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STUDIES ON THE REACTIVITY OF DIAZOALKANES TOWARD ORGANIC ELECTRON ACCEPTORS

（ジアゾアルカンの有機電子受容体に対する反応性に関する研究）

TAKUMI OSHIMA

1982

PREFACE

The work of this thesis was done under the guidance by Professor Toshikazu Nagai and many other members of Nagai Laboratory at the Institute of Chemistry, College of General Education, Osaka University, for seven years since 1975.

The contents of this thesis are composed of the following papers:

(1) Reactions of a Variety of Diazoalkanes with o-Sulfobenzoic Anhydride.
T. Oshima and T. Nagai,
Bull. Chem. Soc. Jpn., 50, 1558 (1977).

(2) Formations and Reactions of Radical Ions in the Systems of Diazocompounds and Electron Acceptors.
T. Oshima, A. Yoshioka, and T. Nagai,
Tetrahedron Lett., 1789 (1977).

(3) ESR and Electronic Absorption Spectra Possibly Assignable to a Radical Ion in the System of Diazoalkane and Electron Acceptor.
T. Oshima and T. Nagai,
Tetrahedron Lett., 3715 (1977).

(4) Polar Effects in the Reactions of a Series of Substituted Diazodiphenylmethanes with Tetracyanoethylene in Benzene.
T. Oshima, A. Yoshioka, and T. Nagai,
J. Chem. Soc. Perkin 2, 1283 (1978).

(5) Formation of Stilbenes and Spiro-oxetanes in the Reactions of Phenyldiazomethanes with Chloranil.
T. Oshima and T. Nagai,
Tetrahedron Lett., 2789 (1979).

(6) Stereochemistry of the Copper Perchlorate or Copper Bromide-Catalyzed Decomposition of Aryldiazomethanes to Stilbenes.
T. Oshima and T. Nagai,
Tetrahedron Lett., 1251 (1980).

(7) Reactions of Aryldiazomethanes with Chloranil.
T. Oshima and T. Nagai,
Bull. Chem. Soc. Jpn., 53, 726 (1980).

(8) Polar Effects in the Reactions of a Series of Substituted Diphenyldiazomethanes with Chloranil.

T. Oshima and T. Nagai,
Bull. Chem. Soc. Jpn., 53, 3284 (1980).

(9) Facile Synthetic Methods of Acetals and Crown Ethers from the Reaction of Diphenyldiazomethane with 2,3-Dichloro-5,6-dicyanobenzoquinone in the Presence of Alcohols.

T. Oshima, R. Nishioka, and T. Nagai,
Tetrahedron Lett., 3919 (1980).

(10) Substituent and Solvent Effects in the Reactions of Diaryldiazomethanes with 2,3-Dichloro-5,6-dicyanobenzoquinone.

T. Oshima and T. Nagai,
Bull. Chem. Soc. Jpn., 54,2039 (1981).

(11) Solvent Effects in the Reaction of Diazodiphenylmethane with Tetracyanoethylene; a New Empirical Parameter of Solvent Basicity.

T. Oshima, S. Arikata, and T. Nagai,
J. Chem. Research, (S)204; (M)2518 (1981).

(12) Products and Kinetic Substituent Effects in the Reactions of Diaryldiazomethanes with 2,5-Dichloro-*p*-benzoquinone.

T. Oshima and T. Nagai,
Bull. Chem. Soc. Jpn., 55, 551 (1982).

(13) Kinetic Solvent Effects in the Decomposition of Diphenyldiazomethane with Chloranil and 2,5-Dichloro-*p*-benzoquinone.

T. Oshima and T. Nagai,
Bull. Chem. Soc. Jpn., 55, 555 (1982).

(14) Solvent Effects in the Conversion of Phenyldiazomethane into Stilbene and Spirooxetane in the Reaction with Chloranil.

T. Oshima, R. Nishioka, and T. Nagai,
Bull. Chem. Soc. Jpn., 55, 904 (1982).

CONTENTS

GENERAL INTRODUCTION

Diazoalkanes(R_2CNN) have been useful intermediates in organic chemistry for many years, and consequently many reactions of these molecules have fully been investigated.[1] A number of extensive reviews of this subject have been published by several workers.[2]

Diazomethane(H_2CNN) is the simplest diazoalkane and as such has served as the prototype for many studies, both experimental and theoretical. From a classical point of view it may be best represented as a resonance hybrid comprising a variety of linear structures with opposing dipoles:[2b]

$$CH_2{=}\overset{+}{N}{=}\overset{-}{N} \longleftrightarrow \overset{+}{C}H_2{-}N{=}\overset{-}{N} \longleftrightarrow \overset{-}{C}H_2{-}\overset{+}{N}{\equiv}N \longleftrightarrow \overset{-}{C}H_2{-}N{=}\overset{+}{N}$$

(1a) (1b) (1c) (1d)

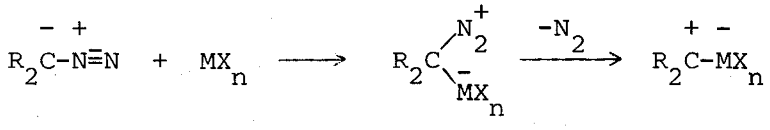
Hence, it is not unreasonable to expect that diazoalkanes, under appropriate conditions, will behave as a carbene or a carbenoid source, as a 1,3-dipole, as an acid or an electrophile, or as a base or a nucleophile.[2b]

According to the initial stage of the reactions, classification can be made as following categories.

(1) Much of the renewed activity in diazoalkane chemistry derives from the tremendous studies of the reactivity and structure of carbene($R_2C{:}$), which are intermediates in the photolysis and thermolysis of diazoalkanes:[3]

$$R_2C{=}\overset{+}{N}{=}\overset{-}{N} \xrightarrow{h\nu,\ \Delta} R_2C{:} \quad + \quad N_2$$

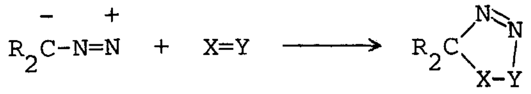
(2) An extensive amount of work has also been done on the decompositions of diazoalkanes with metal halides(Lewis acids). These reactions are thought to involve reactive carbenoids:[4]



$$R_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N \;+\; MX_n \longrightarrow R_2C\begin{smallmatrix}\diagup \overset{+}{N}_2\\ \diagdown \overset{-}{M}X_n\end{smallmatrix} \xrightarrow{-N_2} R_2\overset{+}{C}{-}\overset{-}{M}X_n$$

(3) Other major developments in diazoalkane chemistry include [3+2] cycloaddition with dipolarophiles having X=Y and X≡Y bonds.

Traditionally one associates such work with Huisgen and colleagues:[5]



(4) The basic character of diazoalkanes derives mainly from the resonance structure(1c). Thus, with a protic acid HB, reaction occurs primarily at the nucleophilic carbon atom yielding an alkyl diazonium salt which rapidly decomposes to give the corresponding highly reactive carbonium ion:[6]

$$R_2\overset{-}{C}-\overset{+}{N}\equiv N \quad + \quad \overset{+}{H}\overset{-}{B} \longrightarrow R_2CH\overset{+}{N_2}\ \overset{-}{B} \xrightarrow{-N_2} R_2CH^{+}\ B^{-}$$

(5) On the other hand, the acidic reactivity of diazoalkanes toward nucleophiles increases with increasing contribution of limiting forms like (1c) and (1d) to their overall electron distributions. It has been known that diazoalkanes react with phosphines forming phosphazines:[7]

$$R_2\overset{-}{C}-N=\overset{+}{N} \quad + \quad P(Ph)_3 \longrightarrow R_2\overset{-}{C}-N=N-\overset{+}{P}(Ph)_3 \leftrightarrow R_2C=N-N=P(Ph)_3$$

(6) Electrochemical oxidation of diazoalkanes has been shown to proceed by initial formation of a short-lived intermediate, radical cation:[8]

$$R_2\overset{-}{C}-\overset{+}{N}\equiv N \xrightarrow{-e} R_2\overset{\bullet}{C}-N\equiv\overset{+}{N}$$

As described above, the diazoalkanes show a variety of reaction fashion and play a significant role in the area of organic chemistry from both the synthetic and the mechanistic point of view. However, a few are known of the reactions with organic electron acceptors such as quinones.[9] For instance, Eistert *et al.*[10] have studied the reactions with various quinonoid compounds by employing mainly diazomethane. Therefore, the purpose of the present investigation is to extend the diazoalkane-electron acceptor reactions, to obtain information on the reactivity of diazoalkanes(especially aryl- and diaryldiazomethanes) toward some typical electron acceptors, to discuss the kinetic substituent and solvent effects, and to find a possibility of the synthetic application.

The present thesis is consist of six chapters as follows.

The chapter 1 deals with the fundamental survey of the reactivity of various diazoalkanes toward o-sulfobenzoic anhydride. The two processes giving olefins and keto sultones are described on the basis of the steric and electronic nature of diazoalkanes.

The chapter 2 deals with the product and kinetic studies in the reactions of various substituted diaryldiazomethanes(DDMs) with chloranil, 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ), and 2,5-dichloro-*p*-benzoquinone (DCQ). The betaine and pyrazoline intermediates are assumed respectively to the formation of polyethers and bicyclic diones. The successful Hammett treatments make it possible to quantitatively evaluate the chemical factors governing the reactivity on the basis of the steric and electronic properties of these acceptors.

The chapter 3 deals with the stereochemistry in the conversion of aryldiazomethanes into stilbenes and spirooxetanes in the reaction with chloranil. The solvent effects on the stereochemical course are discussed in terms of the basic and polar solvation of the betaine intermediates.

The chapter 4 deals with the kinetic substituent and solvent effects in the reactions of DDMs with π-acid tetracyanoethylene. A new empirical parameter(D_π) of solvent basicity is proposed from the apparent decrease in rates with the increase of solvent basicity. The successful application of D_π to the other systems is demonstrated.

The chapter 5 deals with the comparison of the solvent effects in the reactions of DDM with chloranil, DDQ, DCQ, and tetracyanoethylene. In view of both the basic solvation of these π-acids and the polar solvation of the transition states, the log k can be correlated with the combination of D_π and the Dimroth-Reichart's E_T values. The extent of the relative contribution of the two parameters is discussed in terms of the electron affinities of the π-acids and of the Hammett parameters.

The chapter 6 deals with a new synthetic application of the betaine intermediate from DDM-DDQ reaction to provide acetals and crown ethers. The effects of the relative amount of glycols used on the product distributions are also discussed.

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Chapter 1 Reaction of Diazoalkanes with o-Sulfobenzoic Anhydride

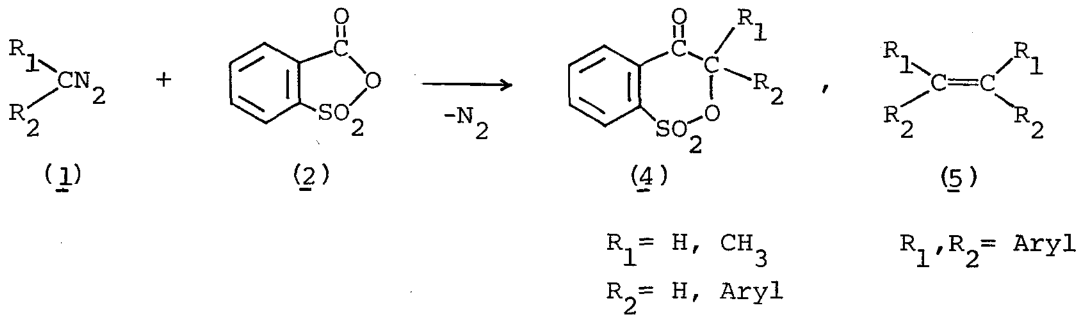
1-1 Introduction

It is well known that diazoalkanes undergo decomposition in the presence of protic acids,[1] a variety of metalic halides,[2] or other Lewis acids[3]— e.g., $ZnCl_2$, Hg_2Cl_2, and BF_3— involving intermediate diazonium ions or carbenoids. However, the decomposition of diazoalkanes under the influence of an organic Lewis acid, i.e., electron acceptor, has not been widely investigated.[4]

Recently, Nagai et. al showed that a mixed sulfonic carboxylic anhydride such as o-sulfobenzoic anhydride can act as an electron acceptor toward tertiary amines, thus giving rise to their radical cations. This Lewis acid behavior of diazoalkanes led me to investigate the decomposition of diazoalkanes using it. This chapter describes the reactions of a variety of diazoalkanes with this new type of electron acceptor. A number of diazoalkanes bearing a relatively small substituent reacted with o-sulfobenzoic anhydride(2) to give the o-(glycoloyl)benzenesulfonic acid sultones (4), while diaryldiazomethanes underwent decomposition to produce the corresponding tetraarylethylenes(5). The kinetics and the mechanism of these reactions were discussed on the basis of the electronic and steric nature of diazoalkanes(1).

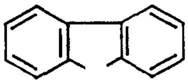
1-2 Results and Discussion

The reactions of a variety of diazoalkanes(1) with o-sulfobenzoic anhydride(2) in dry acetonitrile gave the keto sultones(4) or the tetraarylethylenes(5) depending on the nature of 1(Scheme 1 and Table 1).



Scheme 1.

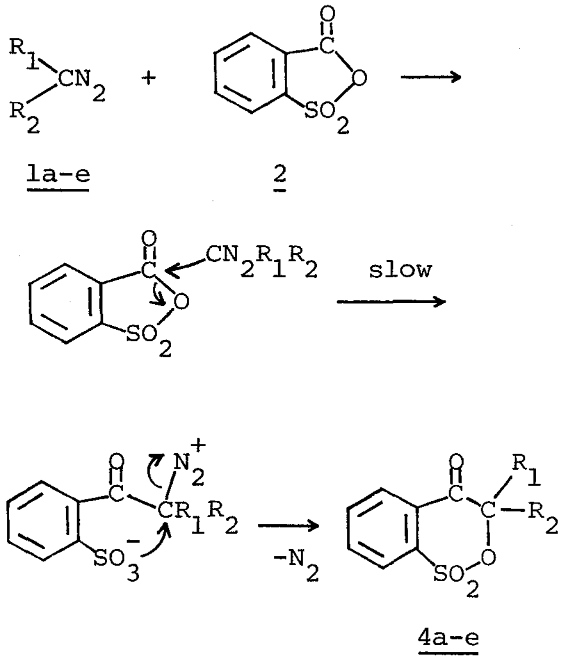
Table 1. Product Distributions from the Reactions of a Number of Diazoalkanes(1) with o-Sulfobenzoic Anhydride(2) in Acetonitrile at Room Temperature[a)]

	R_1	R_2	Products(Yield)[b)]	
1a	H	H	4a(74)	—
1b	H	C_6H_4	4b(71)	—
1c	H	$p\text{-}CH_3C_6H_4$	4c(81)	—
1d	H	$p\text{-}ClC_6H_4$	4d(95)	—
1e	CH_3	C_6H_4	4e(67)	—
1f	C_6H_5	C_6H_4	—	5f(96)
1g	C_6H_4	$p\text{-}CH_3C_6H_4$	—	5g(97)
1h	$p\text{-}CH_3OC_6H_4$	$p\text{-}CH_3OC_6H_4$	—	5h(∿100)
1i			—	5i(75)

a) Reaction time: 1 h. b) The yield is in mole % based on the 1 used.

As may be seen in Table 1, the diazoalkanes(1a-e) which bear a relatively small substituent, R_1, such as H or CH_3, gave the keto sultones(4), while when the R_1 and R_2 substituents were both aryl rings(1f-i), the olefins(5) were isolated instead of the keto sultones. In the course of these reactions it was noticed that the disappearance of diazo-color and the evolution of nitrogen gas occurred very much more rapidly and vigorously in the case of the diaryldiazomethanes(1f-i) than in the case of the monoaryldiazomethanes(1b-e). The marked difference in the product distributions and the reaction velocities suggests that these reactions proceed by way of a different mechanism between the monoaryldiazomethanes and the diaryldiazomethanes.

The kinetic measurements of these reactions provided some information about the mechanism. Keto sultone formation reactions obeyed a clean second order, as is shown in Fig. 1, suggesting a rate-determining nucleophilic attack of diazoalkanes at the carbonyl position of 2(Scheme 2). This is also supported by the tendency for the rate constants to increase with the electron-donating ability of the aryl substituents of these monoaryldiazomethanes: k=1.25(l mol^{-1} min^{-1})(p-Cl), k=2.48(p-H), and k=6.85 (p-CH_3). Taking into account the fact that 2 is a good acylating reagent,[6] it is reasonable to account for this insertion reaction in terms of the nucleophilic attack of the diazo-carbon at the carbonyl position of 2.



Scheme 2.

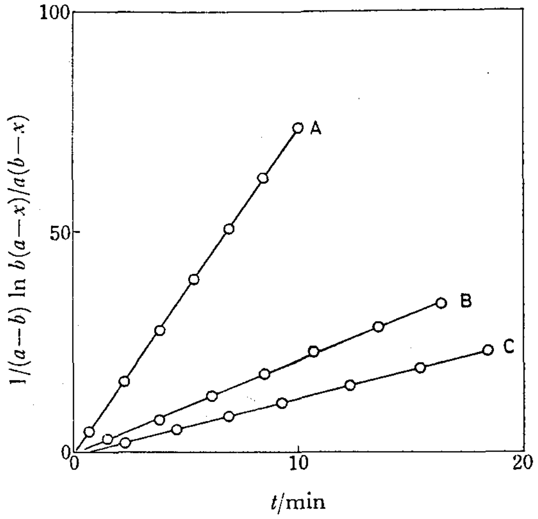


Fig. 1. Second-order kinetic behavior in the reactions of aryldiazometnanes with o-sulfobenzoic anhydride at 23°C; a and b are the initial concentrations of 2 and 1 respectively, x being that of product 4. A: 1c;2.71×10^{-2}M, 2;8.43×10^{-2}M, B: 1b;2.54×10^{-2}M, 2;9.50×10^{-2}M, C: 1d;2.21×10^{-2}M, 2;9.00×10^{-2}M.

On the other hand, as Fig. 2 shows, the olefin-formation reactions progressed quickly even in the presence of a catalytic amount of 2. Here, it is noteworthy that 1g, bearing an electron-donating p-substituent (CH_3), decomposes much faster than 1f. In addition, the IR spectra of equimolar 1 and 2 in acetonitrile showed no change in the two characteristic carbonyl absorptions at 1818 and 1836 cm^{-1} of 2 after the reactions. These facts imply that the decomposition of diaryldiazomethanes does not consume 2 and that it proceeds through a catalytic mechanism.

Considering that 2 invariably contains a trace amount of free acid,[7,8] o-sulfobenzoic acid(3), it seems possible that this free acid induces the

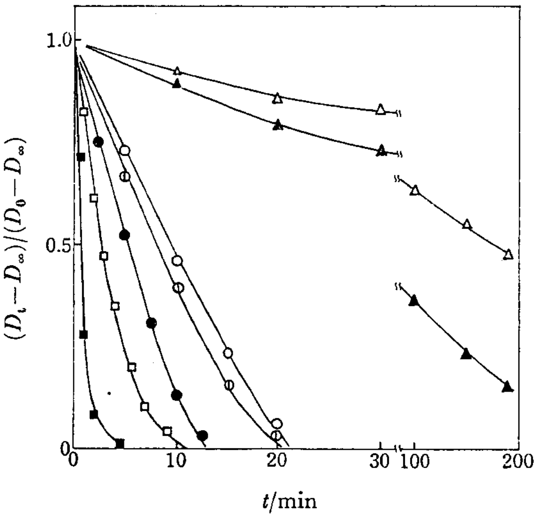


Fig. 2. Decay curves for aryl- and diaryldiazomethanes under the influence of o-sulfobenzoic anhydride(2) or o-sulfobenzoic acid(3) in acetonitrile. D_0 is the initial optical density, D_t and D_∞ being the values when the reaction time is t and when the reaction was complete respectively. Δ: 1b; 2.44×10^{-2} M, 3; 1.15×10^{-3}M, 23°C, ▲: 1c; 3.38×10^{-2}M, 3; 1.15×10^{-3}M, 21°C, ○: 1f; 1.01×10^{-2}M, 2; 2.10×10^{-4}M, 20°C, ●: 1f; 1.01×10^{-2}M, 3; 9.7×10^{-5}M, 20°C, □: 1g; 8.34×10^{-3}M, 2; 2.10×10^{-4}M, 20°C, ■: 1g; 8.34×10^{-3}M, 3; 9.7×10^{-5}M, 20°C, ⦶: 1f; 1.01×10^{-2}M, 2; 2.1×10^{-4}M,* 20°C. * o-Sulfobenzoic anhydride solution used here is identical to that used in the case of marked ○ but has been stood for 1 day in glass stoppered flask.

decomposition of diazoalkanes. The quantitative formation of the tetraarylethylenes in our present reaction is well consistent with that in the acid-catalyzed decompositions of diaryldiazomethanes in aprotic solvents with such strong acids as *p*-toluenesulfonic acid.[1b,9,10,11] Keeping this in mind, the author examined the decompositions of 1 by 3, which had been prepared independently, and compared the decompositions with those by 2(Fig. 2).

As for the reaction leading to 5, the kinetic order by authentic 3 was very similar to that by 2: the kinetic order was close to zero up to the final stage of the reaction, in analogy with that of the *p*-toluenesulfonic acid-catalyzed decomposition of diaryldiazomethanes in dry acetonitrile.[12] Furthermore, a rate acceleration was observed when a solution of 2 which had been stored for one day was employed(Fig. 2). This phenomenon is due to the partial transformation of 2 to 3 by the action of atmospheric moisture, as was confirmed by the UV spectra of 2, as may be seen in Fig. 3.

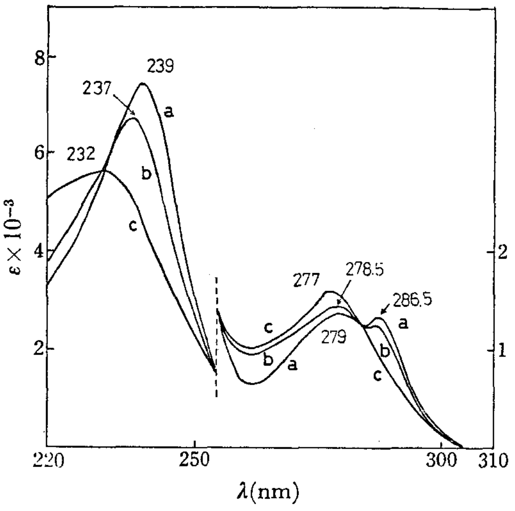


Fig. 3. UV spectra of 2 under the various conditions. a: Measured immediately after preparation, b: measured after 1 day, c: measured after hydrolysis.

When the measurement was done one day later, the intensity in the UV spectrum of 2(Curve b) decreased at λmax =286.5 nm and had new absorption maxima at 237 and 278.5 nm instead of at 239 and 279 nm, with two isosbestic points at 254 and 284 nm. Therefore, it is apparent that the decomposition of diaryldiazomethanes was induced by the trace amount of 3 instead of by 2.

As is well known, the acid-catalyzed reaction of diaryldiazomethanes, involving a rate-determining proton transfer and obeying a pseudo-first order, proceeds by way of intermediate diazonium ions[1b,9,10,11] (or carbonium ions derived from them). Bethell and Callister[11] studied the decomposition of diphenyldiazomethane in dry acetonitrile with perchloric acid, which is fully ionized in this solvent,[13] and found the kinetic order to be pseudo-first, as is formulated in Scheme 3:

$$\mathrm{Ph_2CN_2} \xrightarrow[k_1]{\mathrm{H^+}\ \text{slow}} \mathrm{Ph_2CHN_2^+} \xrightarrow[-\mathrm{N_2}]{} \mathrm{Ph_2CH^+} \xrightarrow[k_2]{\mathrm{Ph_2CN_2}} \mathrm{Ph_2C{=\!=}CPh_2} + \mathrm{N_2} + \mathrm{H^+}$$

Kinetic equation:

$$\frac{-d[\mathrm{Ph_2CN_2}]}{dt} = 2k_1[\mathrm{H^+}][\mathrm{Ph_2CN_2}] = k_1'[\mathrm{Ph_2CN_2}]$$

Scheme 3.

However, at the same time they found that the kinetic order changes to zero when perchloric acid is replaced by *p*-toluenesulfonic acid, which reacts in an undissociated form in dry acetonitrile.[12] As to this zero order decomposition, they thought that the diphenyldiazomethane reacts first to form the benzhydryltoluenesulfonate intermediate, which subsequently undergoes a slow solvolysis to form tetraphenylethylene, as is formulated in Scheme 4:

$$\mathrm{Ph_2CN_2} + \mathrm{HOTs} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Ph_2CHN_2^+}\ {}^{-}\mathrm{OTs} \longrightarrow \mathrm{Ph_2CHOTs}] \xrightarrow{k_4\ \text{slow}} \mathrm{Ph_2CH^+} + {}^{-}\mathrm{OTs}$$

$$\xrightarrow{\mathrm{Ph_2CN_2}} \mathrm{Ph_2C{=\!=}CPh_2} + \mathrm{HOTs} + \mathrm{N_2}$$

Kinetic equation:

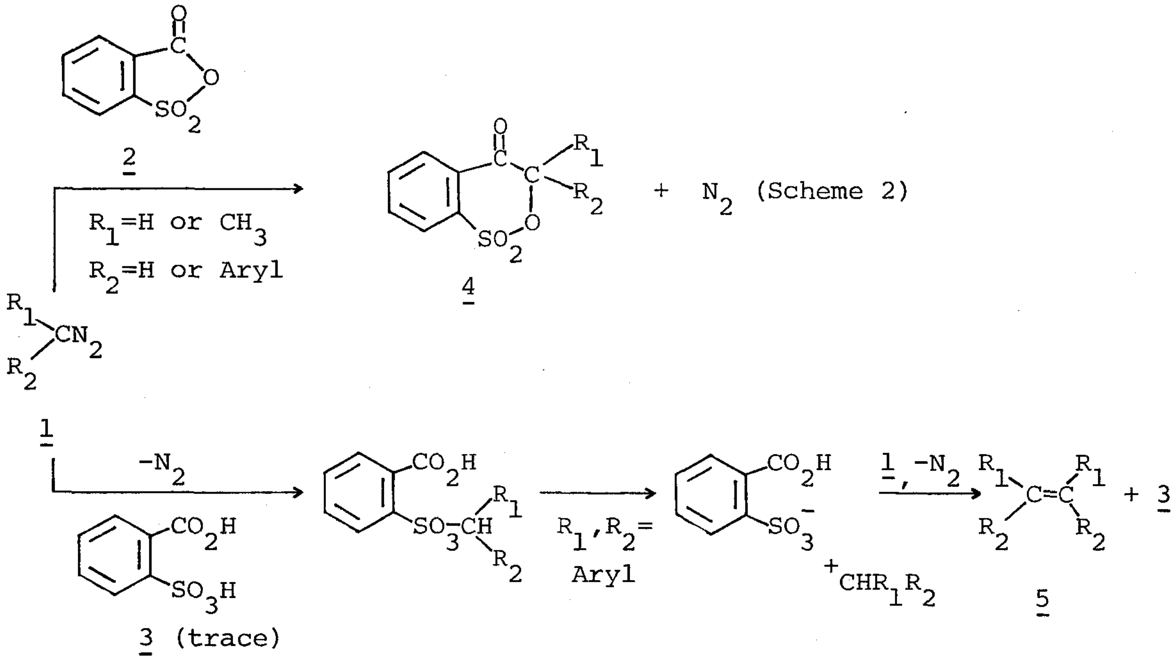
$$\text{if } (k_3/k_{-3})[\mathrm{Ph_2CN_2}] \gg 1,\quad \frac{-d[\mathrm{Ph_2CN_2}]}{dt} = k\ [\mathrm{HOTs}]_{st}$$

$[\mathrm{HOTs}]_{st}$: the stoicheiometric acid concentration

Scheme 4.

In the present system, o-sulfobenzoic acid(3) has both carboxyl and sulfo groups, and its behavior toward diazoalkanes can be regarded as being comparable to *p*-toluenesulfonic acid because the two acids similarly bring about a quantitative olefin formation under zero order kinetics.

The decompositions of monoaryldiazomethanes by the action of 3 were quite slow compared with those of diaryldiazomethanes, even in the presence of about a ten-fold concentration of 3(Fig. 2). This marked change in the decomposition rate between the monoaryldiazomethanes and the diaryldiazomethanes may be attributed to the differences in the stabilities of the intermediate sulfonates. The sulfonates derived from diaryldiazomethanes seem to be much more subject to solvolysis than the corresponding sulfonates from monoaryldiazomethanes. From these observations, the present decomposition reactions are formulated as follows(Scheme 5):



Scheme 5.

In summary, it is concluded that, in the cases of diazomethane and monoaryldiazomethanes, the insertion reaction is preferential because these diazoalkanes have an effective nucleophilicity toward 2; even if the reaction could occur with a trace amount of 3, it would essentially stop at the stage of the sulfonate formation because of its stability against solvolysis. On the other hand, in the cases of diaryldiazomethanes, the lesser nucleophilicity of the diazo-carbon atom toward 2 resulting from the conjugation with the two aromatic rings as well as the steric effects and the readier solvolysis of the sulfonates make the acid-catalyzed decomposition predominant. Thus, the former reaction obeyed a second-order kinetic law, while the latter kinetic order was found to be zero.

1-3 Experimental

The NMR spectra were obtained with a Varian EM-360(60 MHz) instrument, with tetramethylsilane as the internal standard. The IR spectra were recorded on a Hitachi 215 Grating Infrared Spectrophotometer; a 0.1 mm NaCl cell was used for the measurement in solution. The UV spectra were taken with a Union SM-401 spectrophotometer.

Materials. The acetonitrile was purified by careful distillation from phosphorus pentoxide through a 10-in helix-packed column. The middle fractions were collected and stored in a glass-stoppered flask. The o-sulfobenzoic anhydride(2) was prepared by the method of Clarke and Dreger,[14] and recrystallized from benzene; mp 126-127°C, (lit,[14] 126-127°C); IR(in CH_3CN): 1836 and 1818(C=O), 1206, 996, 810 cm^{-1}. The anhydrous o-sulfobenzoic acid(3) was given on the hydrolysis of 2 and was dried *in vacuo* above 105°C; mp 140-141°C; IR(Nujol): 3500-2500(COOH and SO_3H), 1720 (C=O), 1160 and 1020 cm^{-1}(SO_2). Because of moisture-sensitive substance, 2 and 3, placed in a bottle fitted with a sealing cap, were stored in a desiccator, with silica gel as the desiccant. The diazomethane was prepared by the procedure in the literature,[15] and its ethereal solution was dried over potassium hydroxide. The monoaryldiazomethanes and diaryldiazomethanes were synthesized by the methods of Closs and Moss[16] and Smith and Howard[17] respectively. λmax(ε) in CH_3CN: 488 nm(25) for 1b, 495 (25) for 1c, 484(32) for 1d, 525(95) for 1f; these values are essentially identical with those in the literature.[11,16]

p-Tolylphenyldiazomethane(1g); mp 51-53°C, reddish purple needles (from petroleum ether), (lit,[18] 53-55°C), λmax(ε) in CH_3CN: 530 nm(98). Bis(*p*-methoxyphenyl)diazomethane(1h); mp 99°C(dec), purple needles(from ether), (lit,[11] 99-100°C(dec)). 9-Diazofluorene(1i); mp 94-95°C(from EtOH), (lit,[19] 94-95°C). Because of the unstability of the diazo-compounds, they were prepared just before use for the aryldiazomethanes and were purified before use by recrystallization for the diaryldiazomethanes.

Kinetic Measurements. The temperature during the measurements was not especially controlled, but its change was within ±0.5°C. As a rule, solutions of 1, 2, and 3 were made up separately just before use. The change in the optical density at the wavelength of the absorption maximum of 1 in the visible region was followed spectrophotometrically.

The second-order rate constants, k , were determined graphically from the plots of $1/(a-b) \ln b(a-x)/a(b-x)$ against the time

General Procedure. To a three-necked flask(100 ml) equipped with a dropping funnel, a thermometer, and a drying tube of calcium chloride, 2(5 mmol) in dry acetonitrile(25 ml) was introduced, and then 1(5 mmol) in dry acetonitrile(25 ml) was stirred in over a 10-min period. Stirring was then continued for 50 min. In the case of diazomethane, its excess in an ether solution dried over potassium hydroxide was dropped in. The addition of 1 caused the evolution of nitrogen gas. The removal of the solvent *iv vacuo* gave oily reaction mixtures in the cases of 1a-e or solid ones in the cases of 1f-i. The same procedure was used for the o-sulfobenzoic acid-catalyzed decomposition of diaryldiazomethanes(1f-h) by employing a catalytic amount of 3 instead of 2. These catalytic decompositions also gave almost quantitative olefins for 1f-h. These reaction mixtures were submitted to chromatography, using silica gel as the adsorbent. Elution with a petroleum ether — ether gave the olefins(5), while elution with chloroform gave the sultones(4). The olefins, 5f, h, were identified by comparison with authentic samples,[11] while the 5g and 5i were confirmed by elemental analyses: 5g; Found: C, 93.11; H, 6.79%. Calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71%. 5i; Found: C, 94.74; H, 5.11%. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91%. 1,2-Di-*p*-tolyl-1,2-diphenylethylene(5g) showed two kinds of methyl signals to the same extent, centered at δ 2.2 and due to the *cis* and *trans* isomers. The structures of the keto sultones(4a-e) were determined by means of elemental analyses and by measurements of the IR, NMR, and Mass spectra.

o-*Glycoloylbenzenesulfonic Acid Sultone(4a)*: Mp 93-94°C, colorless needles(from CH_3OH), (lit,[20] 93-94°C). IR(Nujol): 1700(C=O), 1367 and 1195 cm^{-1}(SO_2). MS: *m/e*=198(M^+). NMR(δ, $CDCl_3$): 7.7-8.2(m, 4H), 5.25 (s, 2H). Found: C, 48.27; H, 3.17%. Calcd for $C_8H_6O_4S$: C, 48.49; H, 3.05 %.

o-*(Phenylglycoloyl)benzenesulfonic Acid Sultone (4b)*: Mp 54-55°C, colorless needles(from CH_3OH). IR(Nujol): 1703(C=O), 1370 and 1195 cm^{-1}(SO_2). MS: *m/e*=274(M^+). NMR(δ, $CDCl_3$): 7.67-8.17(m, 4H), 7.40(s, 5H), 6.38(s, 1H). Found: C, 61.22; H, 3.77%. Calcd for $C_{14}H_{10}O_4S$: C, 61.32; H, 3.68%.

o-*(Tolylglycoloyl)benzenesulfonic Acid Sultone (4c)*: Mp 123-124°C, pale yellow needles(from CH_3OH). IR(Nujol): 1700(C=O), 1365 and 1195 cm^{-1}(SO_2).

