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STUDIES ON THE REACTION OF CARBAMOYL COMPOUNDS VIA PHOTO-INDUCED ELECTRON TRANSFER

（光電子移動をへるカルバモイル化合物の反応
に関する研究）

1979

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PREFACE

The work of this thesis was performed under the guidance of Professor Yoshinobu Odaira at the Department of Petroleum Chemistry, Faculty of Engineering, Osaka University.

The author is deeply grateful to Professor Yoshinobu Odaira for his continuous guidance and constant encouragement throughout this work. The author would like to express his heartful gratitude to Dr. Yasuo Shigemitsu, Dr. Takuji Miyamoto, Dr. Koji Kimura for their helpful suggestion to his work. He would like to also express his deep thanks to Assistant Professor Yasuhiko Shirota at the Department of Applied Chemistry for his kind indications and useful discussions to the author.

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It is a real pleasure to express the author's gratitude to Dr. Osamu Ikeda in Tamura Laboratory at the Department of Applied Chemistry for his kindness in the measurement of reduction potential. The author's grateful thanks are also due to Ms. Motoko Kobayashi, Ms. Asako Okajima, Ms. Yoko Manabe, and all other members of Odaira Laboratory for their friendship.

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Suita, Osaka
January, 1979

Yuji Tsujimoto

Yuji Tsujimoto

LIST OF WORKS

The contents of this thesis are composed of the following papers (2-7).

(1) The Photoreduction of o-Methoxycarbonylbenzophenone.
Y.Tsujimoto, Y.Shigemitsu, T.Miyamoto, and Y.Odaira,
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(2) Reaction of Tetramethylurea with Photoexcited Carbonyl Compounds.
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(3) Photoureidomethylation of Cyanobenzenes with Tetramethylurea.
Y.Tsujimoto, M.Hayashi, Y.Nishimura, T.Miyamoto, and
Y.Odaira, Chem.Lett., 1977, 677.

(4) Novel Photoureidomethylation to 1,1-Diphenylethylene with Tetramethylurea Involving Electron Transfer.
T.Miyamoto, Y.Tsujimoto, T.Tsuchinaga, Y.Nishimura, and
Y.Odaira, Tetrahedron Lett., 1978, 2155.

(5) A Synthetic Route to 5-Aryl-2-oxazolidinone Derivatives.
Y.Tsujimoto, A.Kosaka, M.Hayashi, T.Miyamoto, and
Y.Odaira, Bull.Chem.Soc.Jpn., in contribution.

(6) Photochemical Carbamoylation of 1,1-Bis(p-cyanophenyl)-ethylene with Some Carbamates.
Y.Tsujimoto, Y.Nishimura, A.Kosaka, H.Kiriyama, T.Miyamoto,
and Y.Odaira, Tetrahedron Lett., in press.

(7) Photoureidomethylation of 9-Cyanophenanthrene with Tetramethylurea Involving the Charge-Transfer Process in the Excited Triplet State.
Y.Tsujimoto, M.Hayashi, T.Miyamoto, Y.Odaira, and Y.Shirota,
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CONTENTS

GENERAL INTRODUCTION

The reactivity of carbamoyl compounds under the sunlight (lightwavelength: 300-1000 nm) is closely connected with a variety of phenomina, for instance, photodeactivation of enzymes and photochemical deformation of proteins with regard to photo-induced mutation of biologically important substances, as well as photodeterioration of polyamide fibers, paints, herbicides with regard to important industrial products against light. It seems that electron transfer plays an important role in the photochemical transformation of substances containing carbamoyl groups. Therefore, fundamental elucidation for such photochemical reaction is of practical significance and urgency.

Recently, lots of novel reactions have been accumulated which proceeds via charge transfer or electron transfer at an initial stage, and these systems are nowadays noticeable fields of organic photochemistry. Such approach towards carbamoyl compounds, however, has taken little interest for organic chemists. Accordingly, it is possible to establish novel synthetic methods of carbamoyl compounds by applying electron (or charge) transfer process to these compounds.

With these in view, the purpose of this thesis is to elucidate photo-induced electron transfer reaction from carbamoyl compounds, such as ureas, amides, carbamates, to obtain basic information for a number of phenomina mentioned above, and to develope a novel synthesis of carbamoyl compounds.

Chapter 1 deals with photoureidomethylation of carbonyl compounds. Chapter 2 is concerned with photocarbamoylation of some electron acceptors.

Chapter 1 PHOTOUREIDOMETHYLATION OF CARBONYL COMPOUNDS

INTRODUCTION

There has been few reports on the photochemical reaction of ureas, except for vapor-phase photolysis[1] and photo-Fries rearrangement of aromatic ureas.[2] This is eminently contrasted with photochemistry of amides,[3] which contain many valuable systems for organic synthesis.

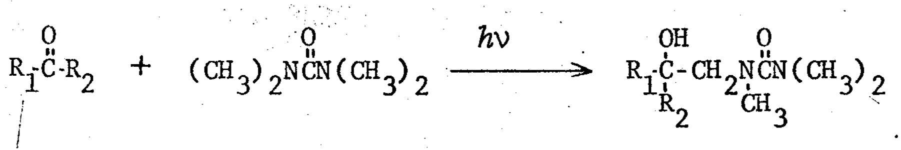
In this chapter is shown an effective hydrogen abstraction from methyl group substituted at nitrogen atom of tetramethylurea in the reaction with photoexcited n-π* triplet of carbonyl compounds, giving β-hydroxyethylureas in one step which can't be obtained conveniently by other routes. It is also mentioned that thermal reaction of β-hydroxyethylureas leads to 2-oxazolidinone derivatives which attracts much attention in the wide field from medicinal chemistry to polymer chemistry.

RESULTS AND DISCUSSION

1-1 PHOTOUREIDOMETHYLATION OF CARBONYL COMPOUNDS. SYNTHESIS OF β-HYDROXYETHYLUREAS

1-1-1 PHOTOUREIDOMETHYLATION OF KETONES (METHOD A)

Irradiation of a mixture of ketones (<u>I</u>) and tetramethylurea (<u>II</u>) in acetonitrile afforded β-hydroxyethylurea derivatives (<u>III</u>) as shown in Table 2 with pinacols (20-40%) as by-products.



$$R_1\overset{O}{\overset{\|}{C}}R_2 + (CH_3)_2N\overset{O}{\overset{\|}{C}}N(CH_3)_2 \xrightarrow{h\nu} R_1\underset{R_2}{\overset{OH}{C}}\text{-}CH_2\underset{CH_3}{N}\overset{O}{\overset{\|}{C}}N(CH_3)_2$$

(I) (II) (III)

Table 1. β-Hydroxyethylureas (III)

		Yield (%)[a]		Mp (°C)
		(III)	(IV)[b]	
a	$R_1=R_2=C_6H_5$	46 44[c]	4 8[c]	147-148.5 -
b	$R_1=C_6H_5$ $R_2=CH_3$	30	11	153-155
c	$R_1=R_2=CH_3$	23	—	Oil
d	$R_1=p\text{-}OCH_3\text{-}C_6H_4$ $R_2=H$	29	0.4	Oil
e	$R_1=p\text{-}CH_3\text{-}C_6H_4$ $R_2=H$	28	—	71.5-72.5
f	$R_1=C_6H_5$ $R_2=H$	26	11	90-91
g	$R_1=p\text{-}CO_2CH_3\text{-}C_6H_4$ $R_2=H$	5 53[d]	2 —	100-100.5
h	$R_1=p\text{-}CN\text{-}C_6H_4$ $R_2=H$	7 11[d]	— —	97-99.5

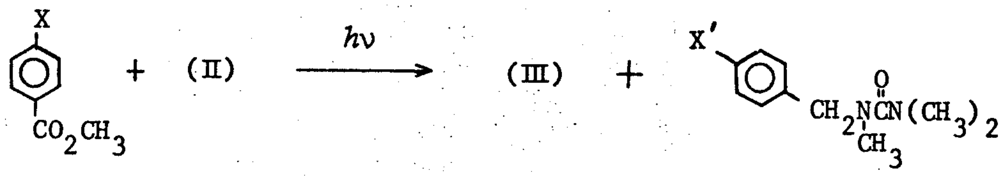
[a] Yield is based on reacted (I) or (V).
[b] Yield of 2-oxazolidinones. [c] The reaction in benzene. [d] Method B.

This method, in spite of low yields of III due to pinacol formation, might contribute to useful and convenient methods for β-hydroxyethylureas which have potential utility for transformation to 2-oxazolidinones.

