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STUDIES
ON
NEW ORGANIC REACTIONS
VIA ORGANOMETAL CARBONYLS

1971

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Introduction

Metal carbonyls have been known to be important catalysts for carbonylation of olefins (Oxo Process) and of acetylenes (Reppe Process) in the organic chemical industries.

Recentry, a great number of organic reactions using metal carbonyls have been studied and on those occasions it has been proved that the complexes, in which organic ligands are bonded to transition metals, have played important roles as active species. For example, in carbonylation reaction, an alkyl complex with σ bond between transition metal and carbon atom is formed first, then it is converted to the corresponding acyl complex by migration of the alkyl group from metal to carbon atom of carbon monoxide coordinated to metal and the acyl complex is decomposed to yield to the carbonylating products.

Therefore, in order to develop the new area in the organic reactions using metal carbonyls, it is thought to be important to find out the formation reaction of the new organo transition metal complexes from metal carbonyls and to clarify the reactivity of those complexes.

From these points of view, studies described in this thesis have been carried out from the following two directions:

1) Although it has been known that both organolithium compounds and organic halides react with mononuclear metal carbonyls to give unstable alkyl- or acylmetal complexes, the complexes derived from the nitrogen or oxygen analogs and metal carbonyls have not yet been investigated. The

clarification of the reaction behaviors and the application for organic syntheses of these unstable complexes were performed.

2) The reaction of the unstable organo transition metal complexes with the reagents containing hetero atoms were investigated.

This thesis consists of three chapters according to the above objects.

In chapter 1, the formation of lithium dimethylcarbamoylnickel carbonylate and its reaction as a nucleophilic reagent are described. Furthermore, the comparison of the carbamoyl complex with the acyl or alkoxycarbonyl complexes derived from the analogous method is also done.

In chapter 2, the formation of urea derivatives from the reaction of alkylmonochloroamines or amide with nickel carbonyl is described.

In chapter 3, some new type reactions of olefin oxides with organometal carbonyl complexes are described.

This thesis is composed of the following reports:

1) The reaction of Phenylacetylene with Nickel Carbonyl and Lithium Dimethylamide.
   S. Fukuoka, M. Ryang and S. Tsutsumi
   J. Org. Chem., 33, 2973 (1968).
2) Reaction of N-Monochloroamines with Nickel Carbonyl.
   S. Fukuoka, M. Ryang and S. Tsutsumi
   Tetrahedron Letters, 2553 (1970).
3) Formation of α,β-Diphenyl-γ-butyrolactone from Styrene Oxide by the Action of Organo Transition Metal Complexes.

S. Fukuoka, M. Ryang and S. Tsutsumi

J. Org. Chem., **35**, 3184 (1970).

4) Reactions of Lithium Dimethylcarbamoylnickel Carbonylate.

S. Fukuoka, M. Ryang and S. Tsutsumi

J. Org. Chem., in contribution.

CHAPTER 1 Formation of Lithium Dimethylcarbamoylnickel Carbonylate and Organic Reactions using the Complex.

It has been known that lithium aroyl- or acylmetal carbonylates $Li[RCOM(CO)_n]$ (R = aryl or alkyl) are formed from the reaction of organolithium compounds with mononuclear metal carbonyls[1], and the iron complex (M = Fe) gives aldehyde (RCHO) by acid hydrolysis[1a] and the nickel complex (M = Ni) gives ketone (RCOR) or α-diketone (RCOCOR) by thermal decomposition and acyloin (RCOCH(OH)R) by acid hydrolysis.[1b] Furthermore, as these complexes have carbon-transition metal bonds, these undergo reaction with unsaturated compounds; e.g., lithium aroyl-(or acyl)nickel carbonylate adds to acetylenic compounds ($R'C{\equiv}CH$) ahd α,β-unsaturated carbonyl compounds ($>C{=}\overset{|}{C}COR''$) to give 1,4-dioxo compounds $RCOCH(R')CH_2COR$ [2] and $RCO\underset{|}{\overset{|}{C}}\overset{|}{C}HCOR''$ [3] respectively.

Lithium carbamoylnickel carbonylate $Li[RR'NCONi(CO)_3]$ is formed from the reaction of lithium amide with nickel carbonyl analogous to the formation of lithium acylnickel carbonylate. In this chapter, I wish to describe the formation, the decomposition behavior and the nucleophilic reactions of lithium dimethylcarbamoylnickel carbonylate. Furthermore, the structure and the reaction behavior of lithium carbamoylnickel carbonylate are compared with those of the analogous complexes, lithium aroyl-(or acy)nickel carbonylate and potassium alkoxycarbonylnickel carbonylate.

1-1 Formation of lithium dimethylcarbamoylnickel carbonylate from the reaction of lithium dimethylamide with nickel carbonyl.

Results and Discussion

Nickel carbonyl undergoes reaction with white suspension of lithium dimethylamide in ether to give red clear solution below 10° without gas evolution. The infrared spectrum of the solution shows peaks of terminal metal carbonyls at 1973 cm^{-1} (vs), 1954 cm^{-1} (s) and a broad peak at 1560 cm^{-1} (m). As the peak at ca.1560 cm^{-1} is thought to be due to both $\nu_{C=O}$ and $\nu_{C=N}$ of the carbamoyl group bonding to nickel atom directly,* and the terminal carbonyl stretching frequencies are lower than that of original nickel carbonyl (2053 cm^{-1}), it is reasonable to consider that lithium dimethylamide added to the carbonyl group of nickel carbonyl to give an anionic carbamoylnickel complex with high electron density on the nickel atom (eq 1). After this work was published, E. O. Fischer et al. has reported the formation of lithium oxydiethylaminocarbene chromium pentacarbonylate etherate from the analogous reaction using lithium diethylamide and chromium hexacarbonyl in ether (eq 2).[8] This suggests

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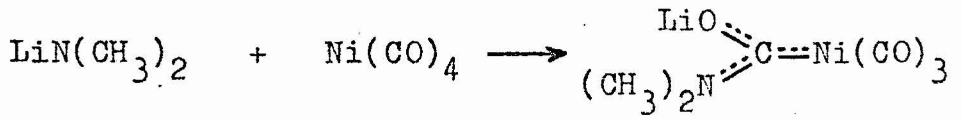
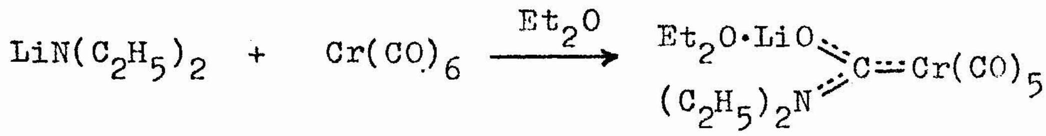
* It has been reported that the neutral carbamoyl transition metal complex shows a $\nu_{C=O}$ peak (m or w) at 1535 ± 10 cm^{-1} in π-$CpFe(CO)_2(CONR_2)$,[4] 1625 cm^{-1} in π-$CpFe(CO)_2(CONHCH_3)$,[5] 1512 cm^{-1} in cis-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$[6] and 1598 cm^{-1} in $(n\text{-}C_3H_7)_2NCOCo(CO)_3(PPh_3)$.[7]

lithium dimethylcarbamoylnickel carbonylate is also a complex with a carbene ligand. The structure of this nickel complex will be discussed in Section 1-6.



$$\mathrm{LiN(CH_3)_2} + \mathrm{Ni(CO)_4} \longrightarrow \begin{matrix}\mathrm{LiO}\\ \mathrm{(CH_3)_2N}\end{matrix}\!\!>\!\mathrm{C{=}Ni(CO)_3} \qquad (1)$$



$$\mathrm{LiN(C_2H_5)_2} + \mathrm{Cr(CO)_6} \xrightarrow{\mathrm{Et_2O}} \begin{matrix}\mathrm{Et_2O\cdot LiO}\\ \mathrm{(C_2H_5)_2N}\end{matrix}\!\!>\!\mathrm{C{=}Cr(CO)_5} \qquad (2)$$

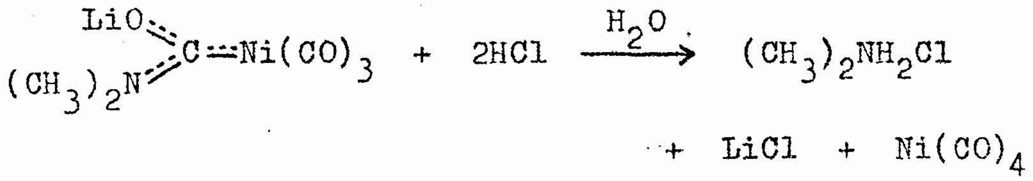
When the solvent was removed from the solution containing lithium dimethylcarbamoylnickel carbonylate under reduced pressure, an orange-red powder was obtained. Attempts to purify this complex were unsuccessful because the powder was very air-sensitive and spontaneous ignition occurred.