MS: *m/e*=288(M^+). NMR(δ, $CDCl_3$): 7.67-8.17(m, 4H), 7.25(s, 4H), 6.37(s,1H), 2.37(s, 3H). Found: C, 62.52; H, 4.23%. Calcd for $C_{15}H_{12}O_4S$: C, 62.50; H, 4.20%.

o-*(*p-*Chlorophenylglycoloyl)benzenesulfonic Acid Sultone (4d)*: Mp 89-90°C, colorless needles(from CH_3OH). IR(Nujol): 1705(C=O), 1360 and 1195 cm^{-1}(SO_2). MS: *m/e*=308, 310(3:1)(M^+). NMR(δ, $CDCl_3$): 7.73-8.33(m, 4H), 7.40(s, 4H), 6.40(s, 1H). Found: C, 54.21; H, 3.35%. Calcd for $C_{14}H_9O_4SCl$: C, 54.40; H, 3.01%.

o-*(Methylphenylglycoloyl)benzenesulfonic Acid Sultone (4e)*: Mp 80-81°C, colorless needles(from CH_3OH). IR(Nujol): 1700(C=O), 1365 and 1194 cm^{-1} (SO_2). MS *m/e*=288(M^+). NMR(δ, $CDCl_3$): 7.67-8.07(m, 4H), 7.27-7.57(m, 5H), 2.28(s, 3H). Found: C, 62.41; H, 4.59%. Calcd for $C_{15}H_{12}O_4S$: C, 62.50; H, 4.20%.

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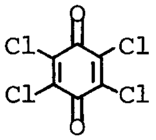
Chapter 2 Substituent Effects on the Reactions of Diaryldiazomethanes with Various Quinones

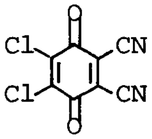
2-1 Introduction

As one area of chemistry of diazoalkanes, continuing interest is being paid to the reactions with quinones from the synthetic and mechanistic points of view.[1] This is because quinones behave as dipolarophiles or electron acceptors with reactive conjugated C=O and C=C bonds. Most of the works have been carried out by use of the simplest diazoalkanes, *e.g.*, diazomethane. For example, epoxides were obtained when diazomethane was allowed to react with tetrasubstituted quinones such as chloranil and 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ), because the C=O bonds are more reactive than the C=C bonds in these quinones.[2] On the other hand, diazomethane is known to react with 2,5-dichloro-*p*-benzoquinone(DCQ) to afford pyrazoline derivative formed by way of [2+3] cycloaddition toward the C=C bonds of the quinone.[3]

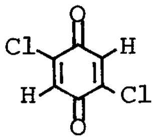
However, little is known of the reactions of aryl- and diaryldiazomethanes with quinones or of kinetic studies of these systems.[4] Thus, the reactions of diaryldiazomethanes(DDMs) with various quinones, *i.e.*, chloranil, DDQ, and DCQ, were kinetically investigated in order to evaluate the chemical factors governing these reactions. The kinetic substituent effects and the mechanism were also discussed on the basis of the concept of charge transfer from diazoalkanes to quinones.



Chloranil



(DDQ)



(DCQ)

2-2 Results and Discussion

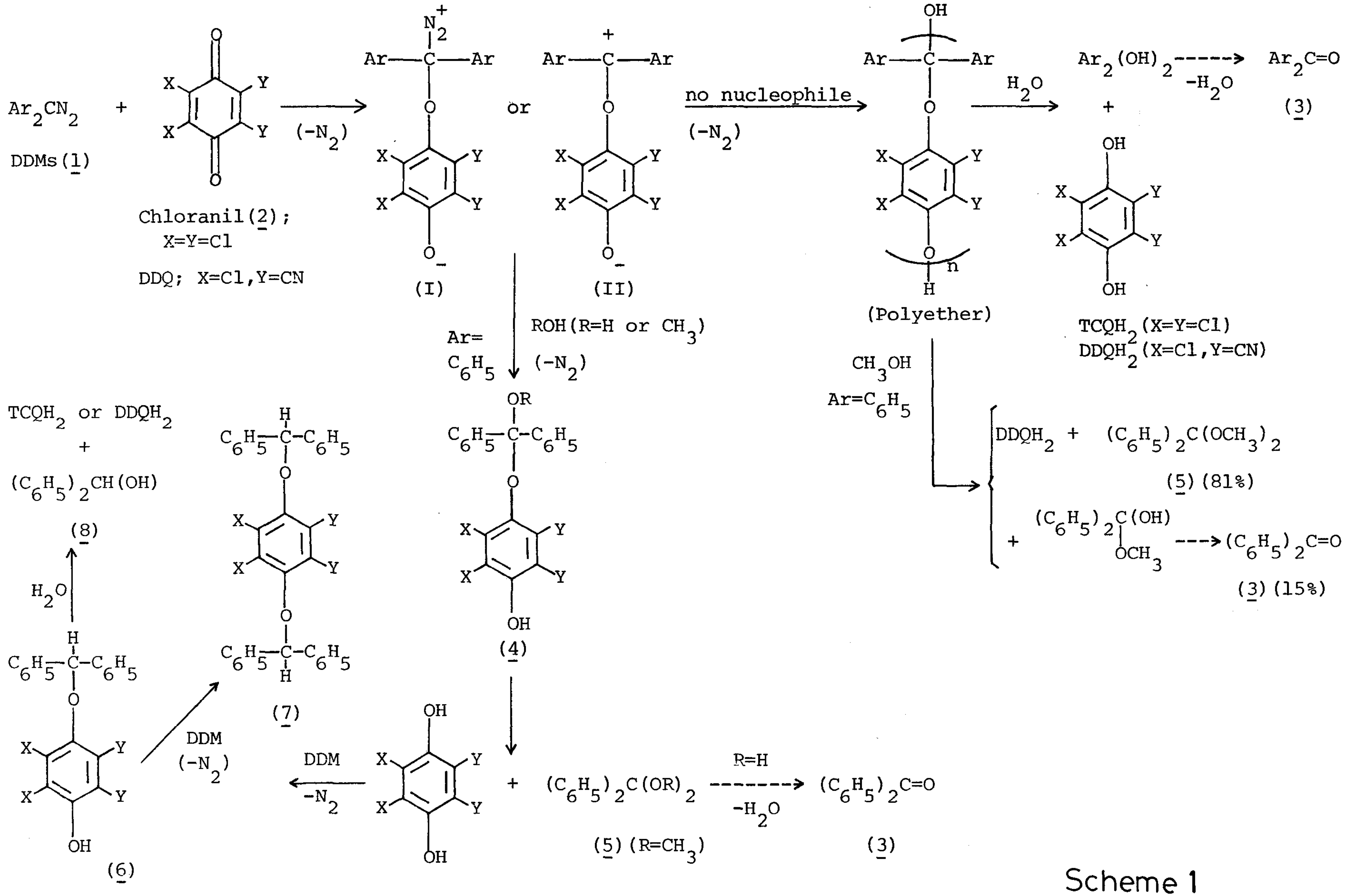
2-2-1 Reactions with Chloranil

(a) Product Study.

The reactions of diphenyldiazomethane(DDM) and its fourteen meta- and para-substituted analogues(DDMs)(1) with an equimolar amount of chloranil(2) were conducted in tetrahydrofuran at 30°C. The decomposition rates were found to be much more accelerated with the increase in the electron-donating abilities of the substituents. For example, the presence of *p*,*p'*-dimethoxy substituents instantaneously brought about the deposition of a white precipitate, accompanied by a vigorous evolution of N_2, while *p*-nito-substituted DDM needed one week for the complete disappearance of the diazo color. All these reactions gave some precipitates or suspensions which were easily degradated into the corresponding substituted benzophenones(3) and tetrachlorohydroquinone($TCQH_2$) on standing in atmospheric moisture or by the addition of aqueous THF. Moreover, the crude reaction mixtures were also completely changed into almost equimolar amounts of the corresponding 3 and $TCQH_2$ on treatment with aqueous THF. These hydrolyses show the stoichiometry to be 1 mol of DDMs to 1 mol of 2, while the total yields of 3 or $TCQH_2$ are, in most cases, greater than 93%. An elemental analysis of the precipitate obtained in the case of DDM exhibited a composition(C; 54.35, H; 2.46%) very close to the combined molecular formula, $C_{19}H_{10}Cl_4O_2$, of diphenylmethylene and 2. The IR spectrum(KBr) of this precipitate showed a weak absorption in the OH region, but no appreciable C=O absorption was observed, indicating that the quinonoid structure of 2 has already been lost.

From this chemical and spectroscopic information, it is natural to consider that the structure of these hydrolyzable products is made up by the polyether linkage depicted in Scheme 1. These polyethers consist of an alternate combination of diarylmethylenes and a chloranil moiety with a benzenoid functionality. Accordingly, it can be suggested that intermediary diazonium betaines(I) or carbonium betaines(II) play an important role in the present polymerization process. The propagation of the polyether linkage may be terminated by the action of residual water present in the solvent, the end groups thus becoming hemiketalic OH and phenolic OH. Therefore, the polymerization degree (*n*) will lie at a lower value with an increase in the water content; the author could not estimate the value of *n* because the precipitates were not soluble in common aprotic solvents and were easily hydrolyzable. The degradation of these polyethers under the influence of water is caused by the successive hydrolytic cleavage of the ether linkage; the dihydroxydiarylmethanes thus formed are easily converted into 3 with a loss of water.

On the other hand, the initial presence of a large amount of water is expected to give, exclusively, the unstable ether(4), capable of undergoing subsequent hydrolysis. Indeed, the presence of a five-fold excess


Ar2CN2
DDMs (1)
+
Chloranil (2); X=Y=Cl
DDQ; X=Cl, Y=CN
(-N2)
(I)
or
(II)
no nucleophile
(-N2)
(Polyether)
H2O
Ar2(OH)2
-H2O
Ar2C=O
(3)
TCQH2 (X=Y=Cl)
DDQH2 (X=Cl, Y=CN)
CH3OH
Ar=C6H5
DDQH2 + (C6H5)2C(OCH3)2
(5) (81%)
+ (C6H5)2C(OH)OCH3
(C6H5)2C=O
(3) (15%)
Ar=C6H5
ROH (R=H or CH3)
(-N2)
(4)
(C6H5)2C(OR)2
(5) (R=CH3)
R=H
-H2O
(C6H5)2C=O
(3)
DDM
-N2
(6)
DDM
(-N2)
(7)
H2O
TCQH2 or DDQH2 + (C6H5)2CH(OH)
(8)

Scheme 1

of water(ROH, R=H) in the DDM-2 system brought about the formation of benzophenone and $TCQH_2$, in addition to small amounts of benzhydrol(8) and tetrachlorohydroquinone dibenzhydryl ether(7) (Scheme 1). These two by-products seem to be derived from the acid-induced decomposition of DDM with the resulting $TCQH_2$; the formation of 8 can be ascribed to the hydrolysis of tetrachlorohydroquinone benzhydryl ether(6) on work-up. A similar reaction was found in the presence of methanol($R=CH_3$), where α,α-dimethoxydiphenylmethane(5, $R=CH_3$) was afforded instead of benzophenone.[5] These solvolysis reactions evidently confirm the occurrence of an intermediate I or II.

(b) Kinetic Study.

As was noticed in the product study, the disappearance of the color of the DDMs was much accelerated by introducing the electron-donating substituents in the meta and the para positions of the aromatic rings of DDMs. In order to estimate these polar effects in more detail, the decompositions of fifteen meta- and para-substituted DDMs were followed spectrophotometrically in the presence of high dilute DDMs with respect to 2; moderate reaction rates were thereby attained, thus avoiding the precipitate formation. The rates determined by monitoring the decrease in the diazo color were found to obey a simple pseudo-first order kinetic law. The rate constants($k$obsd) of the decomposition of DDM with various concentrations of 2 are shown in Table 1; the linear dependence of $k$obsd on the concentration of 2 is held within the limits of experimental error: $10^5 k\text{obsd}/\text{s}^{-1}=535[\text{Chloranil}]-0.31$.

Table 1. Observed first-order rate constants, $k$obsd, for the decomposition of DDM(1.70×10^{-3} mol dm^{-3}) with a large excess of chloranil(2) in tetrahydrofuran at 40°C.

10^2[Chloranil] / mol dm^{-3}	$10^4 k$obsd / s^{-1}
8.33	4.41
6.66	3.59
5.83	3.01
5.00	2.68
4.16	2.17
3.33	1.76

Therefore, the second-order rate constants, *k*, were obtained simply by dividing the *k*obsd by the concentration of 2. The values of *k* thus determined for the meta- and the para-substituted DDMs at various temperatures are given in Table 2, together with the activation parameters.

Table 2. Second-order rate constants, *k*, and activation parameters for the decompositions of the substituted DDMs(1a-o) with chloranil(2) in tetrahydrofuran

DDMs	Substituents	$10^3 k$/l mol^{-1} s^{-1}			$\Delta H^{\neq}$ kJ/mol	$\Delta S^{\neq}$ J/mol K
		30°C	40°C	50°C		
1a	p,p'-OCH_3	197	—	—	—	—
1b	p-OCH_3 p'-CH_3	49.0	—	—	—	—
1c	p-OCH_3	19.5	38.9	69.9	49.3	-115
1d	p,p'-CH_3	15.8	33.1	62.3	53.2	-104
1e	p-OPh	6.67	13.8	25.7	52.3	-114
1f	p-CH_3	6.10	12.0	24.3	53.7	-110
1g	m-CH_3	3.71	7.59	14.9	54.0	-113
1h	p-Ph	3.38	6.03	11.2	46.2	-140
1i	p-F	2.80	5.63	11.3	54.2	-115
1j	p-H	2.43(2.62)[a]	5.35	10.9	58.5	-102
1k	p-Cl	1.29	2.77	5.31	55.0	-119
1l	p,p'-Cl	0.661	1.41	2.94	58.2	-114
1m	m-Cl	0.623	1.38	2.85	59.3	-111
1n	m-NO_2	0.232	—	—	—	—
1o	p-NO_2	0.0790	—	—	—	—

a) The value in parentheses was determined at 30.5°C by the volumetric method employing a 2-molar excess of 2 with respect to DDM.

It can be noted that the *p,p'*-dimethoxy substituents caused a 2500-fold increase in the rate compared with the *p*-nitro substituent at 30°C.
In the case of DDM, the rate of the decomposition was also determined by monitoring the evolved N_2, and second-order rate constant was nearly equal

to that determined by the spectroscopic method. This means that there is no accumulation of any type of intermediate with the N_2 group in the course of the reaction.

The dependence of log k/k_0 on the Hammett σ constants[6] and the Brown σ^+ constants[7] is shown in Fig. 1. For disubstituted DDMs, the σ and σ^+ values used are the sums of the values for the two substituents.

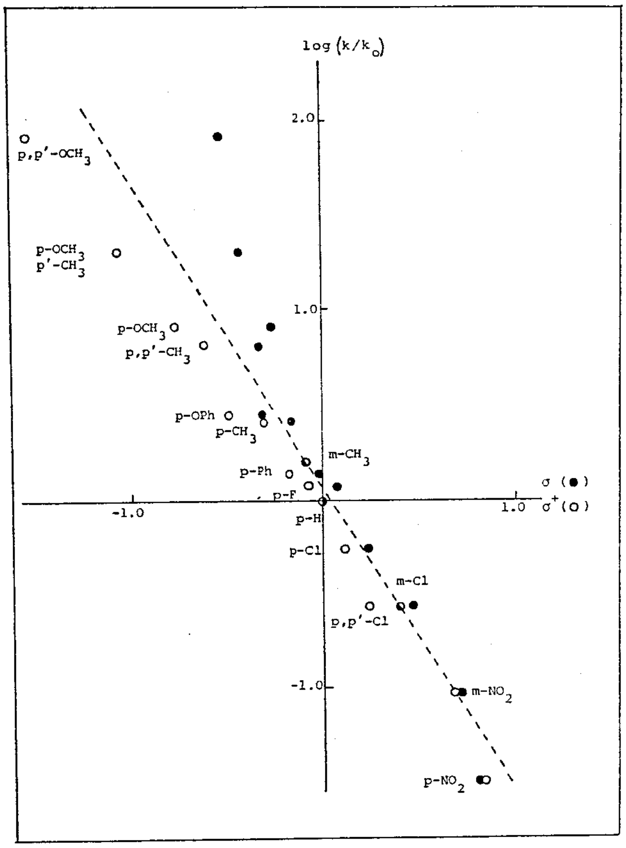


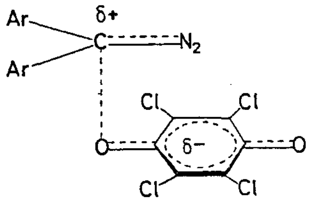
Fig. 1. The plot of log k/k_0 against the Hammett σ(●) and Brown σ^+(○) constants.

Four meta-substituted DDMs gave an excellent linear dependence(ρ= -1.52), r= 0.996(correlation coefficient) when the simple Hammett equation and normal σ values were used. When correlating the series of fifteen meta- and para-substituted DDMs and using the normal σ values, the author obtained substantially worse results(r= 0.933, ρ= -2.10). The correlation line appears to curve upward from the meta line. The replacement of σ by σ^+ caused a considerable improvement in the correlation(r=

0.980, $\rho = -1.37$), though a downward deviation from the meta line is still found for the methoxy-substituted DDMs. Neither the σ nor σ^+ values apparently fit the correlation of the para-substituted DDMs well. Therefore, the author used the two-parameter Yukawa-Tsuno equation,[8] $\log k/k_0 = \rho(\sigma^0 + R\Delta\bar{\sigma}_R{}^+)$, where σ^0, R, and $\Delta\bar{\sigma}_R{}^+$ are the normal substituent constant, the resonance reaction constant, and the resonance substituent constant respectively. The results of regression analysis indicate that the use of a two-parameter equation improves the correlation significantly(Eq. 1):

$$\log k/k_0 = -1.67(\sigma^0 + 0.66\Delta\bar{\sigma}_R{}^+) + 0.009, \quad (r=0.996, s=0.08, n=15) \qquad \text{(Eq. 1)}$$

The negative sign and the magnitude of $\rho(-1.67)$ are consistent with the development of a positive charge at the diazo carbon in the activation process. The value of R=0.66 also confirms that a considerable resonance stabilization of the transition state is required in the present system.



Mechanistically, the formation of polyether and the occurrence of the solvolysis reaction in the present system can be well explained by assuming the participation of the diazonium betaine(I) or the carbonium betaine(II) intermediate. The kinetic data provide some information concerning the transition state. The large negative entropies of activation are indicative of the highly ordered transition state usually encountered in 1,3-dipolar cycloaddition.[9] However, the magnitude of the charge separation, as revealed by the Hammett correlation as well as by the solvent effects,[10] appears unmatched in the isopolar transition states of 1,3-dipolar additions. Therefore, the present system is postulated to proceed through the polar transition state depicted above, though the polar transition state of 1,3-dipolar addition[11] or the radical process[12] can not be ruled out.

2-2-2 Reactions with 2,3-Dichloro-5,6-dicyanobenzoquinone(DDQ)

(a) Product Study.

As well as in the case of chloranil,[13] the reactions of fifteen *meta*- and *para*-substituted DDMs with an equimolar amount of DDQ in benzene at 30°C were much more accelerated with the increase in the electron-donating abilities of the substituents. All these reactions, more or less accompanied by an evolution of N_2, gave resinous products which were highly sensitive to hydroxylic solvents. When these products were hydrolyzed, corresponding benzophenones($\underline{3}$) and 2,3-dichloro-5,6-dicyanohydroquinone($DDQH_2$) were isolated in most cases greater than 95%. These chemical findings strongly suggest the structure of the 1:1 reaction products to be a hydroquinone polyether linkage similar to that considered for the chloranil-DDMs systems.[13] This suggestion is also supported by the representative IR spectrum of the DDQ-DDM system, which exhibited a complete loss of the characteristic carbonyl absorption of DDQ.

The ether linkage may be made up by the successive combination of intermediary diazonium betaines(I) or carbonium betaines(II), as is predicted in Scheme 1. The action of water and methanol can cause the hydrolytic and methanolytic cleavage of the ether bonds to give benzophenones($\underline{3}$) and α,α-dimethoxydiphenylmethane($\underline{5}$), together with $DDQH_2$ (Scheme 1); the *gem*-diols are transformed into $\underline{3}$. In the case of methanolysis, the formation of $\underline{3}$ as a by-product is attributable to the terminal benzhydrol moiety, which primarily degrades into α-methoxy-α-phenylbenzyl alcohol, which is itself easily convertible into $\underline{3}$. Therefore, it is possible to estimate the average polymerization degree (n) from the ratio of $\underline{5}$(81%) to $\underline{3}$(15%); the value over 5 corresponds to n= 6-7.

On the other hand, the initial presence of water and methanol as additives induced solvolysis reactions giving, respectively, $\underline{3}$ and $\underline{5}$, along with $DDQH_2$. These products are thought to be yielded by the successive nucleophilic attack of these additives on the betaine intermediate, as is also depicted in Scheme 1. These reactions were accompanied by trace amounts of benzhydrol(8) and 2,3-dichloro-5,6-dicyanohydroquinone dibenzhydryl ether(7) arising from the acid-induced decomposition of DDM by the resulting $DDQH_2$; 8 seems to be afforded by the hydrolysis of 2,3-dichloro-5,6-dicyanohydroquinone benzhydryl ether(6).

Apparently, the susceptibility of rates to the substituents, the stoichiometry of the reactions, and the solvolysis evidence all confirm that the present diaryldiazomethanes(DDMs)-DDQ systems proceed through a reaction course similar to that of chloranil systems.[13]

(b) Kinetic Study.

The reactions of DDMs with DDQ in benzene can be followed spectrophotometrically by monitoring the disappearance of the absorption of DDQ at 408 nm or that of the combined absorptions of both components at 500 nm in the case of nitro-substituted DDMs(1n,o). These reactions have been found to obey a second-order kinetic law. The rate constants, k, determined for DDMs(1a-o) at various temperatures are listed in Table 3, together with the activation parameters.

Table 3. Second-order rate constants, k, and activation parameters for the reactions of the DDMs(1a-o) with DDQ in benzene

DDMs	Substituents	k/l mol^{-1} s^{-1}			$\Delta H^{\neq}$	$\Delta S^{\neq}$
		30°C	40°C	50°C	kJ/mol	J/mol K
1a	p,p'-OCH_3	256	—	—	—	—
1b	p-OCH_3 p'-CH_3	88.4	—	—	—	—
1c	p-OCH_3	29.1	—	—	—	—
1d	p,p'-CH_3	25.4	—	—	—	—
1e	p-OPh	10.3	—	—	—	—
1f	p-CH_3	8.58	—	—	—	—
1g	m-CH_3	5.49	8.55	12.1	29.5	-133
1h	p-Ph	3.26	4.74	6.68	26.6	-147
1j	p-H	3.05	4.96	7.72	35.2	-119
1i	p-F	1.88	3.04	4.80	35.6	-126
1k	p-Cl	0.935	1.45	2.28	33.7	-134

Table 3. (Continued)

DDMs	Substituents	k/l mol^{-1} s^{-1}			$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
		30°C	40°C	50°C	kJ/mol	J/mol K
1m	*m*-Cl	0.322	0.505	0.778	33.3	-144
1l	*p,p'*-Cl	0.283	0.510	0.831	41.2	-119
1n	*m*-NO_2	0.102	0.188	0.338	46.2	-112
1o	*p*-NO_2	0.0295	0.0594	0.113	52.1	-112

It is noteworthy that the present reactions were much more accelerated with an increase in the electron-releasing abilities of the substituents; the *p,p'*-dimethoxy substituents caused a *ca.* 9000-fold increase in the rates compared with the *p*-nitro substituent, though the chloranil system showed only a 2500-fold increase.[13]

The dependency of log k/k_0 on the Hammett σ[6] and Brown σ^+[7] constants is shown in Fig. 2.

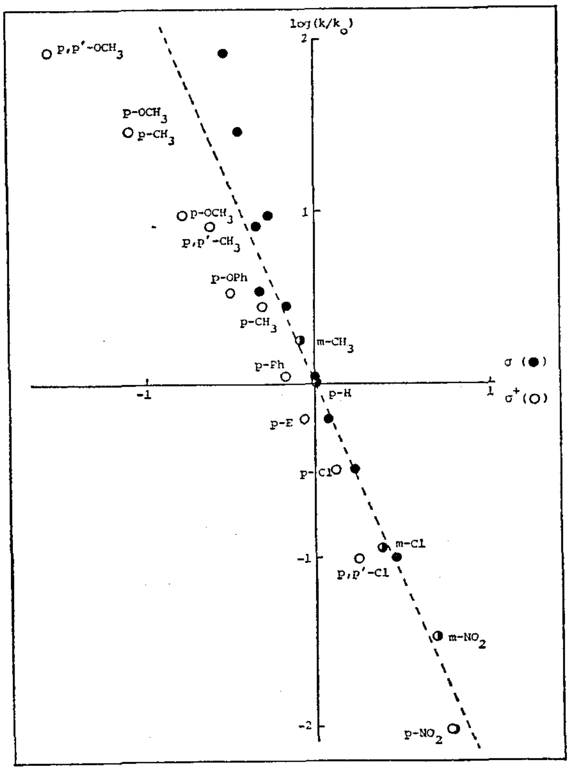


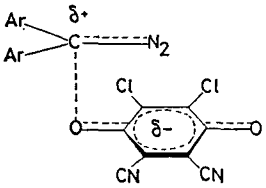
Fig. 2. Plot of log k/k_0 against the Hammett σ(●) and Brown σ^+(○) constants.

As may be noticed, the additivity of the substituent constants holds for the disubstituted DDMs. Four *meta*—substituted DDMs gave a sufficient linear dependence($\rho = -2.19$), $r=0.990$(correlation coefficient) when the simple Hammett equation and normal σ values were used. When correlating all the DDMs and using the normal σ values, I obtained slightly worse results($\rho = -2.65$, $r=0.983$). The correlation line curved somewhat upward from the meta line. The replacement of σ by σ^+ displayed a significant curvature with a ρ value of -1.67($r= 0.976$), wherein the OCH_3 substituents induced the marked deviation from the meta line. Thus, the one-parameter equation did not well fit the correlation of *para*-substituted DDMs. The author used, therefore, the two-parameter Yukawa-Tsuno equation,[8] $\log k/k_0=\rho(\sigma^0 + R\Delta\bar{\sigma}_R^+)$. The two-parameter treatment provided a better correlation(Eq. 2):

$$\log k/k_0= -2.33(\sigma^0 + 0.47\Delta\bar{\sigma}_R^+) + 0.017 \quad (r=0.996, s=0.09, n=15) \qquad \text{(Eq. 2)}$$

The ρ value of -2.33 is consistent with the development of a positive charge at the diazo carbon in the transition state, while the R value of 0.47 indicates an almost equivalent stabilization of the positive charge by both the inductive and the resonance contributions of the *para* substituents.

A comparison of the Hammett parameters between in Chloranil-DDMs systems(Eq. 1) and in DDQ-DDMs systems(Eq. 2) is of usefulness in obtaining some information about the transition states of these similar reactions. As well as the chloranil-DDMs reactions[13] the present DDQ reactions are postulated to proceed throught the polar transition state depicted below, thought the polar transition state of 1,3-dipolar addition can not be ruled out.



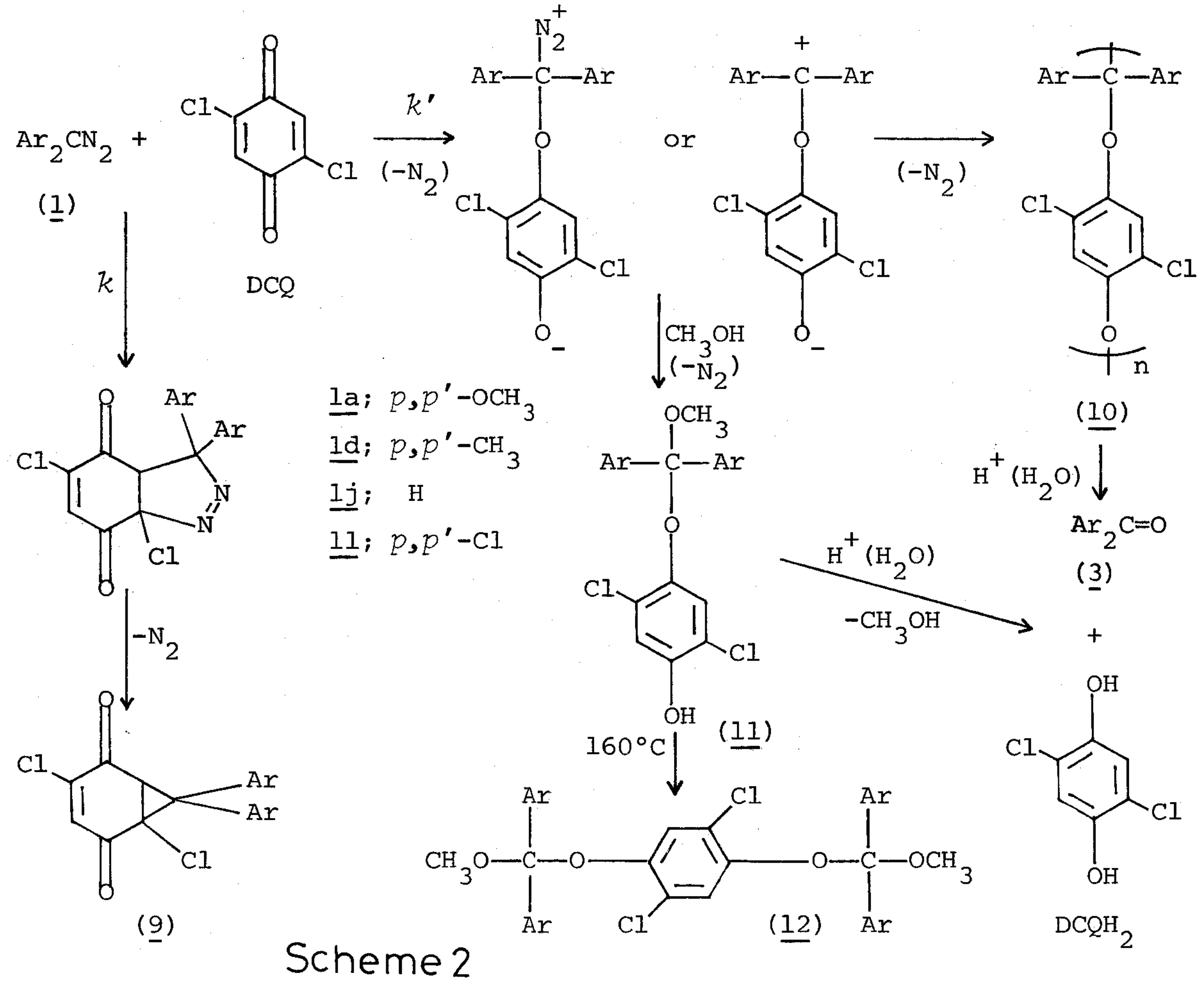
The negatively larger ρ value for DDQ reactions implies that DDQ induces a more positive charge in the diazo carbon, probably because its electron acceptability(1.95 eV) is stronger than that of chloranil(1.37 eV).[14] However, the extent of the resonance stabilization of the positive charge is lower in DDQ reactions(0.47) than in chloranil reactions(0.66)[14]

This discrepancy can be explained by speculating that the higher electron-acceptor ability of DDQ tends to develop more the bond between the diazo carbon and the quinone oxygen. That is, the sp^2 hybridization of the diazo carbon is reduced, and the effect of resonance contribution is thereby lessened, compared to the case of chloranil.

2-2-3 Reactions with 2,5-Dichloro-*p*-benzoquinone(DCQ)

(a) Product Study.

The reactions of disubstituted DDMs(1a,d,j,l) with an equimolar amount of 2,5-dichloro-*p*-benzoquinone(DCQ) were carried out in 1,2-dichloroethane at 30°C. The 1a having the *p,p'*-OCH_3 substituents violently decomposed with an evolution of N_2 and the immediate deposition of white precipitates, while the 1l having the *p,p'*-Cl substituents needed *ca.* 10 h for the complete disappearance of the diazo color. All these reactions gave considerable amounts of white precipitates. Filtrate was evaporated to dryness, followed by column chromatography on silica gel to give bicyclic diones(9)(Scheme 2).



Scheme 2

The ^{1}H NMR spectra showed the vinylic proton at the lower fields (δ, 6.60-6.65) and the cyclopropyl proton at the higher fields (3.58-3.67) in accordance with the bicyclic structure.

The precipitate part isolated in the case of 1a was gradually hydrolyzed into almost equimolar amounts of *p*,*p*′-dimethoxybenzophenone (3a) and 2,5-dichlorohydroquinone(DCQH$_2$) during the manipulation. However, the precipitates for 1d, 1j, and 1l were so stable that the complete hydrolyses needed refluxing for 8-20 h in aqueous methanol containing hydrochloric acid. These hydrolyses gave almost equimolar amounts of benzophenones(3d,j,l) and DCQH$_2$. Next, the author examined the effect of methanol as additive on the reaction features employing DDM(1j). No essential change was found in the yield of 9j, but a different product, 2,5-dichloro-4-[(methoxy)diphenylmethoxy]phenol(11), was provided instead of the precipitate. The 11 was easily hydrolyzed into 3 and DCQH$_2$ under the influence of hydrochloric acid, whereas a short-time heating slightly over its melting point(151°C) smoothly brought about the disproportionation to yield 2,5-dichloro-1,4-bis[(methoxy)diphenylmethoxy]benzene(12) and DCQH$_2$.

It can be suggested that the bicyclic diones(9) may be produced *via* 1,3-dipolar cycloaddition, followed by the rapid elimination of N$_2$ from the resulting pyrazolines, considering that methanol does not participate as an additive. With regard to the structure of white precipitates, poly(2,5-dichlorohydroquinone benzhydryl ether)s(10) are conceivable from the observations that the IR spectra of the stable precipitates for the 1d,j,l showed no carbonyl, but strong absorptions assignable to the ethereal bonds(1050 cm^{-1}, broad), and also that the hydrolyses gave equimolecular amounts of benzophenones and DCQH$_2$. In analogy with the reactions with chloranil[13] and DDQ[15], the formation of polyethers prompted the author to suggest the operation of the same mechanism in these polymerization reactions(Scheme 2). In fact, the presence of methanol as a trapping agent stopped the polymerization completely and afforded the methanolysis product, 11, instead of the polyether, though the [2+3] cycloaddition process leading to 9 was little affected.

The results are summarized in Table 4. The product ratios of 10 to 9 increased in the order of 1a > 1d > 1j > 1l, with the electron-donating ability of the substituents.

Table 4. Product distributions in the equimolar reactions of diaryldiazomethanes(1a,d,j,l) and 2,5-dichloro-*p*-benzoquinone (DCQ) in 1,2-dichloroethane at 30°C

DDMs	Additive	Reaction time(h)	Yield/ %a)		
			9	10	11
1a	—	1	10.5	85.1c)	—
1d	—	1	28.0	67.3c)	—
1j	—	2	38.1	59.7c)	—
1j	CH_3OHb)	2	37.6	—	58.6
1l	—	6	46.3	51.2c)	—

a) Yield as mole percentage based on 1. b) A five-fold molar excess was added with respect to 1j. c) Based on the benzophenones(3a,d,j,l) obtained by the hydrolyses of 10a,d,j,l.