When Ia and II was irradiated under similar conditions in benzene, non-polar solvent, there was not found to be in any significant change in product distribution and conversion of Ia. From this fact, present ureidomethylation is supposed to proceed through hydrogen radical abstraction from II by n-π* triplet of I.^{4}

1-1-2 PHOTOUREIDOMETHYLATION OF AROMATIC ESTERS (METHOD B)

In the previous section, it is shown that photoreaction of ketones with tetramethylurea is applicable to the synthesis of β-hydroxyethylureas. It is impossible, nevertheless, to obtain IIIg,h having electron-withdrawing groups at para positions of benzene rings by method A. To remove this defect in method A, the photoreaction of para-substituted methyl benzoates (V) with II (method B) is designed. Aromatic esters such as V are known to undergo photoreduction at ester groups to give carbinols on irradiation under the presence of hydrogen-donating aromatic solvents.^{5}



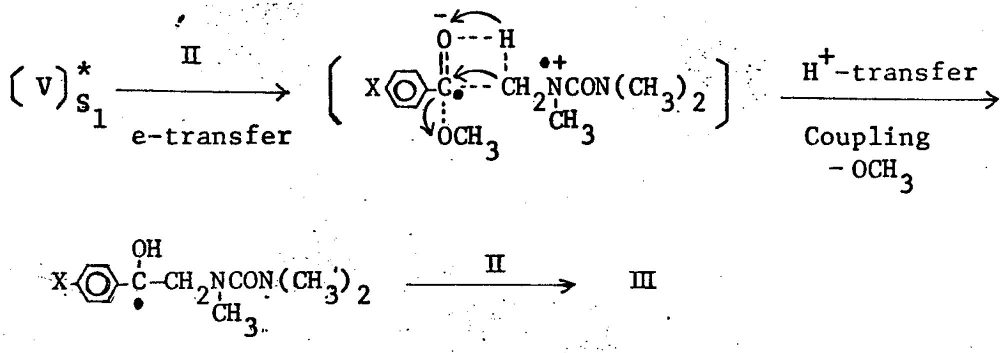
(V) (VI)

	(III)	(VI)
g: $X=CO_2CH_3$	53 %	—
h: X=CN	11 %	15 % ($X'=CO_2CH_3$)

Upon irradiation of an acetonitrile solution of methyl benzoates (Vg,h) and II, the formation of IIIg,h was expectedly achieved. In the case of Vh, the product yield of IIIh is fairly low on account of competitive photoureidomethylation to an aromatic ring (referred to Chapter 2) giving rise to benzylurea (VIh).

Corresponding ureidomethylated products (III) could be detected by trace or not formed in the reaction of electron-rich esters (V: X=H, CH_3). Then the formation of III (by method B) is best explained as shown in Scheme 1 based on this result as well as the fact that singlet exciplex is proposed to be involved in the photoreaction of Vh with toluene.[5] In other words, electron transfer from II to singlet excited esters is followed by almost simultaneously occurring three processes of proton transfer, radical coupling, and demethoxylation, resulting in the production of a ketyl radical, which abstracts hydrogen from II to afford III.

Scheme 1



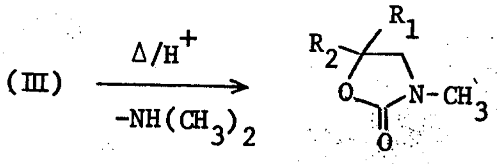
1-2 THERMAL CYCLIZATION OF β-HYDROXYETHYLUREAS. CONVENIENT SYNTHESIS OF 2-OXAZOLIDINONES

Thermal reaction of β-hydroxyethylureas (III) so far obtained was subsequently carried out by two methods; reflux for 10 hr in xylene solution of III (method A), treatment of chloroform solution of III with conc. sulfuric acid at room temperature (method B). The results are tabulated in Table 2.

Table 2. 2-Oxazolidinones (IV)

	Method	Yield (%)[a]	Mp (°C)
a	A	100	137-140
b	B	85	Oil
c	B	80	Oil
d	A	69	65-66
e	A	72	52-53
f	A	79	47-48.5
g	A	73	90.5-91.5
h	A	77	Oil

[a] Yield is based on reacted (III).



(IV)

2-Oxazolidinones are known to be pharmceutically important[6] and to be a monomer source for polycarbamates. Many methods have been contributed to the synthesis of 2-oxazolidinone skeltons,[7] but lots of them consist in the tedious routes by way of multiple steps, and little is well suited for this purpose.[8]

It is therefore concluded that a new route for 2-oxazolidinone derivatives is provided by photoureïdomethylation of carbonyl compounds followed by thermal cyclization.

EXPERIMENTAL

General. All melting points are uncorrected. Ir spectra were recorded with a JASCO IR-G spectrophotometer. Nmr spectra were recorded with tetramethylsilane as an internal standard on a JEOL-PS-100 spectrometer, and chemical shift was presented as δ-value. Mass spectra were taken on a Hitachi RMU-6E spectrometer. Glc analyses and separations were performed on Hitachi gas chromatograph 063 or 163 and on a Varian aerograph model 90-P or 920. All irradiations were carried out with a

500 W high pressure mercury lamp under nitrogen at room teperature.

Materials. Commercially available ketones, aldehydes, esters, and tetramethylurea were purified by usual methods prior to use. Methyl terephthaldehyde (Ig) was obtained by Sommelet reaction.[9] p-Cyanobenzaldehyde (Ih) was prepared by the method of Lieberman et al.[10] Methyl p-cyanobenzoate (Vh) was prepared by the esterification of the corresponding acid.

General Procedure for Photoureidomethylation of Carbonyl Compounds. Method A: Ketones (I) and three molar excess of tetramethylurea (II) were dissolved in acetonitrile. After the solution was bubbled with nitrogen for 15 min, it was irradiated through Pyrex filter for 10 hr. After evaporation of the solvent, unreacted II was recovered under the reduced pressure, the residue was chromatographed on silica gel. The products (III) were eluted with ether-benzene, while IIIc was vacuum distilled (0.55 Torr). Method B: A solution of ester (Vg or Vh) and ten molar excess of II in the same solvent was similarly irradiated through quartz filter for 20 hr. After the irradiation, similar procedures were taken. From volatile parts, methanol was detected by glc (20% PEG, 20 M on Celite 545). Benzylurea (VIh) was confirmed by the comparison with an authentic sample alternatively prepared.

1) N-(β,β-Diphenyl-β-hydroxyethyl)-N,N',N'-trimethylurea (IIIa), mp 147-148.5C (from petroleum ether-benzene); ir (nujol) 3400, 1630, 750, 700 cm^{-1}; mass (m/e) 298 (M^+); nmr (CCl_4) 2.5 (s, 3H), 2.6 (s, 6H), 4.0 (s, 2H), 5.5 (s, 1H, D_2O exchangeable), 7.0-7.6 (m, 10H). Found: C, 72.28; H, 7.48; N, 9.23%. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.45; H, 7.43; N, 9.39%.

2) N-(β-Phenyl-β-methyl-β-hydroxyethyl)-N,N',N'-trimethylurea (IIIb), mp 155-158C; ir (nujol) 3400, 1590, 760, 700 cm^{-1}; mass (m/e) 236 (M^+).

3) N-(β,β-Dimethyl-β-hydroxyethyl)-N,N',N'-trimethylurea (IIIc), bp 86C (0.5 Torr); ir (neat) 1600 cm^{-1}; mass (m/e) 174 (M^+); nmr (neat) 1.3 (s, 6H), 2.8 (s, 6H), 3.0 (s, 3H), 3.3 (s, 2H), 4.7 (s, 1H).

4) N-{β-(p-Anisyl)-β-hydroxyethyl}-N,N',N'-trimethylurea

(IIId), ir (neat) 1600, 820 cm^{-1}; mass (m/e) 252 (M^+); nmr ($CDCl_3$) 2.8 (s, 6H), 2.8 (s, 3H), 3.0, 3.6 (ABX octet, J_{ab}=15 Hz, J_{ax}=3Hz, J_{bx}=9Hz, 2H), 3.8 (s, 3H), 4.9 (ABX q, 1H), 5.9 (brs, 1H, D_2O exchangeable), 6.3-7.4 (A_2B_2, 4H). Found: C, 61.96; H, 8.03; N, 10.90%. Calcd for $C_{13}H_{20}N_2O_3$: C, 61.88; H, 7.99; N, 11.10%.

5) N-{β-(p-Tolyl)-β-hydroxyethyl}-N,N',N'-trimethylurea (IIIe), mp 71.5-72.5C (from benzene-petroleum ether); ir (KBr) 1600, 830 cm^{-1}; nmr ($CDCl_3$) 2.3 (s, 3H), 2.8 (s, 9H), 3.0, 3.6 (ABX octet, J_{ab}=18Hz, J_{ax}=2Hz, J_{bx}=12Hz, 2H), 4.9 (ABX q, 1H), 5.8 (brs, 1H, D_2O exchangeable), 7.0-7.4 (m, 4H). Found: C, 65.92; H, 8.63; N, 11.73%. Calcd for $C_{13}H_{20}N_2O_2$: C, 66.07; H, 8.53; N, 11.86%.

6) N-(β-Phenyl-β-hydroxyethyl)-N,N',N'-trimethylurea (IIIf), mp 88-90C; ir (KBr) 1600; mass (m/e) 222 (M^+); nmr ($CDCl_3$) 2.8 (s, 6H), 2.9 (s, 3H), 3.1, 3.6 (ABX octet, J_{ab}=15Hz, J_{ax}=9Hz, J_{bx}=3Hz, 2H), 4.9 (ABX q, 1H), 5.4 (s, 1H), 7.0-7.5 (m, 5H). Found: C, 64.75; H, 8.29; N, 12.48%. Calcd for $C_{12}H_{18}N_2O_2$: C, 64.84; H, 8.16; N, 12.60%.

7) N-{β-(p-Methoxycarbonylphenyl)-β-hydroxyethyl}-N,N',N'-trimethylurea (IIIg), mp 100-100.5C (from ethanol); ir (KBr) 1715, 1600, 820 cm^{-1}; mass (m/e) 280 (M^+); nmr ($CDCl_3$) 2.8 (s, 9H), 3.1, 3.6 (ABX octet, J_{ab}=20Hz, J_{ax}=4Hz, J_{bx}=15Hz, 2H), 3.9 (s, 3H), 5.0 (ABX q, 1H), 6.4 (d, J=5Hz, D_2O exchangeable), 7.4-8.0 (A_2B_2, 4H). Found: C, 59.83; H, 7.17; N, 9.88%. Calcd for $C_{14}H_{20}N_2O_4$: C, 59.98; H, 7.19; N, 9.99%.