1-2 Decomposition reactions of lithium dimethylcarbamoylnickel carbonylate.

Results and Discussion

(1) Hydrolysis by diluted hydrochloric acid

Hydrolysis of lithium dimethylcarbamoylnickel carbonylate gives only dimethylamine hydrochloride but not dimethylformamide or a nitrogen compound corresponding acyloin (eq 3) and differs from that of lithium aroylmetal carbonylate gives aromatic aldehyde (metal = Fe)[1a] or acyloin (metal = Ni)[1b] (eq 4).



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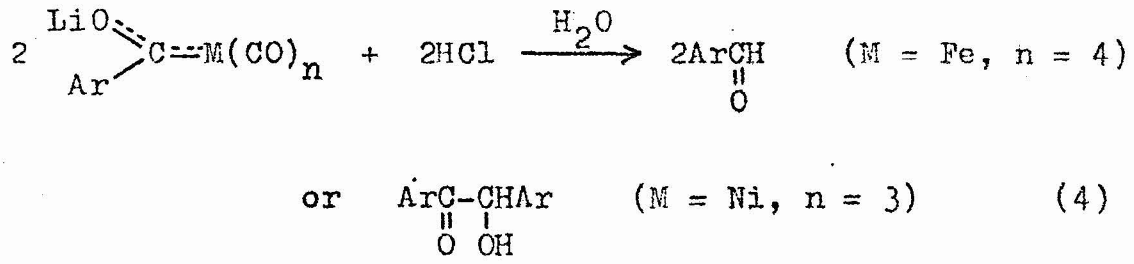
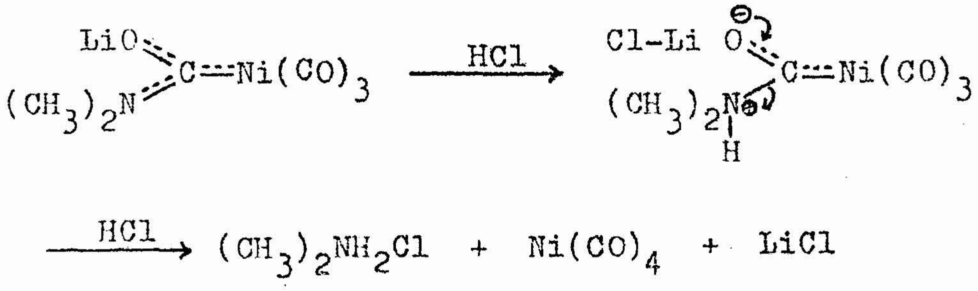


(4)

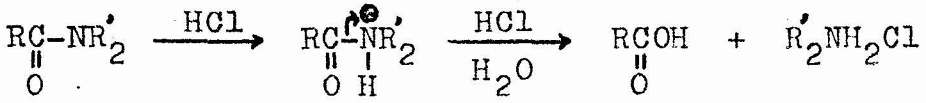
The reaction behavior of lithium dimethylcarbamoylnickel carbonylate toward hydrochloric acid agrees very closely with those of the neutral carbamoyl complexes toward hydrogen chloride (eq 5).[5, 6]

$$(\pi\text{-}C_5H_5)Fe(CO)_2(CONHR) + 2HCl \longrightarrow RNH_2Cl + \left[(\pi\text{-}C_5H_5)Fe(CO)_3\right]Cl \qquad (5)$$

The difference of the reaction behavior in acid hydrolysis between the carbamoyl complex and the aroyl complex can be explained as follows: protonation on nitrogen atom with lone pair electrons takes place initially in the carbamoyl complex like as acid hydrolysis of carboxylic acid amide (eq 6, 7).



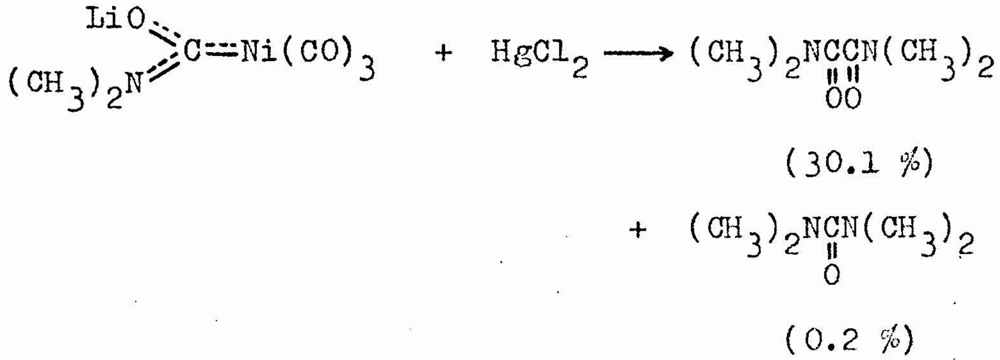
(6)



$$\underset{\|}{RC}\!\!-NR'_2 \;(\text{C}=O) \xrightarrow{HCl} RC(=O)-\overset{\oplus}{N}(H)R'_2 \xrightarrow[H_2O]{HCl} RC(=O)OH + R'_2NH_2Cl \qquad (7)$$

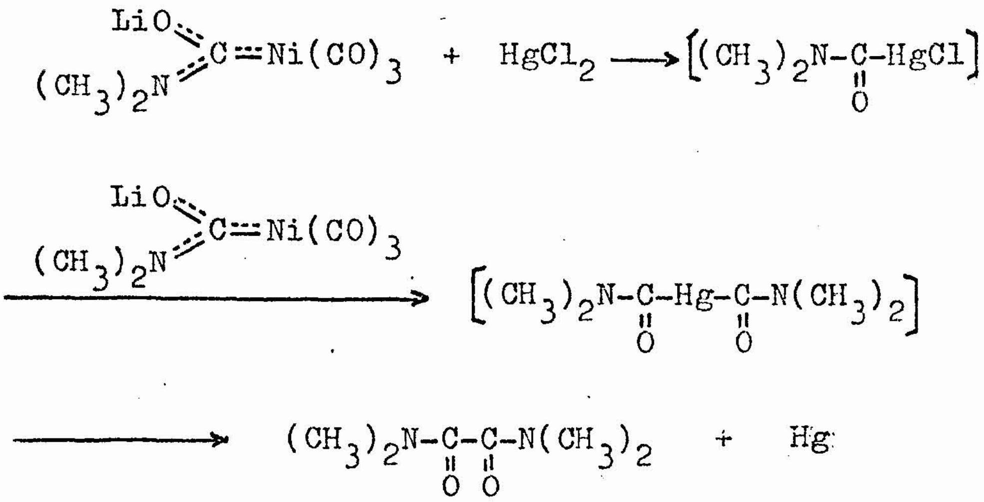
(2) Decomposition by mercuric chloride

Lithium dimethylcarbamoylnickel carbonylate is decomposed by mercuric chloride to give N,N,N',N'-tetramethyloxamide and N,N,N',N'-tetramethylurea (eq 8).



$$LiO(CH_3)_2N{=}C{=}Ni(CO)_3 + HgCl_2 \longrightarrow (CH_3)_2NC(=O)C(=O)N(CH_3)_2 \;(30.1\ \%) + (CH_3)_2NC(=O)N(CH_3)_2 \;(0.2\ \%) \qquad (8)$$

For the formation of N,N,N',N'-tetramethyloxamide, the following scheme is assumed (eq 9).



$$LiO(CH_3)_2N{=}C{=}Ni(CO)_3 + HgCl_2 \longrightarrow [(CH_3)_2N-C(=O)-HgCl]$$

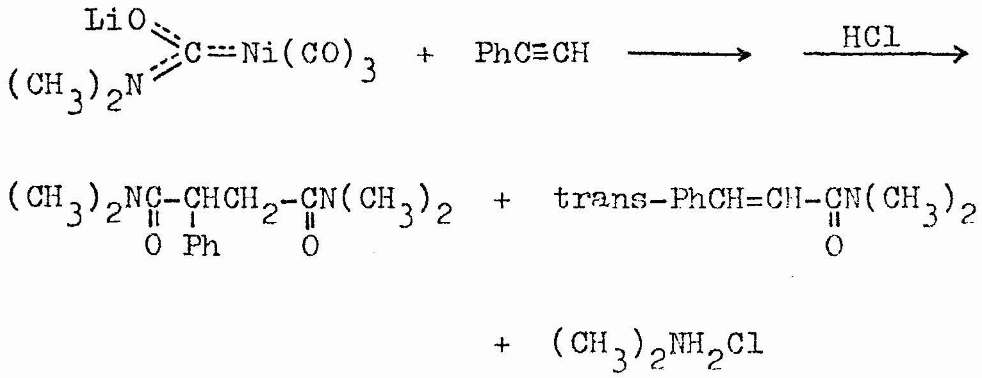
$$\xrightarrow{LiO(CH_3)_2N{=}C{=}Ni(CO)_3} [(CH_3)_2N-C(=O)-Hg-C(=O)-N(CH_3)_2]$$