A comparison of the present results with those observed in the reaction with diazomethane[3] and in the diaryldiazomethanes-chloranil[13] and -DDQ systems[15] is of some interest from the mechanistic point of view. The DCQ is known to react at the C=C bonds with two moles of diazomethane to produce the pyrazoline derivative,[3] while the C=O bonds of DCQ are unreactive toward diazomethane. On the other hand, the diaryldiazomethanes(DDMs) can react at both the C=O and the C=C bonds of DCQ. In contrast to the case of DCQ, the [2+3] cycloaddition process is not anticipated in the reactions of DDMs with chloranil[13] and DDQ,[15] where the C=O bonds selectively participate in the reactions. The lack of such bicyclic diones in the chloranil and DDQ reactions is certainly attributable to the larger steric hindrance due to the bulky Cl and/or CN substituents on either side of the C=C bonds, by which the approach of DDMs(even diazomethane and phenyldiazomethane) to the double bonds is inhibited.

It is also noticed that the polyethers derived from DCQ are more stable against solvolyses than those derived from chloranil or DDQ.[13,15] In addition, the presence of methanol in the chloranil or DDQ reaction inhibited the formation of polyether, as in the present case, but the initially resulting methanolysis products(4) like (11) futher underwent a nucleophilic attack by methanol to be converted into α,α-dimethoxydiphenylmethane and the respective hydroquinones.[13,15] These chemical observations are probably the results of the stronger electron-acceptor ability of chloranil and DDQ moieties than that of DCQ;[14] hence, the ethereal C-O linkage for the chloranil or DDQ reaction is much more subject to hydrolysis and methanolysis than that for the DCQ reaction.

(b) Kinetic Study.

The 1,2-dichloroethane solutions of 1a,d,j,l used for kinetic purposes were diluted by a factor of about 10 compared to those for the product study. Thus, the decompositions of 1a,d,j,l at 30°C could be followed spectrophotometrically over 60-70% reactions without the disturbance due to the suspension of polyethers(10). The observed second-order rate constants increased with the electron-donating ability of the *p*-substituents(Table 5).

Table 5. Observed second-order rate constants, $k$obsd, and the individual rate constants, k, and k', for the process giving bicyclic diones(9) and polyethers(10) in the reactions of 1 with DCQ in 1,2-dichloroethane at 30°C

DDMs	$10^3 k_{obsd}$/l mol^{-1}s^{-1}	$10^3 k$/l mol^{-1}s^{-1}	$10^3 k'$/l mol^{-1}s^{-1}
1a	463	51.0[a)]	412[a)]
1d	81.9	24.1	57.8
1j	14.9	5.81	9.09
1l	3.24	1.54	1.70

a) The values determined by multiplying $k$obsd by the relative yields of 9 and 10.

From the results in Tables 4 and 5, one can easily obtain the individual rate constants leading to the formations of 9 and 10 by multiplying the observed rate constants by the relative product ratios.

The rate constants, k and k', thus determined may also be seen in Table 5.

The dependence of the logarithmic rate constants on the Hammett σ constants[6] is shown in Fig. 3. As may easily be noticed, 9 formation gave an excellent linear dependence(Eq. 3):

$$\log k = -2.51-1.55\sigma \qquad (r=0.996, s=0.0735, n=4) \qquad \text{(Eq. 3)}$$

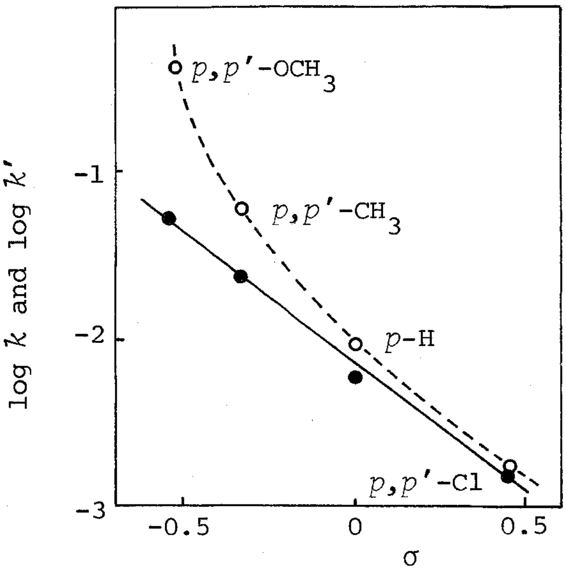
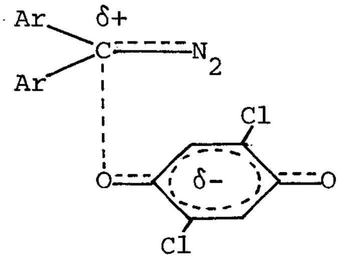


Fig. 3. Plots of log k(●) and log k'(o) against the Hammett σ constants.

However, the correlation line for the 10 process displayed an upward deviation, especially in the OCH$_3$ substituent. The replacement of σ by the Brown σ^+ constants[7] was also unsuccessful, causing a downward deviation. Therefore, the author attempted the two-parameter Yukawa-Tsuno equation.[8] The result of regression analysis indicates that the use of the two-parameter equation improves the correlation significantly (Eq. 4):

$$\log k' = -2.03-1.85(\sigma^0 + 0.515\Delta\bar{\sigma}_R^{+}) \qquad (r=1.00, s=0.0105, n=4) \qquad \text{(Eq. 4)}$$

A comparison of the ρ values in Eqs. 3 and 4 shows a larger susceptibility of the rate of the 10 process on the substituents than that of the 9 process. Also, the value of R=0.515 confirms that a substantial π-resonance stabilization of a transition state operates in the 10 process. By analogy to the mechanism of the reactions of DDMs with chloranil and DDQ, a similar transition state shown below is likely to account for the electronic demand.



On the contrary, the process leading to 9 may be through the 1,3-dipolar addition mechanism, since the rate constants were well correlated with the simple Hammett equation using normal σ values,[16] in accordance with the product analysis, where no essential change was found in the yield of the bicyclic dione(9j), as has been mentioned above.

In summary, it was found that the reactivities of diaryldiazomethanes (DDMs) toward chloranil, DDQ, and DCQ are governed by the structural and electronical nature of these quinones in addition to the substituents of DDMs. The DCQ reacted at both C=C and C=O bonds to give bicyclic diones and polyethers respectively by way of [2+3] cycloaddition and the betaine intermediates. On the other hand, the chloranil and DDQ gave only polyethers because the C=C bonds are sterically masked with the bulky Cl and/or CN substituents. However, the stronger electron acceptability of chloranil and DDQ made the polyethers more solvolyzable than DCQ. The results of the kinetic substituent effects indicated that the usual Hammett equation can be applied for the C=C bond reaction, but Yukawa-Tsuno equation for the C=O bond reactions, with both the negative ρ values, suggesting more or less the charge transfer from diazo carbon to the quinones.

2-3 Experimental

The IR and NMR spectra were recorded on Hitachi 215 and Varian EM-360 spectrometers respectively. The UV spectra were observed with Hitachi 323 and JASCO UVIDEC 505 instruments.

Materials.

The chloranil(2) was of commercial origin and was recrystallized twice from benzene; mp 290°C. The 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was of commercial origin and was recrystallized from dichloromethane; orange yellow needles, mp 213°C. The 2,5-dichloro-*p*-benzoquinone(DCQ) was prepared according to the procedure described by A. R. Ling[17] and was recrystallized from ethanol; pale yellow prisms, mp 164-166°C(lit, 161°C).[17] All the diaryldiazomethanes(DDMs) were made by the oxidation of the corresponding hydrazones with yellow mercury(II) oxide as has been described.[18] The physical properties of these diazoalkanes were all listed elsewhere[19] except for *p,p'*-dimethoxy-(mp 100-101°C (from ether) (lit,[20] mp 99-100°C), UV: λmax=540 nm(ε=85, THF)), *m*-nitro-(mp 53-54°C (petroleum ether-ether)(lit,[21] an oil), UV: 500 nm(ε=138, THF)), and *p*-nitrodiphenyldiazomethane(mp 80-83°C), UV: 500 nm(ε=326, THF)). The THF and benzene were refluxed over lithium aluminum hydride and then fractionated. The 1,2-dichloroethane was refluxed over phosphorus pentaoxide and then fractionated.

Kinetic Measurements.

(a) Reactions with Chloranil.

In order to satisfy the requirements of pseudo first-order treatment, the kinetic reactions were usually carried out in the presence of a 20- to 50-fold molar excess of chloranil with respect to DDMs. The change in optical density at the wavelength of the absorption maxima(524-525 nm) of DDMs(1a-m) was conveniently monitored because chloranil in THF is transparent in this region. The procedure was similar to that described in a previous paper.[19] In the case of the nitro-substituted DDMs(1n,o), however, the temperature of the reaction solutions was kept at 30±0.1°C by the use of a Haake circulator, and the absorption at 500 nm was followed over a 70-percent decomposition at certain time intervals. The pseudo first-order rate constants(*k*obsd) were determined graphically from plots of $-\ln x$ against the time, where x is the concentration of the remaining

DDMs. In all cases, excellent straight lines were obtained. Then, the second-order rate constants(k) obtained by dividing $k$obsd with the initial concentration of chloranil were reproducible to within ±3% (usually two determinations).

(b) Reactions with 2,3-Dichloro-5,6-dicyanobenzoquinone(DDQ).

The kinetic data were obtained according to the standard spectrophotometric methods. Solutions for kinetic experiments were prepared separately just before use in a volumetric flask equipped with a stopper. The DDQ solution(10^{-5}–10^{-3} mol dm^{-3}) was introduced into a stoppered quartz optical cell(10 mm) and kept at the given temperature within ±0.1°C in a thermostat-controlled cell-holder of a Hitachi 323 spectrometer. The reaction was initiated by the quick addition of the requisite volume of a DDMs solution(10^{-5}–10^{-3} mol dm^{-3}), which had been preheated in a water bath to the same temperature as the above cell-holder. The change in the maximum absorption(408 nm, ε=2750) of DDQ in benzene was conveniently monitored over at least two half-lives in the cases of the DDQs(1a-m), for these diazoalkanes and the products are essentially transparent at this wavelength. In the cases of nitro-substituted DDMs(1n,o), the additive absorption of these diazoalkanes(1n; ε=122, 1o; ε=290) and DDQ(ε=361) at 500 nm in benzene was followed. The second-order rate constants, k, were determined graphically from the plots of $\ln\{b(a-x)/a(b-x)\}/(a-b)$ against the time, where a and b are the initial concentrations of the DDMs and DDQ respectively, x being the consumed DDMs or DDQ. The rate constants were reproducible within ±3%(usually two determinations).

*(c) Reactions with 2,5-Dichloro-*p*-benzoquinone(DCQ).*

Values of k were determined spectrophotometrically as described[15] by monitoring the decrease of the absorption of DDMs(1a,d,j,l) at the maximum wavelength(524-540 nm) in the visible region.

Reactions of DDMs with Chloranil(2) in THF.

The reaction of diphenyldiazomethane(DDM, 1j) will be described below as a typical example; the reactions of the other DDMs were carried out similarly until the characteristic color of the diazo compounds had faded. To a THF solution(40 ml) of chloranil(2)(1.0 g, 4.07 mmol) was added, all at once, a THF solution(20 ml) containing DDM(0.79 g, 4.07 mmol) at 30°C. The purple color of DDM slowly disappeared with a slight evolution of N_2. After 6 h standing, the precipitate(0.8 g) which appeared was filtered, dried *in vacuo*, and submitted to IR measurement and elemental analysis. This white precipitate was completely hydrolyzed to benzophenone and $TCQH_2$ on 3 day exposure to atomosphere or by the addition of aqueous THF. The removal of the solvent, followed by the column chromatography(silica gel) of the hydrolyzed mixtures gave almost equimolar amounts of benzophenone(0.34 g, 46.0%) and $TCQH_2$(0.47 g, 46.5%), with benzene and ether as the eluents. The filtrate from the white precipitate was dried *in vacuo*, and the residue was treated with a small portion of aqueous THF for 1 h. The column chromatography of the hydrolyzed mixtures also gave equimolar amounts of benzophenone(0.37 g, 50.0%) and $TCQH_2$(0.52 g, 51.5%). The benzophenones(3a-o) were identified by a comparison of their IR and NMR spectra with those of authentic samples produced by the Friedel-Crafts reaction. The $TCQH_2$ was identified by a comparison of its IR spectrum with that of an authentic sample.[22]

Reaction of DDM with 2 in H_2O-THF.

To a THF solution(40 ml) of 2 (1.0 g, 4.07 mmol), was added, all at once, a THF solution(20 ml) containing DDM(0.79 g, 4.07 mmol) and H_2O (0.36 g, 20 mmol) at 30°C. After 6 h standing, the removal of the solvent, followed by column chromatography, gave tetrachlorohydroquinone dibenzhydryl ether(7)(40 mg, 3.4% based on DDM used), recovered 2(0.10 g, 10%), and benzophenone(0.64 g, 86%) with a petroleum ether-benzene mixture, and then $TCQH_2$(0.85 g, 84%) and benzhydrol(8)(50 mg, 6.7%) with a benzene-ether mixture. The product, 7 , was recrystallized from benzene; mp 190-192°C; IR(KBr): 1407, 949, and 689 cm^{-1}; NMR(δ, $CDCl_3$) 6.43(2H, s) and 7.28(20H, s); Found: C, 66.05; H, 3.89%. Calcd for $C_{32}H_{22}Cl_4O_2$: C, 66.23; H, 3.82%. Compound 7 was identified by a comparison of its IR and NMR spectra with those of an authentic sample given by the reaction of DDM with $TCQH_2$.

Reaction of DDM with 2 in CH_3OH-THF.

The reaction was carried out under conditions similar to those described in the H_2O-THF system. After 6 h standing, the removal of the solvent gave a pasty reaction mixture, the NMR spectrum of which showed the presence of large amounts of α,α-dimethoxydiphenylmethane(5). However, the 5 slowly hydrolyzed into benzophenone in the reaction mixture, so that the product analyses were made according to two different procedures. First, one-half of the reaction mixture was washed with 3×20 ml pentane to extract the 5. The pentane solution was shaken with a small portion of aqueous $NaHCO_3$(5%), washed with water, and dried over sodium sulfate. The concentration of the filtrated solution yielded crystalline 5(0.39 g, 85%), mp 106-107°C; IR(KBr): 1209, 1085, 1053, 987, and 689 cm^{-1}; NMR(δ, $CDCl_3$) 3.10(6H, s, OCH_3) and 7.13-7.57 (10H, m, aromatic H); Found: C, 78.98; H, 7.01%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%. Second, the other half of the reaction mixture was chromatographed(silica gel). Elution with a petroleum ether-benzene mixture successively afforded 7(25 mg, 4%), the recovered 2(0.11 g, 11%), and benzophenone(0.31 g, 84%), while elution with a benzene-ether mixture gave $TCQH_2$(0.42 g, 83%) and 8(30 mg, 8%). Thus, 5 was completely hydrolyzed to give benzophenone during the isolation process by the chromatography.

Reactions of DDMs with DDQ in Benzene. General Procedures:

A benzene solution(10 ml) of DDM(0.50 g, 2.58 mmol) was added, all at once, to a solution of DDQ(0.59 g, 2.60 mmol) in benzene(20 ml). The purple color of DDM suddenly disappeared with the vigorous evolution of N_2. After stirring for 1 h(one overnight standing for the nitro-substituted DDMs), the solvent was evaporated *in vacuo* to give an essentially colorless, resinous product, the IR spectrum of which showed no absorption in the C=O region. The product was then treated with a ten-fold excess of water or methanol for 10 min, with occasional shaking and dried under reduced pressure. The pasty residue thus obtained was triturated with 50 ml of benzene. Filtration gave $DDQH_2$(0.56-0.57 g, 94-96%). The filtrate was washed with aqueous sodium carbonate and dried over anhydrous sodium sulfate. The subsequent evaporation of benzene gave benzophenone(0.45 g, 96%) in the case of treatment with water or α,α-dimethoxydiphenylmethane(5)(0.48 g, 81%) and benzophenone (70 mg, 15%) in the case of treatment with methanol. The relative yields of 5 and benzophenone were determined by means of the NMR spectrum of the product mixture, while pure 5 was obtained by fractional crystallization from pentane. The benzophenones and 5 were identified by a comparison of the IR and NMR spectra with those of authentic samples.[13]

Reaction of DDM with DDQ in H_2O-Benzene.

A benzene solution(10 ml) of DDM(0.50 g, 2.58 mmol) and H_2O(0.23 g, 13 mmol) was added, all at once, to a solution of DDQ(0.59 g, 2.60 mmol) in benzene(20 ml). After stirring for 1 h, the removal of the solvent, followed by column chromatography(silica gel), gave 2,3-dichloro-5,6-dicyanohydroquinone dibenzhydryl ether(7)(35 mg, 5% based on the DDM used), and benzophenone(0.40 g, 85%) with a petroleum ether-benzene mixture, and then $DDQH_2$(0.49 g, 83%) and benzhydrol(8)(30 mg, 6%) with a benzene-ether mixture. The product, 7 , had a mp of 190-191°C(from benzene) (lit,[23] mp 189-190°C), IR(KBr): 2235, 1412, 993, 928, and 695 cm^{-1}; NMR(δ, $CDCl_3$): 6.67(2H, s) and 7.33(20H, s); Found: C; 72.94, H; 4.15, N; 4.94%. Calcd for $C_{34}H_{22}Cl_2N_2O_2$: C; 72.72, H; 3.95, N; 4.99%.

Reaction of DDM with DDQ in CH_3OH-Benzene.

A benzene solution(10 ml) of DDM(0.50 g, 2.58 mmol) and CH_3OH(0.42 g, 13 mmol) was added, all at once, to a solution of DDQ(0.59 g, 2.60 mmol) in benzene(20 ml). After stirring for 1 h, the reaction mixture was evaporated *in vacuo* and the pasty residue was triturated with benzene (50 ml). Filtration gave pure crystalline $DDQH_2$(0.54 g, 91%). The filtrate part was divided in equal parts and was examined by two different methods. One part was washed with aqueous sodium carbonate (5%), dried over sodium sulfate, and evaporated to dryness to give crystalline 5(0.26 g, 87%). The other part was evaporated, followed by column chromatography(silica gel) to give 7(30 mg, 4%) and benzophenone(0.20 g, 85%) with a petroleum ether-benzene mixture, and 8 (15 mg, 6%) with a benzene-ether mixture. Thus, 5 was completely changed into benzophenone on silica-gel-column chromatography.

Reactions of DDMs with DCQ in 1,2-Dichloroethane.

Reaction of DDM is described below as a typical example and the reactions of other diazoalkanes were carried out similarly till the diazo color completely disappeared. To a stirred 1,2-dichloroethane solution(30 ml) of DCQ(1.0 g, 5.65 mmol) was added dropwisely a 1,2-dichloroethane solution(10 ml) containing DDM(1.1 g, 5.67 mmol) at 30°C. After 2 h(1 h for 1a and 6 h for 1l) stirring, the white precipitate appeared was filtered, washed with small portion of 1,2-dichloroethane, and submitted for IR measurement. The precipitate in the case of 1a was easily hydrolyzed into *p,p'*-dimethoxybenzophenone(3a) and $DCQH_2$ on the work-up. While, the precipitates in the case of 1d,j,l were stable to be hydrolyzed only in refluxing aqueous methanol containing hydrochloric acid for 8-20 hr, giving corresponding benzophenones(3d,j,l) and $DCQH_2$. The column chromatography(silica gel) of the hydrolyzed products gave an almost equimolar amount of 3a,d,j,l(benzene as an eluent) and $DCQH_2$(benzene-ether). These compounds were identified by a comparison of their IR spectra with those of authentic samples.[13,17] On the other hand, the filtrate parts were dried *in vacuo*, and the residues were chromatographed on silica gel. Elution with benzene gave pure bicyclic diones(9). The structures of 9 were identified by means of the IR, the NMR, and the elemental analyses.

1,4-Dichloro-7,7-bis(p-methoxyphenyl)bicyclo[4.1.0]hept-3-ene-2,5-dione (9a). Pale yellow prisms(petroleum ether-benzene); mp 148-150°C. IR(KBr): 3055, 1693, 1509, 1243 cm^{-1}. NMR(δ, $CDCl_3$): 3.62(1H, s, cyclopropyl H), 3.73(3H, s, OCH_3), 3.77(3H, s, OCH_3), 6.65(1H, s, vinyl H), 6.8-7.5(8H, m, aromatic H). MS *m/e* 402(M^+). Found: C, 62.64; H, 4.05%. Calcd for $C_{21}H_{16}Cl_2O_4$: C, 62.54; H, 4.00%.

1,4-Dichloro-7,7-di-p-tolylbicyclo[4.1.0]hept-3-ene-2,5-dione(9d). Pale yellow prisms(ether); mp 151-153°C. IR(KBr): 3053, 1684, 1588, 1512, 1291, 1063, 995, 820 cm^{-1}. NMR(δ, $CDCl_3$): 2.27(3H, s, CH_3), 2.30(3H, s, CH_3), 3.62(1H, s, cyclopropyl H), 6.60(1H, s, vinyl H), 7.03(4H, s, aromatic H), 7.1-7.5(4H, m, aromatic H). MS: *m/e* 370(M^+). Found: C, 68.16; H, 4.41%. Calcd for $C_{21}H_{16}Cl_2O_2$: C, 67.94; H, 4.34%.

1,4-Dichloro-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione(9j).

Pale yellow prisms(petroleum ether-benzene); mp 179-180°C. IR(KBr): 3052, 1703, 1689, 1597, 1295, 1062, 996, 709 cm^{-1}. NMR(δ, $CDCl_3$): 3.67(1H, s, cyclopropyl H), 6.61(1H, s, vinyl H), 7.0-7.6(10H, m, aromatic H). MS:*m/e* 342(M^+). Found: C, 66.71; H, 3.59%. Calcd for $C_{19}H_{12}Cl_2O_2$: C, 66.49; H, 3.53%.

*1,4-Dichloro-7,7-bis(*p*-chlorophenyl)bicyclo*[4.1.0]*hept-3-ene-2,5-dione(9l).* Pale yellow prisms(benzene); mp 209-210°C. IR(KBr): 3051, 1701, 1677, 1584, 1485, 1087, 995, 833 cm^{-1}. NMR(δ, $CDCl_3$): 3.58 (1H, s, cyclopropyl H), 6.63(1H, s, vinyl H), 7.1-7.3(8H, m, aromatic H). MS:*m/e* 410(M^+). Found: C, 55.58; H, 2.48%. Calcd for $C_{19}H_{10}Cl_4O_2$: C, 55.37; H, 2.45%.

Reaction of DDM with DCQ in CH_3OH-CH_2ClCH_2Cl.

To a stirred 1,2-dichloroethane solution(30 ml) of DCQ(1.0 g, 5.65 mmol) a 1,2-dichloroethane solution(10 ml) containing DDM(1.1 g, 5.67 mmol) and a 5-fold molar excess of methanol(0.9 g) was added, drop by drop, at 30°C. In contrast to the reactions in the absence of methanol, no precipitate was found. After having been stirred for 2 h, the solvent was evaporated and the trituration of the resinous products with 3×30 ml pentane left 9j(0.72 g, 37%). The combined pentane solution was concentrated to afford 2,5-dichloro-4-[(methoxy)diphenylmethoxy]phenol(11); mp 151°C(dec), IR(KBr): 3520, 1476, 1203, 1002 cm^{-1}, NMR(δ, $CDCl_3$): 3.30(3H, s, OCH_3), 5.17(1H, s, OH), 7.0-7.8(12H, m, aromatic H), MS: *m/e* 343(M^+-OCH_3), Found: C, 64.03; H, 4.13%. Calcd for $C_{20}H_{16}Cl_2O_3$: C, 64.02; H, 4.26%. The 11 was easily hydrolyzed into benzophenone and $DCQH_2$ under the influence of aqueous methanol saturated with hydrochloric acid. When heated at 160°C for 2 min, however, the 11 underwent a disproportionation into 2,5-dichloro-1,4-bis[(methoxy)diphenylmethoxy]benzene(12) and $DCQH_2$. The 12 had a mp of 269-271°C(from benzene); IR(KBr): 1477, 1211, 1091, 991, 697 cm^{-1}, NMR(δ, $CDCl_3$): 3.20(6H, s, OCH_3), 7.0-7.7(22H, m, aromatic H), MS: *m/e* 539(M^+-OCH_3), Found: C, 71.55; H, 4.97; Cl, 12.60%. Calcd for $C_{34}H_{28}Cl_2O_4$: C, 71.45; H, 4.94; Cl, 12.40%.

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Chapter 3 Stereochemistry in the Reactions of Aryldiazomethanes with Chloranil

3-1 Introduction

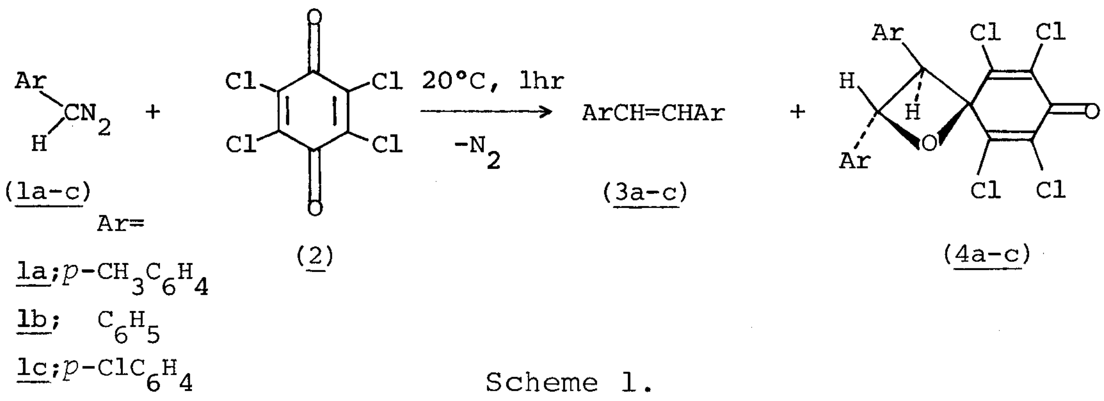
Eistert *et al.*[1] reported that diazomethane adds to the C=O bond of chloranil to afford epoxide. In chapter 2, the author showed that diaryldiazomethanes(DDMs) also add to the C=O bond but provide poly(tetrachlorohydroquinone benzhydryl ether)s instead of the epoxides. The difference in the reaction products is expected to be attributable to the change in the chemical natures of these diazoalkanes. In order to obtain further scope and information about the reactivities of diazoalkanes, it is of interest to know how aryldiazomethanes react with chloranil, because these diazoalkanes are located between diazomethane and diaryldiazomethanes in view of the sterical and electronical points.

This chapter describes the conversion of aryldiazomethanes into stilbenes and spiro-oxetanes in the reactions with chloranil. Stereochemical course of the reaction and the effects of solvents on the product distributions are discussed.

3-2 Results and Discussion

3-2-1 Reactions of Aryldiazomethanes with Chloranil

The reactions of aryldiazomethanes(1a-c) with chloranil(2) gave mainly *cis*- and *trans*-stilbenes(3a-c) and *trans*-spiro-oxetanes(4a-c), as is shown in Scheme 1. Besides 3 and 4, small amounts of several

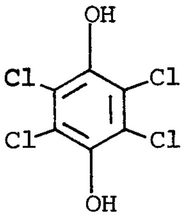


Scheme 1.

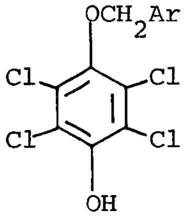
products were isolated: benzaldehydes(5'a-c), tetrachlorohydroquinone ($TCQH_2$), tetrachloro-4-(benzyloxy)phenols(6a-c), tetrachloro-1,4-bis(benzyloxy)benzenes(7a-c), and tetrachloro-4-[4'-(benzyloxy)butoxy]-phenols(8a-c).

ArCH=O

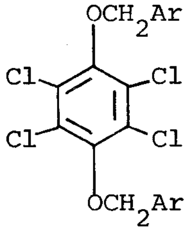
(5'a-c)



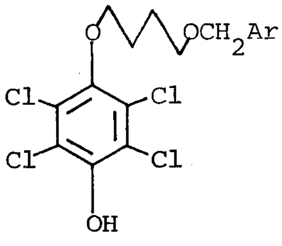
$TCQH_2$



(6a-c)



(7a-c)



(8a-c)

The 8 products were obtained only in the THF solution because these compounds incorporated the THF molecule. Since these by-products were afforded by the action of the residual water present in the solvent, a detailed mechanism will be presented later for the case of the reactions in the presence of CH_3OH or CF_3CH_2OH(see Section 3-2-2). The reaction conditions and the product distributions are summarized in Table 1.

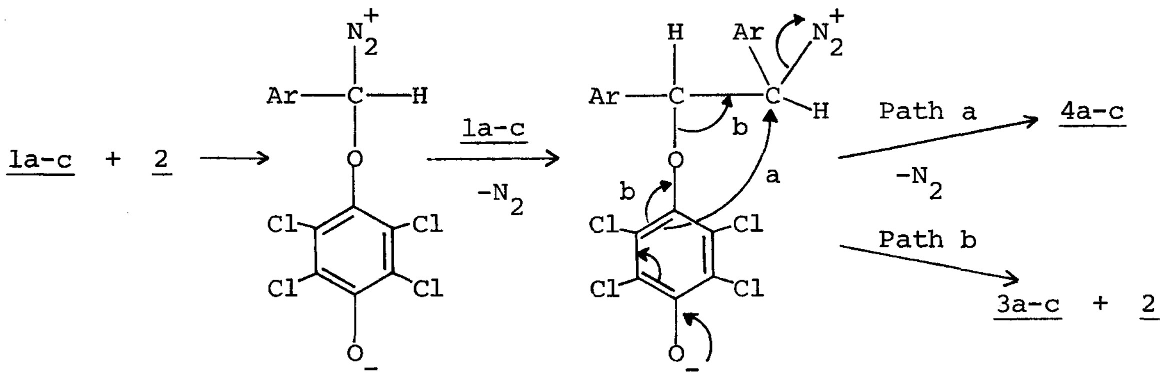
Table 1. Product distributions in the reactions of aryldiazomethanes (1a-c) with chloranil(2) in THF or CH_2ClCH_2Cl at 20°C[a)]

1a-c and 2 (mmol)		Solv.	Yield/ %[b)]						
			3(*cis/trans*)	4	5'	$TCQH_2$	6	7	8
1a(7.35)	2(2.03)	THF	69.0(2.4)	15.6	6	2	4	0.5	0.5
1b(8.47)	2(2.03)	"	75.5(2.8)	8.1	6	1	2.5	0.5	2.5
1b(8.47)	2(4.06)	"	73.7(2.8)	7.5	7	1.5	2.5	0.5	3
1c(6.58)	2(2.03)	"	72.3(3.2)	6.2	10	1	4	1	3
1a(7.35)	2(3.25)	CH_2Cl–CH_2Cl	60.0(2.2)	31.7	4	0.5	2	1	—
1b(8.31)	2(2.03)		59.7(2.5)	26.4	6	2	3.5	1	—
1c(5.92)	2(2.03)		59.5(2.9)	20.6	11	3	5	2	—

a) Reaction time 1 h. b) Yield as mole percentage based on 1 used.

In both THF and 1,2-dichloroethane, 3 were major products. The yield of 4 was considerably greater in 1,2-dichloroethane than in THF. Here, particular attention should be paid to the stereochemistry of 3 because the thermodynamically less stable *cis*-isomers were about 2 to 3 times more numerous than the *trans*-isomers, depending on the solvents and on the substituents of 1. On the other hand, 4 were shown to be the only stable *trans*-isomers by comparison with an authentic sample produced by the photoaddition of *trans*-3b and 2, and also by the fact that the thermal decomposition of 4 at slightly over their melting points for several minutes gave *trans*-3 and 2. As is exemplified in the case of 1b in THF, the ratio of 1 to 2 had no essential influence on the product distributions.

Mechanistically, the formation of 4 needs an intermediate because *cis*- or *trans*-3 was quantitatively recovered after 5-hs' mixing with an equimolar amount of 2 in THF or 1,2-dichloroethane at room temperature. The most reasonable process is the occurrence of the diazonium betaine intermediate(II) which can produce 4 or 3 by way of Path(a) or Path(b), as is shown in Scheme 2.



(I) (II)

Scheme 2.

Though II may be formed through the nucleophilic attack of 1 on the first diazonium betaine(I, or carbonium betaine given by the loss of N_2), the mechanism giving I remains unknown. However, three possible routes can be suggested. The first one is the radical-ion formation, followed by the simultaneous recombination presumed in the previous communication.[2] Radical cations of diazoalkanes have already been postulated or actually detected in the electrochemical oxidation[3] or in the reaction with copper(II) perchlorate.[4] However, no direct evidence for the presence of the radical cation of 1 could be obtained in the present system, though the radical anion of 2 was detected in the measurements of ESR and electronic absorption spectra.[2] The second possible route is the formation of 2,5-dihydro-1,3,4-oxadiazole through 1,3-dipolar cycloaddition between 1 and 2; the follow-up ring opening or loss of N_2 gives I or carbonium betaine. In fact, 1,3,4-oxadiazole was isolated in the reaction of diazomethane with duroquinone.[5] Other examples of the favoring of the 1,3,4-structure of oxadiazole were found in the reactions of DDM with diphenylketene[6] and of aryldiazomethanes with hexa- and pentafluoroacetones.[7] The last possible route is the direct attack of the diazo carbon on the oxygen atom of 2. Whichever route is adopted, it has to explain the observation that the qualitative N_2 evolution or disappearance of diazo color was accelerated in the order of 1a > 1b > 1c.