8) N-{β-(p-Cyanophenyl)-β-hydroxyethyl}-N,N',N'-trimethylurea (IIIh), mp 97-99.5C (from benzene); ir (KBr) 3400, 2200, 1600, 825 cm^{-1}; nmr ($CDCl_3$) 2.8 (s, 6H), 3.1 (s, 3H), 3.2, 3.4 (ABX octet, J_{ab}=20Hz, J_{ax}=6Hz, J_{bx}=12Hz, 2H), 5.0 (ABX q, 1H), 6.0 (brs, 1H, D_2O exchangeable), 7.2-7.6 (m, 4H). Found: C, 63.31; H, 7.05; N, 16.76%. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.96%.

Alternate Synthesis of N-(p-Methoxycarbonylbenzyl)-N,N',N'-trimethylurea (VIh). VIh was prepared from p-methoxycarbonylbenzyl bromide and excess of trimethylurea under the presence of potassium amide in liquid ammonia according to the method by

Bryant et al.[11] Spectroscopic data: bp 120C (0.6 Torr); ir (neat) 1700, 1600 cm^{-1}; nmr ($CDCl_3$) 2.5 (s, 3H), 2.6 (s, 6H), 3.8 (s, 3H), 4.4 (s, 2H), 7.2-8.0 (A_2B_2, 4H). Found: C, 62.22; H, 7.39; N, 10.90%. Calcd for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.19%.

General Procedure for Synthesis of 2-Oxazolidinones (IV). Method A: A solution of III (0.35-0.45 mmol) in xylene (8 ml) was heated under reflux for 10 hr. After removal of the solvent, the residue was chromatographed on silica gel. Elution with ether-benzene gave IV. Method B: A solution of III (0.5-0.6 mmole) in chloroform (5 ml) with a trace of conc. sulfuric acid was stirred for 4 hr at room temperature. After the mixture was washed with water, the organic layer was dried over calcium chloride. Evaporation of the solvent left the residual oil, which was separated by glc (10% FFAP).

1) 3-Methyl-5,5-diphenyl-2-oxazolidinone (IVa), mp 137-140C (from benzene); ir (KBr) 1750, 740, 700 cm^{-1}; mass (m/e) 253 (M^+); nmr (CCl_4) 2.8 (s, 3H), 4.0 (s, 2H), 7.0-7.5 (m, 10H). Found: C, 75.67; H, 5.79; N, 5.47%. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53%.

2) 3,5-Dimethyl-5-phenyl-2-oxazolidinone (IVb), ir (neat) 1740, 760, 690 cm^{-1}; mass (m/e) 191 (M^+); nmr (CCl_4) 1.7 (s, 3H), 2.8 (s, 3H), 3.5 (s, 2H), 7.0-7.5 (m, 5H).

3) 3,5,5-Trimethyl-2-oxazolidinone (IVc), ir (neat) 1740 cm^{-1}; mass (m/e) 129 (M^+); nmr (CCl_4) 1.4 (s, 6H), 2.8 (s, 3H), 3.2 (s, 2H).

4) 5-(p-Anisyl)-3-methyl-2-oxazolidinone (IVd), mp 65-66C (from ethanol); ir (KBr) 1740 cm^{-1}; nmr ($CDCl_3$) 2.9 (s, 3H), 3.4, 3.8 (ABX sextet, $J_{ab}=J_{ax}=J_{bx}=8Hz$, 2H), 3.8 (s, 3H), 5.4 (ABX t, 1H), 6.8-7.4 (m, 4H). Found: C, 63.57; H, 6.36; N, 6.57%. Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76%.

5) 3-Methyl-5-(p-tolyl)-2-oxazolidinone (IVe), mp 52-53C (from ether); ir (KBr) 1730, 825 cm^{-1}; nmr ($CDCl_3$) 2.3 (s, 3H), 2.9 (s, 3H), 3.4, 3.9 (ABX sextet, $J_{ab}=J_{ax}=J_{bx}=12Hz$, 2H), 5.4 (ABX t, 1H), 7.2-7.4 (m, 4H). Found: C, 68.86; H, 6.91; N, 7.35%. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33%.

6) 3-Methyl-5-phenyl-2-oxazolidinone (IVf), mp 47-48.5C (from benzene-petroleum ether); ir (KBr) 1730, 750, 690 cm^{-1};

nmr ($CDCl_3$) 2.9 (s, 3H), 3.4, 3.9 (ABX sextet, $J_{ab}=J_{ax}=J_{bx}=$ 10Hz, 2H), 5,4 (ABX t, 1H) 7.2-7.4 (m, 5H). Found: C, 67.88; H, 6.20; N, 7.72%. Calcd for $C_{10}H_{10}NO_2$: C, 67.78; H, 6.26; N, 7.91%.

7) 5-(p-Methoxycarbonylphenyl)-3-methyl-2-oxazolidinone (IVg), mp 90.5-91.5C (from ether-petroleum ether); ir (KBr) 1730, 1715, 820 cm^{-1}; mass (m/e) 235 (M^+); nmr ($CDCl_3$) 2.9 (s, 3H), 3.4, 3.9 (ABX sextet, $J_{ab}=J_{ax}=J_{bx}=$10Hz, 2H), 3.8 (s, 3H), 5.5 (ABX t, 1H), 7.3-8.0 (A_2B_2, 4H). Found: C, 60.98; H, 5.49; N, 5.82%. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96%.

8) 5-(p-Cyanophenyl)-3-methyl-2-oxazolidinone (IVh), ir (neat) 2200, 1740 cm^{-1}; nmr ($CDCl_3$) 2.9 (s, 3H), 3.4, 4.0 (ABX sextet, $J_{ab}=J_{ax}=J_{bx}=$12Hz, 2H), 5.5 (ABX t, 1H), 7.4-7.8 (A_2B_2, 4H). Found: C, 64.94; H, 5.15; N, 14.09%. Calcd for $C_{11}H_9N_2O_2$: C, 65.33; H, 4.98; N, 13.86%.

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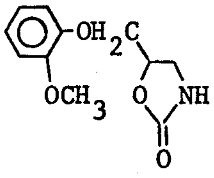
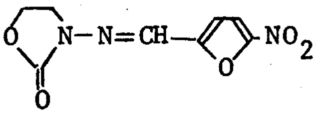
6) See to ref 7. Two drugs are drawn at bottomside as examples.



Methoxadone
(psychopharmcological
compound)



Furazolidone
(drug against typhoid)

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PHOTOCARBAMOYLATION OF ELECTRON ACCEPTORS

INTRODUCTION

In the previous chapter is made clear the possibility of a new synthetic chemistry using carbamoyl compounds by the observation of photochemical hydrogen transfer with great ease from tetramethylurea.

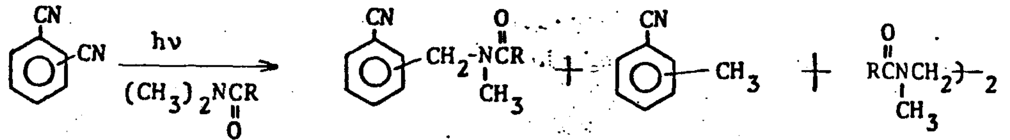
In this chapter is described precisely photo-induced electron transfer reaction from carbamoyl compounds to electron acceptors, such as aromatic nitriles (Section 1), 1,1-diphenylethylenes (Section 2).

RESULTS AND DISCUSSION

2-1 PHOTOCARBAMOYLATION OF AROMATIC NITRILES

2-1-1 PHOTOUREIDOMETHYLATION OF AROMATIC NITRILES

When a mixture of dicyanobenzenes (I) and tetramethylurea (II) in acetonitrile was irradiated, benzylurea derivatives (III) were given, accompanied with tolunitriles (IV),[1] and dimeric urea (V).



(I) a:*ortho* b:*para*

(II) R:$N(CH_3)_2$

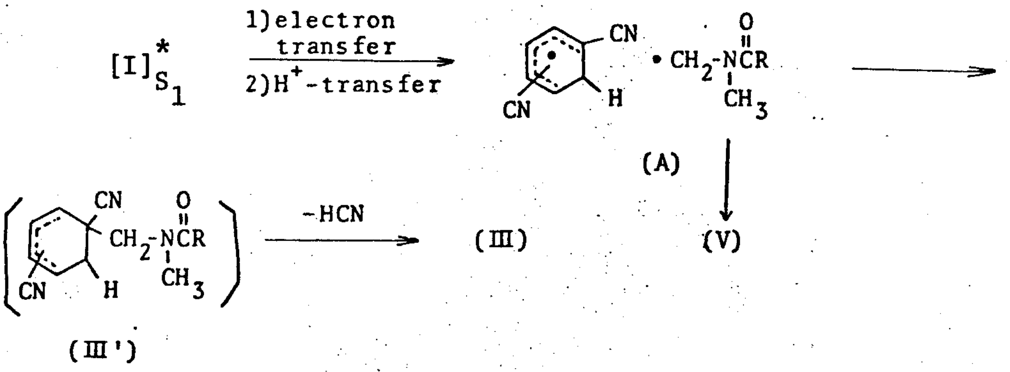
(III-a) 27% (III-b) 19%

(IV-a) < 1% (IV-b) 18%

(V)

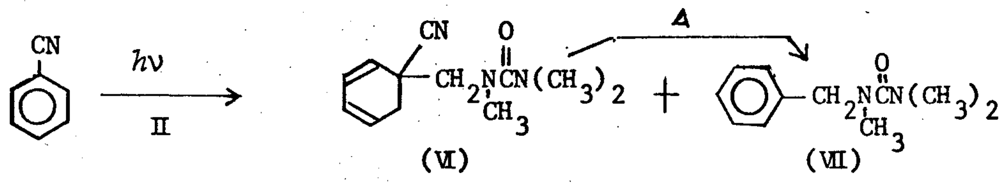
Similar irradiation in benzene, non-polar solvent, resulted in the suppression of ureidomethylation. Furthermore, dicyanobenzene fluorescenece was efficiently quenched with II, and piperylene did not affect ureidomethylation. From these observations, the reaction pathway is schematically shown in Scheme 2.