$$\longrightarrow (CH_3)_2N-C(=O)-C(=O)-N(CH_3)_2 + Hg \qquad (9)$$

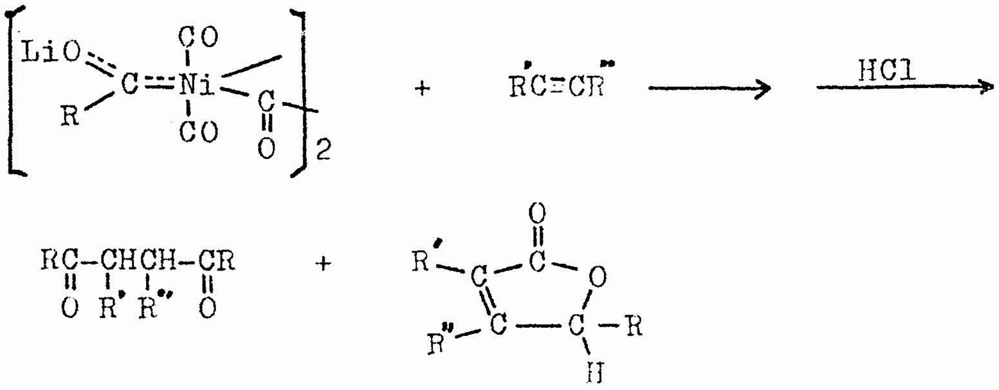
1-3 Reaction of lithium dimethylcarbamoylnickel carbonylate with phenylacetylene.

Results and Dicussion

Lithium dimethylcarbamoylnickel carbonylate undergoes reaction with phenylacetylene to give 2-phenyl-N,N,N',N'-tetramethylsuccinamide as a main product and N,N-dimethylcinnamamide as a minor one (eq 10) like as lithium acylnickel carbonylate adds to acetylenic compound to give 1,4-dioxo compound as a main product and unsaturated five-membered-ring lactone as a minor one (eq 11).[2]

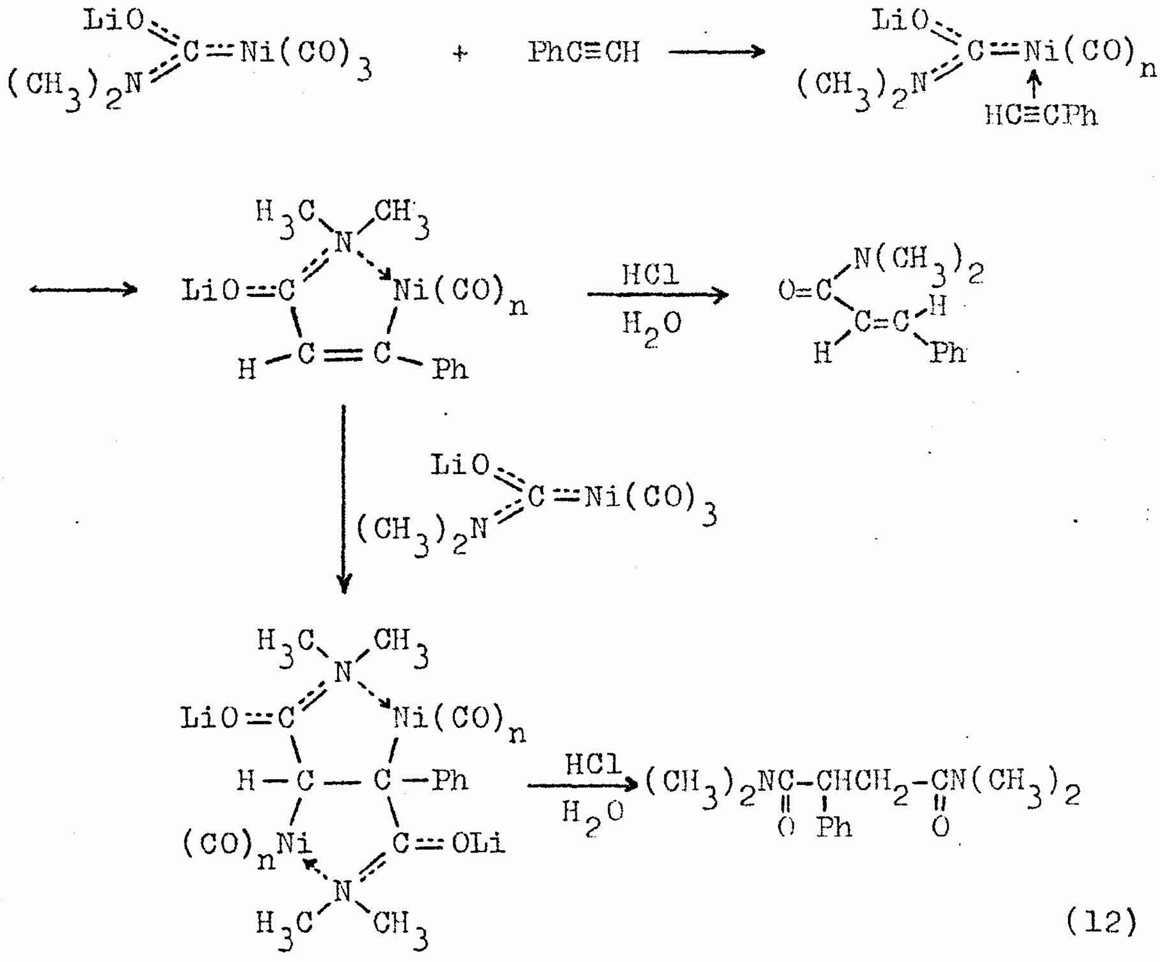


(10)



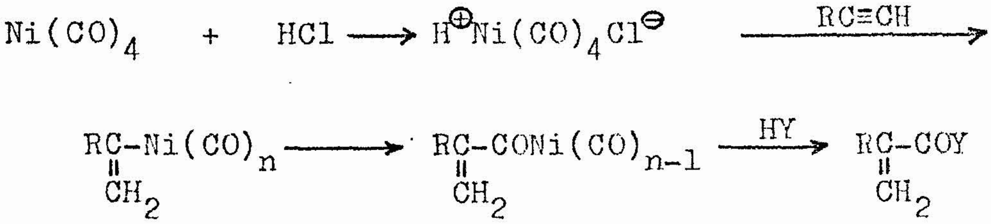
(11)

A mechanism of the formation of 2-phenyl-N,N,N',N'-tetramethylsuccinamide and trans-N,N-dimethylcinnamamide is assumed as follows (eq 12).



(12)

Compared with the Reppe reaction, the formation of trans-N,N-dimethylcinnamamide in this reaction is interesting. In the Reppe reaction, monosubstituted acetylenes react with nickel carbonyl and hydrochloric acid in the presence of water, or an alcohol, or an amine to give compounds of the type $RC(COY)=CH_2$ ($Y = OH, OR', NR''_2$). In the above reaction it was thought that a proton of the hydronickel carbonyl adds to the terminal carbon atom of the monosubstituted acetylenes and nickel adds to the inner carbon atom to give an alkylnickel complex and the insertion of carbon monoxide into the carbon-nickel bond occurs, followed by hydrolysis, alcoholysis, or aminolysis (eq 13),[9] but in an acylmetal complex with a carbon-metal σ bond, the acyl group generally tends to add to the terminal carbon of the monosubstituted acetylenes.



$$Ni(CO)_4 \quad + \quad HCl \longrightarrow H^{\oplus}Ni(CO)_4Cl^{\ominus} \quad \xrightarrow{\quad RC\equiv CH \quad}$$

$$\underset{\substack{\| \\ CH_2}}{RC}\text{-}Ni(CO)_n \longrightarrow \underset{\substack{\| \\ CH_2}}{RC}\text{-}CONi(CO)_{n-1} \xrightarrow{HY} \underset{\substack{\| \\ CH_2}}{RC}\text{-}COY \qquad (13)$$

In fact, in the case of the reaction of phenylacetylene with a carbamoylnickel complex, a cinnamamide derivative is obtained but not an atropic acid amide derivative (a product of the Reppe reaction).

From acetylenic compounds and nickel carbonyl, acrylic acid derivatives can be obtained by the Reppe reaction,[10] but succinic acid derivatives cannot be obtained. Natta et al. have reported that succinic acid was obtained by the reaction of acetylene with carbon monoxide (250 atm) using $Co_2(CO)_8$ as a catalyst at 110°.[11] On the other hand a succinamide derivative is easily obtained under mild conditions by the present reaction. (Recently, Chiusoli et al. have reported the formation of dimethyl maleate and dimethyl muconate from acetylene and carbon monoxide in methanol containing palladium dichloride and thiourea.[12])

Table I shows the yields of 2-phenyl-N,N,N',N'-tetramethylsuccinamide, trans-N,N-dimethylcinnamamide and dimethylamine hydrochloride under several reaction conditions.