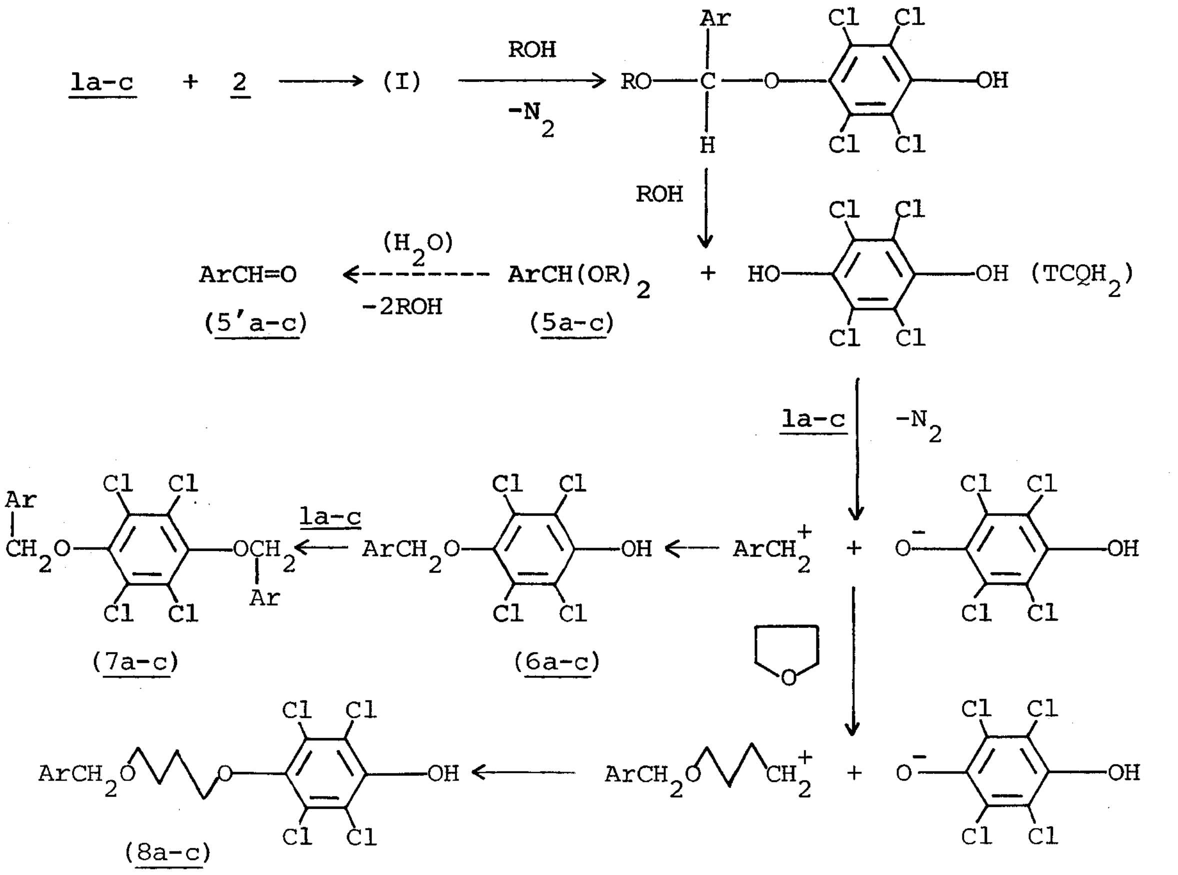
3-2-2 Effects of Additive CH_3OH or CF_3CH_2OH

To establish the validity of the I intermediate in the present reaction, it is useful to attempt capturing it with suitable nucleophilic reagents. Indeed, marked changes in the product distributions were found on the addition of CH_3OH or CF_3CH_2OH, as is summarized in Table 2. The reactions in the presence of CH_3OH gave only a trace amount of 3; instead, they afforded mainly acetals(5) and $TCQH_2$, along with 6, 7, and 8. The 5 were isolated as benzaldehydes(5') because of the easy degradation under the present acidic conditions as exhibited in the NMR measurement(see Experimental). These phenomena indicate that I undergoes a nucleophilic attack by CH_3OH rather than by 1 to turn into the redox products, as is formulated in Scheme 3. Furthermore, in this Scheme the formation of $TCQH_2$ may be responsible for the products, 6, 7, and 8, because this hydroquinone is so acidic as to decompose 1, as was confirmed in a comparative experiment using 1b and $TCQH_2$(Table 2). Both 6 and 7 are simple mono- and dietherification products of $TCQH_2$ with 1; however,

Table 2. Product distributions in the reactions of 1a-c with 2 in THF-CH_3OH or THF-CF_3CH_2OH and in the reaction of 1b with $TCQH_2$ in THF[a)]

1a-c, 2, and		Additive[b)]	Yield/ %[c)]						
(mmol)	$TCQH_2$		3	4	5′	$TCQH_2$	6	7	8
1a(7.35)	2(6.10)	CH_3OH	trace	ND[d)]	53	23	22	2	7
1b(8.47)	2(8.50)	"	trace	ND	52	13	19	3	18
1c(6.58)	2(6.10)	"	trace	ND	46	12	15	2	17
1b(8.47)	2(8.50)	CF_3CH_2OH	58(2.6)[e)]	6	24	11	3.5	1	3.5
1b(8.47)	$TCQH_2$ (8.47)	—	—	—	—	—	43	7	47

[a)] Reaction time 1 h, at 20°C. [b)] A four-fold excess was added with respect to 1. [c)] Yield as mole percentage based on 1.
[d)] Not detected. [e)] *cis/trans* ratio.



Scheme 3

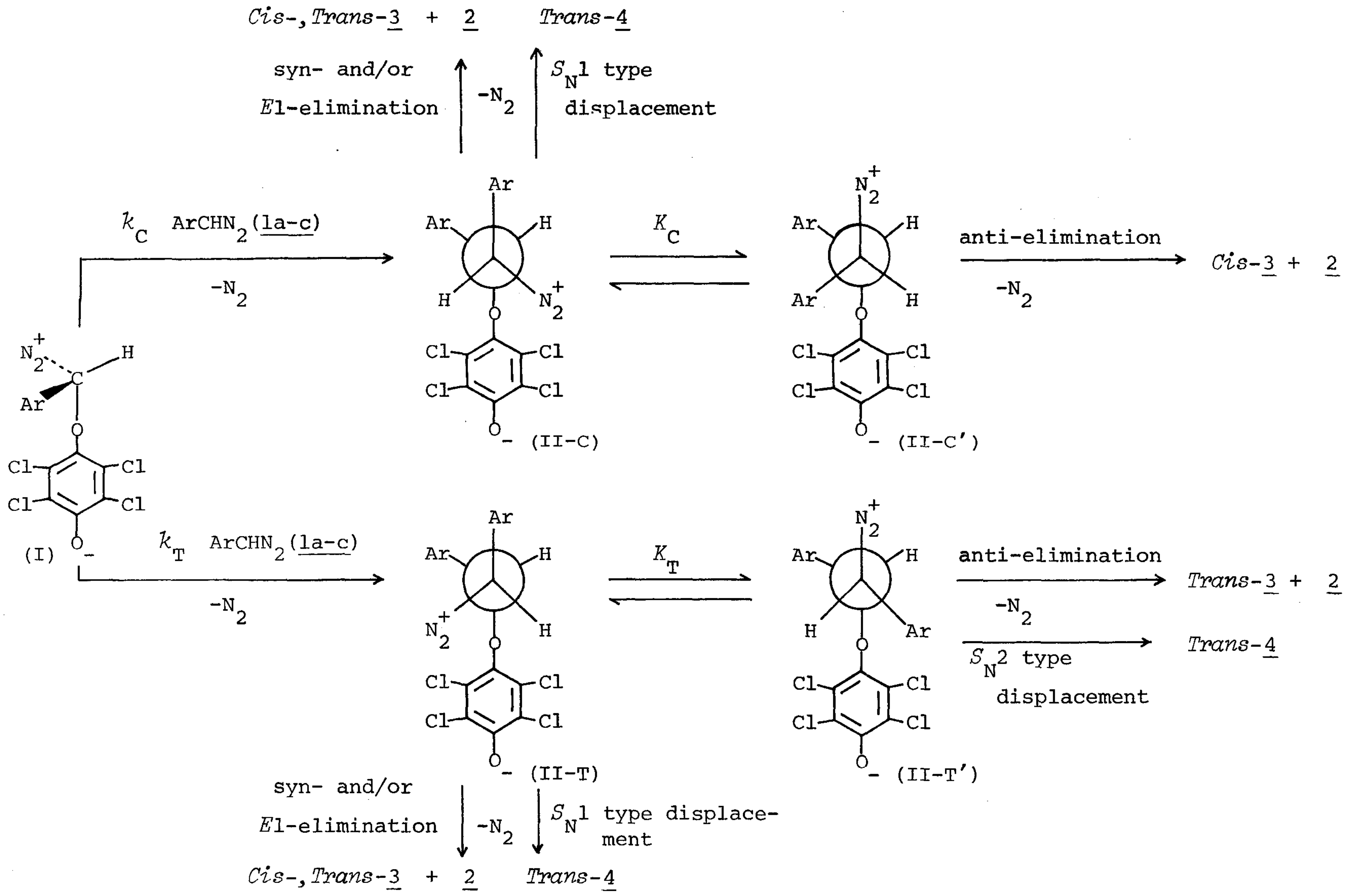
8 noticiably arises from the THF ring opening caused by the attack of the resulting benzyl cations.

On the contrary, the presence of CF_3CH_2OH allowed the substantial formation of 3b and 4b because of the lesser nucleophilic ability of this alcohol compared with CH_3OH. Keeping these results in mind, the appearance of small amounts of 5′, $TCQH_2$, 6 , 7 , and 8 in the absence of an additive may be attributed to the action of the residual water(ROH, R=H) present in the solvent in spite of careful drying; here unstable *gem*-diols seem to be produced instead of 5.

3-2-3 Stereochemistry in the Formation of Stilbenes and Spiro-oxetanes

Why does the major Path(b) preferentially yield *cis*-isomers rather than *trans*-ones, while the minor Path(a) selectively yields *trans*-isomers? These stereochemical phenomena can be well interpreted by considering the transition state leading to II and the subsequent N_2 elimination process giving 3 and 4. The nucleophilic attack of 1 on I should occur favorably through the transition state where the steric repulsion is as small as possible and where the opposite charges which appear attract each other.

As is pictured in Scheme 4, I contains a large chloranil moiety with a negative charge, a medium-sized aryl group, and a small H atom on the side remote from the N_2^+ group. Therefore, the approach of 1 to I from this side predominantly give such stable conformers as II-C and II-T, avoiding the most striking steric repulsion between the chloranil moiety and the aryl group of 1, and also satisfying the electronic requirement mentioned above. It should be noted here that the threomer II-C has a lower free energy than the erythromer II-T because the former can release some of the steric repulsion by placing the small H atom on the most hindered space between the chloranil moiety and the aryl group. Accordingly, the formation of II-C is more accelerated than II-T($k_C > k_T$). However, in the conformational rotation to II-C′ and II-T′, the equilibrium constant, K_C , is apparently smaller than K_T because II-C′ has the highest free energy among these four isomers from the sterical point of view(Scheme 4). In view of the steric orientations of these


Cis-, Trans-3 + 2
Trans-4
syn- and/or
E1-elimination
-N2
SN1 type
displacement
kC ArCHN2(1a-c)
-N2
Ar
H
N2+
KC
Ar
Cl
O
(II-C)
(II-C′)
anti-elimination
-N2
Cis-3 + 2
N2+
C
(I)
kT ArCHN2(1a-c)
-N2
KT
(II-T)
(II-T′)
anti-elimination
-N2
Trans-3 + 2
Trans-4
SN2 type
displacement
syn- and/or
E1-elimination
-N2
SN1 type displacement
Cis-, Trans-3 + 2
Trans-4

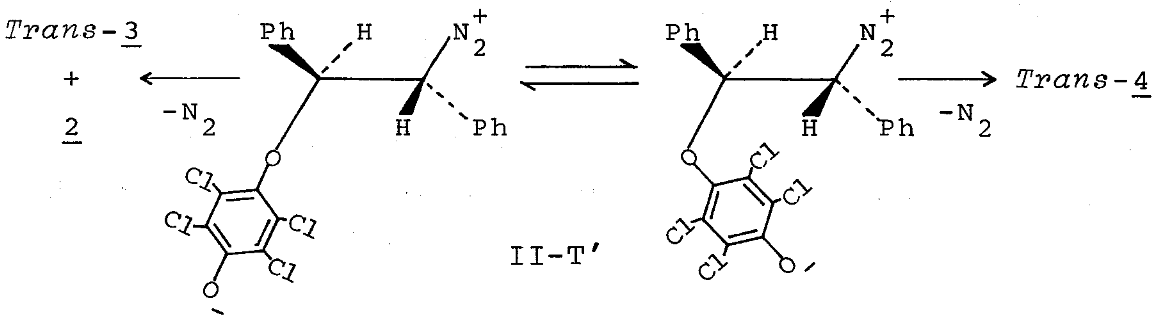
Scheme 4

isomers, it may be thought that the stereochemistry of the products depends on how great extent the respective isomers contribute to the product formations. As is represented in Scheme 4, the more populous II-C and II-T will afford *cis*-*trans* mixtures of 3 *via* the syn- and/or *E*1-type elimination, and *trans*-4 *via* the intramolecular S_N1-type displacement. On the other hand, the less populous II-C′ will prefer to give *cis*-3 *via* the anti-elimination. II-T′ will prefer to give *trans*-3 *via* the anti-elimination and *trans*-4 *via* the intramolecular S_N2-type displacement(Scheme 4).

From these stereochemical considerations, the present high yield of *cis*-3 can be reasonably explained as being responsible for the significant contribution of II-C′. Otherwise, the product distributions from the other conformers, II-C, II-T, and II-T′, would result in an excess formation of *trans*-3 relative to *cis*-3, conflicting with the present results(Table 1). Therefore, it may be suggested that the rate of the product formation from II-C′ and II-T′ is much more rapid than that from II-C and II-T.

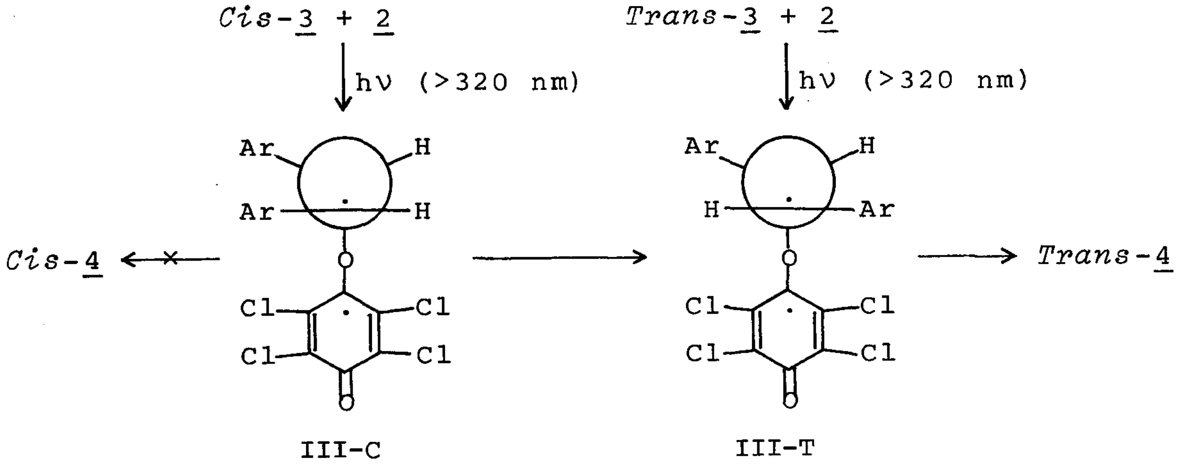
A further examination of Table 1 indicates the presence of the substituent effects on the product distributions. The substituents of 1 affect the relative ratios of II-C to II-T, since the stronger the nucleophilicity of 1, the weaker the stereoselective attack of 1 on I becomes, as is supposed by the reactivity selectivity principle(RSP).[8] This assumption is good agreement with the facts that the *cis*/*trans* ratio of 3 decreases, with the increase in the nucleophilic activity of 1.

It should be also noted here that the S_N2-type displacement giving *trans*-4 is only possible when the bent ether linkage of these rotamers can be aligned so as to build up a four membered ring with the central C-C bond as represented in the conformational equilibrium of II-T′(Scheme 5).



Scheme 5

However, II-C′ will not be transformed into such a crowded structure on account of the unfavorable phenyl-phenyl cis repulsion. This steric repulsion is the reason why *cis*-4 was not formed in the present reaction. In accordance with this sterical idea, we obtained *trans*-4b alone in 77.8 or 79.2% yield on the 3-h irradiation of a benzene solution of *trans*- or *cis*-stilbene containing an equimolar amount of 2(50 mmol dm^{-3}), using a high-pressure mercury lamp at 20°C: photochemical oxetane formation from olefins and C=O compounds is well known to proceed *via* a biradical intermediate,[9] such as III-C(from *cis*-stilbene) and III-T(from *trans*-stilbene); the former seems to afford no *cis*-4 because of the highly crowded orientation as well as II-T and II-C′, but it does afford *trans*-4 after pre-transformation into the stable III-T(Scheme 6).



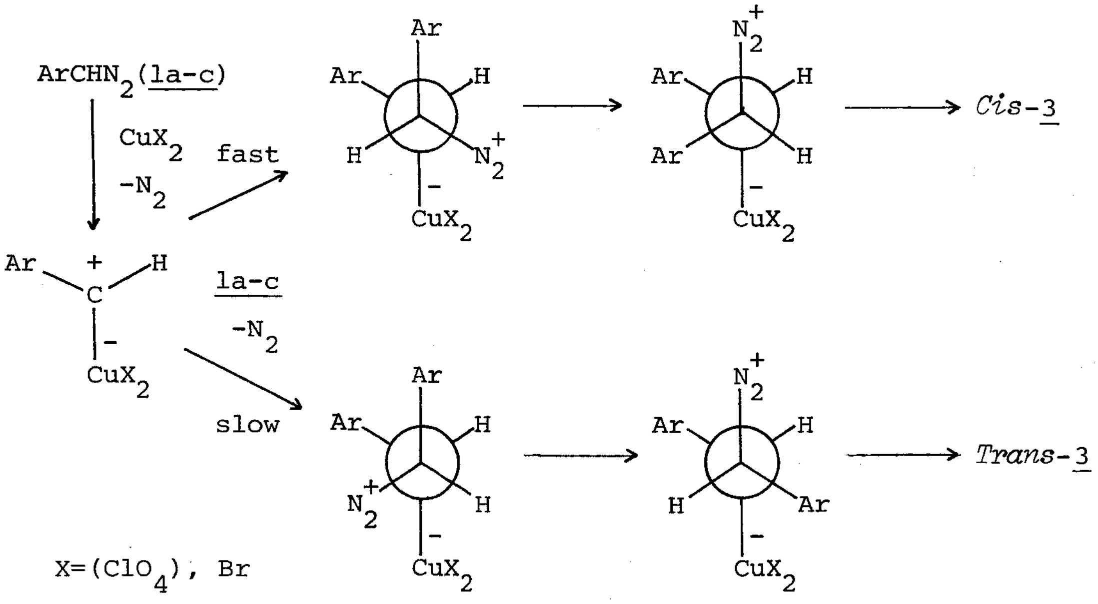
Scheme 6

As an evidence in support of the stereochemical consideration above mentioned, the author found that 1a-c easily decompose to *cis*- and *trans*-3a-c when treated with a small amounts of Lewis acid such as copper perchlorate or copper bromide. The preferential formation of *cis*-isomer is particularly noteworthy (Table 3).[10] Mechanistically, copper carbenoid intermediate can be put forward for this case. Therefore, the intriguing stereochemical results can be reasonably explained by considering the subsequent attack of 1a-c toward the resulting carbenoid on the basis of the steric and the electronic effects in a similar manner as the present reaction of 1a-c with 2(Scheme 7).

Table 3. *Cis:trans* ratios of stilbenes(3a-c) in the reactions of aryldiazomethanes(1a-c) with copper perchlorate or copper bromide in acetonitrile[a)]

$ArCHN_2$(1a-c) (mmol)		Catalyst[b)] (mmol)	Temp. (°C)	Reaction time(hr)	ArCH=CHAr(3a-c) Yield(%) (*cis/trans*)[c)]
		$Cu(ClO_4)_2$			
1a	2.10	0.01	20	1	80.2(1.59)
1b	2.00	0.01	40	1	73.5(1.74)
1b	2.00	0.01	20	1	86.2(1.81)
1b	2.00	0.01	0	2	81.9(1.93)
1c	2.60	0.01	20	1	92.5(2.47)
		$CuBr_2$			
1a	2.10	0.01	20	1	79.5(1.36)
1b	2.00	0.01	20	1	77.2(1.52)
1c	2.60	0.01	20	1	85.5(2.23)

a) In 10 ml of solvent. b) Acetonitrile solution(0.2-0.3 ml) was added.
c) Determined by high performance liquid chromatography.



Scheme 7

The high *cis*-to-*trans* ratio of 3 in the decomposition of 1a-c with catalytic ammonium cerium(IV) nitrate has already reported by Trahanovsky and his coworkers.[11] Anselme *et al*. also observed the predominant formation of *cis*-3 from the action of lithium-bromide on 1a-c.[12] However, unequivocal explanation of the high yield of the *cis*-isomer is lacking.

3-2-4 Solvent Effects

(a) Cis- *to* trans-*Products Ratios*.

As shown in Table 1, THF brings about the higher *cis*:*trans* ratios of 3 and the lower relative yields of 4 than 1,2-dichloroethane. This section is aimed to make the more penetrating interpretation about the effects of solvents on the stereochemical phenomena and on the product distributions. The results in a wide variety of aprotic solvents are tabulated in Table 4.

Table 4. Product distributions on the reaction of phenyldiazomethane (1b) with chloranil(2) in various aprotic solvents

	Solvent	Relative Yields[a)]	
		3 (*cis*/*trans*)	4
1	Diethyl ether	67.7(5.01)	32.3
2	Dibutyl ether	65.3(4.89)	34.7
3	Dipropyl ether	66.7(4.75)	33.3
4	Carbon tetrachloride	57.7(4.55)	42.3
5	Dimethoxymethane	69.6(4.46)	30.4
6	Tetrahydropyran	78.4(4.32)	21.6
7	Cyclohexanone	86.2(4.03)	13.8
8	Butyl acetate	83.2(3.97)	16.8
9	1,4-Dioxane	70.9(3.94)	29.1
10	1,2-Dimethoxyethane	81.9(3.89)	18.1
11	Tetrahydrofuran	78.9(3.77)[b)]	21.1
12	Benzene	60.3(3.70)	39.7
13	Chloroform	59.4(3.65)	40.6
14	Methyl acetate	81.1(3.53)	18.9

Table 4. (Continued)

	Sovlent	Relative Yields[a)]	
		3 (*cis*/*trans*)	4
15	Isopropyl acetate	79.4(3.45)	20.6
16	Ethyl methyl ketone	87.1(3.40)	12.9
17	1,1-Dichloroethane	63.9(3.39)	36.1
18	1,2-Dichloroethane	61.6(3.34)[b)]	38.4
19	Propyl acetate	77.8(3.16)	22.2
20	Nitrobenzene	78.7(3.08)	21.3
21	Butyronitrile	82.3(2.97)	17.7
22	Propionitrile	77.7(2.96)	22.3
23	Acetone	82.9(2.89)	17.1
24	Dichloromethane	59.4(2.88)	40.6
25	Ethyl acetate	81.3(2.71)	18.7
26	Benzonitrile	71.1(2.31)	28.9
27	Acetonitrile	78.2(2.23)	21.8
28	Nitromethane	72.6(1.92)	27.4

[a)] Total yields of 3 and 4 exceeded 50% in most cases.

[b)] The present values determined by the high performance liquid chromatographic analyses are somewhat different from the data obtained by an usual column chromatographic separation method and NMR measurements(see Table 1), probably because of the degradation of 4 into *trans*-3 and 2 in the column chromatographic treatment.

It is noteworthy that the thermodynamically less stable *cis*-3 was preferentially formed, *ca*. 2 to 5 times more than *trans*-3. The isomer ratios of 3 were high in acyclic ethers, such as diethyl ether and dipropyl ether, but considerably decreased in nitro compounds and nitriles. However, 4 was found to be a stable *trans*-isomer in any solvent, and its relative yields increased in the nonpolar solvents, such as benzene and carbon tetrachloride.

In the nucleophilic attack of 1, basic and polar solvents tend to stabilize the cation center of I, and thereby appear to suppress its reactivity. As a guiding principle of chemical behavior, the reactivity-selectivity principle(RSP)[8] suggests that the less reactive the diazonium betaine, I , the more stereoselective will be the attack of 1. Assuming that most of the 3 and 4 arise from the II-C′ and II-T′ conformers, as has been mentioned above, the molar ratios of *cis*-3 to the sum of *trans*-3 and 4 may be said to be approximately parallel to the rate ratio(k_C/k_T).

Keeping these considerations in mind, the author preliminarily attempted to correlate the logarithms of the molar ratios of *cis*-3 to the sum of *trans*-3 and 4 with such empirical solvent-basicity parameters as D_{π}[13], Kagiya's $\Delta\nu_D$[14], Gutmann's *DN*[15], and Kamlet-Taft's β.[16]

When correlated with these conventional parameters, the regression equations are as follows: log *cis*-3/(*trans*-3 + 4) = $0.142+0.149D_{\pi}$ (r=0.782, n=24), = $-0.00512+0.0027\Delta\nu_D$ (r=0.731, n=22), = $-0.0337+0.0115DN$ (r=0.808, n=14), and = $-0.142+0.698\beta$ (r=0.727, n=13), where r and n are the correlation coefficients and the number of data points respectively. However, the correlations with the solvent-polarity parameters, *i.e.*, the Kirkwood function[17] of dielectric constants ε, $f(\varepsilon)=(\varepsilon-1)/(2\varepsilon+1)$ and Dimroth and Reichart's E_T values,[18] provided worse results for f(ε), (r=0.156, n=23) and for E_T, (r=0.102, n=20). Thus, the specific role of the solvent basicity is much more important than its polarity effects. These statistical results are substantially in accordance with the above assumption that the further stereoselective formation of II-C is achieved by the nucleophilic solvation of the cation of I. The better correlation with D_{π} than with $\Delta\nu_D$ or β is suggestive of a soft acidity of the cation center(N_2^+) of I, because the indicator compounds employed for the determination of D_{π} and $\Delta\nu_D$ or β are typical soft-acid TCNE and hard-acid methanol or phenol respectively.[19] Though D_{π} is a slightly less successful parameter than *DN*, the ten more available values for D_{π} force the author to adopt this parameter in the present discussion.

The more basic and the more polar the solvents are, the easier the conformational rotation into II-C′ and II-T′ will be. Thus, II-C′ and II-T′ play a much more significant role in the product distributions, ultimately increasing the net amount of *cis*-3. Therefore, we attempted to improve the above unsatisfactory correlation by the use of two parameters, D_π and the polarity parameter, f(ε) or E_T. Equations 1 and 2 were obtained for the D_π-f(ε) and D_π-E_T systems respectively.

$$\log \frac{\textit{cis}\text{-}\underline{3}}{\textit{trans}\text{-}\underline{3} + \underline{4}} = -0.105+0.169D_\pi+0.632\mathrm{f}(\varepsilon) \qquad (r=0.863, s=0.0684, n=23) \quad \text{(Eq. 1)}$$

$$\log \frac{\textit{cis}\text{-}\underline{3}}{\textit{trans}\text{-}\underline{3} + \underline{4}} = -0.0957+0.155D_\pi+0.00589E_T \qquad (r=0.801, s=0.0801, n=20) \quad \text{(Eq. 2)}$$

The positive coefficients of both D_π and f(ε) or E_T are in harmony with the hypothesis that the solvent with a more basic and polar nature induces a more stereoselective formation of II-C than II-T and promotes the conformational transformation into II-C′ and II-T′. A plot of log *cis*-3/(*trans*-3 + 4)(obs) *versus* log *cis*-3/(*trans*-3 + 4)(calc) according to Eq. 1 is shown in Fig. 1.

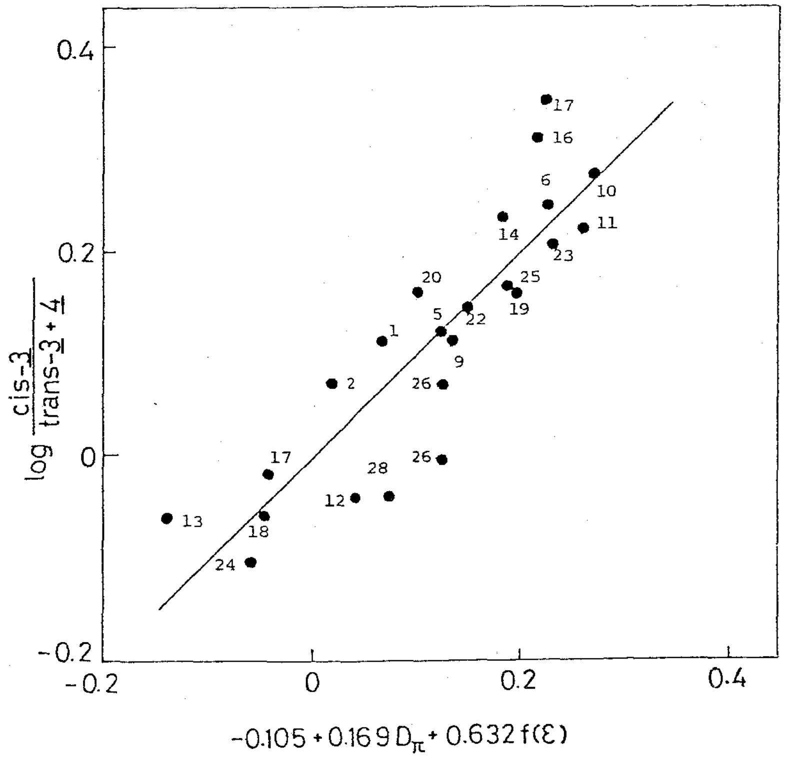


Fig. 1. Plot of log *cis*-3/(*trans*-3 + 4)(obs) *versus* log *cis*-3/(*trans*-3 + 4)(calc) according to Eq. 1; for point number, see Table 4.

It is noticeable that nonpolar solvents, such as benzene and carbon tetrachloride, afforded exceptionally lower *cis*-3 values with respect to the *trans*-products; *i.e.*, the logarithmic ratios were below null. These phenomena may be attributed to the more significant participation of the minor syn- and/or *E*1-type elimination and S_N1-type displacement, most probably from II-C. The reason for this may be that the conformational rotation into II-C′ is energetically more costly compared to the corresponding transformation of II-T into II-T′.

(b) *Spiro-oxetane(4) to* trans-*Stilbene(3) Ratios.*

It is also interesting to examine the solvent effects on the competitive S_N2-type and anti-elimination processes, giving 4 and *trans*-3, from II-T′, because the solvent-dependent equilibrium situation between the extended and the crowded structures, as represented in Scheme 5, plays a significant role in these product ratios. The more basic and more polar solvents are liable to separate the opposite charges of II-T′, so that the amount of 4 decreases as a result of the reduced contribution of the crowded structure. On the other hand, in the less basic and less polar solvents the opposed charges should come close together; thus, the growing participation of the crowded structure increases the formation of 4. A similar type of solvent contribution to product distributions can be expected for the minor S_N1- and/or *E*1-type elimination processes. In consideration of this, the author attempted to correlate the logarithms of the molar ratios of 4 to *trans*-3 with the linear combination of two parameters, D_π and f(ε) or E_T. Equations 3 and 4 were thus obtained:

$$\log \frac{\underline{4}}{trans\text{-}\underline{3}} = 1.07-0.232D_\pi-2.37f(\varepsilon) \quad (r=0.921,\ s=0.0937,\ n=23) \text{ (Eq. 3)}$$

$$\log \frac{\underline{4}}{trans\text{-}\underline{3}} = 2.16-0.259D_\pi-0.0514E_T \quad (r=0.930,\ s=0.0883,\ n=20) \text{ (Eq. 4)}$$

The negative coefficients in both the basicity and the polarity parameters are consistent with the solvation environment expected above.

A comparison of the coefficients in Eqs. 1 and 2 with those in Eqs. 3 and 4 shows that the effects of the solvent basicity are more enhanced in log *cis*-3/(*trans*-3 + 4) than in log 4/*trans*-3. The reverse is necessarily true for the contribution of the solvent polarity. A plot of log 4/*trans*-3(obs) *versus* log 4/*trans*-3(calc) according to Eq. 4 is shown in Fig. 2.

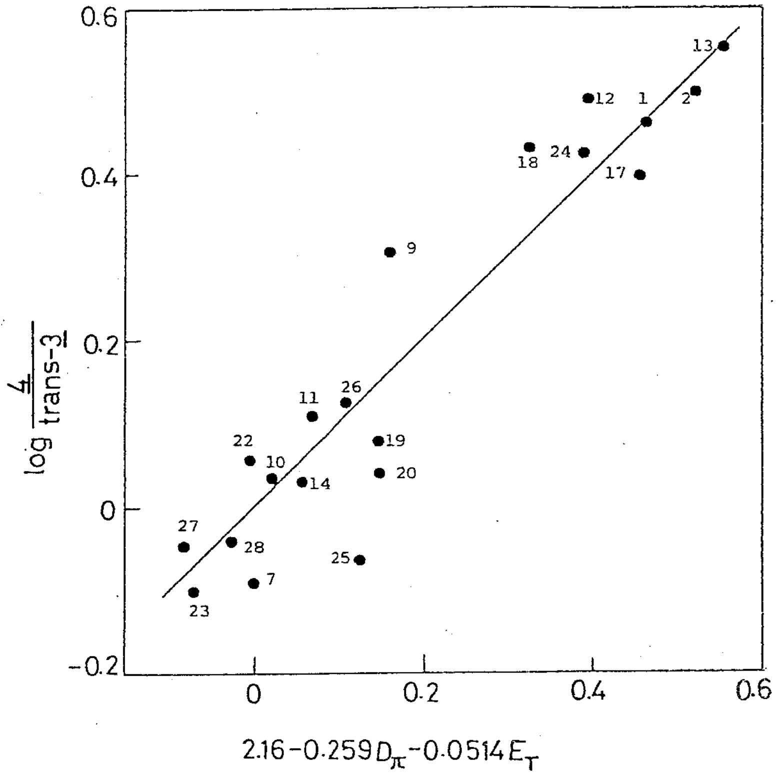


Fig. 2. Plot of log 4/*trans*-3(obs) *versus* log 4/*trans*-3(calc) according to Eq. 4; for point numbers, see Table 4.

This figure consists of two solvent groups except for 1,4-dioxane. One group on the high side contains aliphatic chlorinated solvents(very low D_π and moderate high E_T) and acyclic ethers and benzene(moderate high D_π and very low E_T). Therefore, the high 4:*trans*-3 ratios can be ascribed to the low D_π or E_T values; that is, these solvents can not well stabilize the cation or anion center of II, increasing the population of the crowded structures. On the other hand, the other group on the low side is characterized by such solvent properties as a relatively strong nucleophilicity(high D_π) and/or electrophilicity(high E_T). Thus, the ketones, such as acetone and cyclohexanone, reduce the 4:*trans*-3 ratios much more because of both the effective nucleophilic and electrophilic solvations of the respective cation N_2^+ and anion chloranil moieties of II, consequently decreasing the population of the crowded structures. Though the esters have D_π values very close to those of ketones, the 4:*trans*-3 ratios appreciably increased on account of the slight decrease in E_T values. Similarly, though the E_T values for nitro compounds and nitriles are higher than those for ketones, the less basic properties (lower D_π) of these solvents induce more formation of 4.

In summary, aryldiazomethanes(1) behave differently toward chloranil (2) than in the epoxide and polyether formation in the cases of diazomethane[1] and diaryldiazomethanes[20]. Stilbenes(3) and spiro-oxetanes (4) were formed from the diazonium or carbonium betaine intermediate under the stereocontrolled conditions which furnished *cis*-rich for 3 and only the *trans*-isomer for 4. Thus, the stereochemistry and the product distributions were markedly affected by the basicity and polarity of the solvents.