Scheme 2



In the scheme, i.e., an initial electron transfer (discussed fully in the next part) is followed by proton transfer to yield a radical pair (A). Coupling of radical pair leads to an unstable adduct (III'), which is easily aromatized to give III with the elimination of hydrogen cyanide.

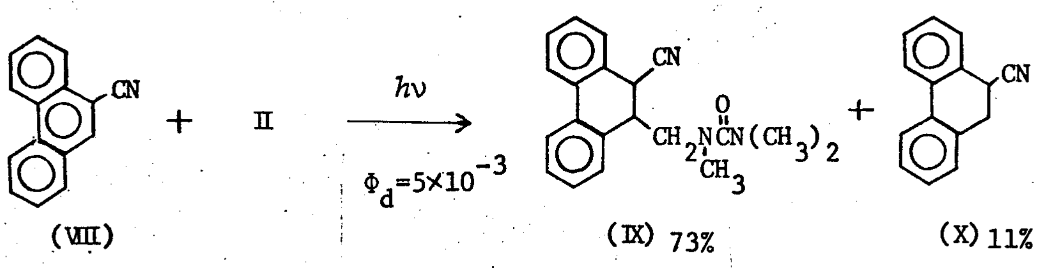
The intermediacy of III' in this reaction was found to be valid by taking the run with benzonitrile.



Irradiation of benzonitrile with II[2] was carried out under same conditions, then urea (VI) having a cyclohexadiene structure could be isolated, together with benzylurea (VII). Pyrolysis of VI at 250 C provided rapidly VII, which supports the intermediary of III'.

In the case of cyanobenzenes was made clear evident photoureidomethylation to an aromatic ring through an electron transfer to excited singlet nitriles. The yield of ureidomethylated products, however, is not always satisfactory, which made go on to the experiment with poly-fused aromatic nitriles.

When photoreaction of 9-cyanophenanthrene (VIII) with excess of II was undertaken in a Pyrex tube, ureidomethylated product (IX) was obtained in good yield.



The present reaction is regioselective, i.e., the opposite oriented product is not permitted to form in which ureidomethyl group is attached to 9-C site. In addition, the solvent dependency is remarkable (yield of IX: 3% in benzene). The reaction mechanism is developed in the following section.

2-1-2 REACTION MECHANISM FOR PHOTOUREIDOMETHYLATION. CONSIDERATION OF INITIAL PHOTOCHEMICAL STAGE

Quenching of aromatic nitrile fluorescence by II was undertaken to obtain information regarding the excited species in the photoureidomethylation of aromatic nitriles. The results are summarized in Table 3.

It is immediately understood that efficient quenching takes place except for the case of 9-cyanophenanthrene (VIII). The result of simple calculation using the equation developed by Rehm and Weller[3] shows that the free energy change (ΔG) for the electron transfer process in the lowest singlet state of aromatic nitriles is significantly exothermic, indicating that the electron transfer process would be probable in the cyanobenzenes-tetramethylurea system.

On the contrary to this, the fluorescence intensity of VIII was never reduced and its lifetime (τ_f) showed constant value (τ_f=24 nsec with or without II). This rules out the intervention

Table 3. Quenching of Aromatic Nitrile Fluorescence by II.

Aromatic Nitrile	$k_q\tau$[a] (l/mole)	$E_{1/2}(V)$[b]	$\Delta E_{0,0}$[c] (kcal/mole)	ΔG[e] (kcal/mole)
Benzonitrile	45.5	-2.77	104[d]	-13.4
o-Dicyanobenzene	78.5	-2.12	98.6[d]	-22.9
p-Dicyanobenzene	87.5	-2.03	98.6[d]	-25.0
1-Cyanonaphthalene	55.0	-2.30	85.8	-5.8
9,10-Dicyanoanthracene	109.0	-1.32	72.2	-14.9
9-Cyanophenanthrene	<0.1	-2.24	78.2	0.2

[a] The slope of Stern-Volmer plot for the fluorescence quenching (in acetonitrile). [b] The half-wave reduction potential was measured by polarography with dropping mercury as working electrode in dimethylformamide (vs. Ag/Ag^+ 0.1N). [c] The excitation energy of the lowest excited singlet state of aromatic nitriles. [d] Data from "Handbook of Photochemistry", S.L.Murov, Marcel Dekker, Inc., New York, 1973. [e] $\Delta G = 23.06(E_{p/2} - E_{1/2} - e^2/\varepsilon r) - \Delta E_{0,0}$. The half-peak potential for oxidation of II (irreversible process, $E_{p/2}$) was determined to be 1.22V(vs. Ag/Ag^+ 0.1N) by cyclic voltammetry with platinum as working electrode in acetonitrile. The Coulombic attraction term in acetonitrile ($e^2/\varepsilon r$) is reported to be 0.05eV(1.2 kcal/mole), D.Rehm and A.Weller, *Israel J.Chem.*, 8, 259(1970).

of singlet species of VIII in the reaction pathway. Accordingly phosphorescence quenching of VIII was taken to inquire into the triplet state participation. As shown in Figure 1, the phosphorescence of VIII was partially quenched in the presence of large amounts of II. Noteworthy is the fact that whereas the intensity of the phosphorescence decreases in the presence of II, its lifetime (τ_p) was not affected at all by II (τ_p=2.4 sec in the presence and absence of II). The result suggests that the interaction of II with an excited nitrile takes place in the non-relaxed excited triplet state of VIII generated after the isoenergetic intersystem crossing of the 9-cyanophenanthrene singlet state.

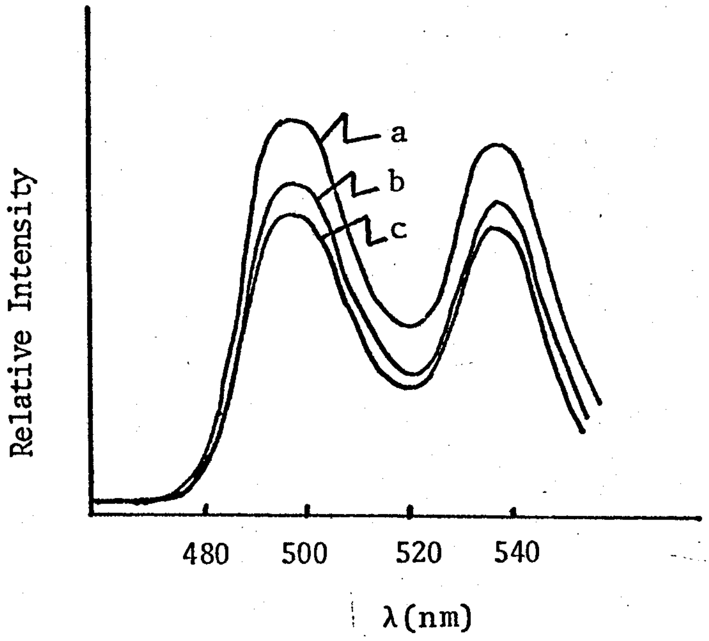


Fig. 1. Quenching of the 9-cyanophenanthrene (VIII) phosphorescence by tetramethylurea (II) in MTHF at 77°K.

a: [VIII] =10^{-3} M

b: [VIII] =10^{-3} M + [II] =10^{-1} M

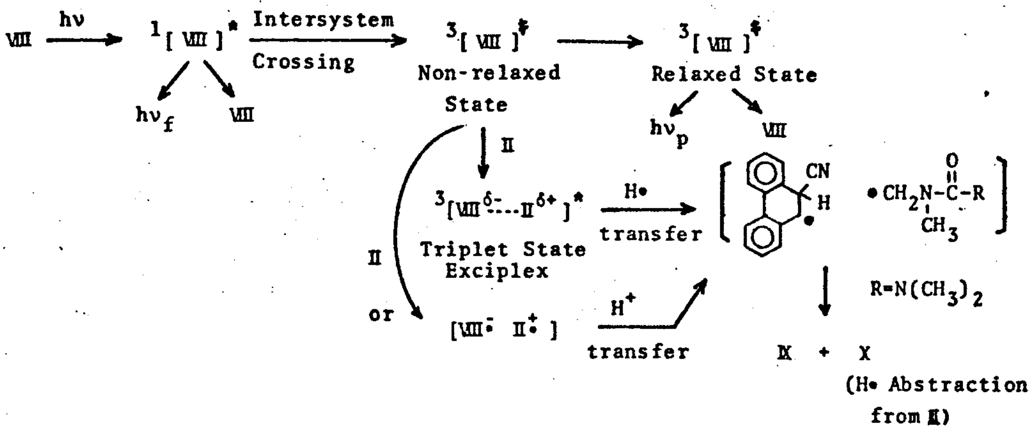
c: [VIII] =10^{-3} M + [II] =1 M

Excited wavelength: 320 nm

By taking into account the results described above as well as solvent dependecy and regioselectivity, the two possible mechanisms as shown in Scheme 3 are suggested for the photoureidomethylation of VIII.