Table I

Reaction of Lithium Dimethylcarbamoylnickel Carbonylate with Phenylacetylene

			% yield*		
Solv.	Temp, °C	Time, hr	$PhCHCON(CH_3)_2$ | $CH_2CON(CH_3)_2$	$PhCH$ ‖ $HCCON(CH_3)_2$	$(CH_3)_2NH_2Cl$
Et_2O	20	4	40.7	0.6	12.4
Et_2O	-70	33	7.5	4.5	28.8
THF	20	4	14.1	0.2	10.1
THF	-70	33	6.0	0.8	20.8

*Yields were calculated based on lithium dimethylamide used.

1-4 Reaction of lithium dimethylcarbamoylnickel carbonylate with organic halides.

Recently, anionic organometal carbonylate have been shown to be effective nucleophilic reagents in organic syntheses: e.g., nucleophilic acylation of organic halides[13] and conjugated enones[3] using lithium acylmetal carbonylates derived from organolithium compounds and mononuclear metal carbonyls, and alkoxycarbonylation of organic halides[14] using nickel carbonyl and potassium alkoxide.

In this and the next sections, the reactions of lithium dimethylcarbamoylnickel carbonylate as a nucleophilic carbamoylation reagent will be described. The reaction of alkyl carbamoyl chloride with carbanion has been well known as a method for electrophilic carbamoylation accompanying a carbon-carbon bond formation.[15] On the other hand, the anionic carbamoyl group ought to show an opposite reaction behavior to the cationic one and would be considered to develop a new type of organic reaction. On account of the difficulty to form it, however, there are few reports on nucleophilic carbamoylation except the reaction system of biscarbamoylmercury compounds and n-butyllithium at very low temperature.[16]

Results and Discussion

Treatment of lithium dimethylcarbamoylnickel carbonylate with several organic halides, RX or RCOX, in ether results in formation of the acid amides $RCON(CH_3)_2$. The examples cited in Table II illustrate the synthesis of N,N-dimethyl acid amides using the indicated reactants and reaction conditions.

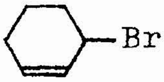
In general, the reactivity sequence of alkyl halides in the nucleophilic substitution reaction is RI > RBr > RCl, but alkyl iodides such as methyl iodide, n-butyl iodide and also t-butyl bromide do not undergo dimethylcarbamoylation under these conditions. It is probably owing to acceleration of the reactivity by the coordination of the double bond to nickel that alkenyl halides which are more unsusceptible to nucleophilic substitution than alkyl halides undergo dimethylcarbamoylation easily. In the reaction with allylic halides also, the same factor and/or the formation of a stable π-allyl complex probably play important roles.

The formation of N,N-dimethylcrotonamide from allyl bromide suggests the existence of a π-allyl complex as an intermediate.

Table II

Dimethylcarbamoylation of Organic Halides

$$\mathrm{Li}\left[(CH_3)_2NCONi(CO)_3\right] + RX\ (\text{or } RCOX) \longrightarrow RCON(CH_3)_2{}^{a}$$

Organic Halides (RX or RCOX)	Reaction time, hr and temp, °C	$RCON(CH_3)_2$ % yield[b]
trans-PhCH=CHBr	7, 10	96.0
PhI	5, 37	98.2
$PhCH_2Br$	12, 33	64.8[c]
$CH_2=CHCH_2Br$	0.5, 15	35.9[d]
	10, 20	99.3
CH_3COCl	0.5, 22	75.9[e]
$n\text{-}C_4H_9COCl$	0.5, 22	97.1[e]
PhCOCl	5, 30	95.6[e]

[a] Reactants ratio; $LiN(CH_3)_2$: $Ni(CO)_4$: halide = 1 : 2 : 2.

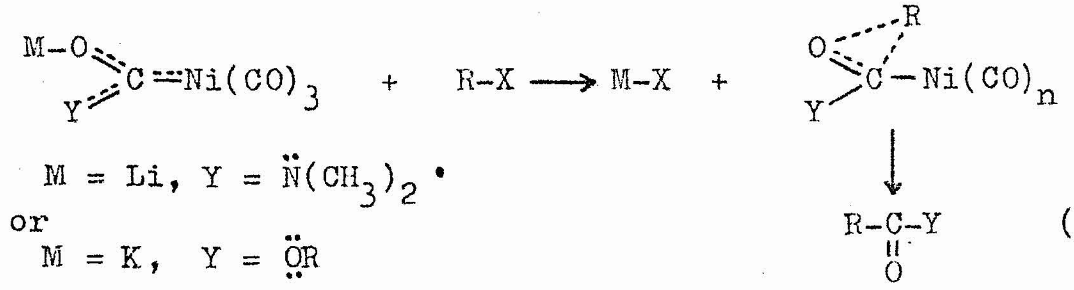
[b] Yields were calculated based on $LiN(CH_3)_2$ used.

[c] Other product; $PhCH_2N(CH_3)_2$ 33.2 %.

[d] Product; $CH_3CH=CHCON(CH_3)_2$.

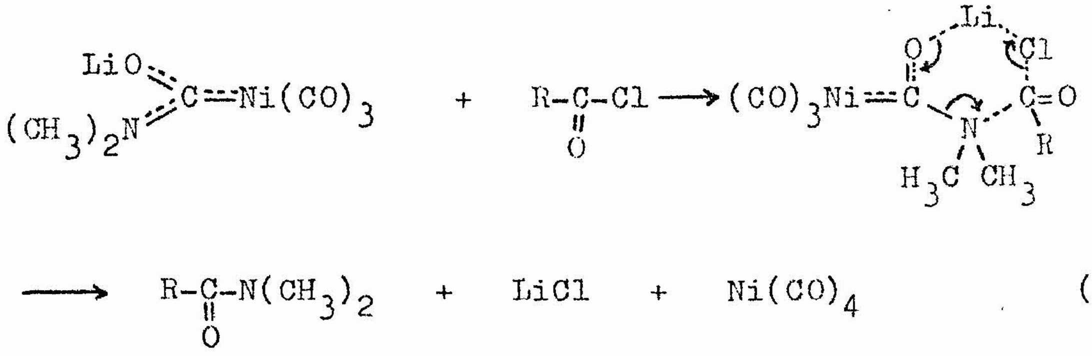
[e] None of $RCOCON(CH_3)_2$ was detected.

The tendency of the reactivity of lithium dimethylcarbamoylnickel carbonylate toward organic halides resembles with that of the complex in alkoxycarbonylation[14] using nickel carbonyl and potassium alkoxide. The analogous reactivity suggests the active species in both systems have closely related structures, and both dimethylcarbamoylation and alkoxycarbonylation of organic halides may be described schematically by the following (eq 14).



(14)

In the reaction with acyl chloride, N,N-dimethyl acid amides are obtained but not N,N-dimethyl α-keto acid amides. This shows the cationic acyl group attacked to nitrogen atom (eq 15) like as proton did so in acid hydrolysis of lithium dimethylcarbamoylnickel carbonylate (eq 6).

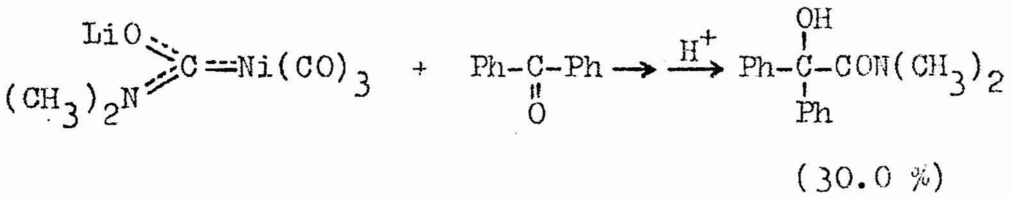


(15)

1-5 Reaction of lithium dimethylcarbamoylnickel carbonylate with carbonyl compounds.

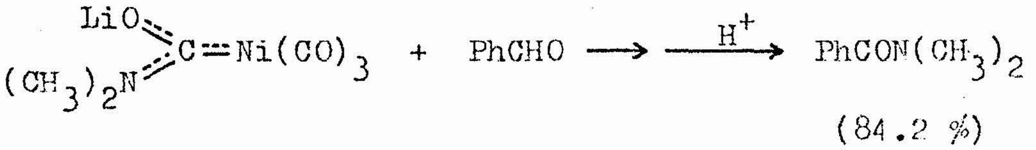
Results and Discussion

Treatment of lithium dimethylcarbamoylnickel carbonylate with benzophenone in tetrahydrofuran results in formation of α-phenyl-N,N-dimethylmandelamide after hydrolysis (eq 16).