3-3 Experimental

The NMR spectra were obtained with a Varian EM-360 instrument. The IR and UV spectra were recorded with a Hitachi 215 infrared spectrometer and a 323 spectrophotometer respectively. The ESR spectra were observed with a JEOL JES-NE2X instrument. The *cis*:*trans* ratios of 3 and the overall yields of 3 and 4 were determined by column chromatographic separation(on silica gel) and NMR measurements, or by means of JASCO tri-rotor high-performance liquid chromatography(H. P. L. C.) using naphthalene as the internal standard. The H. P. L. C. analysis was carried out at room temperature using a 250×4.5 mm column packed ODS (octadecyl silane)on silica gel; methanol-water(4:1 by volume); flow rate, 1.0-1.5 ml/min. The UV detector was calibrated at 280 nm with standard mixtures of known concentrations of *cis*- and *trans*-3 and 4. The average error in the *cis*:*trans* ratio was *ca.* 3% or better. The relative retention times were as follows: naphthalene(1.0), *cis*-3(1.8), *trans*-3(2.3), and 4(4.5).

Materials.

The chloranil(2) was commercially obtained and was purified by recrystallization from dry THF; mp 290°C. The oily aryldiazomethanes (1a-c) were prepared just before use by the method of Closs and Moss[21] and were used without further purification. All solvents used were purified by the usual method.[22]

Reactions of Aryldiazomethanes(1a-c) with Chloranil(2).

These reactions were carried out in THF and 1,2-dichloroethane. The general procedures are exemplified in the case of 1a in THF as follows. To a stirred solution of 2 (0.5 g, 2.03 mmol) in 20 ml of dry THF, the author added, drop by drop, a THF solution(10 ml) containing 1a(0.97 g, 7.35 mmol) over a 10-min period at 20°C. The color of the solution was suddenly darkened by the addition of 1a, and then it gradually faded with the vigorous evolution of N_2. After 1 h's standing, the removal of the solvent *in vacuo* gave a pasty reaction mixture. The washing of this mixture with 3×20 ml pentane and then with a small portion of ether left recovered 2(130 mg) and 4a(260 mg, 15.6%); the amount of 4a was determined by the NMR measurement using an internal standard($CHCl_2CHCl_2$, δ= 5.8(s)), while its analytical sample was obtained by fractional crystallization from benzene-petroleum ether. The evaporation of the solvent (pentane-ether) gave an oily residue(1.21 g), which was submitted to NMR measurement. The spectrum showed the formation of excess *cis*-3a compared with its *trans*-isomer, as was confirmed by subsequent chromatographic treatment(on silica gel). Elution with pentane gave, successively, *cis*-3a(374 mg, 49%) and *trans*-3a(155 mg, 20%), while elution with a petroleum ether-benzene mixture gave 7a(8 mg, 0.5%), 2(55 mg), 5'a (53 mg, 6%), 6a(103 mg, 4%), and 8a(16 mg, 0.5%), and subsequent elution with a benzene-ether mixture gave $TCQH_2$(40 mg, 2%) and a small amount of an unidentified solid. The structures of 3a-c, 4a-c, 6a-c, 7a-c, and 8a-c were determined by elemental analyses, and the IR and the NMR spectra.

p,p'-Dimethylstilbene(*cis*-3a); colorless oil. NMR(δ, $CDCl_3$): 2.28(6H, s, CH_3), 6.45(2H, s, vinyl H), 6.88-7.20(8H, q, aromatic H). Found: C, 92.13; H, 7.82%. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74%.

p,p'-Dimethylstilbene(*trans*-3a); colorless leaflets(ether); mp 179-180°C.

NMR(δ, CDCl$_3$): 2.30(6H, s, CH$_3$), 6.90(2H, s, vinyl H), 6.95-7.40(8H, q, aromatic H). Found: C, 92.24; H, 7.80%. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74%.

Stilbene(*cis*-3b); colorless oil. NMR(δ, CDCl$_3$): 6.57(2H, s, vinyl H), 7.22(10H, s, aromatic H). Found: C, 92.94; H, 6.69%. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71%.

Stilbene(*trans*-3b); colorless leaflets(ether); mp 123-124°C. NMR (δ, CDCl$_3$): 7.07(2H, s, vinyl H), 7.17-7.57(10H, m, aromatic H). Found: C, 93.20; H, 6.70%. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71%.

p,p'-Dichlorostilbene(*cis*-3c); colorless oil. NMR(δ, CDCl$_3$): 6.47 (2H, s, vinyl H), 7.07(8H, s, aromatic H). Found: C, 67.38; H, 4.06%. Calcd for $C_{14}H_{10}Cl_2$: C, 67.50; H, 4.02%.

p,p'-Dichlorostilbene(*trans*-3c); colorless leaflets(ether); mp 178-181°C. NMR(δ, CDCl$_3$): 7.0(2H, s, vinyl H), 7.37(8H, s, aromatic H). Found: C, 67.09; H, 4.11%. Calcd for $C_{14}H_{10}Cl_2$: C, 67.50; H, 4.02%.

2,3,5,6-Tetrachloro-trans-*3',4'-di*-p-*tolylspiro* [*2,5-cyclohexadiene-1,2'-oxetan*]*-4-one (4a)*. Colorless prisms(benzene-petroleum ether); mp 154°C(dec). IR(KBr): 1675, 1111, 953, 800, 718 cm^{-1}. NMR(δ, CDCl$_3$): 2.35(3H, s, CH$_3$), 2.40(3H, s, CH$_3$), 4.93(1H, d, *J*=9.3 Hz), 6.67(1H, d, *J*=9.3 Hz), 6.83-7.60(8H, m, aromatic H). UV: λmax(THF) 260, 306.5 nm (ε=12900, 6270). Found: C, 58.48; H, 3.56%. Calcd for $C_{22}H_{16}Cl_4O_2$: C, 58.18; H, 3.55%.

2,3,5,6-Tetrachloro-trans-*3',4'-diphenylspiro* [*2,5-cyclohexadiene-1,2'-oxetan*]*-4-one (4b)*. Colorless prisms(benzene-petroleum ether); mp 150°C (dec). IR(KBr): 1671, 1092, 955, 762 cm^{-1}. NMR(δ, CDCl$_3$): 4.98 (1H, d, *J*=9.1 Hz), 6.72(1H, d, *J*=9.1 Hz), 6.90-7.83(10H, m, aromatic H). UV: λmax(THF) 259, 295 nm(ε=11400, 6995). Found: C, 56.62; H, 2.91%. Calcd for $C_{20}H_{12}Cl_4O_2$: C, 56.37; H, 2.84%.

2,3,5,6-Tetrachloro-trans-*3',4'-bis*(p-*chlorophenyl*)*spiro* [*2,5-cyclohexadiene-1,2'-oxetan*]*-4-one (4c)*. Colorless prisms(benzene-petroleum ether); mp 172°C (dec). IR(KBr): 1676, 1100, 952, 821, 726 cm^{-1}. NMR (δ, CDCl$_3$): 4.87(1H, d, *J*=8.9 Hz), 6.60(1H, d, *J*=8.9 Hz), 6.83-7.50(8H, m, aromatic H). UV: λmax(THF) 260.5, 296 nm (ε=13600, 7320). Found: C, 48.74; H, 2.13%. Calcd for $C_{20}H_{10}Cl_6O_2$: C, 48.52; H, 2.04%.

*2,3,5,6-Tetrachloro-4-(*p*-methylbenzyloxy)phenol (6a)*. Colorless needles(benzene-petroleum ether); mp 134-135°C. IR(KBr): 3390, 1435, 1391, 958, 708 cm^{-1}. NMR(δ, $CDCl_3$): 2.35(3H,s), 4.92(2H,s), 5.83(1H, s, OH), 7.05-7.50(4H, q, aromatic H). Found: C, 47.81; H, 2.88%. Calcd for $C_{14}H_{10}Cl_4O_2$: C, 47.76; H, 2.86%.

2,3,5,6-Tetrachloro-4-(benzyloxy)phenol (6b). Colorless prisms (benzene-petroleum ether); mp 142-143.5°C. IR(KBr): 3390, 1436, 1386, 945, 708 cm^{-1}. NMR(δ, $CDCl_3$): 4.92(2H,s), 5.85(1H, s, OH), 7.13-7.50 (5H, m, aromatic H). Found: C, 46.09; H, 2.44%. Calcd for $C_{13}H_8Cl_4O_2$: C, 46.14; H, 2.37%.

*2,3,5,6-Tetrachloro-4-(*p*-chlorobenzyloxy)phenol (6c)*. Colorless needles(benzene); mp 174-175°C. IR(KBr): 3400, 1344, 1152, 1082, 808 cm^{-1}. NMR(δ, $CDCl_3$): 4.93(2H,s), 5.95(1H, s, OH), 7140(4H, s, aromatic H). Found: C, 41.88; H, 1.97%. Calcd for $C_{13}H_7Cl_5O_2$: C, 41.91; H, 1.89%.

*2,3,5,6-Tetrachloro-1,4-bis(*p*-methylbenzyloxy)benzene (7a)*. Colorless needles(benzene); mp 211-212°C. IR(KBr): 2911, 1424, 1352, 956, 799 cm^{-1}. NMR(δ, $CDCl_3$): 2.38(6H,s), 5.00(4H,s), 7.17-7.67(8H, q, aromatic H). Found: C, 58.06; H, 4.02%. Calcd for $C_{22}H_{18}Cl_4O_2$: C, 57.92; H, 3.98%.

2,3,5,6-Tetrachloro-1,4-bis(benzyloxy)benzene (7b). Colorless needles (ether); mp 169-171°C. IR(KBr): 1421, 1358, 959, 752, 694 cm^{-1}. NMR (δ, $CDCl_3$): 4.97(4H,s), 7.1-7.35(10H, m, aromatic H). Found: C, 56.04; H, 3.38%. Calcd for $C_{20}H_{14}Cl_4O_2$: C, 56.10; H, 3.30%.

*2,3,5,6-Tetrachloro-1,4-bis(*p*-chlorobenzyloxy)benzene (7c)*. Colorless needles(benzene); mp 236-237°C. IR(KBr): 1418, 1355, 959, 801 cm^{-1}. NMR(δ, $CDCl_3$): 4.96(4H,s), 7.15(8H, s, aromatic H). Found: C, 48.63; H, 2.46%. Calcd for $C_{20}H_{12}Cl_6O_2$: C, 48.33; H, 2.43%.

*2,3,5,6-Tetrachloro-4-[4'-(*p*-methylbenzyloxy)butoxy]phenol (8a)*. Pale yellow prisms(benzene); mp 86-87°C. IR(KBr): 3150, 1441, 1381, 1168, 1030, 709 cm^{-1}. NMR(δ, $CDCl_3$): 1.66-2.07(4H, m, CH_2CH_2), 2.33(3H, s, CH_3), 3.33-3.73(2H, m, OCH_2), 3.76-4.17(2H, m, OCH_2), 4.45(2H, s, OCH_2Ar), 5.93(1H, s, OH), 7.13(4H, s, aromatic H). Found: C, 51.08; H, 4.31%. Calcd for $C_{18}H_{18}Cl_4O_3$: C, 50.97; H, 4.28%.

2,3,5,6-Tetrachloro-4-[4'-(benzyloxy)butoxy]phenol (8b). Pale yellow prisms(benzene); mp 84-85°C. IR(KBr): 3240, 1445, 1384, 1171, 1041, 714

cm^{-1}. NMR(δ, $CDCl_3$): 1.70-2.10(4H, m, CH_2CH_2), 3.40-3.80(2H, m, OCH_2), 3.80-4.10(2H, m, OCH_2), 4.43(2H, s, OCH_2Ar), 5.83(1H, s, OH), 7.18(5H, s, aromatic H). Found: C, 49.78; H, 4.03%. Calcd for $C_{17}H_{16}Cl_4O_3$: C, 49.78; H, 3.93%.

*2,3,5,6-Tetrachloro-4-[4'-(*p*-chlorobenzyloxy)butoxy]phenol (8c).* Pale yellow prisms(benzene); mp 77-78°C. IR(KBr): 3140, 1425, 1371, 1152, 1025, 699 cm^{-1}. NMR(δ, $CDCl_3$): 1.70-2.07(4H, m, CH_2CH_2), 3.40-3.70(2H, m, OCH_2), 3.80-4.10(2H, m, OCH_2), 4.77(2H, s, OCH_2Ar), 5.90(1H, s, OH), 7.23(4H, s, aromatic H). Found: C, 45.99; H, 3.36%. Calcd for $C_{17}H_{15}Cl_5O_3$: C, 45.92; H, 3.40%.

Reactions of 1a-c with 2 in THF-CH_3OH.

The reactions were carried out in THF containing CH_3OH. The general procedures may be illustrated by the case of 1a. To a stirred solution of 2(1.50 g, 6.10 mmol) author added a THF solution(10 ml) of 1a (0.97 g, 7.35 mmol) over a 10-min period at 20°C. After 1 h's standing the removal of the solvent *in vacuo* gave a pasty reaction mixture. The washing of this mixture with 3×20 ml ether left only the recovered 2 (0.49 g); the subsequent evaporation of the ether solution gave oily products. The NMR spectrum of the oily products showed the presence of α,α—dimethoxy-*p*-tolylmethane(5a); (δ, $CDCl_3$), 3.28(6H, s, OCH_3) and 5.30(1H, s, $CH(OR)_2$). However, this acetal was easily degradated to *p*-tolualdehyde on work-up. Therefore, the acetal was identified as the aldehyde(5a'). The column chromatographic treatment of the oily products gave, successively, 3a(trace), 7a(35 mg, 2%), 2(60 mg), and 5a'(470 mg, 53%), 6a(565 mg, 22%), 8a(220 mg, 7%), and $TCQH_2$(420 mg, 23%).

Reaction of 1b with 2 in THF-CF_3CH_2OH.

To a stirred solution of 2(2.09 g, 8.50 mmol) in THF(50 ml) containing CF_3CH_2OH(3.4 g) the author added a THF solution(10 ml) of 1b (1.0 g, 8.47 mmol) over a 10-min period at 20°C. After 1 h's standing, the removal of the solvent *in vacuo* gave a pasty reaction mixture. The washing of the mixture with 3×20 ml ether left 2(1.2 g) and 4b(110 mg, 6%). The ether was evaporated *in vacuo*, and the residue(1.7 g) was chromatographed. Contrary to the case of CH_3OH, a relatively large amount of 3b(442 mg, 58%, *cis/trans*=2.6) was obtained, together with 5b′(220 mg, 24%), TCQH$_2$(230 mg, 11%), 6b(100 mg, 3.5%), 7b(20 mg, 1%) and 8b(120 mg, 3.5%).

Reaction of 1b with TCQH$_2$ in THF.

An equimolar mixture of 1b(1.0 g, 8.47 mmol) and TCQH$_2$ in THF(50 ml) gave 6b(1.23 g, 43%), 7b(0.13 g, 7%), and 8b(1.63 g, 47%).

General Procedure for H. P. L. C. Analysis.

To a solution or suspension of 2(0.5 g) in a solvent(30 ml) was added drop by drop a solution of 1b(0.5 g) in the same solvent(10 ml) for 10 min at 20°C. After 1 h′s stirring, the solvents(except for benzene) boiling below 100°C were evaporated and the pasty residue was redissolved in benzene(40 ml). In the case of the higher boiling solvents, the reaction solutions were submitted to the following treatment without any work-up. In these reaction solutions, naphthalene(100 mg) was dissolved as an internal standard and the two milliliter aliquots were diluted with benzene until the total volume of solution rose to 25 ml. The sample solutions thus prepared were analyzed by H. P. L. C..

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Chapter 4 Kinetic Substituent and Solvent Effects in the Reactions of Diaryldiazomethanes with Tetracyanoethylene

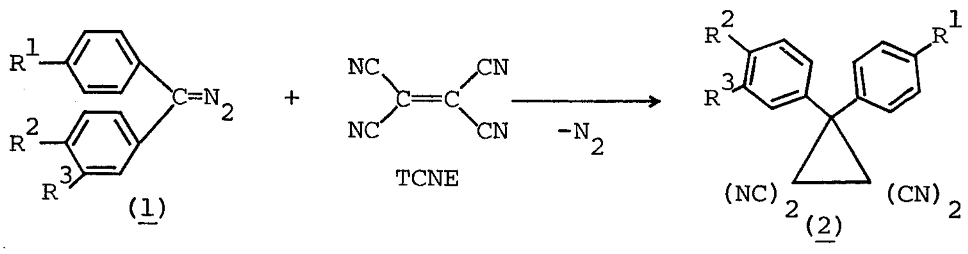
4-1 Introduction

In the preceding chapters 1-3, the author described the reactivities of various diazoalkanes toward o-sulfobenzoic anhydride and a variety of quinones all which contain the reactive C=O groups. This chapter aims to extend the reactions of diazoalkanes to the other type of organic electron acceptors. For this purpose, tetracyanoethylene(TCNE) with an electron deficient C=C bond was used to study the reactivities of diazoalkanes. Reactions of TCNE with diazoalkanes have already been carried out using diazomethane,[1] ethyldiazoacetate.[2] However, the reaction with diaryldiazomethanes is not known. Therefore, the author wants to describe the studies on the reactions of *meta*- and *para*-substituted diaryldiazomethanes(DDMs) with TCNE and discuss the kinetic substituent and solvent effects. From the kinetic solvent effects which reflect the strong basic solvation of TCNE molecule, a new empirical solvent basicity parameter, D_π , was proposed and the application to the other reaction systems was also demonstrated.

4-2 Results and Discussion

4-2-1 Kinetic Substituent Effects

The reactions of diphenyldiazomethane(DDM) and its *meta*- and *para*-substituted derivatives(DDMs) with an equimolar quantity of TCNE in benzene at room temperature gave nearly quantitatively the corresponding 1,1-diaryl-2,2,3,3-tetracyanocyclopropanes(Scheme 1 and Table 1).



	a	b	c	d	e	f	g	h	i	j	k	l	m	n
R^1=	OCH_3	OCH_3	CH_3	OPh	CH_3	Ph	H	H	F	I	Cl	Br	Cl	H
R^2=	CH_3	H	CH_3	H	H	H	H	H	H	H	H	H	Cl	H
R^3=	H	H	H	H	H	H	CH_3	H	H	H	H	H	H	Cl

Scheme 1.

TABLE 1

Yields and physical data for 1,1-diaryl-2,2,3,3-tetracyanocyclopropanes (2a—n)[c]

Compound	R^1 (*para*)	R^2 (*para*)	R^3 (*meta*)	Yield (%)	M.p. (°C)	Formula	Found (%)[a] C	H	N
(2a)	OCH_3	CH_3	H	96	212—213	$C_{21}H_{14}N_4O$	74.3 (74.6)	4.2 (4.2)	16.5 (16.6)
(2b)	OCH_3	H	H	89	206—207.5	$C_{20}H_{12}N_4O$	74.2 (74.1)	3.9 (3.7)	17.3 (17.3)
(2c)	CH_3	CH_3	H	97	263—265	$C_{21}H_{14}N_4$	77.9 (78.2)	4.5 (4.4)	17.2 (17.4)
(2d)	OPh	H	H	96	231.5—233.5	$C_{25}H_{14}N_4O$	77.9 (77.7)	3.6 (3.7)	14.4 (14.5)
(2e)	CH_3	H	H	98	243—245	$C_{20}H_{12}N_4$	78.2 (77.9)	4.0 (3.9)	18.1 (18.2)
(2f)	Ph	H	H	93	249.5—251.5	$C_{25}H_{14}N_4$	81.4 (81.1)	3.7 (3.8)	14.8 (15.1)
(2g)	H	H	CH_3	91	247—248	$C_{20}H_{12}N_4$	77.7 (77.9)	3.9 (3.9)	18.1 (18.2)
(2h)	H	H	H	97	276—278[b]	$C_{19}H_{10}N_4$	77.5 (77.5)	3.5 (3.4)	19.1 (19.0)
(2i)	F	H	H	91	233—234.5	$C_{19}H_9FN_4$	72.6 (73.1)	3.0 (2.9)	17.8 (17.9)
(2j)	I	H	H	95	244—245	$C_{19}H_9IN_4$	54.3 (54.3)	2.2 (2.1)	13.5 (13.3)
(2k)	Cl	H	H	94	236—238	$C_{19}H_9ClN_4$	69.7 (69.4)	2.8 (2.8)	17.1 (17.0)
(2l)	Br	H	H	92	249—250	$C_{19}H_9BrN_4$	61.4 (61.1)	2.4 (2.4)	15.1 (15.0)
(2m)	Cl	Cl	H	93	278—280	$C_{19}H_8Cl_2N_4$	62.6 (62.8)	2.4 (2.2)	15.4 (15.4)
(2n)	H	H	Cl	94	240.5—242.5	$C_{19}H_9ClN_4$	69.9 (69.4)	2.7 (2.8)	16.9 (17.0)

[a] Required values in parentheses. [b] Lit.,[13] 276—278 °C.

[c] I.r., n.m.r., and mass spectral data are given in Supplementary Publication No. SUP 22352 (3 pp.).

It was noticed that the disappearance of the color of the diazo-compounds(1) and the evolution of nitrogen gas were much accelerated by introducing electron-donating substituents in the *meta*- or *para*-positions of the aromatic rings of the diazo-compounds(1). In order to estimate this tendency in more detail, the reactions were followed spectrophotometrically, and were found to obey clean second-order kinetics. The values of the rate constants in benzene at various temperatures are given in Table 2 together with the activation parameters.

TABLE 2

Second-order rate constants k (l mol^{-1} s^{-1}) and activation parameters for the reactions of the substituted DDMs (1a—n) with TCNE in benzene

	10^2k 30 °C	40 °C	50 °C	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J mol^{-1} K^{-1}
(1a)	3 830 ± 30				
(1b)	605 ± 12				
(1c)	330 ± 4				
(1d)	83.8 ± 1.3	140 ± 4	200 ± 5	34.1 ± 0.5	−134 ± 2
(1e)	63.0 ± 1	111 ± 4	156 ± 3	34.1 ± 0.4	−136 ± 3
(1f)	19.7 ± 0.3	36.2 ± 0.4	57.2 ± 0.3	41.6 ± 0.5	−121 ± 3
(1g)	17.5 ± 0	32.7 ± 0.6	49.5 ± 1.5	39.7 ± 0.5	−128 ± 2
(1h)	9.72 ± 0.08	17.0 ± 0.3	26.8 ± 0.5	39.2 ± 0.8	−135 ± 3
(1i)	6.43 ± 0.04	11.5 ± 0.25	18.2 ± 0.2	40.0 ± 0.8	−135 ± 3
(1j)	2.85 ± 0.03	4.63 ± 0.05	7.72 ± 0.03	37.4 ± 0.3	−150 ± 2
(1k)	2.40 ± 0.02	4.55 ± 0.01	6.70 ± 0.2	44.2 ± 0.7	−130 ± 3
(1l)	2.23 ± 0.07	4.17 ± 0.05	6.78 ± 0.03	45.2 ± 0.6	−127 ± 4
(1m)	0.697 ± 0.004	1.30 ± 0.03	2.15 ± 0.03	43.5 ± 0.4	−142 ± 5
(1n)	0.583 ± 0.014	0.927 ± 0.005	1.33 ± 0.04	31.2 ± 0.5	−184 ± 6

From the second-order rate constants k, it can be noted that p-OCH_3 and p'-CH_3 substituents cause a 400-fold increase of the rate compared with the unsubstituted case, while m-Cl markedly retarded the reaction. This implies that the rate-determining step of the reactions is influenced by the electronic character of the diazo-carbon. It was found that the correlation is better when log k is plotted against σ^+ than against σ. In the normal Hammett treatment, large apparent deviations were observed for (1a and 1b) which have strong electron-donating substituents, OCH_3. For disubstituted DDM the σ^+ values used are the sums of the σ^+ values for the two substituents. A least squares treatment of these results (for 30°C) yielded equation(1).

$$\log k = -2.67\sigma^+ -1.23 \quad (r=0.989,\ s=0.07,\ n=14) \qquad (1)$$

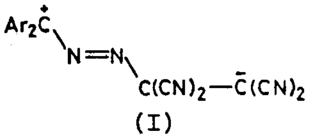
A moderately good fit was also obtained with similar values as for 30°C when this treatment was applied to results at 40 and 50°C[equations (2) and (3), respectively].

$$\log k = -2.78\sigma^+ -0.98 \quad (r=0.967,\ s=0.15,\ n=11) \qquad (2)$$

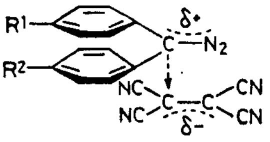
$$\log k = -2.74\sigma^+ -0.79 \quad (r=0.966,\ s=0.16,\ n=11) \qquad (3)$$

The existence of a better correlation with the substituent constants σ^+ and the very large negative ρ value indicate that polar resonance structure might contribute to stabilization of the transition state.

Reactions of diazoalkanes with TCNE have already been carried out using diazomethane [1] and ethyl diazoacetate[2], and gave respectively 3,3,4,4-tetracyano-1-pyrazoline and 4-ethoxycarbonyl-5-tricyanovinyl-1,2,3-triazole. For diazomethane it has been postulated that the 1,3-dipolar cycloaddition with TCNE gives a pyrazoline which is easily transformed into 1,1,2,2-tetracyanocyclopropane. On the other hand, for DDMs the magnitude of ρ and the correlation with σ^+ almost certainly rule out a isopolar concerted 1,3-dipolar cycloaddition for which correlations[3] are with σ and yield small ρ values, *e.g.* in the addition of substituted phenyl azides to maleic anhydride(ρ -0.8) and *N*-phenylmaleimide(ρ -1.1). By contrast, a two-step mechanism through the zwitterion intermediate(I), resulting from nucleophilic attack of the terminal nitrogen of the diazoalkane on TCNE, fits the results. However, such nucleophilic behavior of the terminal nitrogen is rarely found, although electrophilic attack is known for the reaction with phosphine.[4] Furthermore, if this were true, the reaction would not require such a high degree of order in the transition state as expected from the large negative entropies of activation($\Delta S^{\ddagger}$). These values are appropriate to a concerted process.[5]



(I)



(II)

The electron-transfer mechanism sufficiently explains the problem in view of the highly ordered transition state(II) where the molecules are probably oriented in two separate planes to maximize the overlap between DDM and TCNE as in Diels-Alder reactions.[6] When powdered TCNE was dissolved in a benzene solution of DDM and the system degassed, the mixture immediately showed an ESR signal of 11 lines with a spacing of 1.56G at 20°C which appears to be identical with the spectrum observed by Phillips and Rowell[7] for $TCNE^{\overline{\cdot}}$ (Fig. 1). Changing the solvent from benzene to THF or acetonitrile brought about a change in the signal; only seven lines were descernible in THF, while in acetonitrile a single line was observed (Figure). This reduction and disappearance of the fine structure in

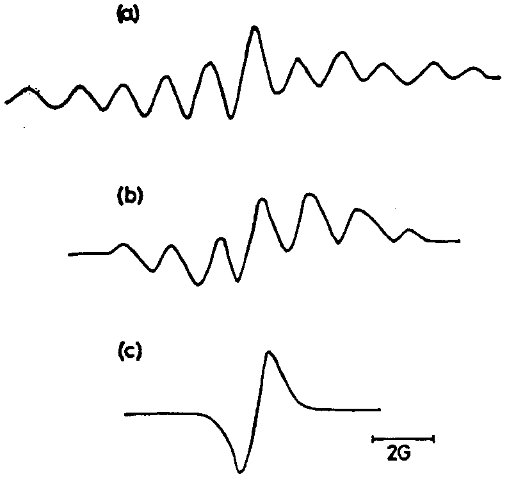
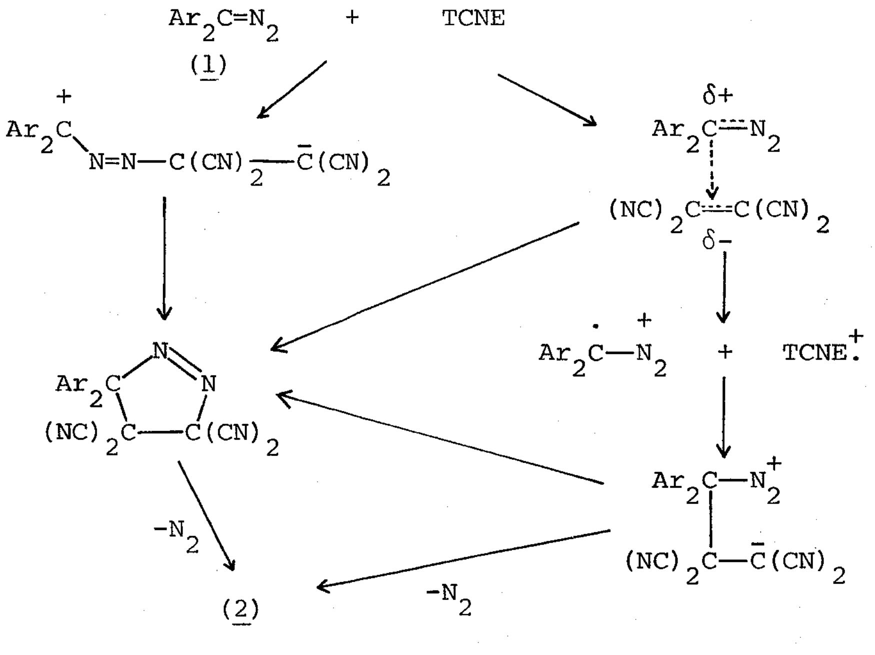


Fig. 1. ESR spectra of the reaction of DDM with TCNE in (a) benzene, (b) THF, and (c) acetonitrile at 20°C

polar solvents is attributable to fast electron exchange between TCNE$\bar{\cdot}$ and neutral TCNE.[8] In spite of the appearance of the radical anion of TCNE in benzene, the counter radical cation possibly derived from DDM could not be detected under these conditions. The failure to detect DDM$\overset{+}{\cdot}$ in the ESR measurements does not support the electron-transfer mechanism; however the possibility that the radical is too unstable to be detected compared with TCNE$\bar{\cdot}$ should be considered. Bethell *et al.*[9] observed no signal assignable to DDM$\overset{+}{\cdot}$ in the decomposition of DDM with $Cu(ClO_4)_2$ above 0°C. In addition, DDM$\overset{+}{\cdot}$ is known to react with further DDM in a chain process yielding tetraphenylethylene in the absence of additive.[10] The corresponding olefins were not isolated in the present case and this seems to be the result of the essential suppression of the chain process by preferential collapse with TCNE$\bar{\cdot}$. Taking into account these considerations, the reaction probably proceeds by an initial rate-determining electron transfer from the diazoalkanes to TCNE, followed by collapse of the radical ion pair to give the zwitterion or the pyrazoline from which nitrogen is lost yielding the related cyclopropane, though the participation of the two-step mechanism through(I) or the polar transition state of 1,3-dipolar addition giving pyrazoline can not be fully ruled out(Scheme 2).



Scheme 2

4-2-2 Kinetic Solvent Effects. A New Empirical Parameter of Solvent Basicity

In this section, the author intends to provide a new solvent basicity parameter, D_π, based on kinetic solvent effects. There are few parameters concerning solvent basicity toward a π-acceptor Lewis acid. Therefore, the present parameter concerning solvent interaction with TCNE as a typical π-acceptor seems useful to describe solvent effects on the various physical and chemical properties influenced by an interaction between solvent and π-acceptor.

The second-order rate constants, $\bar{k}$, of the reaction of DDM and TCNE at 30°C in a wide range of aprotic solvents are shown in Table 3, together with the conventional solvent basicity parameters.

Table 3. Second-order rate constants $\bar{k}$ (l mol^{-1} s^{-1}) for the reaction between DDM and TCNE in various solvents, with solvent basicity parameters

	Solvent	$\frac{\bar{k}}{30°C}$	$\Delta\nu_D$ a)	β b)	DN c)	D_π
1.	Chloroform	3.51	-17	NHBA d)	—	-1.56
2.	Dichloromethane	1.95	-12	NHBA	—	-1.30
3.	1,1-Dichloroethane	1.64	—	NHBA	—	-1.23
4.	1,2-Dichloroethane	1.62	2	NHBA	0	-1.22
5.	Bromobenzene	1.03	-1	0.062	—	-1.03
6.	Diisopropyl ether	0.933	75	0.466	—	-0.982
7.	Chlorobenzene	0.778	-2	0.071	—	-0.903
8.	Fluorobenzene	0.639	—	—	—	-0.818
9.	Nitromethane	0.515	6	—	2.7	-0.724
10.	Nitrobenzene	0.372	21	—	4.4	-0.583
11.	Methyl chloroacetate	0.332	27	—	—	-0.533
12.	Acetonitrile	0.268	49	0.31	14.1	-0.440
13.	Benzonitrile	0.243	38	0.409	11.9	-0.398
14.	Di-*n*-butyl ether	0.229	77	0.453	—	-0.372
15.	Diethyl ether	0.193	78	0.466	19.2	-0.298
16.	Propionitrile	0.184	52	—	16.1	-0.277

Table 3. (Continued)

Solvent	$\frac{\bar{k}}{30°C}$	$\Delta\nu_D$[a]	β[b]	*DN*[c]	D_π
17. Methyl benzoate	0.163	—	—	—	-0.225
18. Benzene	0.0972	0	0.100	0.1	0.000
19. Methyl ethyl ketone	0.0646	57	—	—	0.177
20. Methyl acetate	0.0619	36	0.454	16.5	0.196
21. Ethylbenzene	0.0617	4	—	—	0.197
22. Cyclohexanone	0.0556	66	0.534	—	0.243
23. Acetone	0.0533	64	0.478	17	0.261
24. Ethyl acetate	0.0500	39	0.446	17.1	0.289
25. 1,3-Dioxolane	0.0467	58	—	—	0.318
26. Propyl acetate	0.0447	—	—	—	0.337
27. Ethyl carbonate	0.0440	33	—	—	0.344
28. Isopropyl acetate	0.0404	—	—	—	0.381
29. Dimethoxymethane	0.0402	—	—	—	0.383
30. Toluene	0.0392	2	0.112	—	0.394
31. Tetrahydropyran	0.0281	93	0.544	—	0.539
32. 1,4-Dioxan	0.0250	77	0.369	14.8	0.590
33. Tetrahydrofuran	0.0223	90	0.55	20	0.639
34. 1,2-Dimethoxyethane	0.0192	71	0.405	24	0.704[e] (0.000)

[a] Wave-number shift of the O-D stretching vibration of CH_3OD, as between benzene and the solvent. Mainly from ref. 11. Nos. 14 and 27 were obtained from the results in ref. 12.

[b] Kamlet-Taft β scale: hydrogen-bonding donor acceptor ability; ref. 13.

[c] Gutmann's *DN*(donor number), ref. 14.

[d] NHBA(non-hydrogen bond acceptor solvents).

[e] Values for two centered and one centered(in parentheses) associations.

Inspection of the results evidently shows that the rate did not correlate well with the solvent polarity. Dipolar solvents, *e.g.*, nitro compounds, nitriles, and ketones, unusually decreased the rate compared to chloroform and dichloromethane. However, the rates were found generally to decrease with increasing solvent basicity. Values of the rate constants in the more basic THF and 1,4-dioxan were less than that in the least basic chloroform by a factor of about 150.