One of these two pathways involves the initial hydrogen atom transfer from II to VIII via the intermediate non-emitting triplet exciplex. The charge-transferred nature of the complex will be more enhanced in polar solvents leading to the stabilization of the complex, and the charge-transferred nature of the complex or the geometry will be responsible for the regioselectivity observed for the reaction. An alternative mechanism involves the intermediacy of radical ion pair generated by electron transfer. The electron transfer will be facilitated in polar solvents, and the following proton transfer and the resulting radical coupling processes account for the formation of <u>IX</u>. The free energy change for the electron transfer process in the lowest triplet state of <u>VIII</u> is highly endothermic (ΔG=20.9 kcal/mol), indicating that electron transfer would be impossible; however, if the electron transfer occurs in the non-relaxed excited triplet state of <u>VIII</u> as suggested from the phosphorescence quenching measurement, there is energy gain favorable for the electron transfer.[4]

Scheme 3

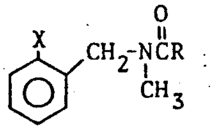


There is recently growing evidence that the exciplex and cation-anion radicals generated by the electron transfer are intermediate in numerous photochemical reactions. Although whether the charge-transfer process takes place in the excited singlet or triplet state depends upon the reaction system, the examples of the charge-transfer which occur in the excited singlet state have been more accumulated than those involving the excited triplet state. In particular, only few definite examples are avilable with regard to the reaction involving the intermediacy of the triplet state exciplex.[5] The results obtained suggests more or less important points to organic photochemistry from this viewpoint.

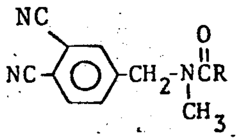
2-1-3 PHOTOAMIDOMETHYLATION OF AROMATIC NITRILES

Based on the photoureidomethylation of aromatic nitriles, photoreaction of aromatic nitriles was carried out in the presence of N,N-dimethylacetamide (XI) in place of II.

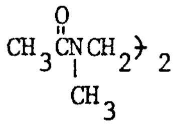
As irradiation of o-dicyanobenzene (Ia) with XI was performed in acetonitrile, amidomethylated products (XIII), (XIV) were isolated with dimeric amide (XII).



(XIII) X=CN, R=CH_3



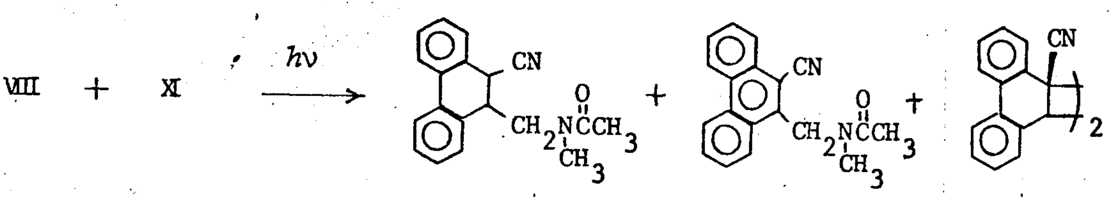
(XIV) R=CH_3



$(CH_3\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{N}}CH_2\text{+}_2$

(XII)

In the reaction of VIII and excess of XI, two kinds of amidomethylated products (XV), (XVI) were also obtained with the formation of cyclodimer of VIII.



(XV) 21% (XVI) 2% 61%

This result is clearly contrasted with the photoureidomethylation of VIII and a little higher ionization potential of XI[6] compared with II might bring about inefficiency of an initial electron transfer.

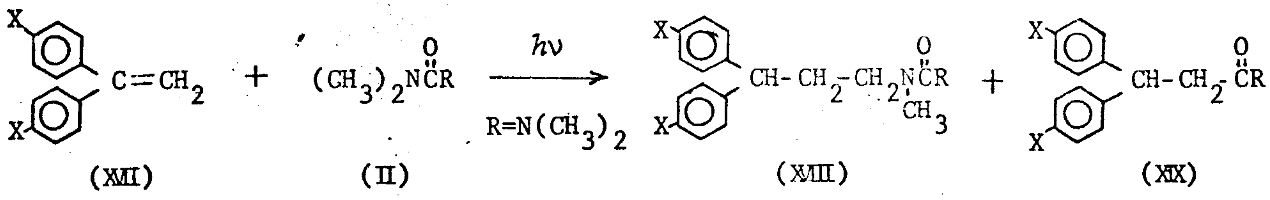
2-2 PHOTOCARBAMOYLATION OF 1,1-DIPHENYLETHYLENES

2-2-1 PHOTOUREIDOMETHYLATION AND PHOTOAMIDATION OF 1,1-DIPHENYLETHYLENES

In the previous section, the possibility was shown that photo-induced electron transfer from carbamoyl compounds was applicable to a new synthetic chemistry. This section deals with photocarbamoylation of olefinic parts which is useful for organic synthesis. 1,1-Diphenylethylenes (XVII) was selected as electron acceptors.

It is already known that photochemical acylation takes place due to an amide bond fission in the irradiation of 1,1-diphenylethylene with N,N-dimethylbenzamide.[7] The similar photoreaction with N,N-dimethylacetamide, however, was found only to afford an acylated product in trace amount.[8] Therefore the experiment with tetramethylurea (II) was examined first of all.

On irradiation of a mixture of XVII and excess of II in acetonitrile, there was found ureidomethylated products (XVIII), amidated products (XIX) derived from an urea bond scission as shown in Table 4. It was also clarified that the reaction mixture contained small amounts of 1,1,4,4-tetraphenylbutane, dimeric urea (V) and tetramethyloxamide in the case of XVIIc.



The photoureidomethylation was sensitized with xanthone (E_T=74 kcal/mol) or phenanthrene (E_T=62 kcal/mol), and quenched effectively with piperylene (E_T=59 kcal/mol), demonstrating that an excited triplet of XVII is in operation in the present ureidomethylation.

The ureidomethylation was markedly suppressed when the reaction of XVIIc with II was taken in non-polar solvents (yield of XVIIIc; 1% in benzene, 5% in cyclohexane). In addition, it is apparent that the yield of XVIII increases with increasing electron affinity of olefins and the similar tendency is seen as for the conversion of XVII.

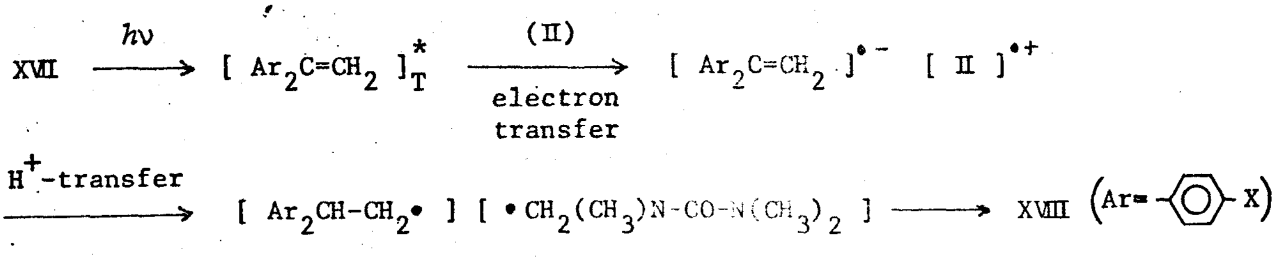
Table 4. Photoreaction of 1,1-Diphenylethylenes (XVII) with II.

X	Conv of XVII (%)	Yield(%)[a] (XVIII)	(XIX)
a OCH_3	19	7	25
b CH_3	13	27	12
c H	17	29	6
d CO_2CH_3	71	92	-
e CN	99	95	-

[a] Yield is based on consumed XVII.

From these results as well as the fact that anti-Markownikoff adduct is obtained, the probability can be safely precluded that an initial hydrogen abstraction of triplet olefins is followed by coupling of the resulting radicals.[9] It is therefore concluded that an electron transfer from II to triplet of XVIId,e occurs at initial stage (Scheme 4).

Scheme 4

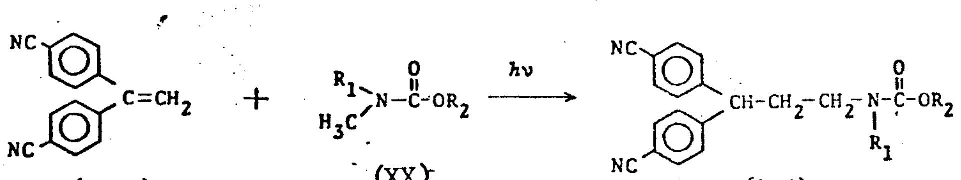


The orientation observed in XVIII is chiefly dependent on the electronic structure of radical anions generated after electron transfer. Judging from the formation of head-to-head dimer of XVIIc (1,1,4,4-tetraphenylbutane), as well as the reaction of XVIIc with sodium,[10] anion center is supposed to localize on aryl groups substituted carbon (α-carbon).

On the other hand, amidation occurred in considerable yields with suppression of ureidomethylation in the cases of XVIIa-c. The mechanism for the photoamidation is rather obsecure, but bond fission of urea bond may take place by non-vertical energy transfer from excited olefins to II. The only example for photochemical urea bond fission is photo-Fries rearrangement of aromatic ureas[11] except for vapor-phase photolyses,[12] and it is interesting to photochemistry of carbamoyl compounds that an aliphatic urea is subjected to urea bond fission observed in this system.