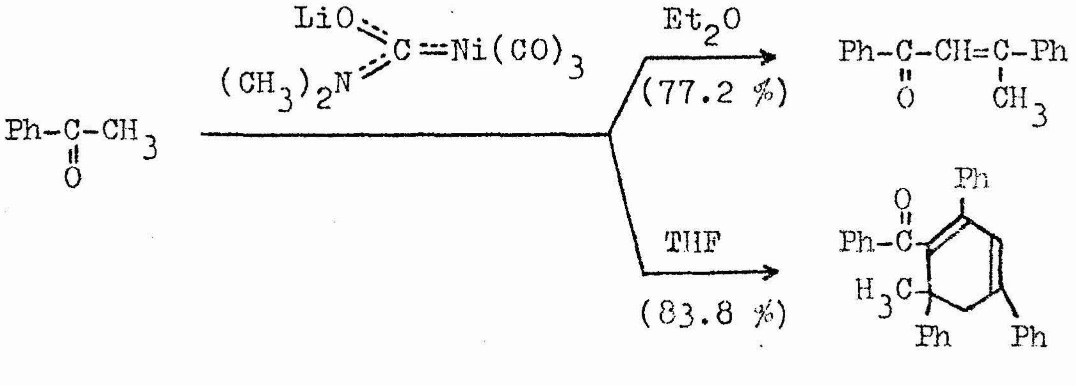
(16)

Benzaldehyde reacts with lithium dimethylcarbamoylnickel carbonylate to give N,N-dimethylbenzamide but not N,N-dimethylmandelamide (eq 17). The formation of N,N-dimethylbenzamide suggests that decarbonylation took place in the course of the reaction, although the mechanism is not clear.



(17)

In the presence of lithium dimethylcarbamoylnickel carbonylate, acetophenone condenses to give α-methylchalcone in ether and 1-methyl-1,3,5-triphenyl-2-benzoyl-cyclohexadiene-(2,4) in tetrahydrofuran (eq 18).



(18)

1-6 Discussion on the structures and the reactivity of the anionic organonickel carbonylates, lithium dimethylcarbamoylnickel carbonylate, lithium acyl(or aroyl)-nickel carbonylate and potassium t-butoxycarbonylnickel carbonylate.

Results and Discussion

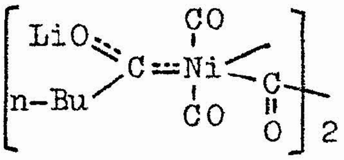
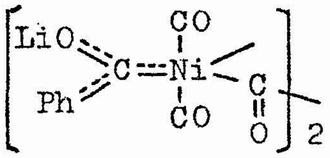
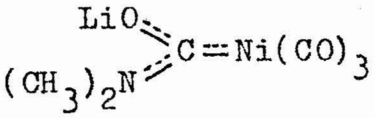
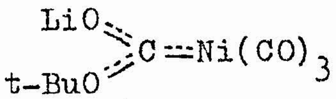
The above three types of complexes have been shown to be important as nucleophilic reagents, but it is difficult to study on their structures in the isolated state because of their instability. So in this section, I will discuss the subjects on the basis of the information obtained from the carbonyl stretching frequencies of the complexes in the infrared spectra in ether.

Table III shows the assumed structures and the carbonyl stretching frequencies of the complexes derived from the reactions indicated in the first column. The terminal carbonyls of the complexes absorb at lower frequencies than that of original neutral nickel carbonyl as shown in Table III. This suggests that these are anionic complexes with high electron density on the nickel atom. These are assumed to be complexes with carbene type ligands analogous to lithium oxycarbene complexes from organolithium compounds and VI-group metal carbonyls [1c] or iron pentacarbonyl[17](eq 19), and lithium oxyaminocarbene complex [8] from lithium diethylamide and chromium hexacarbonyl.

$$\mathrm{LiR} \quad + \quad \mathrm{Fe(CO)_5} \longrightarrow \mathrm{Fe(CO)_4[C(OLi)R]} \qquad (19)$$

Table III

The Carbonyl Stretching Frequencies of the Anionic Organonickel Carbonylate in Ether at 20°

Formation Reaction	Assumed Structure		Terminal CO (cm^{-1})
n-BuLi + $Ni(CO)_4$		(I)[a]	1985, 1962
PhLi + $Ni(CO)_4$		(II)[b]	1962, 1915
(CH) NLi + $Ni(CO)_4$		(III)	1973, 1954
t-BuOK + $Ni(CO)_4$		(IV)	1963, 1920

cf. $Ni(CO)_4$ absorbs at 2053 cm^{-1} in ether.

[a] Bridging CO: 1845, 1819, 1795 cm^{-1}.

[b] Bridging CO: 1855, 1745 cm^{-1}. Reference (13).

The fact that the sequence of the terminal carbonyl stretching frequencies is (I) > (III) > (IV) ~ (II) shows the electron density on nickel atom increases in the order of (I) < (III) < (IV) ~ (II). This result suggests the following effects: (1) the σ-donating character of the carbene ligand becomes enhanced by the electron donating group (R_2N-, R'O-); (2) the nonbonding electron pair on heteroatom in (III) or (IV) fills the vacant p-orbital of the carbene carbon in a certain degree, so the back donation from nickel to carbene carbon decreases. (In (II), the π-electrons of phenyl group probably play the same role as the nonbonding electron pair on heteroatom.) Therefore, the negative charge is relatively localized on the carbene carbon in (III) or (IV) than (I), and the double bond character between the carbene carbon and nickel is smaller in (III) or (IV) than that in (I), and it is expected that the nucleophilic reactivity of (III) or (IV) toward organic halides is greater than that of (I), although (I) has the bridging carbonyls and hence the dinuclear structure has been proposed.[13] Indeed, (III) and (IV) are very reactive toward iodobenzene and give N,N-dimethylbenzamide and t-butyl benzoate respectively in spite of the inactiveness of (I). This suggests the terminal carbonyl stretching frequency can be used in a certain extent as a measure of nucleophilicity of the anionic organometal carbonylates.

As concerns the structure, (III) or (IV) is assumed to be a mononuclear complex in which the carbene ligand and the three carbon monoxide ligands are bonding to nickel tetrahedrally on the basis of the following facts: (1) no carbon monoxide evolution is observed during the formation reaction; (2) the infrared spectrum shows two terminal carbonyl absorptions (C_{3v} symmetry: two infrared active terminal viblations).

Experimental Section

General.—All reactions were carried out under nitrogen. All melting points and boiling points were uncorrected. Gas-liquid partition chromatographic analyses were performed on a Yanagimoto GCG-5DH instrument using 2.5 m × 3 mm or 3.75 m × 3 mm columns packed with 5 % SE-30 or 20% PEG-20M, or on a Hitachi K53 instrument using 1.5 m × 3 mm columns packed with SF-96 or 20% PEG-20M (carrier gas, He). The infrared spectra of the ether solution of the complexes were taken on a Hitachi-Perkin-Elmer 225 infrared recording spectrophotometer using KBr cell and those of the other organic compounds were taken on a Shimazu IR 27 spectrophotometer. The nmr spectra were taken on a Jasco JNM-G-60 instrument and the mass spectra were taken on a Hitachi RMU-6 instrument.

Preparation of the Ether Solution of Lithium Dimethylcarbamoylnickel Carbonylate.—To dimethylamine (25 mmol) dried with potassium hydroxide was added dropwise n-butyllithium (5 mmol) in n-hexane at 0°, then the excess dimethylamine and the n-hexane were removed under reduced pressure at 40°. The ether (15 ml) solution of nickel carbonyl (10 mmol) was added to the ether (40 ml) suspension of lithium dimethylamide (white) obtained above below 10° and the mixture was stirred for 1 hr. No carbon monoxide evolution was observed during the reaction. Thus obtained red clear solution containing about 9 mol % of lithium dimethylcarbamoylnickel carbonylate was used for the infrared spectrum measurement. This solution showed peaks of carbonyl stretching vibrations at 1973 (vs), 1954 (s) and 1560 cm^{-1} (m, broad).

Preparations of the Ether Solutions of Lithium Pentanoylnickel Carbonylate and Potassium t-Butoxycarbonylnickel Carbonylate.—The ether solution of lithium pentanoylnickel carbonylate was prepared by addition of nickel carbonyl (10 mmol) in ether (15 ml) to the n-hexane solution of n-butyllithium (5 mmol) bellow -40° and stirring for 1 hr. After allowing to warm to 20°, the infrared spectrum of this deep red solution was taken, and showed peaks at 1985 (vs), 1962 (s), 1845 (m), 1819 (m) and 1795 cm^{-1} (m).
A similar method was used for the preparation of potassium t-butoxycarbonylnickel carbonylate using potassium t-butoxide (2.5 mmol) prepared from 0.1 g (2.5 mg atom) of potassium and t-butanol in ether (40 ml) in place of lithium dimethylamide. Thus obtained red solution showed peaks at 1973 (vs) and 1920 cm^{-1} (s) in the terminal metal carbonyl region.