In order to understand the influence of solvent on rate, solvation effects on both reactants and transition state must be taken into consideration. The present kinetic solvent effects apparently imply that the transition state has not been efficiently stabilized by dipole-dipole interaction but that the solvation of the reactants, undoubtedly the TCNE molecule, by the basic solvents may significantly contribute to the rate decrease. TCNE is in fact well known to form donor-acceptor complexes with basic solvents such as aromatic hydrocarbons,[15] THF, and 1,4-dioxan.[16] The relative strengths of such an interaction between solute TCNE and various solvents could be estimated by the hypsochromic shift of the $\pi-\pi^*$ absorption of TCNE with increasing solvent basicity as seen in Table 4.

Table 4. Solvent effects on the UV absorption spectrum of TCNE and DDM

Solvent	TCNE		DDM
	λmax/nm (log ε)		λmax/nm (log ε)
Chloroform	267.7 (4.16)	277.6 (4.15)	290.5 (4.35)
Dichloromethane	267.4 (4.13)	277.7 (4.09)	289.5 (4.32)
Acetonitrile	262.5 (4.20)	271.5 (4.16)	287.2 (4.40)
Propiononitrile	263.0 (4.22)	272.3 (4.18)	287.1 (4.39)
Ethyl acetate	259.0 (4.18)	270a) (4.08)	287.3 (4.36)
Propyl Acetate	258.5 (4.19)	270a) (4.09)	287.6 (4.38)
Isopropyl acetate	257.2 (4.19)	270a) (4.08)	287.5 (4.35)
Tetrahydrofuran	260.5 (4.08)	270a) (4.02)	289.0 (4.37)
1,4-Dioxan	259.5 (3.98)		288.7 (4.39)

a) Shoulder

The two distinct absorption peaks of TCNE in non-basic chloroform and dichloromethane hypsochromically moved *ca.* 5 nm in nitriles, and further shifted to shorter wavelength(7-10 nm), accompanied by the deterioration of the longer wavelength peak with solvent variation from nitriles to esters and cyclic ethers. These solvatochromic effects indicate that, with increasing solvent basicity, the energy of the ground state of TCNE is lowered more than that of the excited state owing to the basic solvation, and this produces a hypsochromic shift. By contrast, absorption of DDM essentially remained unchanged in such a variation of solvents, reflecting the lower solvation of DDM.

(a) The D_π Scale of Solvent Basicity.

Keeping the above considerations in mind, author introduces a solvent electron donor power, D_π , toward a π-acceptor soft acid, using equation(4),

$$D_\pi = \log \bar{k}_0 - \log \bar{k} \qquad (4)$$

where $\bar{k}_0$ is the second-order rate constant at 30°C in benzene as reference solvent, and $\bar{k}$ is the rate constant in another solvent. By definition, the D_π value of benzene is zero and the + or - sign refers to a stronger or weaker base with respect to benzene. The D_π values thus determined are given in the last column of Table 3. In an actual application of the empirical D_π values, a solvent dependent physicochemical quantity Q can be expressed by the familiar form of a linear free energy(LFE) relationship(equation 5),

$$Q = Q_0 + mD_\pi \qquad (5)$$

where m is a constant describing the sensitivity of the property Q to solvent basicity D_π (m = -1, $Q_0 = \log \bar{k}_0$ for DDM-TCNE system by definition).

(b) Comparison of D_π with $\Delta\nu_D$, β , and DN.

As a solvent basicity parameter, a number of workers have employed the infrared O-D or O-H stretching frequency of CH_3OD[11,12,17] (or CH_3OH),[18] PhOH,[19] and $4\text{-}FC_6H_4OH$[18,20] in the pure media. For example, Kagiya, Sumida, and Inoue proposed $\Delta\nu_D$, the frequency shift of the O-D stretching band of CH_3OD, as between benzene and the solvent.[11] Alternative conventional solvent basicity parameters are the Kamlet-Taft β scale[13] and Gutmann's *DN*(donor number).[14] The β scale is defined as a solvent hydrogen-bond acceptor ability and is constructed from the magnitudes of enhanced solvatochromic shift in a given solvent of such indicator compounds as 4-nitroaniline and 4-nitrophenol relative to their alkylated derivatives. The *DN* is the negative enthalpy of formation of adducts between the Lewis acid $SbCl_5$ and a given solvent molecule as Lewis base in dilute 1,2-dichloroethane solution.

Values of $\Delta\nu_D$, β , and *DN* are available for 28, 17, and 14 of the solvents measured by author(Table 3). These three measures of solvent basicities do not correspond exactly(a plot of $\Delta\nu_D$ against β or *DN* shows a some scatter of points) but there is a general parallelism. The relationships between these conventional parameters and D_π are shown in Figs. 2-4.

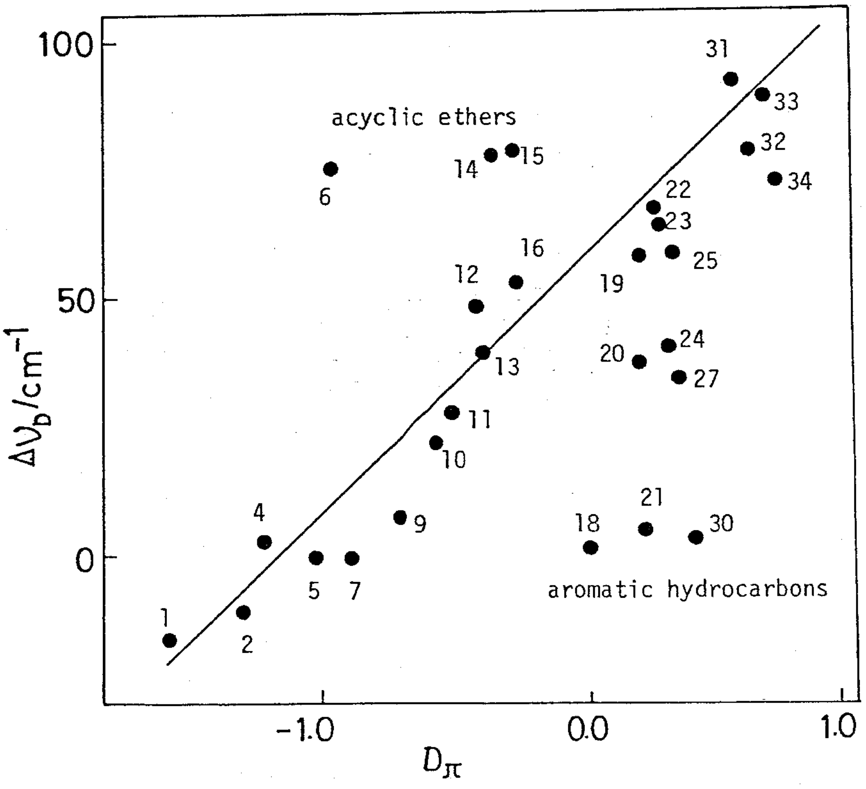


Fig. 2. Correlation between D_π and $\Delta\nu_D$; for point numbers, see Table 3

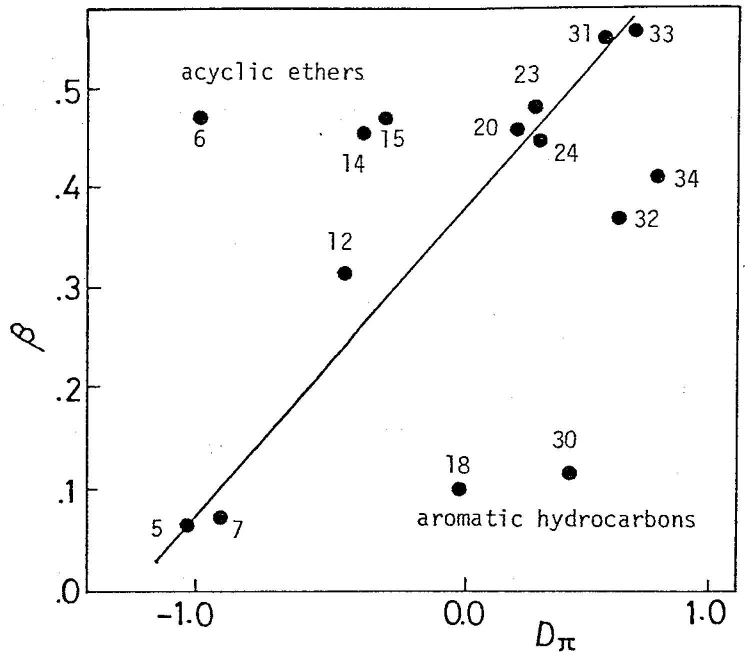


Fig. 3. Correlation between D_π and β ; for point numbers, see Table 3

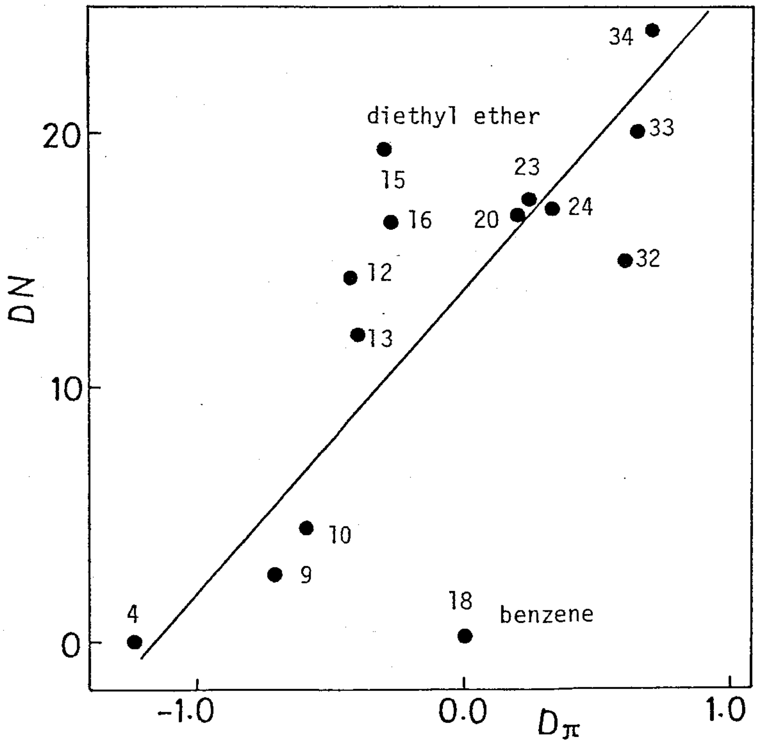


Fig. 4. Correlation between D_π and DN; for point numbers, see Table 3

It is seen that these parameters exhibit substantially linear correlations with corresponding D_π values if the data for aromatic hydrocarbons and sterically hindered acyclic ethers are always excluded, together with those for some particular solvents: esters(Fig. 2), 1,2-dimethoxyethane (Figs. 2 and 3), 1,4-dioxan(Figs. 3 and 4).

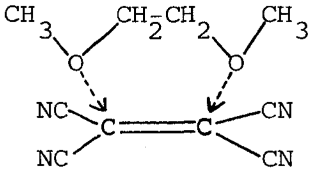
(c) Rationale for the Separation into Families.

Since $\Delta\nu_D$ is a measure of the solvent hydrogen-bond acceptor ability toward CH_3OD, a straightfoward application of $\Delta\nu_D$ to estimate the solvent Lewis basicity toward TCNE appears ambiguous. This is also the case with the β scale. As an example, the author will rationalize the separation into families when $\Delta\nu_D$ was plotted against the D_π values.

It should be noted that TCNE is essentially different from CH_3OD in the following points: (a) first, TCNE is a Lewis acid (π-acceptor) and CH_3OD is a Brønsted acid; (b) next, the HSAB(Hard and Soft Acid and Base) theory[21] classifies TCNE as a typical soft acid and CH_3OD as a typical hard acid; (c) and finally, CH_3OD is a smaller molecule than TCNE and its acidic site is one dimensional in contrast to the planer C=C bond system of TCNE. In addition, some attention should also be paid to the solvent Lewis basicity. Based on the type of orbitals involved in the bonding interaction with acids, solvents can be divided into several categories; *e.g.*, n-, π-donor solvents.[22] Nitro compounds, nitriles, ketones, esters, and ethers belong to n-donor bases, while aromatic hydrocarbonds are π-donor bases. Accordingly, n-donor solvents form n-donor — π-acceptor complexes with TCNE and π-donor solvents make up π-donor — π-acceptor complexes. This Lewis acid-base approach can be extended on the basis of the HSAB principle[21] : hard and soft acids prefer to bind hard and soft bases, respectively. As well as the acids, solvents can be classified as hard or soft beses depending on their chemical constitution and associating partners. The n-donor solvents whose n-electron clouds are small and not easily distorted are rather hard bases toward the soft acid TCNE. By contrast, π-donor solvents are typical soft bases owing to the large and easily distortable π-electrons so that TCNE more strongly interacts with aromatic hydrocarbons than with the above examined n-donor solvents. This is the reason why the aromatic hydrocarbons gave the large negative deviations in the plot of $\Delta\nu_D$ against D_π.

The inductive and steric influence of chloro and bromo substituents will affect the π-basicity of aromatic ring to reduce the strength of the interaction with TCNE; halogenated benzenes do not appreciably stabilize TCNE.[15] It should be noted, however, that the introduction of NO_2 and CN groups on the aromatic ring completely changes the solvent basic nature from π-donor to n-donor as realized in the cases of nitrobenzene and benzonitrile, because these substituents can be regarded as the bonding sites.

The upward deviation of the three acyclic ethers from the cyclic group may be explained in terms of the steric hindrance caused by the alkyl groups of the ethers. In contrast to the case of the smaller CH_3OD, solvation of TCNE might be reduced by the introduction of the sterically hindering alkyl substituents on the ethereal oxygen in proportion to the size. Indeed, the rate constants increase with Taft's steric constants, E_s,[23] in order of diisopropyl(E_s = -0.47) > di-*n*-butyl(-0.39) > diethyl ether(-0.07). However, such a steric repulsion was not anticipated in the cyclic ethers where the basic oxygen atoms are not disturbed in the bonding interaction with TCNE. Interestingly, the lowest rate for 1,2-dimethoxyethane suggests the formation of a stable quasi six-membered ring as illustrated below.



Finally, esters such as methyl acetate, ethyl acetate, and ethyl carbonate were far apart from the main n-donor solvent family as seen in Fig. 2. As to the location of the ester group on the right hand side of the nitrile group in spite of the lower $\Delta\nu_D$ values, the author can imagine that the ester function possesses a considerable softness so as to make a more stable complex with TCNE than nitriles do. In fact, esters induced a greater hypsochromic shift than nitriles, comparable with THF and 1,4-dioxan.

Consequently, the negative deviations for aromatic hydrocarbons in all cases obviously show that TCNE is a more soft acid than the indicator acid compounds employed in determining $\Delta\nu_D$, β , and *DN*. On the other hand, the greater deviations for hindered ethers may be attributed to the greater steric susceptibility of TCNE in comparison to the above indicator acids. Thus, the relationships in Figs. 2-4 evidently limit the application of $\Delta\nu_D$, β , and *DN* for the evaluation of solvent basicity toward a π-acceptor acid.

(d) *Application of the D_π Scale to Other Reactions.*

The author tested the validity of the D_π scale in the interpretation of kinetic solvent effects in reactions involving a protic or π-acceptor acid as a reactant.

Chapman and Shorter[24] have done extensive work on the role of the solvent in the reaction of DDM with benzoic acid(hard protic acid).

$$\underset{\text{(DDM)}}{Ph_2CN_2} \quad + \quad PhCOOH \xrightarrow[-N_2]{} Ph_2CHOCOPh$$

Values of D_π are available for 21 of their solvents and the plot of log k against D_π is shown in Fig. 5.

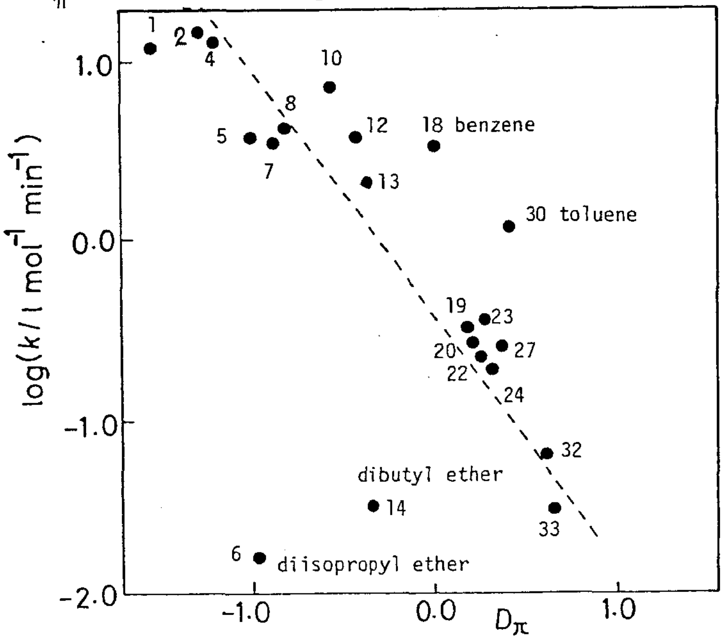
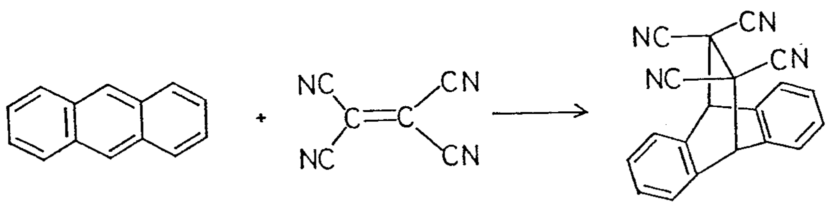


Fig. 5. Correlation between D_π and log k of the reaction of DDM with benzoic acid in various solvents at 37°C; for numbers, see Table 3.

The reaction tends to be fast in the weakly basic solvents and slow in the strongly basic solvents. However, the positive deviations for aromatic hydrocarbons such as benzene and toluene imply a weaker basic character of these solvents toward the hard acid(benzoic acid). However, the large negative deviations for di-*n*-butyl ether and diisopropyl ether indicate the release of steric repulsion in these cases. Thus, the application of D_{π} to the hard acid system is limited in view of both the HSAB concepts[21] and the steric factor.

Brown and Cookson[25] have studied solvent effects in the kinetics of Diels-Alder addition of TCNE to anthracene. The second-order rate



constants at 30°C increased by a factor of 70 in going from o-xylene to chloroform. The author has found that these workers's data for which D_{π} values are known are well correlated as can be seen in Fig. 6.

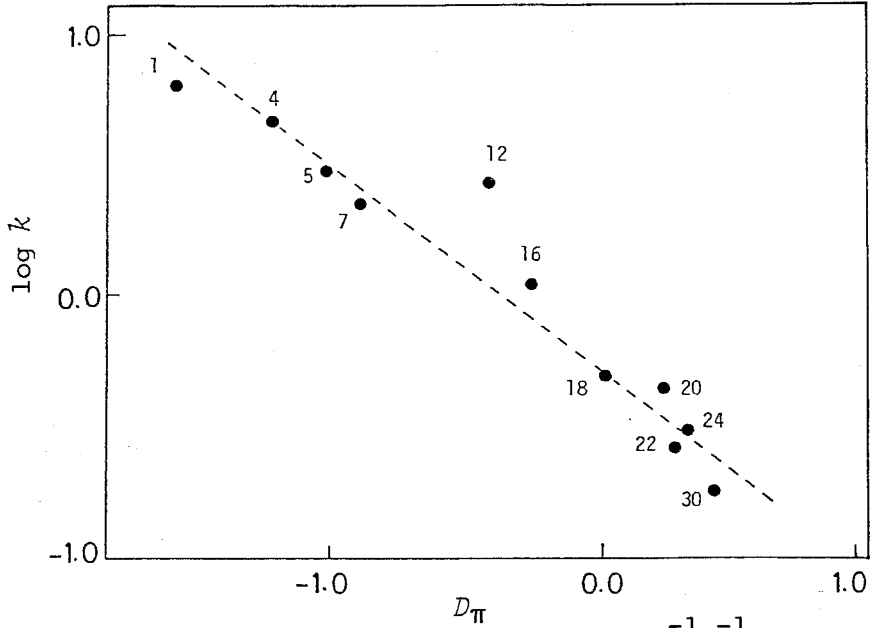
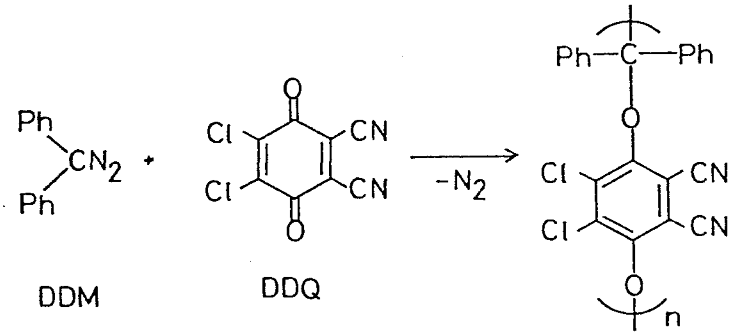


Fig. 6. Correlation between D_{π} and log k(1 mlo^{-1}s^{-1}) of the reaction of TCNE with anthracene at 30°C: log k= -0.273-0.763D_{π} (r=0.962, n= 11). For point numbers, see Table 3.

According to the LEF treatment in equation(5), the *m* value of this anthracene-TCNE system is -0.76, suggesting a lower susceptibility to solvent basicity compared to the model DDM-TCNE system($m = -1$). This is probably because anthracene molecule behaves as an electron donor and thereby the electron-accepting ability of TCNE is lowered.

As quinones are π-acceptor acids as well as TCNE, the decomposition of DDM with 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) is thought to undergo to a considerable extent similar solvent effects to those in the TCNE reactions. This reaction was found to obey the second-order kinetic law, giving the corresponding poly(2,3-dichloro-5,6-dicyanohydroquinone benzhydryl ether).[26]



A plot of log *k* for DDQ reaction against D_π values shows a substantially linear correlation except for 1,2-dimethoxyethane as seen in Fig. 7 and equation(6).

$$\log k = 0.623 - 1.10 D_\pi \quad (r=0.977,\ s=0.161,\ n=26) \qquad (6)$$

This linear dependence of log *k* on D_π values means that the stabilization of the initial DDQ molecule due to the solvent basicity effectively contributes to the increase of the free energy of activation. The coefficient(*m* value) of D_π in equation(6) lying slightly below -1 refers to the somewhat more sensitive dependence of the DDQ reaction on the solvent basicity in comparison to the TCNE reaction. The enhanced upward shift for 1,2-dimethoxyethane may be rationalized in view of the specific two-centered association with TCNE as mentioned above, which is not found in the case of DDQ. Therefore, it is necessary to adopt a reduced D_π value for the one-centered association of 1,2-dimethoxyethane.

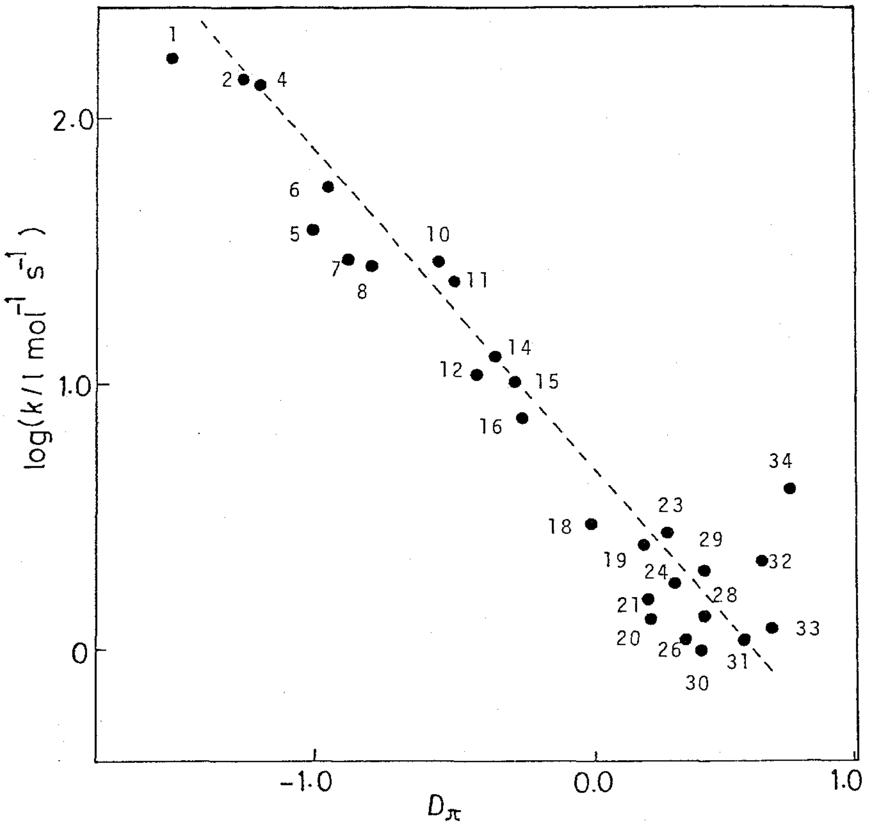


Fig. 7. Correlation between D_π and log k(l mol^{-1} s^{-1}) of the reaction of DDM with DDQ in various solvents at 30°C; for point numbers, see Table 3

According to the linear correlation in equation(6), the author propose an alternative D_π value of 0.000 for the one-centered association(also represented by the parenthesized value in Table 3).

As has been demonstrated in chapter 3, the D_π parameter is found to be applied to the description of the solvent effects on the stereochemical course in the reaction of aryldiazomethanes with chloranil.[27] Further usage of the D_π will be seen in the next chapter where the solvent contributions to the reactions of DDM with chloranil and 2,5-dichloro-*p*-benzoquinone are discussed.

In summary, TCNE easily decomposed diaryldiazomethanes(DDMs) to provide quantitatively diaryltetracyanocyclopropanes. The kinetic studies indicated that the transition state may be stabilized by the resonance contribution of the substituents of DDMs; log k were well correlated with Brown's σ^+ constants with ρ value of -2.67 at 30°C in benzene.

It was found that the rate constants generally decreased with the increase of solvent basicity, so the relative values of log *k*(benzene as reference solvent) could be defined as a solvent basicity parameter(D_π) applicable to the physicochemical properties induced by the participation of soft acids(π-acceptors).

4-3 Experimental

Materials. TCNE was prepared by the method of Carboni[28] and purified by sublimation at least three times; mp 200°C. Diaryldiazomethans (DDMs) were synthesized from the corresponding hydrazones by oxidation with yellow mercury(II) oxide as described by Smith and Howard.[29] The crystalline diazo-compounds were recrystallized from ether or light petroleum, and the oils were ascertained not to contain hydrazones by NMR measurements. The diazo-compounds prepared and some of their physical properties are listed in Table 5. All solvents were dried and purified according to the standard procedures.[30]

Table 5. Physical properties of DDMs(<u>1a-n</u>) $(XC_6H_4)(YC_6H_4)CN_2$

DDMs	X	Y	Mp(°C)	Lit.mp(°C)	Ref.	λmax(C_6H_6)/nm	(ε)
<u>1a</u>	4-OCH_3	4-CH_3	75-78	—	—	544	(91)
<u>1b</u>	4-OCH_3	H	55-56	56	31	527	(98)
<u>1c</u>	4-CH_3	4-CH_3	102-103	100-101	32	538	(89)
<u>1d</u>	4-OPh	H	53-54	—	—	531	(102)
<u>1e</u>	4-CH_3	H	55-56	53-55	33	532	(102)
<u>1f</u>	4-Ph	H	118-119	118-120	31	529	(140)
<u>1g</u>	3-CH_3	H	Oil	—	—	528	(98)
<u>1h</u>	H	H	29-30	29	32	527	(102)
<u>1i</u>	4-F	H	34-36	34-35	34	529	(86)
<u>1j</u>	4-I	H	Oil	—	—	525	(78)
<u>1k</u>	4-Cl	H	31-33	26-27	32	526	(104)
<u>1l</u>	4-Br	H	35-36	39-41	34	524	(81)
<u>1m</u>	4-Cl	4-Cl	105-106	70	32	524	(120)
<u>1n</u>	3-Cl	H	Oil	—	—	520	(84)

Kinetic Measurements. Solutions for kinetic experiments were prepared separately just before use in a volumetric flask with a stopper. TCNE solution (*ca.* 10^{-2}M) was introduced into a stoppered quartz optical cell (10 mm) and kept at the given gemperature (±0.05°C) in a thermostatically controlled cell-holder of a Hitachi 323 spectrophotometer. The reaction was initiated by rapid addition of the requisite volume of the diazo-compound solution (*ca.* 10^{-2}M), preheated in the bath to the same temperature as the cell-holder. The change in the optical density of the maximum of the diazo-compound was followed continuously over at least two half-lives for 1a-l and one half-life for 1m and 1n. The second-order rate constants (k) were determined graphically according to the procedure described in chapter 2.

Product Analyses. In benzene solution(10 ml), diazo-compound (200 mg) and an equimolar quantity of TCNE were mixed at room temperature and the solution was shaken to dissolve TCNE completely. Evolution of nitrogen gas was vigorous for 1a-i with accompanying precipitation of the cyclopropane products, moderate for 1j-l, and slow for 1m and 1n. The mixtures were still allowed to stand for 1 h for 1a-i, 6 h for 1j-l, and overnight for 1m and 1n. Samples for analysis were prepared by recrystallization from benzene, and the structures were confirmed by IR, NMR, and mass spectra and elemental analyses.

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Chapter 5 Solvent Effects in the Reactions of Diphenyldiazomethane with Various Quinones

5-1 Introduction

The chapter 2 dealt with the reactions of diaryldiazomethanes(DDMs) with quinones from the standpoint of kinetic substituent effects. The rate constants increased with the electron donating ability of the substituents, thus the reactions were postulated to proceed through the polar transition state with the partial positive charge on the diazo-carbon. More detailed information regarding the reaction features may be obtained from the studies of the kinetic solvent effects.

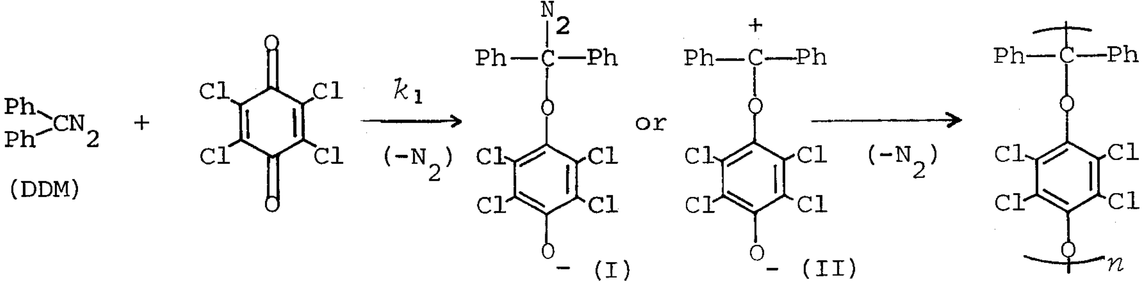
The chapter 4 was concerned with the kinetic solvent effects in the reaction of diphenyldiazomethane(DDM) with TCNE, and the apparent role of the solvent basicity in the rate retardation made the author propose a new empirical parameter of solvent basicity, D_π.

In this chapter, the author wants to describe the solvent effects on the rates in the reactions of DDM with chloranil, 2,5-dichloro-*p*-benzoquinone(DCQ), and 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) in terms of the basic solvation of the initial states and of the polar solvation of the transition states. Thus, the linear free energy(LFE) treatment of these results will be examined with the aid of the solvent basicity(D_π) and polarity(f(ε) or E_T) parameters.

5-2 Results and Discussion

5-2-1 Reaction with Chloranil

The DDM-chloranil reaction is found to afford poly(tetrachlorohydroquinone benzhydryl ether) by way of a diazonium or carbonium betaine intermediate, I or II (Scheme 1).[1]



Scheme 1

Table 1. Second-order rate constants k(1 $mol^{-1}s^{-1}$) for the reactions of diphenyldiazomethane(DDM) with chloranil, 2,5-dichloro-*p*-benzoquinone(DCQ), and 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) in various solvents at 30°C, with the solvent basicity and the polarity parameters

Solvent[b)]	chloranil	DCQ			DDQ	D_π	E_T	f(ε)
	10^3k_1	10^3kobsd(2/3)[a)]	10^3k_2	10^3k_3	k_4			
Chloroform(1)	30.7	15.5(0.535)	5.40	10.1	169	-1.56	39.1	0.359
Dichloromethane(2)	—	13.5(0.611)	5.12	8.38	146	-1.30	41.1	0.420
1,2-Dichloroethane(4)	30.5	14.3(0.611)	5.65	9.25	134	-1.22	41.9	0.431
Bromobenzene(5)	12.1	7.26(0.681)	2.94	4.32	39.2	-1.03	37.5	0.373
Diisopropyl ether(6)	—	— —	—	—	56.8	-0.982		0.329
Chlorobenzene(7)	10.1	6.32(0.685)	2.57	3.75	30.8	-0.903	37.5	0.377
Fluorobenzene(8)	8.90	5.56(0.690)	2.27	3.29	27.6	-0.818	38.1	0.373
Nitromethane(9)	32.3	15.9(0.670)	6.44	9.46	—	-0.724	46.3	0.479
Nitrobenzene(10)	24.4	—	—	—	30.3	-0.583	42.0	0.479
Methyl chloroacetate(11)	—	—	—	—	25.1	-0.533		
Acetonitrile(12)	23.4	13.4(0.711)	5.57	7.83	11.2	-0.440	46.0	0.480
Benzonitrile(13)	—	11.1(0.618)	4.24	6.86	—	-0.398	42.0	0.471
Dibutyl ether(14)	—	—	—	—	12.8	-0.372	33.4	0.291
Diethyl ether(15)	—	—	—	—	10.3	-0.298	34.6	0.345
Propionitrile(16)	14.5	10.8(0.676)	4.35	6.45	7.85	-0.277	43.7	0.473
Benzene(18)	2.66	3.38(0.954)	1.65	1.73	3.05	0.000	34.5	0.230
Ethyl methyl ketone(19)	6.43	8.02(0.496)	2.66	5.36	2.58	0.177	41.3	0.461
Methyl acetate(20)	6.29	5.23(0.848)	2.40	2.83	1.34	0.196	40.0	0.396
Ethylbenzene(21)	2.42	3.07(0.706)	1.27	1.80	1.56	0.197	—	0.241

Table 1. (Continued)

Solvent[b)]	chloranil	DCQ			DDQ	D_π	E_T	f(ε)
	10^3k_1	10^3kobsd(2/3)	10^3k_2	10^3k_3	k_4			
Cyclohexanone(22)	5.69	7.01(0.501)	2.34	4.67	—	0.243	40.8	0.460
Acetone(23)	5.68	7.48(0.685)	3.04	4.44	2.91	0.261	42.2	0.464
Ethyl acetate(24)	5.34	4.65(0.710)	1.93	2.72	1.81	0.289	38.1	0.385
Propyl acetate(26)	5.30	5.26(0.697)	2.16	3.10	1.13	0.337	37.5	0.385
Isopropyl acetate(28)	—	—	—	—	1.38	0.381		
Dimethoxymethane(29)	—	—	—	—	2.10	0.383		
Toluene(30)	1.65	2.46(0.864)	1.14	1.32	1.03	0.394	33.9	0.239
Tetrahydropyran(31)	—	3.39(0.670)	1.36	2.03	1.12	0.539	—	0.377
1,4-Dioxane(32)	1.79	2.93(0.655)	1.16	1.77	2.22	0.590	36.0	0.223
Tetrahydrofuran(33)	2.43	2.37(0.634)	0.92	1.45	1.27	0.639	37.5	0.407
1,2-Dimethoxyethane(34)	—	—	—	—	4.20	0.704		

a) Product ratios(2/3) were determined by means of high performance liquid chromatography; the yield of 3 was taken as the amount of benzophenone after hydrolysis of 3.

b) Solvent numbers are common in Chapter 4.