2-2-2 PHOTOCARBAMOYLATION OF 1,1-BIS(P-CYANOPHENYL)ETHYLENE WITH CARBAMATES

As a variety of carbamates have been known to have physiological properties, they have been widely utilized as antileukemic agents, tranquilizers, herbicides etc.[13] In this part is described novel synthesis of methylene-chain extended carbamates by two units starting from simple carbamates.



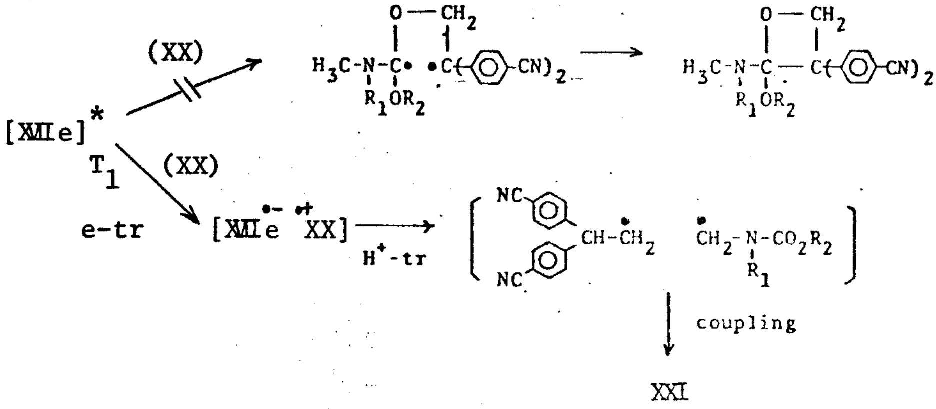
(XVIIe) (XX) (XXI)

a: $R_1=R_2=CH_3$	90%
b: $R_1=CH_3$, $R_2=C_2H_5$	85%
c: $R_1=CH_3$, $R_2=CH(CH_3)_2$	84%
d: $R_1=C_6H_5$, $R_2=CH_3$	96%
e: $R_1=H$, $R_2=CH_3$	55%
f: $R_1=p\text{-}CN\text{-}C_6H_4$, $R_2=CH_3$	37%

Upon irradiation of an acetonitrile solution of 1,1-bis-(p-cyanophenyl)ethylene (XVIIe) and excess of carbamates (XX), carbamoylation occurred smoothly to give adducts (XXI) in preferable yields (especially in the cases of XXa-d).

Though aminooxetans are known to form in the reaction of ethyl carbamates with photoexcited 1,1-diphenylethylene,[14] initial electron transfer takes place preferentially from XX to triplet of XVIIe to inhibit oxetan formation between the olefin (XVIIe) and carbonyl function of XX (Scheme 5).

Scheme 5



EXPERIMENTAL

General. Uv spectra were taken on a Hitachi Perkin-Elmer UV-VIS spectrophotometer. Emission spectra were recorded with a Hitachi MPE-2A fluorescence spectrophotometer. Reduction potential was recorded with Yanagimoto P8 polarograph or with a set of electronics (Nikko Keisoku NPS-2 potential sweeper and Hokuto Denko PS-500B potentialstat). All other apparatus were similar to those used in Chapter 1.

Materials. 1-Cyanonaphthalene was prepared by the method of Newman.[15] 9-Cyanophenanthrene (VIII) was prepared according to the procedure of Coleman et al.[16] 9,10-Dicyanoanthracene was prepared similarly as above. 1,1-Diphenylethylene (XVIIc) or 1,1-Bis(p-tolyl)ethylene (XVIIb) was obtained by Grignard reaction.[17] 1,1-Bis(p-anisyl)ethylene (XVIIa) was prepared by the method of Al-Attar et al.[18] 1,1-Bis(p-cyanophenyl)-ethylene was prepared as following; p,p'-dibromobenzophenone was prepared by Friedel-Crafts reaction from bromobenzene and carbon tetrachloride followed by hydrolysis. Subsequent Grignard reaction with methyl magnesium bromide and further cyanation by cuprous cyanide gave cyano-olefin (XVIIe).[19] 1,1-Bis(p-methoxycarbonylphenyl)ethylene (XVIId) was prepared from XVIIe according to the method of Yukawa et al.[20] N-Mono-substituted or N-disubstituted carbamates were obtained by the action of the corresponding amine into chloroformate in ether. p-Cyano-N-methylaniline was obtained by the method of Ashley et al.[21] All other materials were commercially available and purified by conventional methods before use.

Preparation of Authentic Samples. 1,1,4,4-Tetraphenylbutane was obtained by the procedure of Gilman et al.[22] Dimeric urea (1,1'-ethylenebis[1,3,3-trimethyl]urea)(V) was prepared by the method of Boon.[23] Dimeric amide (1,1'-ethlenebis[1-methyl]-acetamide)(XII) was given by the method of Friedman et al.[24] N,N-Dimethyl-β,β-diphenylpropionamide (XIXc) from β,β-diphenyl-propionic acid[25] according to the procedure of Gilbert.[26] Bis (p-anisyl) or bis(p-tolyl) derivatives (XIXa,b) were similarly prepared by using substituted cinnamic acids in the preparation of propionic acids. Tetramethyloxamide was prepared by the action of gaseous dimethyl amine into oxalyl chloride[27] in ether.

Photoureidomethylation of Aromatic Nitriles.

1) Photoureidomethylation of Benzonitrile. A solution of benzonitrile (20g, 0.194 mol) and tetramethylurea (II, 22.5g, 0.194 mol) was irradiated in acetonitrile (600 ml) through quartz filter for 1 hr. After the irradiation, the solvent and the unreacted starting materials were removed off under the reduced pressure. The remaining materials were distilled at 0.5-0.8 Torr. The distillate was subjected to preparative glc (10% FFAP). N-Benzyl-N-methyl-N',N'-dimethylurea (VII)(45.6 mg, 1%) and dimeric urea (V) was obtained and confirmed by comparison with authentic samples, respectively. 1-Cyano-1-trimethyl-

ureidomethyl-2,4-cyclohexadiene (VI) was obtained in 12% yield and characterized as following data; ir (neat) 2240, 1630, 720 cm^{-1}; mass (m/e) 192 (M^+-HCN); nmr ($CDCl_3$) 2.8 (s, 9H), 3.0 (s, 2H), 3.5 (d, 2H), 5.8 (m, 2H). Flash thermolysis of VI was performed on glc (injection temperature: 250C, 10% FFAP) to afford VII in approximately 50% yield.

2) Photoureidomethylation of Dicyanobenzenes. A solution of o- or p- dicyanobenzene (I, 2.5g, 20 mmol) and II (2.3g, 20 mmol) in 200 ml acetonitrile was irradiated in quartz tube for 10 hr. Unreacted materials were filtered off and the remaining residue was distilled or chromatographed on silica gel. Tolunitriles (IV) were identified by the identity with authentic samples (<1% for IVa, 18% for IVb). Separation by glpc (10% FFAP) gave analytical samples of N-(cyanobenzyl)-N-methyl-N',N'-dimethylureas (III) and characterized by spectroscopic data. For IIIa (19%); mp 58-59C (from ether-petroleum ether); ir (KBr) 2230, 1620, 810 cm^{-1}; mass (m/e) 217 (M^+); nmr (CCl_4) 2.6-2.8 (two s, 9H), 4.3 (s, 2H), 7.2-7.6 (A_2B_2, 4H). Found: C, 66.15; H, 6.76; N, 19.44 %. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34%. For IIIb (27%); ir (neat) 2220, 1620, 760 cm^{-1}; mass (m/e) 217 (M^+); nmr (CCl_4) 2.7 (s, 9H), 4.4 (s, 2H), 7.2-7.6 (m, 4H). Found: C, 66.65; H, 6.90; N, 19.52%. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34%.

3) Photoureidomethylation of 9,10-Dicyanoanthracene. An acetonitrile solution of 9,10-dicyanoanthracene (200mg, 1.5 mmol) and large excess of II was irradiated in Pyrex vessel. After the removal of the solvent and II in vacuo, the residue was chromatographed on silica gel. Elution with ether-benzene gave an ureidomethylated product, 9,10-dihydro-9,10-dicyano-9,10-bis(trimethylureidomethyl)anthracene; mp 190C dec (from ethanol); ir (KBr) 2220, 1640, 770 cm^{-1}; mass (m/e) 342 [M^+- $CH_2N(CH_3)CON(CH_3)_2$]; nmr ($CDCl_3$) 2.1-2.4 (two s, 18H), 4.3 (s, 4H), 7.4-7.8 (m, 8H). Found: C, 68.09; H, 6.76; N, 17.94%. Calcd for $C_{26}H_{30}N_6O_2$: C, 68.10; H, 6.59; N, 18.33%.

4) Photoureidomethylation of 9-Cyanophenanthrene. A solution of 9-cyanophenanthrene (VIII, 2.3g, 11 mmol) and ten molar excess of II in acetonitrile (180 ml) was irradiated in Pyrex vessel for 20 hr. After the irradiation, the solvent and unreacted II was

evaporated under the reduced pressure, then the residue was chromatographed on silica gel. Elution with benzene-petroleum ether afforded 9,10-dihydro-9-cyanophenanthrene (X) (454 mg, 11%), mp 78-80C (from ethanol); nmr($CDCl_3$) 3.0 (d, J=8Hz, 2H), 3.9 (t, 1H), 7.0-7.8 (m, 8H). 9,10-Dihydro-9-cyano-10-trimethylureidomethylphenanthrene (IX), 73%; mp 94-95C (from ethanol); ir (KBr) 2230, 1630 cm^{-1}; mass (m/e) 319 (M^+); nmr ($CDCl_3$) 2.7 (s, 3H), 3.3 (d, J=8Hz, 2H), 3.4-3.7 (m, 1H), 4.3 (d, J=4Hz, 1H), 7.2-7.8 (m, 8H). Found: C, 75.10; H, 6.67; N, 13.10%. Calcd for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63; N, 13.16%.