Hydrolysis of Lithium Dimethylcarbamoylnickel Carbonylate.—The ether solution of lithium dimethylcarbamoylnickel carbonylate (25 mmol) was hydrolyzed by adding of 25 ml of 3 N hydrochloric acid at room temperatures and the solvents was removed and remained yellowish green solid was extracted with ethanol. The ethanol extract was concentrated and distilled giving 1.01 g (62 %) of hygroscopic crystals of dimethylamine hydrochloride (bp 148-150°/10 mm): mp in tube 169-170.5°(recrystallized from ethanol); ir (KBr) 2960 ($\nu_{as\ C-H}$), 2800 ($\nu_{s\ C-H}$), 2450 (ν_{N^+-H}), 1595 (δ_{NH_2}), 1475 (δ_{asCH_3}), 1025 (ν_{C-N}); nmr ($CDCl_3$) τ 7.26 (t, 6H), 0.5-1.3 (broad, 2H). No compounds resulting from carbon monoxide insertion were obtained.

Reaction of Lithium Dimethylcarbamoylnickel Carbonylate with Mercuric Chloride.—The THF solution of lithium dimethylcarbamoylnickel carbonylate (25 mmol) was treated with mercuric chloride at room temperatures for 5 hr, and the mixture was extracted with CH_2Cl_2 . The dichloromethane extract was distilled to give the fraction (bp 40-60°/5 mm), which was analyzed by glpc (column: SE-30, 2.5 m, 120-200°; He 7.5 ml/min) to contain 0.055 g (30.1 %) of N,N,N',N'-tetramethyloxamide and 0.002 g (0.2 %) of N,N,N',N'-tetramethylurea. Mercury and lithium chloride were also obtained as inorganic products. N,N,N',N'-tetramethyloxamide: mp 75-76°(from ether); ir (KBr) 1620-1650 cm^{-1} (vs). N,N,N',N'-tetramethylurea: ir 1640 cm^{-1}.

Reaction of Lithium Dimethylcarbamoylnickel Carbonylate with Phenylacetylene.—Phenylacetylene (5.1 g, 50 mmol) was added to the ether solution of lithium dimethylcarbamoylnickel carbonylate (50 mmol) and the mixture was stirred for 4 hr at 20°. After removal of the ether and the remaining nickel carbonyl under reduced pressure, benzene (150 ml) was added and then hydrolyzed by 2 N hydrochloric acid (80 ml) with cooling. From the water-soluble part, 0.50 g (12.4 %) of dimethylamine hydrochloride was obtained. The benzene-soluble part was dried ($MgSO_4$), concentrated, and distilled to give fractions (1) bp 100-150°(0.6 mm) and (2) bp 150-200° (0.6 mm) in yields of 2.23 g and 0.55 g, respectively. A part of these fractions was separated by column chromatography (silica gel, petroleum ether (bp 35-65°)) to give triphenylbenzene (mixture of 1,3,5- and 1,2,4-): mp 108-112° (from petroleum ether-benzene); white crystals; nmr τ 2.5-3.0 (m), and all-trans-1,4-diphenylbutadiene (mp 147.5-149° (from petroleum ether-benzene), white needles) which is confirmed by a comparison of the infrared spectrum and a mixture melting point determination with an authentic sample prepared by a Wittig reaction of cinnamyl bromide with benzaldehyde. By the recrystallization of these fractions using petroleum ether-benzene, 2-phenyl-N,N,N',N'-tetramethylsuccinamide, and trans-N,N-dimethylcinnamamide were obtained. A gas chromatographic analysis (column: SE-30, 2.5 m, 200°; He 7.5 ml/min) of the fractions (1) and (2) showed that these fractions consisted of 2.52 g (40.7 %) of 2-phenyl-N,N,N',N'-tetramethylsuccinamide, 0.05 g (0.6 %) of trans-N,N-dimethylcinnamamide, a trace of triphenylbenzene, and a trace of all-trans-1,4-diphenylbutadiene. 2-Phenyl-N,N,N',N'-tetramethylsuccinamide: mp 93.1-93.8°(white crystals); ir (KBr) 3025 (w), 2980 (w), 2810 (m), 1645 (sh), 1630 (vs), 1620 (sh), 1590 (m), 1495 (m), 1458 (m), 1415 (m), 1390 (s), 1268 (s), 1130 (s), 765 (s), 725 (m), 703 cm^{-1} (s); nmr ($CDCl_3$) τ 7.6 (m, 1H), 7.1 (s, 12H), 6.6 (m, 1H), 5.6 (m, 1H), 2.8 (s, 5H).

Anal. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12; N, 11.28; mol wt, 248. Found: C, 67.60; H, 8.20; N, 11.27; mol wt, 258 (osmometer in benzene at 25°).

The structure of trans-N,N-dimethylcinnamamide, mp 100.6-101.5°(white needles), was confirmed by mixture meltimg point determination and infrared (conjugated $\nu_{C=0}$ and $\nu_{C=C}$; 1655 and 1600 cm^{-1}) and nmr ($CDCl_3$, 6.93(s, 3H), 7.02 (s, 3H), 2.70 (s, 5H)) spectral comparison with an authentic sample. The same reaction was carried out under different conditions. The results obtained are listed in Table I.

Reaction of Lithium Dimethylcarbamoylnickel Carbonylate with Organic Halides.—The experimental execution of dimethylcarbamoylation reaction is illustrated for the synthesis of trans-N,N-dimethylcinnamamide from trans-β-bromostyrene. To the ether solution (60 ml) of lithium dimethylcarbamoylnickel carbonylate prepared from 25 mmol of lithium dimethylamide and 50 mmol of nickel carbonyl was added dropwise 9.15 g (50 mmol) of trans-β-bromostyrene in 10 ml of ether below 10° and the mixture was stirred for 7hr at that temperature. After allowing to warm to room temperatures, carbon monoxide was bubbled through the mixture for 1 hr to dispel any remaining nickel carbonyl. Then anhydrous ethanol (30 ml) was added and the solution was distilled under reduced pressure to give 4.2 g of yellowish white crystals (bp 120-140°/0.7 mm), which were identified to be trans-N,N-dimethylcinnamamide by glpc and irs comparison with an authentic sample (yield, 96.0 %). N,N-Dimethyl-3-cyclohexene carboxylic acid amide (bp 98-99°/0.5 mm) obtained from 3-bromocyclohexene was identified by the irs ($\nu_{C=0}$ 1645 cm^{-1}), the mass spectrum (m/e; P=153, 81, 72) and the nmr spectrum (τ ; 8.2-

8.5 (m, 5H), 7.3 (s, 6H), 6.9 (m, 1H), 4.5-4.7 (m, 2H)). N,N-Dimethylcrotonamide from the reaction with allyl bromide was isolated by preparative glpc and identified by the irs (conjugated $\nu_{C=O}$ and $\nu_{C=C}$; 1620 and 1665 cm^{-1}), the mass spectrum (m/e; P=113, 98, 69, 41) and the nmr spectrum (τ ; 8.3 (d, 3H), 7.1 (s, 6H), 3.9 (d, 1H), 2.5 (m, 1H)). The other N,N-dimethyl acid amides cited in Table II were identified by glpc and irs comparison with authentic samples.

Reaction of Lithium Dimethylcarbamoylnickel Carbonylate with Benzophenone.—To the THF solution (60 ml) of lithium dimethylcarbamoylnickel carbonylate prepared from 25 mmol of lithium dimethylamide and 37 mmol of nickel carbonyl was added 4.55 g (25 mmol) of benzophenone in 20 ml of THF and the mixture was stirred for 20 hr at 67°. After hydrolysis by adding of 30 ml of 3 N hydrochloric acid at room temperatures, the solution was concentrated by removal of the THF under reduced pressure and was extracted with ether. The ethereal extract was washed with water saturated with sodium chloride until a neutral solution was obtained and dried with anhydrous magnesium sulfate. The extract was distilled under reduced pressure after removal of the ether to give fractions (1) bp 120-125°/0.7 mm, 3.32 g and (2) bp 140-145°/0.7 mm, 0.50 g. The fraction (1) consisted of the recovered benzophenone. By the recrystallization of the fraction (2) using petroleum ether-benzene, white crystals of α-phenyl-N,N-dimethylmandelamide (mp 103°) were obtained. This compound was identified by the irs (KBr, ν_{O-H} 3300 cm^{-1},

$\nu_{C=O}$ 1620 cm^{-1}), the mass spectrum (m/e; P=255, 183, 105), the nmr spectrum (τ; 7.3 (broad, 6H), 4.1 (s, 1H, this peak disappeared by adding of D_2O), 2.7 (s, 10H)) and the elemental analysis.

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.18; H 6.66; N, 5.38. (Yield, 30.0 % based on benzophenone consumed.) .