The second-order rate constants over a wide range of aprotic solvents are shown in Table 1, together with the D_{π}[2] and the solvent polarity parameters, the Kirkwood function of the dielectric constants ε, $f(\varepsilon) = (\varepsilon-1)/(2\varepsilon+1)$,[3] and Dimroth and Reichart's E_T values.[4] This table also contains the data for the reactions with 2,5-dichloro-*p*-benzoquinone(DCQ) and 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ).

An inspection of the results shows that the rates did not correlate well only with the usual solvent basicity or polarity parameter. Dipolar solvents, *e.g.*, nitro compounds and nitriles, tended to increase the rates, while the basic aromatic hydrocarbonds and cyclic ethers decrease them. A preliminary correlation of log k_1 with the conventional basicity parameters, such as $\Delta\nu_D$,[5] the β scale,[6] and *DN*,[7] yielded worse results because of the marked deviation of the aromatic hydrocarbons: log k_1= $-0.0048\Delta\nu_D-1.97$(r=0.35, n=18), log k_1= -0.198 -2.23(r=0.10, n=11), and log k_1= $-0.028DN$ -1.76(r=0.45, n=11). However, a plot of log k_1 against D_{π} values showed a better correlation, suggesting the stabilization of the initial state as a result of the basic solvation of the chloranil molecule; log k_1= $-0.536D_{\pi}-2.23$(r=0.826, n=20) (Fig. 1).

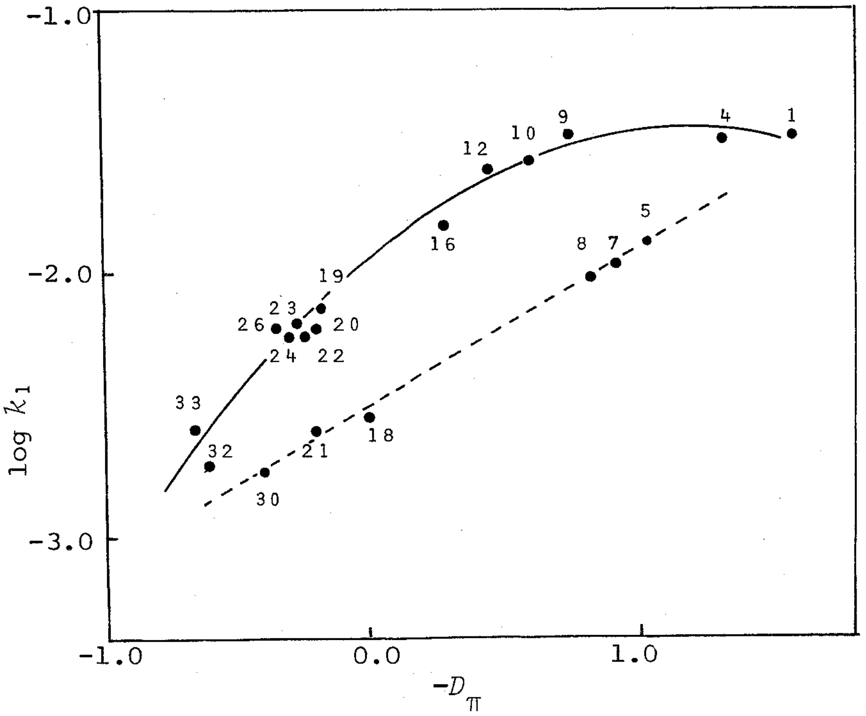


Fig. 1. Plot of log k_1 against D_{π}. Solvent Nos., see Table 1.

The six nonpolar aromatic hydrocarbons and derivatives(Solv. Nos. 5, 7, 8, 18, 21, and 30) were well correlated(slope= -0.600, r=0.998), but the dipolar solvents displayed an inverted U-shaped deviation. The apparent acceleration by the dipolar solvents may be attributed to the stabilization of the transition state by the dipole-dipole interaction. The effects of the substituents on the rate supported the polar transition state with a partial positive charge on the diazo-carbon: log k/k_0= -1.67(σ^0 + 0.66$\Delta\bar{\sigma}_R^+$) + 0.009,[1] at 30°C in THF. However, the correlation of log k_1 with f(ε) (r=0.69) or E_T (r=0.74) was less satisfactory than that with D_π. This implies that the chloranil reaction is more dependent on the basic property(D_π) of the solvents.

To obtain a more satisfactory regression, it is useful to examine the multiple correlation of log k_1 with D_π values and with E_T or f(ε) as the solvent polarity parameter. The two parameter equations consisting of linear combination of D_π and E_T or f(ε) improved the correlation, as may be seen in Eq. 1 for 19 solvents and in Eq. 2 for 20 solvents:

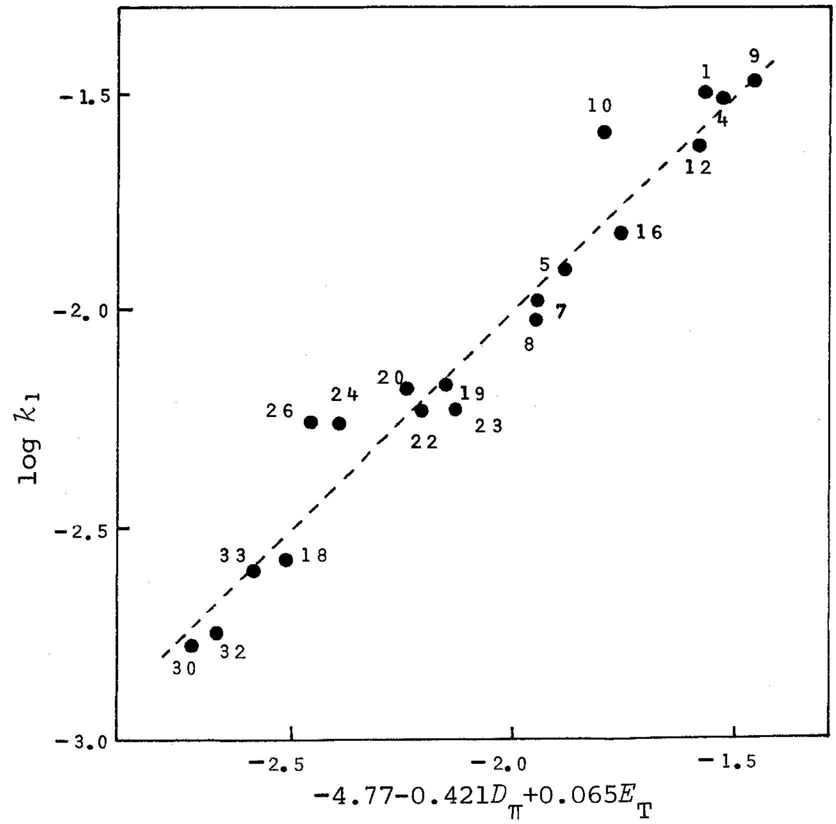


Fig. 2. Plot of log k_1(obsd) against log k_1(calcd) according to Eq. 1, for point numbers, see Table 1.

Chloranil-DDM reaction:

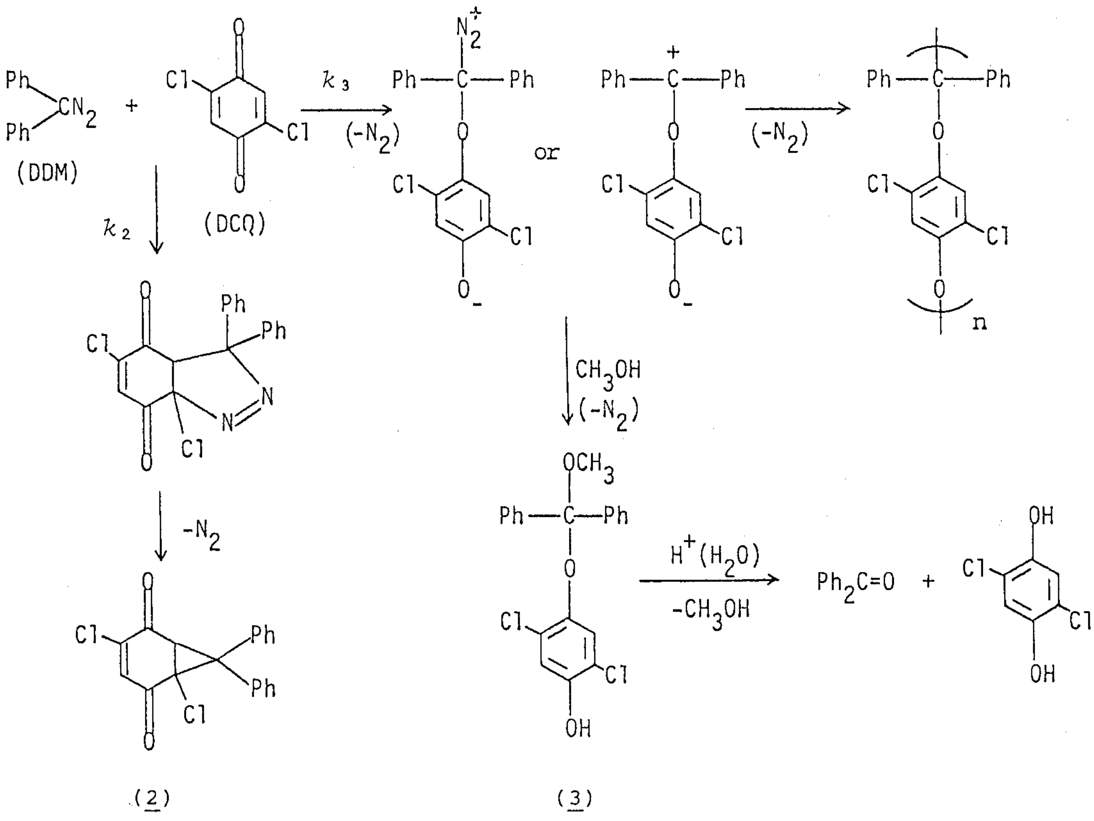
$$\log k_1 = -4.77-0.421D_{\pi}+0.0650E_{T} \qquad (r=0.977,\ s=0.0945,\ n=19) \tag{1}$$

$$\log k_1 = -3.16-0.450D_{\pi}+2.45f(\varepsilon) \qquad (r=0.963,\ s=0.120,\ n=20) \tag{2}$$

The Kirkwood function, f(ε), appears less successful than E_T, as is shown by the values of *r* in Eqs. 1 and 2. A plot of log k_1(obsd) *vs*. log k_1(calcd) according to Eq. 1 is shown in Fig. 2.

5-2-2 Reaction with 2,5-Dichloro-*p*-benzoquinone

The 2,5-dichloro-*p*-benzoquinone(DCQ) decomposed DDM to give two products, bicyclic dione(2) and poly(2,5-dichlorohydroquinone benzhydryl ether)(Scheme 2).[8]



Scheme 2

The formation of 2 may be explained as arising from the initial product, pyrazoline, followed by the loss of N_2; the polyether may then be thought to be made up by the polymerization of a diazonium or carbonium betaine intermediate, like *I* or *II*. The participation of the betaine intermediate was evidenced by the isolation of 2,5-dichloro-4-[(methoxy) diphenylmethoxy]phenol(3) in the reaction carried out in the presence of a small amount of CH_3OH;[8] 3 was easily hydrolyzed into benzophenone and 2,5-dichlorohydroquinone. Thus, the yield was taken as the amount of benzophenone. However, no essential change was noticed in the observed rate constants or in the yield of 3 between the reaction in the absence and in the presence of a small amount of CH_3OH as an additive, as exemplified by a 1,2-dichloroethane solution.[8] Therefore, the author made product and kinetic studies of the solvents containing a 5 molar excess of CH_3OH with respect to DDM, and then the total and the relative yields of 2 and benzophenone after the hydrolysis were conveniently determined by means of high-performance liquid chromatography. The combined yields of 2 and 3 amount to more than 95% in all the solvents used. The observed second-order rate constants(k_{obsd}) were divided into the individual rate constants, k_2 and k_3, for the paths leading, respectively, to 2 and 3, by combining them with their relative yields. The kinetic data and the relative product yields are shown in Table 1.

An examination of the results shows that, although the variation in the rate constants with the changing solvent is considerably low, k_2 and k_3 depend on both the basicity and the polarity of the solvents, as in the case of a chloranil reaction; $\log k_2 = -1.35 + 0.584 \log k_1$ (r=0.962, n=19) and $\log k_3 = -1.05 + 0.66 \log k_1$ (r=0.946, n=19), where k_1 is the rate constant in the chloranil-DDM reaction. For a comparison of k_2 and k_3, a similar but slightly greater dependence of k_3 on the properties of the solvents can be anticipated from the linear correlation: $\log k_3 = 0.392 + 1.08 \log k_2$ (r=0.973, n=22).

For example, a single-parameter correlation of the logarithmic rate constants with the D_π, E_T, and f(ε) values is as follows: $\log k_2 = -2.65 - 0.289 D_\pi$ (r=0.769, n=22), $\log k_2 = -4.87 + 0.0582 E_T$ (r=0.797, n=20), $\log k_2 = -3.38 + 2.05 f(\varepsilon)$ (r=0.673, n=22), and $\log k_3 = -2.48 - 0.311 D_\pi$ (r=0.743, n=22), $\log k_3 = -5.02 + 0.0664 E_T$ (r=0.807, n=20), $\log k_3 = -3.37 + 2.46 f(\varepsilon)$ (r=0.727, n=22). A comparison of the r values of these correlations indicates that both k_2 and k_3 are more affected by the solvent polarity(E_T) than by the basicity(D_π). This trend is the opposite of that found in the chloranil reaction. Attempts to obtain more satisfactory correlations were done using two parameters, D_π and E_T or f(ε). The results are shown as Eqs. 3 and 4 for log k_2 and as Eqs. 5 and 6 for log k_3:

DCQ-DDM reaction:

$$\log k_2 = -4.45-0.205D_\pi+0.0460E_T \quad (r=0.962,\ s=0.0176,\ n=20) \qquad (3)$$

$$\log k_2 = -3.24-0.240D_\pi+1.55f(\varepsilon) \quad (r=0.912,\ s=0.110,\ n=22) \qquad (4)$$

$$\log k_3 = -4.57-0.218D_\pi+0.0535E_T \quad (r=0.953,\ s=0.090,\ n=20) \qquad (5)$$

$$\log k_3 = -3.22-0.249D_\pi+1.94f(\varepsilon) \quad (r=0.926,\ s=0.113,\ n=22) \qquad (6)$$

As the case of the chloranil reaction, both the equations involving D_π and E_T gave better correlations than the corresponding expressions involving D_π and f(ε). The superiority of the E_T parameter may be ascribed to the intrinsic combined measures of solvent polarity and acidity,[9] by which the specific solvation of the transition state with the negatively charged quinone moiety is effected. Furthermore, a comparison of the coefficients of D_π and E_T in Eqs. 3 and 5 shows that the $\underline{3}$ path receives more influence of the solvent polarity than does the $\underline{2}$ path; the absolute coefficients of D_π increased *ca.* 6%, but the corresponding values of E_T increased *ca.* 16%, in going from Eq. 3 to Eq. 5. The plots of log k_2(obsd) *vs.* log k_2(calcd) and log k_3(obsd) *vs.* log k_3 (calcd), according to, respectively, Eq. 3 and Eq. 5, are shown in Fig. 3. The greater suceptibility of the $\underline{3}$ path to the solvent polarity than the $\underline{2}$ path can be ascribed to the more-charged transition state suggested by the kinetic substituent effects: $\log k_2 = -2.15-1.55\sigma$ and $\log k_3 = -2.03 -1.85(\sigma^0 + 0.515\Delta\bar{\sigma}_R{}^+)$.[8]

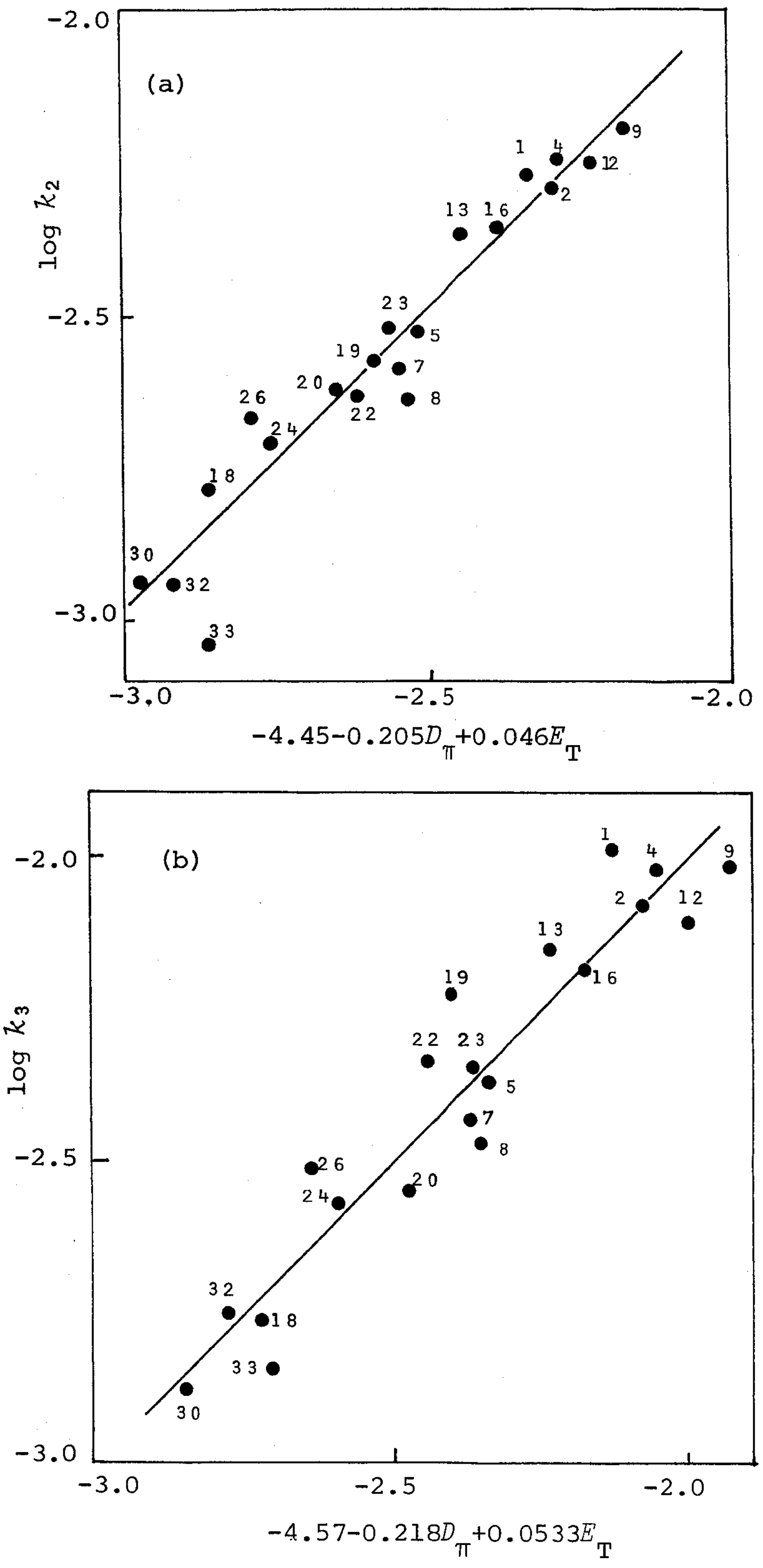


Fig. 3. (a) Plot of log k_2(obsd) *vs*. log k_2(calcd) accordig to Eq. 3; (b) Plot of log k_3(obsd) *vs*. log k_3(calcd) according to Eq. 5; for point numbers, see Table 1.

5-2-3 Comparison of the Kinetic Solvent Effects

One can now compare the kinetic solvent effects in the reactions of DDM with various π-acceptor acids, *i.e.*, chloranil, DCQ, DDQ, and TCNE.

In contrast to the cases of chloranil-, DCQ-DDM reactions, 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ)-DDM reaction giving the corresponding polyether[10] as well as the chloranil reaction was found to be correlated only with the D_π parameter as in Eq. 7(for Figure; see chapter 4).

DDQ-DDM reacrion:

$$\log k_4 = 0.623 - 1.10 D_\pi \quad (r=0.977,\ s=0.161,\ n=26) \tag{7}$$

In formulating the D_π scale in 34 aprotic solvents,[2] the author used the difference between the logarithmic rate constants of the TCNE-DDM reaction in benzene(as a reference solvent) and the solvent at 30°C, so the log k_5 can be described by this modified form:

TCNE-DDM reaction:

$$\log k_5 = -1.01 - D_\pi \tag{8}$$

A comparison of the intercepts and the slopes in Eqs. 7 and 8 indicates that the DDQ reaction is *ca.* 30 times faster in the benzene solution(D_π= 0) and depends slightly more on the solvent basicity than the TCNE reaction. On the contrary, the chloranil and DCQ reactions, both having substantially the same orders of rates, gave rates about 50 times lower in benzene and showed a less effective contribution of the D_π compared to the TCNE reaction, as may be seen in the coefficients of D_π in Eqs. 1, 3, and 5. It should also be noted that these equations are characterristic in incorporating the solvent-polarity parameter.

The solvation effects in both initial and transition states must be taken into account in order to understand the influence of the solvent on the rate. In the initial states, the basic solvation of the π-acceptor acids is the chief factor influencing the rate constants, as exemplified the UV blue shifts and the appearance of the charge-transfer absorption of TCNE[11,12] and chloranil[13] on going to more basic solvents[†] (Table 2). As for the data for TCNE, one can see them in Table 4 in chapter 4.

Table 2. Solvent effects in the UV spectra of chloranil.[a)]

	λmax/nm (log ε)		
Chloroform	292.0 (4.35)	374.0 (2.37)	
Acetonitrile	287.0 (4.32)	367.5 (2.39)	
Ethyl acetate	287.0 (4.27)	364.0 (2.40)	
Tetrahydrofuran	283.5 (4.23)	330[b)] (3.16)[c)]	
1,4-Dioxane	285.5 (4.20)	330[b)] (3.20)[c)]	
Fluorobenzene	285.5 (4.12)	330[b)] (3.27)[c)]	
Benzene	283.5 (4.16)	332 (3.33)[c,d)]	346[d,e)]
Toluene	286.5 (4.19)	362 (3.27)[c,d)]	365[d,e)]

a) Measured at 25°C. b) Shoulder. c) Measured in 7.0 × 10^{-4} mol/l. d) Due to charge-transfer absorption.
e) Values taken from Ref. 13.

One can easily notice the parallelism between the absolute coefficients of D_π and the electron affinity of these π-acids in the order of DDQ(1.95 eV) > TCNE(1.80) > chloranil(1.37) > DCQ(1.1).[14] This means that the extent of the basic solvation can be related to the π-acceptor ability of these acids. On the other hand, the transition states may be stabilized by the dipole-dipole interaction in the polar media, since the kinetic substituents effects of all these reactions suggest charged transition states.

Here again, the author summarizes the Hammett parameters, ρ, with the correlation fashion: TCNE reaction; -2.67(with Brown's σ^+)[15], DDQ; -2.33(Yukawa-Tsuno equation)[10], chloranil; -1.67(Yukawa-Tsuno

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[†] By contrast, the π-π^* absorption of DDM in the ultraviolet region remained essentially unchanged during such a variation of solvents, reflecting the lower solvation of DDM; see Table 4 in chapter 4.

equation)[1], and DCQ; -1.85(for the path giving 3, Yukawa-Tsuno equation) and -1.55(for path giving 2, with normal σ).[8] If the ρ values may be taken as a suitable estimate of the charge appearance of the transition state, the TCNE and DDQ reactions are more likely to be stabilized by the polar solvent than are the chloranil and DCQ reactions. An examination of Eqs. 1-8, however, shows that the DDQ reaction is satisfactorily correlated only with D_π, while the chloranil and DCQ reactions are well expressed by a linear combination of D_π and a polarity parameter, such as E_T and f(ε). This apparent discrepancy can be easily explained by the relative significance of the stabilizations in the initial and transition states in comparison with that for the model TCNE-DDM reaction. By definition, the D_π parameter inherently reflects the influence of the solvent, not only on the initial state, but also on the transition state of the TCNE-DDM reaction. The free energies of the solvation of the initial state(ΔG_B) are, of course, greater than those of the transition state(ΔG_P), as was demonstrated earlier by the statistically better correlation of the logarithmic rate constants with the conventional basicity parameters, such as $\Delta\nu_D$, β , and *DN*, than those with E_T and f(ε).[2] This situation is schematically shown in Fig. 4, together with the other cases of DDQ, chloranil, and DCQ reactions.

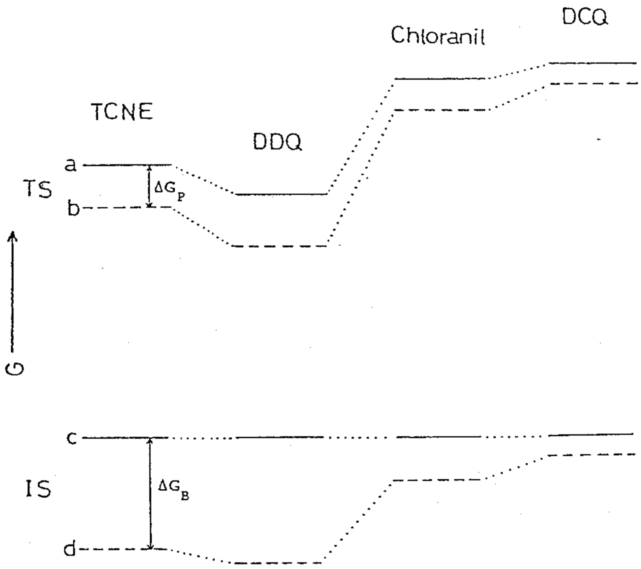

Fig. 4. Solvent effect upon reactants and transition states;
TS: transition states in nonpolar(a) and in polar(b) solvents;
IS: initial states in nonbasic(c)(depicted arbitrarily in the same level) and basic(d) solvents.

In the case of DDQ reaction, lack of the polarity parameter and the slight excess sensitivity to the D_{π}, therfore, may be ascribed to essentially the same $\Delta G_P/\Delta G_B$ ratios but to somewhat greater individual values with compared to TCNE reaction. On the other hand, the incorporation of the polarity parameter in chloranil and DCQ reaction is the results of the significant decrease in the basic solvation, thereby the relative role of ΔG_P may be pronounced with respect to ΔG_B.

Recently, Krygowski and Fawcett proposed a similar two-parameter regression with the aid of E_T and DN, where Q is a physicochemical quantity and α, β are the regression coefficients.[9] Application of this empirical equation to the present chloranil and DCQ reaction, how-

$$Q = Q_0 + \alpha E_T + \beta DN$$

ever, resulted in much worse correlation because DN is inadequate to describe the softness of aromatic solvents.

In summary, the second-order rate constants(k) in the reactions of DDM with chloranil, DCQ, DDQ, and TCNE increased with the solvent polarity and decreased with the solvent basicity. The kinetic solvent effects could be interpreted in terms of the effects of the polarity and basicity of the solvents respectively to the transition and to the initial states. The extent of the relative contributions of the two effects may be estimated by both the Hammett ρ values of these reactions and the electron affinity(EA) of these acceptors. Thus, the multiple linear correlations of the log k with a function of the basicity(D_{π}) and the polarity(E_T) were successful.

5-3 Experimental

The bicyclic dione(2):benzophenone ratios and the overall yields of 2 and benzophenone were determined by means of JASCO tori-roter high-performance liquid chromatography(H. P. L. C.), using biphenyl as the internal standard. The H. P. L. C. analysis was carried out at room temperature using a 250×4.5 mm column packed with ODS(octadecylsilane) on silica gel; methanol-water(7:3 by volume); flow rate, 1 ml/min. The UV detector was calibrated at 245 nm with standard mixtures of known concentrations of benzophenone, 2 , and biphenyl. The relative retention times were as follows;benzophenone (0.53), 2(0.68), and biphenyl (1.0).

Materials. The diphenyldiazomethane(DDM) was synthesized as has been described by Smith and Howard[16] and recrystallized from light petroleum; mp 29-30°C. The chloranil and DDQ were of commercial origin and were purified by recrystallization as has described.[1,10] The DCQ was prepared according to the procedure described by Ling[17] and was recrystallized from ethanol; mp 164-166°C. All the solvents were dried and purified according to the standard procedures.[18]

Kinetic Measurements. The values of k were determined spectrophotometrically as has previously been described[1,8] by the use of Hitachi 323 and JASCO UVIDEC-505 instruments. The absorption cells were thermostated at 30±0.1°C with a Haake circulator. The mean deviations for k were ±3%(usually two determinations)

5-4 References

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Chapter 6 An Application of Diphenyldiazomethane-Quinone Reaction to Syntheses of Acetals and Crown Ethers

6-1 Introduction

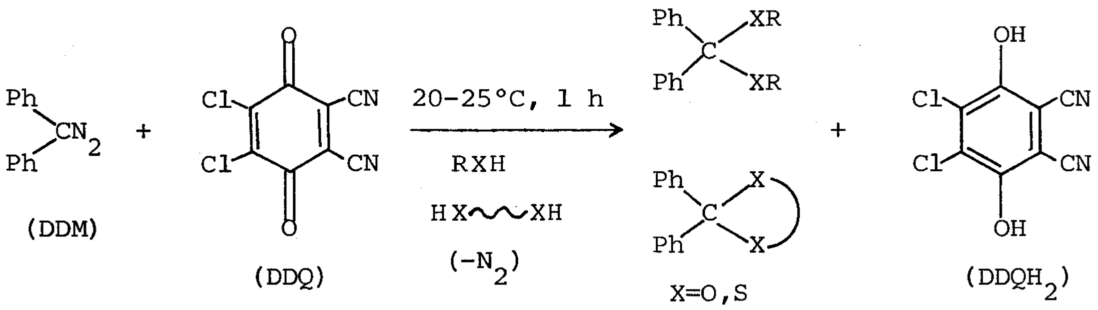
In the preceding several chapters, the author studied the reactions of diaryldiazomethanes(DDMs) with various quinones mainly from the mechanistic viewpoint with the aid of the information of the kinetic substituent and solvent effects. This chapter is concerned with the synthetic utilization of the DDM-quinone systems in order to provide acetals and crown ethers. Acetals are generally produced from the reactions between alcohols and carbonyl compounds with a suitable Brønsted or Lewis acid catalyst.[1] On the other hand, since the pioneering work of Pedersen on the preparation and properties of macrocyclic polyethers (crown ethers),[2] there have been numerous reports of syntheses of a wide variety of crowns.[3] The general methods proposed for the synthesis of crown compounds are a modified Williamson ether syntheses by the reactions of oligoethylene glycols with oligoethylene glycol dichlorides or ditosylates[2,4] and of oligoethylene glycols with arensulfonyl or alkanesulfonyl chlorides,[5] in the presence of suitable template metal cations.

The author wants to report a novel synthetic method of various cyclic and non-cyclic benzophenone acetals, thioacetals , and crown ethers incorporated with a diphenylmethylene subunit in high yields by means of the reaction of DDM with DDQ under the influence of the corresponding alcohols, thiols, and oligoethylene glycols.

6-2 Results and Discussion

6-2-1 Formation of Acetals

The reaction of diphenyldiazomethane(DDM) and a stoichiometric amount of 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) in the presence of 3 to 5 fold molar excess of alcohols proceeds with a vigorous evolution of nitrogen gas to afford benzophenone acetals in good yields together with 2,3-dichloro-5,6-dicyanohydroquinone($DDQH_2$) (Method A). This system was found to be efficient even if the alcohols were separately added after the termination of the reaction(Method B). These results are shown in Scheme 1 and Table 1.



Scheme 1

Table 1. Formation of Acetals and Thioacetals in the DDM-DDQ-Alcohols, -Thiols Systems.