Fluorescence Quenching of Aromatic Nitriles with II. An acetonitrile solution of aromatic nitriles (10^{-4} mol/l) with various concentration of II (0-0.1 mol/l) was prepared. The aromatic nitrile fluorescence was measured using a number of excitation wavelengths as shown below.

	Excitation wavelength (nm)
Benzonitrile	254
o-Dicyanobenzene	248
p-Dicyanobenzene	254
1-Cyanonaphthalene	314
9,10-Dicyanoanthracene	424
9-Cyanophenanthrene	310

The change in fluorescence maxima was monitored and the intensity ratio (F_o/F) was plotted vs the concentration of II according to the Stern-Volmer equation ($F_o/F = 1+K[I]$, $K=k_q\tau$). In each case, a linearity was obtained, and quenching constant ($k_q\tau$) was calculated from the slope.

Measurement of Lifetime of 9-Cyanophenanthrene Fluorescence.

An acetonitrile solution of VIII (5.5×10^{-4} mol/l) with II (0, 0.01 mol/l, 0.1 mol/l) was prepared in Pyrex tube and degassed. The samples were excited with 337 nm using N_2-laser and the decay curves were monitored by conventional electronics.[28] The first-order decay was obtained when the intensity was plotted against the time. The lifetime was calculated using the equation ($\ln F/F_o = kt$, $\tau_f = 1/k$).

Phosphorescence Quenching of 9-Cyanophenanthrene. A solution of VIII (10^{-3} mol/l) in 2-methyltetrahydrofuran (MTHF) containing II (0, 0.1 mol/l, 1.0 mol/l) was prepared and degassed. Using an excitation wavelength of 320 nm, the decrease of phosphorescence was monitored. The lifetime was measured by observing one emission band (532 nm). It was calculated similarly as described in measurement of fluorescence lifetime.

Measurement of Half-Wave Reduction Potential of Aromatic Nitriles and Half-Peak Oxidation Potential of II. The half-wave reduction potential of aromatic nitriles ($E_{1/2}$) was measured by polarography. Polarographic measurements were made in a three electrode cell[29] with a dropping mercury as working electrode, and a silver-silver perchlorate electrode in dimethylformamide was used as the reference electrode [Ag|$AgClO_4$ (0.1 mol/l); $(C_4H_9)_4NClO_4$ (0.1 mol/l) as a supporting electrode]. Polarographic solutions were approximately 10^{-3} mol/l in the compound studied.

The half-peak potential of II ($E_{p/2}$) was measured by cyclic voltammetry using a three-electrode cell of conventional design. The voltammetric measurement was made with platinum as working electrode. A silver-silver nitrate electrode in acetonitrile was used as the reference electrode [Ag|$AgNO_3$ (0.1 mol/l); $(C_4H_9)_4NBF_4$ (0.1 mol/l) as a supporting electrode]. The concentration of II was nearly 10^{-3} mol/l.

Quantum Yield Measurement. The solution was prepared by dissolving VIII (4.93×10^{-5} mol/l) and II in acetonitrile. Monochromatic light at 313 nm was isolated through a Toshiba UV-29 glass filter from resonance lines of a high pressure mercury arc. The light intensity (I_o) was determined by potassium ferrioxalate actinometry[30] or by applying the quantum yield for the photocycloaddition of 1-cyanonaphthalene.[31] The decrease in the absorbance at 311 nm (As) was monitored to determine the quantum yield for the decrease of VIII (Φ_d). The calculation was based on the equation; $\ln(e^{As}-1)=-1000\Phi_d I_o t + \text{const}$.

Photoamidomethylation of Aromatic Nitriles.

1) Photoamidomethylation of o-Dicyanobenzene. A solution of o-dicyanobenzene (Ia, 3.0g, 0.156 mol/l) and equimolar of N,N-dimethylacetamide (XI) in acetonitrile was irradiated in a quartz tube for 20 hr. After evaporation of the solvent, unreacted Ia

was filtered off , and the residue was chromatographed on silica gel. Elution with ether-benzene (1:9) afforded N-(o-cyanobenzyl)-N-methylacetamide (XIII) (520 mg, 23%), ir (neat) 2220, 1635, 760 cm^{-1}; mass (m/e) 188 (M^+); nmr (CCl_4) 2.1 (s, 3H), 3.0 (s, 3H), 4.6 (s, 2H), 7.2-7.6 (m, 4H). Found: C, 70.18; H, 6.43; N, 14.88%. Calcd for $C_{11}H_{12}N_2O$: C, 70.28; H, 6.47; N, 14.93%. Further elution with ether-benzene (3:7) gave N-(3,4-dicyanobenzyl)-N-methylacetamide (XIV) (90 mg, 4%), mp 134-135C (from ethanol); ir (KBr) 2220, 1625, 820 cm^{-1}; mass (m/e) 213 (M^+); nmr ($CDCl_3$) 2.0 (s, 3H), 3.0 (s, 3H), 4.6 (s, 2H), 7.5-7.9 (m, 3H). The presence of dimeric amide (XII) was confirmed by comparison with an authentic sample.

2) Photoamidomethylation of VIII. An acetonitrile solution of VIII (2.3g, 0.07 mol/l) and ten molar excess of XI (9.6g) was irradiated in Pyrex tube for 20 hr. After the removal of the solvent and unreacted XI, the remaining oil was separated by silica gel column chromatography. Elution with benzene gave cyclodimer of VIII (977 mg, 61%). N-(9-Cyanophenanthrylmethyl)-N-methylacetamide (XVI) was eluted with ether-benzene (1:9), 47 mg, 2%; mp 200-210C (from chloroform-ethanol); ir (KBr) 2200, 1620, 740 cm^{-1}; mass (m/e) 288 (M^+); nmr ($CDCl_3$) 2.2 (s, 3H), 2.8 (s, 3H), 5.4 (s, 2H), 7.6-8.8 (m, 8H). Elution with the same solvent continuously gave 9,10-dihydro-9-cyano-10-(N-methylacetamidomethyl)phenanthrene (XV, 487 mg, 21%), mp 133-134C (from ether-benzene); ir (KBr) 2230, 1630, 740 cm^{-1}; mass (m/e) 290 (M^+). Found: C, 78.30; H, 6.14; N, 9.53%. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65%. Amide (XV) was determined to be composed of two geometrical isomers from nmr spectrum: 1.4 (s), 2.8 (s), 3.7 (m), 4.4 (m) for cis-isomer, 2.0 (s), 2.6 (s), 3.4 (m), 4.2 (d) for trans-isomer. The ratio (cis/trans) was calculated to be 2:3. Dehydroganation of XV by n-butyllithium-tetramethylethylenediamine complex[32] gave XVI in 21% yield.

Photoureidomethylation and Photoamidation of 1,1-Diphenylethylenes. A mixture of 1,1-diphenylethylenes (XVII) (0.02 mol) and tetramethylurea (II) (0.1 mol) in acetonitrile was irradiated through quartz filter for 20 hr. After the removal of volatile parts, the residue was chromatographed on silica gel.

Elution with ether-benzene afforded products, propionamide derivatives (XIX) were confirmed by the identity with authentic samples (yield calculated on glc, SE-30).

1) with 1,1-Diphenylethylene (XVIIc). 1,1-Diphenyl-2-(N-methyl-N',N'-dimethylureidomethyl)ethane (XVIIIc, 29%), ir (neat) 1635, 750, 690 cm^{-1}; mass (m/e) 296 (M$^+$); nmr (CCl_4) 2.3 (m, 2H), 2.7 (m, 9H), 3.0 (m, 2H), 3.8 (t, 1H), 7.1 (m, 10H). 1,1,4,4-Tetraphenylbutane, V, tetramethyloxamide were detected also in this system from the comparison with authentic samples.

2) with 1,1-Bis(p-anisyl)ethylene (XVIIa). 1,1-Bis(p-anisyl)-2-(N-methyl-N',N'-dimethylureidomethyl)ethane (XVIIIa, 7%), ir (neat) 1600, 825 cm^{-1}; mass (m/e) 356 (M$^+$); nmr (CCl_4) 2.2 (m, 2H), 2.6 (m, 9H), 3.0 (m, 2H), 3.8 (t, 1H), 3.7 (s, 6H), 6.6, 7.0 (A_2B_2, 8H). N,N-Dimethyl-β,β-bis(p-anisyl)propionamide (XIXa, 25%), ir (neat) 1610, 825 cm^{-1}; mass (m/e) 313 (M$^+$); nmr (CCl_4) 2.7 (s, 6H), 4.0 (d, 2H), 3.7 (s, 6H), 4.4 (t, 1H), 6.6, 7.0 (A_2B_2, 8H).