Reaction of Lithium Dimethylcarbamoylnickel Carbonylate with Benzaldehyde.—Treatment of 2.65 g (25 mmol) of benzaldehyde with lithium dimethylcarbamoylnickel carbonylate (25 mmol) by the method mentioned in the case of benzophenone resulted in formation of 1.68 g of N,N-dimethylbenzamide (84.2 % based on benzaldehyde consumed), which was identified by glpc, irs comparison with an authentic sample and the mass spectrum (m/e; P=149, 105).

Reaction of Lithium Dimethylcarbamoylnickel Carbonylate with Acetophenone.—To the ether solution of lithium dimethylcarbamoylnickel carbonylate (25 mmol) was added 6.00 g (50 mmol) of acetophenone and the solution was stirred for 24 hr at 18°. After hydrolysis by adding of 30 ml of 3 N hydrochloric acid, the solution was extracted with ether. The extract was washed with water saturated with sodium chloride and dried with anhydrous magnesium sulfate, then was distilled under reduced pressure. The first fraction (bp 115°/80 mm, 2.50 g) was acetophenone recovered and the second fraction (bp 150-185°/2 mm, 2.61 g) was shown to contain 2.50 g of α-methylchalcone by a glpc analysis. This compound was isolated by preparative glpc and identified by the irs (conjugated $\nu_{C=O}$ and $\nu_{C=C}$; 1660 and 1600 cm^{-1}), the mass spectrum (m/e; P=222, 115, 105) and the nmr spectrum (τ ; 7.5 (s, 3H), 2.9 (s, 1H), 2.0-2.8 (m, 10H)). (77.2 % based on acetophenone consumed.) In the same reaction using THF as a solvent (67°, 10 hr), 3.00 g (25 mmol) of acetophenone was converted to 2.23 g of 1-methyl-1,3,5-triphenyl-2-benzoyl-cyclohexadiene-(2,4) (mp 134-135° from petroleum ether-benzene), which was identified by the irs ($\nu_{C=O}$ 1670 cm^{-1}; $\nu_{C=C}$ 1640 and 1620 cm^{-1}), the mass spectrum (m/e; P=426, 411, 321, 105), the nmr spectrum (τ ; 8.4 (s, 3H), 6.9 (s, 2H), 3.9 (s, 1H), 2.5-3.1 (m, 20H)) and the elemental analysis.

Anal. Calcd for $C_{32}H_{26}O$: C, 90.10; H, 6.14. Found: C, 90.06; H, 6.01.

(Yield, 83.8 % based on acetophenone used.)

CHAPTER 2 Reaction of Nickel Carbonyl with N-Monochloroamines (or amide) and with t-Butylhypochlorite.

It has been well known that several organic monohalides which contain unsaturated bonds (e.g., $>C=C<$, $>C=O$, $-C\equiv C-$) at the β,γ-position to the halogenes add oxidatively to metal carbonyls to give cationic complexes, $RM(CO)_nX$ or $RCOM(CO)_{n-1}X$, which decompose to give coupling products R-R and ketones RCOR (or α-diketones RCOCOR), and furthermore these complexes undergo reactions with olefins or with acetylenes to give the alkylated or acylated compounds.[18]

On the other hand, few studies of the reaction of metal carbonyls with the reagents having heteroatom-halogen bond have been reported except the reaction of N,N-dichloroamines with nickel carbonyl in wet benzene giving N,N′-dialkylureas.[19]

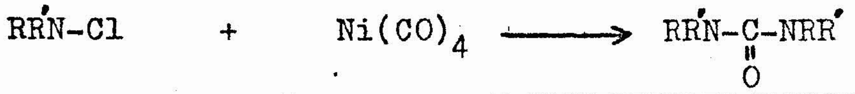
So it seems to be interesting to study whether compounds with heteroatom-halogen bond, haloamine (RR′N-X) or hypohalite (RO-X), shows analogous reactivity. In this chapter, I will describe the formation of cationic carbamoylnickel complexes as precursors to urea derivatives by the oxidative addition of N-monochloroamines (or amide) to nickel carbonyl and the reaction of t-butyl hypochlorite with nickel carbonyl.

2-1 Reaction of nickel carbonyl with N-monochloroamines (or amide).

Results and Discussion

Treatment of N-monochloroamine with nickel carbonyl in ether results in formation of the urea derivative. The examples cited in Table IV illustrate the reaction of N-monochloroamines (or amide) with nickel carbonyl using the indicated reaction conditions.

Table IV



$$RR'N\text{-}Cl + Ni(CO)_4 \longrightarrow RR'N\text{-}\underset{\underset{O}{\|}}{C}\text{-}NRR'$$

R	R'	Solvent	Temp (°C)	Time (hr)	% yield[a]
CH_3	CH_3	Et_2O	17-30	6	10.0[b]
C_2H_5	C_2H_5	Et_2O	15-20	20	10.1[c]
C_2H_5	H	Et_2O	20-30	15	17.2
$PhCH_2$	H	Et_2O	20-30	14	17.0
PhCO	H	$CHCl_3$	45	2.5	52.5[d]

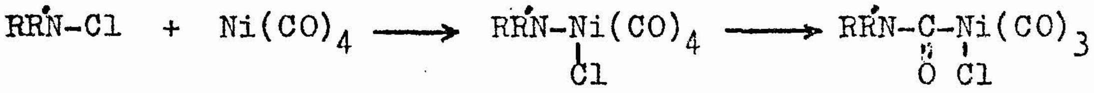
[a] Yields were calculated based on N-monochloroamines (or amide) used.

[b] Other product: $(CH_3)_2NCOCl$ (trace).

[c] Other products: $(C_2H_5)_2NCOCl$ (1.9 %), $(C_2H_5)_2NCO_2C_2H_5$(trace).

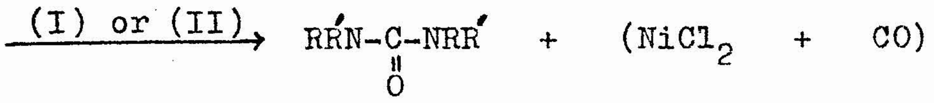
[d] Other product: $PhCONH_2$ (38.0 %).

A possible mechanism for the formation of urea derivatives seems to be analogous to that of the reaction of organic monohalides with metal carbonyl, although the formation of the intermediates (II) and (III) have not yet been confirmed by irs studies (eq 20).



$$RR'N\text{-}Cl + Ni(CO)_4 \longrightarrow RR'N\text{-}\underset{\underset{Cl}{|}}{Ni}(CO)_4 \longrightarrow RR'N\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{Cl}{|}}{Ni}(CO)_3$$

(I) (II) (III)



$$\xrightarrow{\text{(I) or (II)}} RR'N-\underset{\underset{O}{\|}}{C}-NRR' \quad + \quad (NiCl_2 \quad + \quad CO) \qquad (20)$$

The formation of dialkylcarbamoyl chloride is explained in terms of the decomposition of (III). The intermediates (II) and (III) were expected to cause the addition of amino carbamoyl group to olefinic or acetylenic bond because the organo transition metal σ-complexes have been well known to add to unsaturated bonds (e.g., $>C=C<$, $-C\equiv C-$, $>C=O$).[2,3,20] Anionic carbamoylnickel complex also adds to phenylacetylene to give a succinamide derivative and a cinnamamide derivative as mentioned in Section 1-3. But contrary to the expectation, the attempted reaction of N-chloroethylamine or N-chlorobenzylamine with nickel carbonyl in the presence of acrylonitrile or phenylacetylene gave a urea derivative alone.

N-Chlorobenzamide which is one of the nitrogen compounds corresponding to α-haloketone reacts with nickel carbonyl to give carbon monoxide inserted product, N,N'-dibenzoylurea, although α-haloketones react with nickel carbonyl without carbon monoxide insertion to give two types of dimerization products, 1,2-diacylethanes(in THF) and β-epoxy ketones (in DMF).[21,22] It is probably owing to the easiness of the migration of amino group in the aminonickel carbonyl complex (II) from nickel to the carbon atom of the coordinated carbon monoxide compared with that of alkyl group in the alkylnickel carbonyl complex because of the larger nucleophilicity of nitrogen atom than carbon atom. Addition of benzyl bromide to the reaction system of N-chlorobenzamide and nickel carbonyl did not cause the formation of the carbamoylated product.

2-2 Reaction of nickel carbonyl with t-butyl hypochlorite.

Results and Dicussion

Treatment of t-butyl hypochlorite with nickel carbonyl in n-hexane results in formation of a trace amount of di-t-butyl carbonate and bluish purple precipitate. The precipitate seems to be nickel$^{(II)}$ di-t-butyl alkoxide, $Ni^{II}(OBu\text{-}t)$, prepared from di-t-butyl peroxide and bis(cycloocta-1,5-diene)nickel by Schott and Wilke.[23]

Experimental Section

General.—All reactions were carried out under nitrogen. Gas-liquid partition chromatographic analyses were performed on the same instruments mentioned in CHAPTER 1.