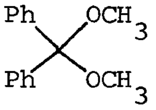
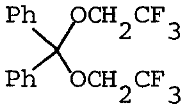
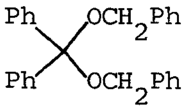
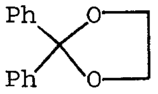
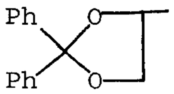
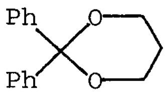
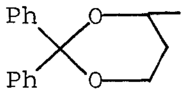
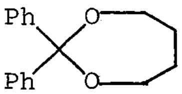
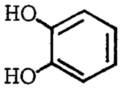
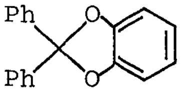
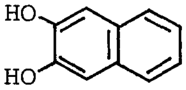
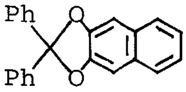
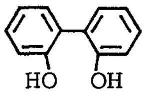
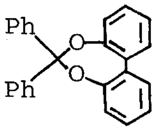
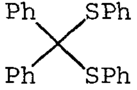
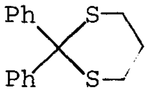
No	Alcohols and Thiols	Methods	Products	Yields(%)a)	MP(°C)	Found(%)b)	
						C	H
1	CH_3OH	A		87 85c)	106-107	78.98 (78.92)	7.01 (7.06)
		B		78			
2	CF_3CH_2OH	B		54	95-96	56.26 (56.04)	4.08 (3.87)
3	$PhCH_2OH$	A		73	107-109	85.37 (85.22)	6.30 (6.37)
4	$HO(CH_2)_2OH$	A		81	54-55	79.66 (79.61)	6.22 (6.25)
5	$HOCH_2CH(OH)CH_3$	A		74	68-69	80.08 (79.96)	6.70 (6.72)
6	$HO(CH_2)_3OH$	A		84	113-115	79.88 (79.96)	6.65 (6.72)
7	$HOCH_2CH_2CH(OH)CH_3$	A		78	89-91	80.18 (80.27)	7.11 (7.15)

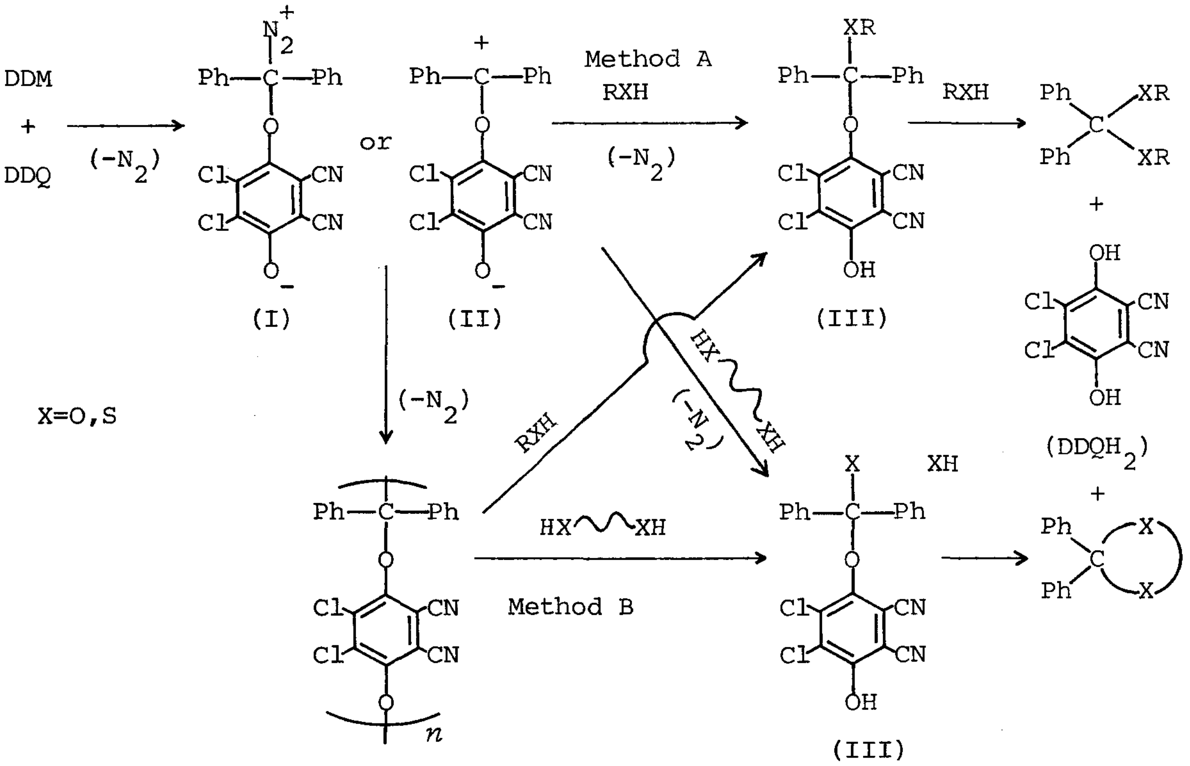
Table 1. (Continued)

No	Alcohols and Thiols	Methods					
8	HO$(CH_2)_4$OH	A		75	124-126	80.19 (80.27)	7.03 (7.15)
9		B		65	93.5-91.5	83.27 (83.18)	5.15 (5.15)
10		B		54	158-159.5	85.15 (85.15)	4.95 (4.98)
11		B		50	166-167	85.68 (85.68)	5.13 (5.19)
12	PhSH	B		79	138-139	77.88 (78.07)	5.19 (5.25)
13	HS$(CH_2)_3$SH	A		53	111-112.5	70.55 (70.53)	5.97 (5.93)
14	H_2O	B	$Ph_2C=O$	95	48-50		

a) Isolated yield based on DDM used. b) Required values in the parenthesis. c) Obtained from DDM-chloranil-CH_3OH system, Ref. 6.

Mechanistically, formations of acetals are well interpreted in terms of the occurrence of diazonium(I) or carbonium betaine(II) intermediate and the following nucleophilic attack of alcohols(Scheme 2). The resulting hydroquinone benzhydryl ethers(III) lead to the acetals by way of the external or the internal nucleophilic attack by the hydroxyl and the mercapt groups. As was expected, presence of water (R=H, X=O) resulted in the formation of benzophenone given by the loss of water from the initial product, α,α-dihydroxydiphenylmethane(Table 1, No. 14).[7] In Method B, it seems that I or II temporarily polymerizes and then the addition of alcohols and thiols causes the nucleophilic cleavage of the ether linkage to afford III.

The present methods utilize the decomposition of DDM by DDQ and the strong dehydrogenating ability of this quinone.[8]

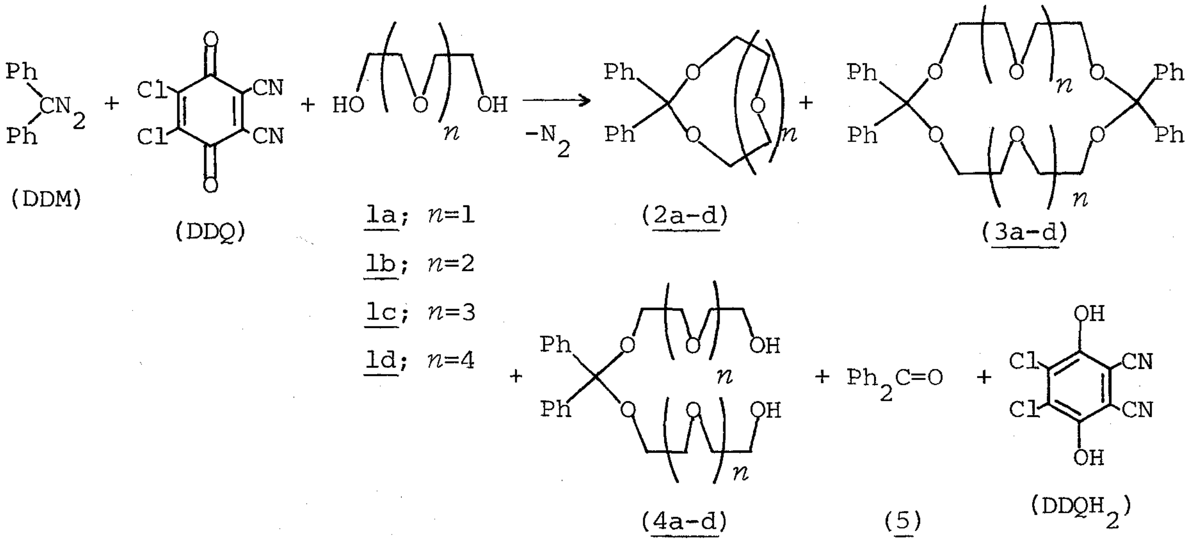


Scheme 2

6-2-2 Formation of Crown Ethers

(a) Reaction of DDM with DDQ in the Presence of Oligoethylene Glycols (Method A).

Reaction of DDM with DDQ in the presence of 1, 3, and 5 equivalent of di-, tri-, tetra-, and pentaethylene glycols(1) in dry benzene at 20-25°C gave three macroethereal products, 2, 3, and 4, incorporated with diphenylmethylene moiety together with benzophenone(10-20%) and almost quantitative amount of 2,3-dichloro-5,6-dicyanohydroquinone($DDQH_2$) (Scheme 3). The reaction conditions and the product distributions are seen in Table 2. The two macrocyclic products 2 and 3 have structures formally made by the dehydrocyclization of oligoethylene glycols toward diphenylmethylene with the aid of DDQ; 3 have a dimeric formula of 2. The non-cyclic macroethers 4 possess diol structures of 2 molecule of glycols being linked at the central carbon atom of diphenylmethylene.



Scheme 3

Table 2. Reaction Conditions and Product Distribution

Run	Glycols a) (rel. equiv)	Method	Reaction time, (h)	Products (%) b) 2	3	4	5
1	1a (1)	A	2	45	5	18	9
2	1a (3)	A	2	38	3	37	9
3	1a (5)	A	2	10	trace	43	3
4	1a (0.5)	B	2	84c)	0	0	25
5	1b (1)	A	2	27	13	21	16
6	1b (3)	A	2	12	5	52	16
7	1b (5)	A	2	8	trace	68	14
8	1b (0.5)	B	2	79c)	0	0	27
9	1b (1)	B	2	47	5	6	15
10	1b (3)	B	2	23	8	18	17
11	1c (1)	A	2	38	5	18	18
12	1c (1)	A	4	41	6	15	16
13	1c (3)	A	2	15	2	36	21
14	1c (5)	A	2	7	trace	44	18
15	1c (0.5)	B	2	70c)	0	0	23
16	1d (1)	A	2	48	trace	19	16
17	1d (0.5)	B	2	89c)	0	0	22
18	1e (0.5)	B	2	70c)	0	0	16

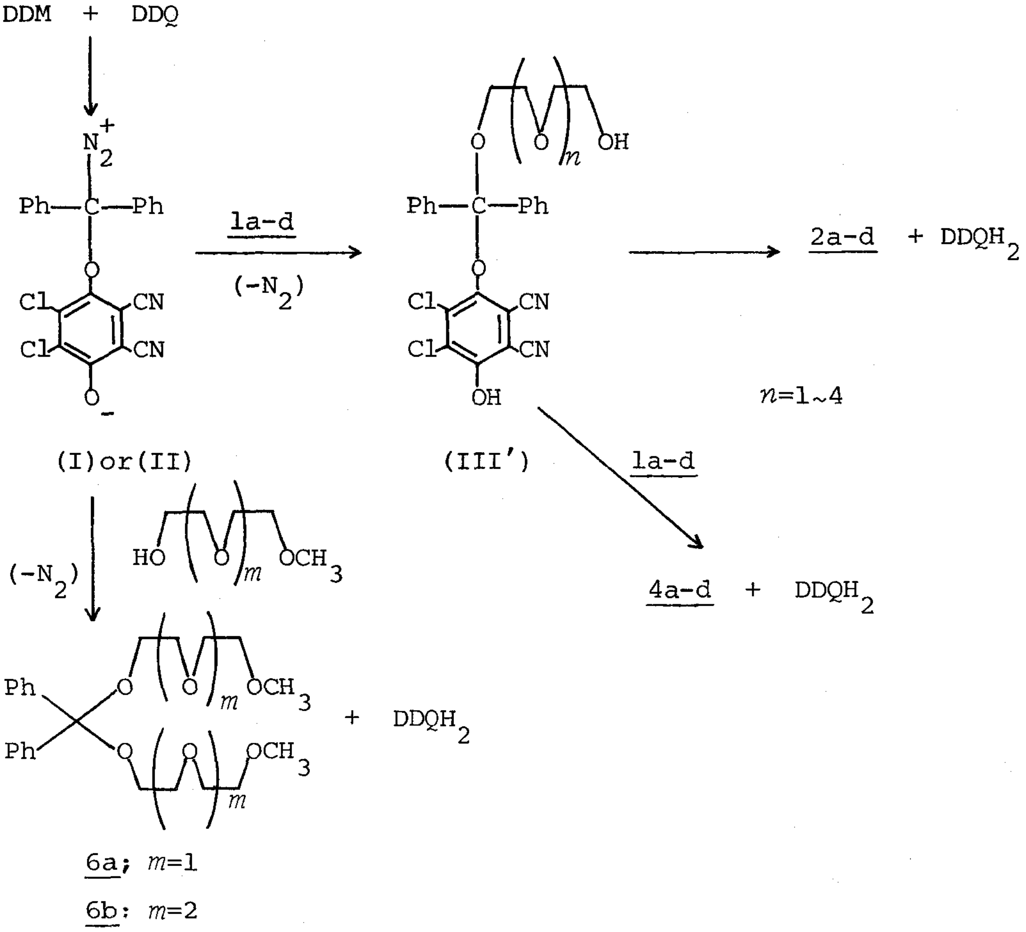
Table 2. (Continued)

a) 1a: di-, 1b: tri-, 1c: tetra-, 1d: penta-, and 1e: hexa-ethylene glycol.

b) Unless otherwise noted, based on DDM used.

c) Based on glycols.

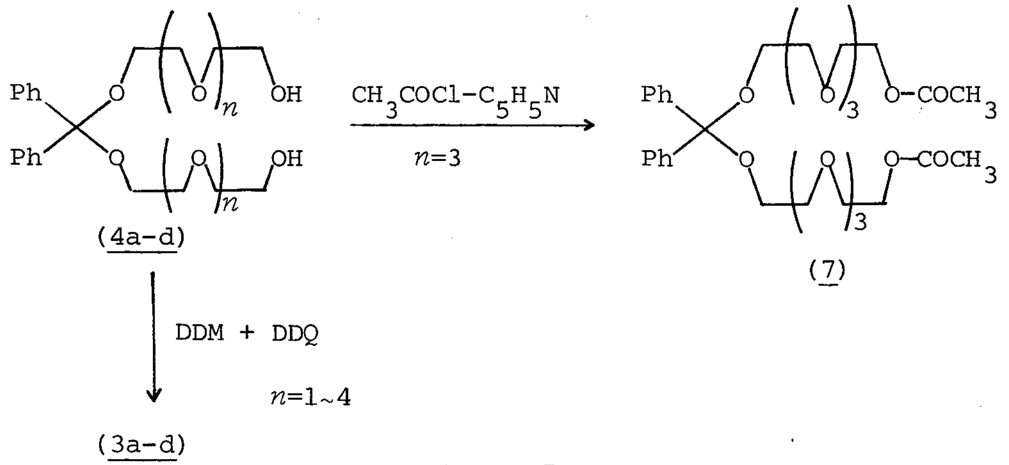
These overall redox reactions can be explained to proceed *via* diazonium betaine(I) or carbonium betaine(II) intermediate as well as the reactions with alcohols. The nucleophilic attack of the oligoethylene glycols to this intermediate is expected to provide a relatively unstable product(III′) which leads to cyclic 2 *via* an internal S_N2 displacement in competition with an external S_N2 attack of another glycol to afford non-cyclic 4 (Scheme 4).



Scheme 4

In accordance with the schematic diagram, reaction with di- and triethylene glycol monomethyl ethers has been found to give only non-cyclic macroethers 6. On the other hand, the formation of 3 is rationalized as the results of the nucleophilic attack of the resulting 4 toward the betaine intermediate and the follow-up internal S_N2 displacement as well as the case of 2. The evidence of such an intermediary 4 was realized by the observation that 4 were easily transformed into 3 when treated with DDM and DDQ(see Scheme 5). As was noted in the case of reaction with alcohols, the present reaction system is very sensitive to water, so the reagents and the equipments must be carefully dried before use. Thus, the unfortunate occurrence of benzophenone(5) can be ascribed to the residual water.

The purified 2 and 3 were all colorless prisms except for oily 3d, and the structures of these ethereal macrocyclic compounds were ascertained by the IR, NMR, mass spectra, and the elemental analyses. The IR spectra of oily 4 showed the strong hydroxyl absorption at 3450-3470 cm^{-1} and the several characteristic bands assignable to the ethereal bonds at 1020-1140 cm^{-1}. Mass spectra of 4 revealed m/e = M^+-$(OCH_2CH_2)_nOH$ as the base peaks. The compound 4 were separated by a high performance liquid chromatography(HPLC), but their elemental analyses deviated due to the hygroscopic property. Therefore, the author confirmed the diol structures by acetylation into 7. Further evidence was offered by the cyclization into 3 when treated with DDM and DDQ (Scheme 5)



Scheme 5

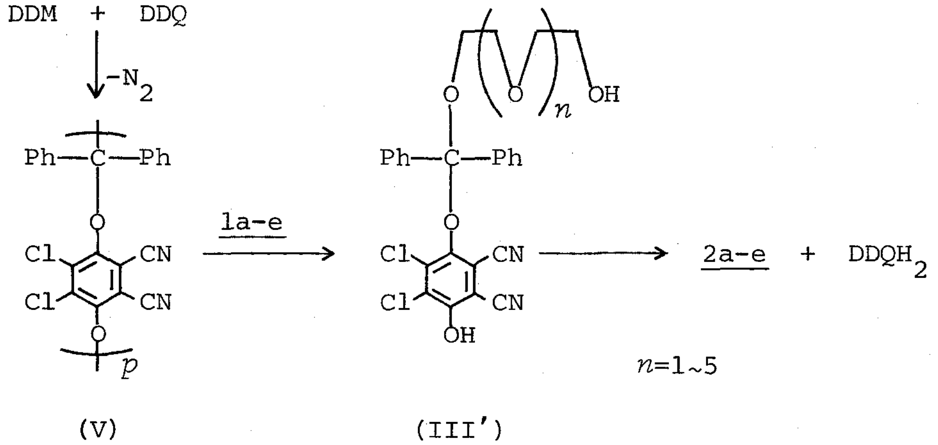
As is seen in Table 2, increase of oligoethylene glycols used in Method A brings about the considerable decrease in the yields of cyclic 2 and 3. But the yields of non-cyclic 4 reversely increased with such an increament of glycols. These results mean that the intramolecular cyclization giving 2 was highly disturbed by the growing intermolecular reaction giving 4 with the increasing amounts of glycols.

Being markedly different from the conventional synthetic methods of macrocyclic compounds,[9] the present reactions can be made under the mild conditions without any special template cation, high dilution technique, or the elevated temperature. And, relatively short reaction times(2 h) is sufficient to complete the reactions. Extended reaction times(4 h) did not greatly effect the product distributions; essentially similar percentages of 2 , 3 , and 4 were performed in the case of triethylene glycol (Run 11 and 12). The facile preparation of these macrocyclic compounds can be essentially ascribed to the property of DDQ as a good oxidizing agent[10] in addition to the easy formation of the diazonium betaine. Indeed, the precipitate of reduced $DDQH_2$ begins to appear at the early stage of the reactions.

(b) Reaction of DDM with DDQ followed by the Addition of Oligoethylene Glycols (Method B).

The rapid reaction of DDM with DDQ is found to give a resinous poly(2,3-dichloro-5,6-dicyanohydroquinone benzhydryl ether) (V) generated by the successive combination of diazonium betaine, if any hydrolytic or solvolytic additive is absent.[7] Since the polyether undergoes rapid hydrolysis and methanolysis to give same products as those obtained from the Method A treatment,[7] the author attempted to utilize its solvolytic property in the cyclization of oligoethylene glycols.

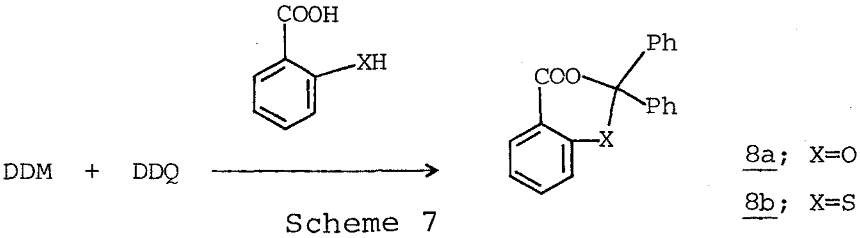
Dropwise addition of 0.5 equivalent of glycols into the reaction solution of DDM and DDQ gave 2 in 70-90% yields(based on glycols used) without any detectable formation of 3 and 4. The selective and convenient formation of the desired 2 may be performed by both the slow addition and the small amounts of glycols. Under these conditions, most of glycols exclusively attack the diphenylmethylene moieties in the polyether linkage so that the resulting III′ has an enough time to undergo internal S_N2 displacement because free glycols are rarely present in the reaction solutions(Scheme 6).



Scheme 6

As represented in the case of triethylene glycol(Run 9 and 10), however, the increased addition(1 or 3 equivalent) of glycol resulted in the production of 3 and 4 in addition to the major 2. This phenomenon can be similarly ascribed to the further solvolysis of resulting III′ by the increased glycol as already demonstrated in Method A. The present Method B, of course, yields about twice more cyclic 2 than the corresponding Method A(Run 5 and 9) because former method furnishes the reaction conditions with the more III′ and less glycol especially at the early stage of the reaction.

Although a complete comparison has not been established for the other glycols, Method B with equivalent of glycols appears to be preferable to Method A for the more production of 1:1 macrocyclic 2. Further advantage of Method B is the possible extention to the acidic reagents which can decompose DDM.[11] For example, salicylic and thiosalicylic acids can be successfully cyclized in treatment according to Method B (Scheme 7).



Scheme 7

6-3 Experimental

Infrared spectra were recorded on a Hitachi 260-10 spectrometer. Proton NMR spectra were taken at 90 MHz on a Varian EM-390 spectrometer. Mass spectral data were obtained with a Hitachi RMU-6E mass spectrometer. at an ionization potential of 70 eV. Hight performance liquid chromatography(HPLC) analyses were accomplished using naphthalene as an internal standard with a JASCO TRI ROTOR high pressure liquid chromatograph equipped with a 25 cm × 4 mm column packed with octadecyl silane on silica gel and with methanol-water(5:1) as an eluent.

Materials. Alcohols and thiols were purified by distillation or by crystallization from benzene. DDM was prepared according to the procedure described by Smith and Howard.[12] DDQ, salicylic and thiosalicylic acids, di- and triethylene glycol monomethyl ethers were of commercial origin and were used without further purification.
The 1,2-dichloroethane was dried over phosphorous pentaoxide and fractionated. Benzene was refluxed over lithium aluminum hydride and was fractionated.

Reaction of DDM with DDQ in the Presence of Alcohols and Thioalcohols.

The representative procedure is as follows(Method A). To a stirred suspension of DDQ(0.59 g, 2.60 mmol) in 1,2-dichloroethane(20 ml) was added 10 ml of 1,2-dichloroethane solution containing DDM(0.50 g, 2.60 mmol) and methanol(0.40 g, 12.5 mmol) in one portion at 20°C.
The characteristic purple color of DDM suddenly faded with the vigorous evolution of N_2. After stirring for 1 h, the solvent was evaporated *in vacuo* and the pasty reaction mixture was triturated with 3×20 ml benzene. The combined benzene solution was washed several times with aqueous sodium carbonate(5%), dried over anhydrous sodium sulfate, and evaporated to give α,α-dimethoxydiphenylmethane(0.51 g, 87%) together with a small amount of benzophenone(0.04 g, 8.5%). The solidy residue was chromatographed(on silica gel) to affoed 2,3-dichloro-5,6-dicyanohydroquinone(0.55 g, 92%) with benzene-ether mixture(4:1) as an eluent.
In other cases, no effort to isolate the hydroquinone was made, namely, benzene(60 ml) was poured into the pasty or solidy reaction mixtures to extract the acetals. The benzene extract was washed with aqueous

sodium carbonate(5%), dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The fractional crystallization of the residue in ether or column chromatographic treatment on aluminium oxide using petroleum ether-benzene(4:1) as an eluent gave the analytically pure samples. In Method B, alcohols were added after the termination of the reaction of DDM and DDQ, and then the same work-up technique as for Method A was adopted to isolate the products.

Reaction of DDM with DDQ in the Presence of Oligoethylene Glycols (Method A).

General procedure was described in the case of triethylene glycol. To a stirred suspension of DDQ(1.18 g, 5.2 mmol) in benzene(20 ml) was added dropwise over 1 h at 20-25°C a benzene solution(10 ml) of DDM (1.0 g, 5.2 mmol) and equiv. of triethylene glycol(0.78 g, 5.2 mmol). After further 1 h stirring, the precipitated $DDQH_2$ was filtered off and was washed with benzene(20 ml× 3). The washing and filtrate parts were combined, washed with 5% aqueous sodium carbonate(10 ml × 3) and then with NaCl saturated water(10 ml× 5), dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give a pale brown viscous oil. The oily products were column chromatographed on alumina. Careful successive elution gave benzophenone with light petroleum-benzene(1:1), 1:1 macrocyclic 2d with benzene-ether(1:3), 2:2 macrocyclic 3b with ether, and 1:2 non-cyclic 4b with benzene-methanol(20:1). In the case of diethylene glycol, 2:2 macrocyclic 3a was eluted with benzene-ether(1:1) before 1:1 product 2a. Column chromatographic separation of 3c and 4c, or 3d and 4d was unsuccessful so that the yields of these compounds were determined by means of the HPLC using naphthalene as an internal standard. As the 4c and 4d isolated by the HPLC were colorless hygroscopic oil, structural evidence was performed by the conversion into 3c and 3d in treatment with DDM and DDQ and also by esterification with acetylchloride. The structures of 1:1 and 2:2 macrocyclic compounds 2 and 3 were determined as follows.

Diphenyl-8-crown-3 (2a): mp 101-103°C (from ether); IR(KBr) 2910, 1130, 1110 cm^{-1}; NMR($CDCl_3$) δ 3.7-3.8(m, OCH_2CH_2O, 8H), 7.1-7.6(m, Ph, 10H); MS *m/e* 270(M^+). Found: C,75.52; H,6.71%. Calcd for $C_{17}H_{18}O_3$: C,75.53; H,6.71%.

Diphenyl-11-crown-4 (<u>2b</u>): mp 105-106°C (from ether); IR(KBr) 2900, 1128, 1107 cm^{-1}; NMR($CDCl_3$) δ 3.7-3.8(m, OCH_2CH_2O, 12H), 7.1-7.6(m, Ph, 10H); MS *m/e* 314(M^+). Found: C,72.58; H,7.06%. Calcd for $C_{19}H_{22}O_4$: C,72.59; H,7.05%.

Diphenyl-14-crown-5 (<u>2c</u>): mp 89-90°C (from ether); IR(KBr) 2885, 1132, 1102 cm^{-1}; NMR($CDCl_3$) δ 3.8-3.9(m, OCH_2CH_2O, 16H), 7.1-7.6(m, Ph, 10H); MS *m/e* 358(M^+). Found: C,70.46; H,7.28%. Calcd for $C_{21}H_{26}O_5$: C,70.37; H, 7.31%.

Diphenyl-17-crown-6 (<u>2d</u>): mp 61-62°C (from ether); IR(KBr) 2880, 1138, 1105 cm^{-1}; NMR($CDCl_3$) δ 3.5-3.8(m, OCH_2CH_2O, 20H), 7.1-7.5(m, Ph, 10H); MS *m/e* 402(M^+). Found: C, 68.78; H,7.58%. Calcd for $C_{23}H_{30}O_6$: C,68.63; H,7.51%.

Diphenyl-20-crown-7 (<u>2e</u>): mp 62-63°C (from ether); IR(KBr) 2890, 1140, 1107 cm^{-1}; NMR($CDCl_3$) δ 3.7-3.9(m, OCH_2CH_2O, 24H), 7.2-7.6(m, Ph, 10H); MS *m/e* 446(M^+). Found: C,67.31; H,7.78%. Calcd for $C_{25}H_{34}O_7$: C,67.24; H,7.68%.

Tetraphenyl-16-crown-6 (<u>3a</u>): mp 182-183°C (from ether); IR(KBr) 2876, 1090, 1018 cm^{-1}; NMR($CDCl_3$) δ 3.3-3.8(m, OCH_2CH_2O, 16H), 7.1-7.6(m, Ph, 20H); MS *m/e* 540(M^+). Found: C,75.57; H,6.73%. Calcd for $C_{34}H_{36}O_6$: C,75.53; H,6.71%.

Tetraphenyl-22-crown-8 (<u>3b</u>): mp 167-168°C ; IR(KBr) 2875, 1096, 1018 cm^{-1}; MS *m/e* 628(M^+). Found: C,72.32; H,6.90%. Calcd for $C_{38}H_{44}O_8$: C,72.59; H,7.05%. NMR spectrum could not be obtained because of the insolubility in common solvents.

Tetraphenyl-28-crown-10 (<u>3c</u>): mp 89-91°C (from ether); IR(KBr) 2875, 1090, 1015 cm^{-1}; NMR($CDCl_3$) δ 3.4-3.8(m, OCH_2CH_2O, 32H), 7.2-7.7(m, Ph, 20H); MS *m/e* 716(M^+). Found: C,70.35; H,7.31%. Calcd for $C_{42}H_{52}O_{10}$: C,70.37; H,7.31%.

Tetraphenyl-34-crown-12 (<u>3d</u>): Colorless oil; IR(neat) 2880, 1098, 1025 cm^{-1}; NMR($CDCl_3$) δ 3.3-3.7(m, OCH_2CH_2O, 40H), 7.1-7.6(m, Ph, 20H); MS *m/e* 804(M^+). Found: C,68.69; H,7.58%. Calcd for $C_{46}H_{60}O_{12}$: C,68.63; H,7.51%.

Reaction with Di- and Triethylene Glycol Monomethyl Ethers.

This reaction was made by use of 2 equiv. of monomethyl ethers according to Method A. Column chromatographic treatment(on alumina) of the reaction mixtures gave colorless oily 6a and 6b with benzene-methanol(20:1) as an eluent.

6a: 85% yield; IR(neat) 2870, 1095, 1020 cm^{-1}; NMR($CDCl_3$) δ 3.35(s, OCH_3, 6H), 3.4-3.7(m, OCH_2CH_2O, 16H), 7.1-7.5(m, Ph, 10H); MS *m/e* 285 ($M-(OCH_2CH_2)_2OCH_3$). Found: C,68.00; H,7.93%. Calcd for $C_{23}H_{32}O_6$: C,68.29; H,7.97%.

6b: 90% yield; IR(neat) 2875, 1100, 1022 cm^{-1}; NMR($CDCl_3$) δ 3.36(s, OCH_3, 6H), 3.4-3.8(m, OCH_2CH_2O, 24H), 7.2-7.6(m, Ph, 10H). MS *m/e* 329 ($M-(OCH_2CH_2)_3OCH_3$). Found: C,65.53; H,8.28%. Calcd for $C_{27}H_{40}O_8$: C,65.83; H,8.19%.

Reaction of DDM with DDQ followed by Addition of Oligoethylene Glycols (Method B).

General procedure was described in the case of triethylene glycol. To a stirred suspension of DDQ(1.18 g, 5.2 mmol) in benzene(20 ml) was added all at once a benzene solution(10 ml) of DDM(1.0 g, 5.2 mmol) at 20-25°C. The reaction was very vigorous with the violent evolution of N_2 and gave a resinous product. The 0.5 equiv. of triethylene glycol (0.39 g, 2.6 mmol) in benzene(10 ml) was added dropwise over 1 h to the reaction solution. After further 1 h stirring followed by the treatment with a small amount of water, the precipitated $DDQH_2$ was filtered off and washed with benzene(20 ml × 3). The same workup technique as for Method A was adopted to give a pale brown viscous oil. The oily products were column chromatographed (alumina) with light petroleum-benzene(1:1) as an eluent to afford benzophenone, and then with benzene-ether(1:3) to afford 1:1 macrocyclic 2b, but possible 3b and 4b were not detectable in the case of 0.5 equiv. using of glycol. While, addition of 1 or 3 equiv. of triethylene glycol brought about the formation of 3b and 4b in addition to 2b.

Conversion of 4 into 3.

This reaction was made by employing 0.5 equiv. of 4 with respect to DDM and DDQ according to Method B. The converted products 3 were isolated by column chromatography on alumina with ether or ether-methanol (20:1) as an eluent. The yields were respectively 65%(3a), 74%(3b), 58%(3c), and 73%(3d).

Acetylation of 4b.

To a benzene solution(10 ml) of 4b(300 mg, 0.47 mmol) was added all at once a benzene solution(10 ml) of acetylchloride(100 mg, 1.27 mmol) and pyridine(150 mg, 1.9 mmol). After 1 h standing, precipitated salt was filtered off and washed with benzene(10 ml × 3). The washing and filtrate were combined, washed with 5% aqueous sodium carbonate(5 ml × 3) and then with NaCl saturated water(5 ml × 3), dried over anhydrous sodium sulfate, and evaporated *in vacuo* over 50°C to give a pale yellow viscous oil. The oily products were gel chromatographed(Sephadex LH-20, Pharmacia), with methanol as an eluent, to afford 7. Colorless oil; 80% yield; IR(neat) 2780, 1735, 1235, 1105 cm^{-1}; NMR($CDCl_3$) δ 2.0(s, $COCH_3$, 6H), 3.3-3.7(m, OCH_2CH_2O, 28H), 4.0-4.2(m, CH_2OCO, 4H), 7.1-7.5(m, Ph, 10H); MS *m/e* 401(M-$(OCH_2CH_2)_4OCOCH_3$). Found: C,62.07; H,7.60%. Calcd for $C_{33}H_{48}O_{12}$: C,62.24; H,7.60%.

Reaction with Salicylic and Thiosalicylic acids.

To a stirred reaction solution of DDM(1.0 g, 5.2 mmol) and DDQ(1.18g, 5.2 mmol) in benzene(20 ml) was added dropwise for 1 h a benzene solution (10 ml) of salicylic acid(0.72 g, 5.2 mmol) or thiosalicylic acid(0.80 g, 5.2 mmol). After further 1 h stirring, the precipitated $DDQH_2$ was filtered off and washed with benzene(20 ml × 3). The same workup technique as for Method B was adopted to give a crude reaction mixture as a brown paste. The 8a and 8b were isolated by alumina column chromatography with benzene-methanol(20:1) as an eluent.

8a: mp 104-106°C (from benzene); 55% yield; IR(KBr) 1742, 1301, 765 cm^{-1}; NMR($CDCl_3$) δ 7.2-7.6(m, aromatic H). Found: C,79.72; H,4.67%. Calcd for $C_{20}H_{14}O_3$: C,79.46; H,4.67%.

8b: mp 178-180°C (from benzene); 62% yield; IR(KBr) 1721, 1275, 748 cm^{-1}; NMR($CDCl_3$) δ 7.2-7.8(m, aromatic H). Found: C,75.76; H,4.63%. Calcd for $C_{20}H_{14}O_2S$: C,75.45; H,4.43%.

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CONCLUSION

The results obtained from the present investigation may be summarized as follows;

(1) In the reactions with o-sulfobenzoic anhydride, diazomethane and aryldiazomethanes gave the keto sultones derived from the nucleophilic attack of these diazoalkanes, whereas diaryldiazomethanes(DDMs) underwent the acid-catalyzed decomposition to produce the tetraarylethylenes. These results indicated that the reactivity of diazoalkanes is much more governed by the intrinsic steric and the electronic nature.

(2) The DDMs were found to react with chloranil and 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) at their C=O bonds giving the polyethers. On the other hand, DDMs reacted with 2,5-dichloro-*p*-benzoquinone(DCQ) to provide the bicyclic diones and the polyethers. The diazonium or carbonium betaine intermediate was assumed for the formation of polyethers, while the 1,3-dipolar addition toward the C=C bond of DCQ was claimed for the bicyclic dione processes. The difference in the reaction fashion may be ascribed to the steric effects of these quinones. The results of the kinetic substituent effects indicated that the polyether processes can be well correlated with the Yukawa-Tsuno equation and the bicyclic dione processes with normal Hammett equation, both having the negative ρ values. The relative magnitude of the Hammett parameters were interpreted in terms of the electron acceptability of the quinones.

(3) In the reaction with chloranil, aryldiazomethanes gave stilbenes (*cis*-isomer rich) and spirooxetanes(*trans* only) in marked difference from the polyethers in the cases of DDMs. These stereochemical results could be explained by consideration of the configuration and conformation of the diazonium betaine intermediate. The stereochemical courses were found to be highly influenced by both the solvent basicity and polarity.

(4) Reactions of DDMs with tetracyanoethylene(TCNE) gave quantitatively diaryltetracyanocyclopropanes. The kinetic substituent effects suggested the polar transition state with positive charge on diazocarbon. The kinetic solvent effects indicated the strong basic

solvation of TCNE molecule, so a new basicity parameter, D_π , was derived and proposed. This parameter was found to be successfully applicable to the π-acid systems.

(5) It was found that the reactions of DDM with chloranil, DDQ, and DCQ undergo the basic solvation of the initial states to an appreciable extent and the polar solvation of the transition states. Thus, linear free energy relationships were furnished between log k and the solvent parameters D_π and E_T values.

(6) As a synthetic application of DDM-quinone reactions, acetals and crown ethers were yielded in high yields by the redox reaction of DDM-DDQ system in the presence of alcohols and oligoethylene glycols.

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