3) with 1,1-Bis(p-tolyl)ethylene (XVIIb). 1,1-Bis(p-tolyl)-2-(N-methyl-N',N'-dimethylureidomethyl)ethane (XVIIIb, 27%), ir (neat) 1630, 810 cm^{-1}; mass (m/e) 324 (M$^+$); nmr (CCl_4) 2.2 (m, 2H), 2.3 (s, 6H), 2.7 (m, 9H), 3.0 (m, 2H), 3.7 (t, 1H), 7.0 (m, 8H). N,N-Dimethyl-β,β-bis(p-tolyl)propionamide (XIXb, 12%) ir (neat) 1630, 810 cm^{-1}; mass (m/e) 281 (M$^+$); nmr (CCl_4) 2.3 (s, 6H), 2.8 (s, 6H), 2.9 (d, 2H), 4.5 (t, 1H), 7.0 (m, 8H).

4) with 1,1-Bis(p-methoxycarbonylphenyl)ethylene (XVIId). 1,1-Bis(p-methoxycarbonylphenyl)-2-(N-methyl-N',N'-dimethylureidomethyl)ethane (XVIIId, 92%), ir (neat) 1710, 1630 cm^{-1}; mass (m/e) 412 (M$^+$); nmr ($CDCl_3$) 2.4 (m,2H), 2.7(m, 9H), 3.1 (m, 2H), 3.9 (s, 6H), 4.0 (t, 1H), 7.2, 8.0 (A_2B_2, 8H).

5) with 1,1-Bis(p-cyanophenyl)ethylene (XVIIe). 1,1-Bis(p-cyanophenyl)-2-(N-methyl-N',N'-dimethylureidomethyl)ethane (XVIIIe, 95%), mp 101-102.5C; ir (KBr) 2220, 1630, 830 cm^{-1}; mass (m/e) 346 (M$^+$); nmr (C_6D_6) 2.0 (m, 2H), 2.5 (m, 9H), 2.8 (m, 2H), 3.5 (t, 1H), 6.8, 7.1 (A_2B_2, 8H). Found: C, 72.78; H, 6.36; N, 16.21%. Calcd for $C_{21}H_{22}N_4O$: C, 72.80; H, 6.40; N, 16.17%.

Photocarbamoylation of XVIIe. An acetonitrile solution of XVIIe (2g, 0.09 mol/l) and five molar excess of carbamates (XX) was irradiated in Pyrex vessel for 20-50 hr. After the removal of the solvent and unreacted XX in vacuo, the residual substances were separated by silica gel column chromatography. Carbamoylated compounds were eluted with ether-benzene.

1) Methyl N-{3,3-bis(p-cyanophenyl)propyl}-N-methylcarbamate (XXIa, 90%), mp 113-115C; ir (KBr) 2250, 1685, 825 cm^{-1}; mass (m/e) 333 (M^+); nmr ($CDCl_3$) 2.3 (m, 2H), 2.8 (s, 3H), 3.2 (m, 2H), 3.6 (s, 3H), 4.1 (t, 1H), 7.4, 7.6 (A_2B_2, 8H). Found: C, 72.00; H, 5.68; N, 12.51%. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.61%.

2) Ethyl N-{3,3-bis(p-cyanophenyl)propyl}-N-methylcarbamate (XXIb, 85%), ir (neat) 2250, 1680, 820 cm^{-1}; mass (m/e) 347 (M^+); nmr ($CDCl_3$) 1.2 (t, J=8Hz, 3H), 2.2-2.6 (m, 2H), 2.8 (s, 3H), 3.1-3.3 (m, 2H), 4.1 (t, J=8Hz, 1H), 4.8 (q, J=8Hz, 2H), 7.2-7.8 (m, 8H).

3) i-Propyl N-{3,3-bis(p-cyanophenyl)propyl}-N-methylcarbamate (XXIc, 84%), mp 103-104C (from ethanol); ir (KBr) 2250, 1680, 820 cm^{-1}; mass (m/e) 361 (M^+); nmr ($CDCl_3$) 1.2 (d, J=5Hz, 6H), 2.2-2.6 (m, 2H), 2.9 (s, 3H), 3.1-3.4 (m, 2H), 4.2 (t, J=8Hz, 1H), 4.8 (septet, J=5Hz, 1H), 7.2-7.8 (m, 8H). Found: C, 72.97; H, 6.36; N, 11.70%. Calcd for $C_{22}H_{23}N_3O_2$: C, 73.10; H, 6.41; N, 11.63%.

4) Methyl N-{3,3-bis(p-cyanophenyl)propyl}-N-phenylcarbamate (XXId, 96%), ir (neat) 2210, 1685, 820 cm^{-1}; mass (m/e) 395 (M^+); nmr ($CDCl_3$) 2.4 (m, 2H), 3.6 (s, 3H), 3.6 (t, J=8Hz, 2H), 4.1 (t, J=8Hz, 1H), 7.0-7.6 (m, 13H).

5) Methyl N-{3,3-bis(p-cyanophenyl)propyl}carbamate (XXIe, 55%), ir (neat) 2220, 1690, 820 cm^{-1}; mass (m/e) 329 (M^+); nmr ($CDCl_3$) 2.3 (m, 2H), 3.1 (m, 2H), 3.6 (s, 3H), 4.1 (t, 1H), 5.0 (brs, 1H), 7.2-7.6 (m, 8H).

6) Methyl N-{3,3-bis(p-cyanophenyl)propyl}-N-(p-cyanophenyl)-carbamate (XXIf, 37%), ir (neat) 2240, 1695, 830 cm^{-1}; mass (m/e) 420 (M^+); nmr ($CDCl_3$) 2.4 (m, 2H), 3.6 (s, 3H), 3.7 (m, 2H), 4.0 (t, 1H), 7.2-7.8 (m, 12H).

REFERENCES AND FOOTNOTES

1) Based on the result that p-tolunitrile (IVb) was obtained as a major product (35%) in the photolysis of IIIb in acetonitrile, tolunitriles (IV) are thought to be derived from further photoreaction of III. Similar results are also reported in the photoreaction of I and triethylamine, see to; K.Tsujimoto, K.Miyake, and M.Ohashi, Chem.Commun., 1976, 386.
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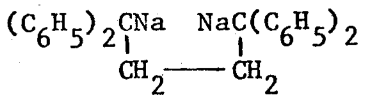

$$\begin{array}{ccc}(C_6H_5)_2CNa & & NaC(C_6H_5)_2\\ | & & | \\ CH_2 & — & CH_2\end{array}$$

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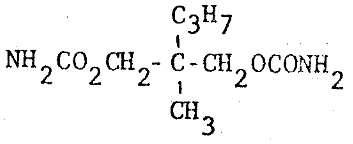
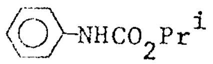


$NH_2CO_2CH_2\text{-}\underset{CH_3}{\overset{C_3H_7}{C}}\text{-}CH_2OCONH_2$

Meprobamate (tranquilizer)

$NH_2CO_2CH_2CCl_3$

Voluntal
(hypnotics)



herbicide

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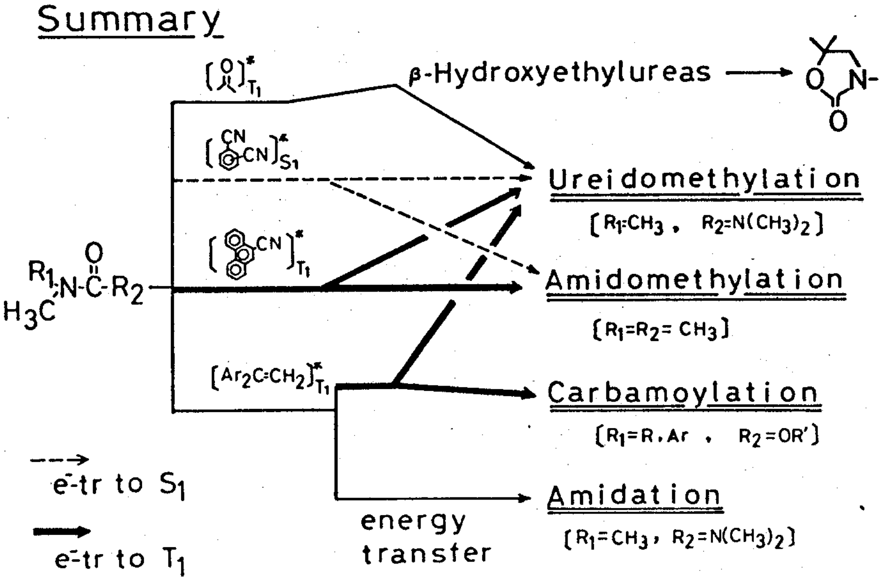
CONCLUDING REMARKS

The results obtained in this study may be summarized as following.



In Chapter 1, it has been shown that hydrogen abstraction from tetramethylurea, an aliphatic urea whose photochemical reaction is scarcely known, occurs smoothly in the presence of photoexcited carbonyl compounds to give β-hydroxyethylureas in one step, which is not easily available by other routes. In simple thermal reaction of β-hydroxyethylureas has been elucidated high-yield formation of 2-oxazolidinone derivatives, which attracts much attention in wide field such as from drug chemistry to polymer chemistry.

In Chapter 2, it has been made clear that photocarbamoylation takes place through electron transfer from a variety of carbamoyl compounds to photoexcited electron acceptors, such as aromatic nitriles and 1,1-diphenylethylenes, i.e., photoureidomethylation with tetramethylurea, photoamidomethylation with N,N-dimethylacetamide, photocarbamoylation with methylcarbamates. In these reactions, consideration has been made on their photochemical initial stage. Noteworthy is the elucidation of electron (or charge) transfer in the triplet state of which examples are scarce. It has also shown that a new type of reaction would occur in the system where electron transfer is retarded (photoamidation of olefins due to urea bond fission).

Finally, the author would hope that the present study should contribute to novel synthetic chemistry of carbamoyl compounds.