Materials.—N-Monochloroamines were prepared from amines and sodium hypochlorite in ether and the chlorine was determined by the methods described in the literatures.[24,25] N-Chlorobenzamide was prepared by bubbling of chlorine through ca. 3 N hydrochloric acid saturated with benzamide and recrystallized from hot water (mp 117°);[26] t-Butylhypochlorite was prepared by bubbling of chlorine through the aq sodium hydroxide solution containing t-butanol.[27]

Reaction of Nickel Carbonyl with N-Monochloroamines.—The typical experimental execution is illustrated by the procedure for the reaction with N-chlorodiethylamine. To 75 ml of ethereal solution of N-chlorodiethylamine (73 mmol) prepared from diethylamine hydrochloride and 10 % aq sodium hypochlorite in ether was added dropwise 12.4 g (73 mmol) of nickel carbonyl in 20 ml of ether at 15° with stirring. In the course of the reaction, grayish white precipitates were formed along with carbon monoxide evolution (3000 ml of the gas was collected after stirring for 20 hr at 15-20°). The reaction mixture was filtered and the filtrate was distilled under reduced pressure after removal of the ether to give 0.77 g of oily liquid (bp 120-135°/115 mm), which was analyzed by glpc (Polyester and PEG-20M, 180, He 10 ml/min) and found to contain 0.64 g (10.1 %) of tetraethylurea, 0.19 g (1.9 %) of diethylcarbamoyl chloride and a trace amount of ethyl diethylcarbamate. A coupling product, tetraethylhydrazine was not detected. Tetraethylurea was identified by glpc and irs comparison with an authentic sample prepared from the reaction of diethylamine with phosgene. Ethyl diethylcarbamate was isolated by preparative glpc and identified by the irs ($\nu_{C=0}$ 1755 cm^{-1}) and the mass spectrum (m/e; P=135, P+2=137, 100, 72). The other products cited in Table IV were identified by glpc and irs comparison with authentic samples.

Reaction of Nickel Carbonyl with N-Chlorobenzamide.— To a chloroform (60 ml) solution of N-chlorobenzamide (3.9 g, 25 mmol) was added 4.2 g (25 mmol) of nickel carbonyl in 10 ml of chloroform at 45°. After stirring for 2.5 hr, yellow ochre precipitates (5.7 g) were formed and 2000 ml of carbon monoxide was evolved. From the ether and dichloromethane extracts of the precipitate, white crystals (3.91 g) were obtained. The crystals were separated by sublimation to give 1.15 g (38.0 %) of benzamide (below 80°/0.2 mm) and 1.76 g (52.5 %) of N,N'-dibenzoylurea (remained at 80°/0.2 mm). N,N'-Dibenzoylurea (mp 218° from benzene, lit.[28] 218°) was identified by irs comparison with that of cited in lit.[28] (ν_{N-H} 3260 cm^{-1}; $\nu_{C=O}$ 1755 (vs), 1690 (w), 1670 (s) cm^{-1}), the mass spectrum (m/e; P=268, 147, 121, 105) and the nmr spectrum (τ; 1.9-2.6 (m, 10H), -1.9 (s, 2H)).

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.07; H, 4.39; N, 10.43.

Reaction of Nickel Carbonyl with t-Butyl Hypochlorite. —To a n-hexane (20 ml) solution of 3.4 g of t-butyl hypochlorite was added 25 mmol of nickel carbonyl in 20 ml of n-hexane at -30° and the solution was allowed to warm to room temperatures with stirring. Carbon monoxide evolution was observed near at 0°, and bluish purple precipitates were formed. The mixture was extracted with ethyl acetate after removal of the n-hexane and the extract was concentrated, analyzed by glpc and found to contain a trace amount of di-t-butyl carbonate. The precipitate was not purified.

CHAPTER 3 Reactions of Organometal Carbonyl Complexes with Olefin Oxides.

A large number of studies on organic syntheses by means of organometal complexes and the reagents containing hetero-atoms at the reaction sites have been published. For example, it has been well known that the syntheses of cyclic amides or imides from the nitrogen compounds (Schiff bases, azo compounds, unsaturated amides, unsaturated amines, aromatic nitriles) and metal carbonyls under pressure of carbon monoxide, the syntheses of formamides or ureas or oxamides from amines and metal carbonyls, or from amines in the presence of palladium dichloride under pressure of carbon monoxide, and the syntheses of amides or esters by aminolysis or alcoholysis of the acylmetal complexes.[29]

As concerns with epoxides, it has been known that the compounds are transformed to the corresponding ketones by the action of cobalt tetracarbonyl anion or dicobalt octacarbonyl.[30] In the presence of carbon monoxide, carbon monoxide insertion reactions occur to give β-hydroxy carboxylic acid esters in alcohol solution[31] and α,β-unsaturated acids in benzene solution.[32] Furthermore, under the oxo conditions, α,β-unsaturated aldehydes are produced.[33]

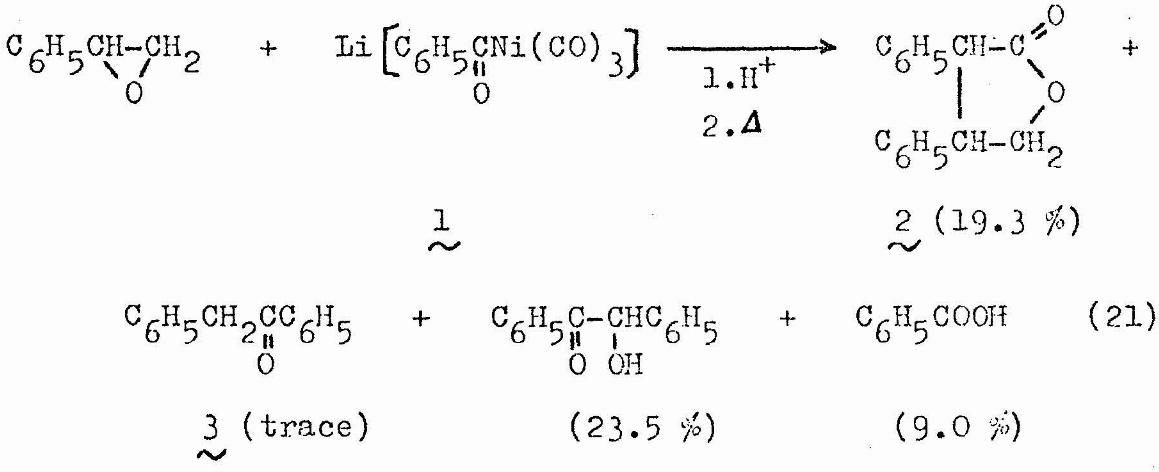
Although the interesting reaction behaviors of σ-organometallic compounds toward olefins, acetylenes, ketones, or aldehydes have been revealed during these ten years, the reactivity of alkyl or acyl transition metal complexes toward epoxides has not yet been defined. However, the facility with which π-methallylnickel bromide reacts with styrene oxide to give 2-methyl-4-phenyl-5-hydroxypentene-1[34] suggests that analogous reactions of alkyl or acyl transition metal complexes might be important in organic synthesis.

Lithium acylmetal carbonylates, prepared by the reaction between organolithium compounds and metal carbonyls, are efficient nucleophilic acylating agents, and many useful organic reactions using these reagents, such as syntheses of aldehydes,[1a] acyloins,[1b] α-diketones,[1b] unsymmetrical ketones,[1b,13] and 1,4-dioxo compounds[2,3] have been reported. The reaction of lithium aroylnickel carbonylate with styrene oxide was carried out and it was found that the product is not the expected aroylphenylethyl alcohol but α,β-diphenyl-γ-butyrolactone, which seemed to be produced by dimerization and hydrogen abstraction of styrene oxide. In this chapter, I will describe the formation of α,β-diphenyl-γ-butyrolactone from styrene oxide by the action of lithium aroylnickel carbonylate or dibenzyliron tetracarbonyl (and sodium benzyliron tetracarbonylate), which is a new type of transformation of olefin oxide and would promise a unique synthetic route to lactones from olefin oxides, and other some new type of reactions of olefin oxides in the presence of organometal carbonyl complexes.

3-1 Formation of α,β-diphenyl-γ-butyrolactone from styrene oxide by the action of organo transition metal complexes.

Results and Discussion

Styrene oxide undergoes reaction with lithium benzoylnickel carbonylate (**1**) to give trans-α,β-diphenyl-γ-butyrolactone (**2**), benzyl phenyl ketone (**3**), benzoin, and benzoic acid. The latter two compounds are produced by the hydrolysis of **1**,[1b] and the former two seem to be the products derived from the reaction between styrene oxide and **1** (eq 21).



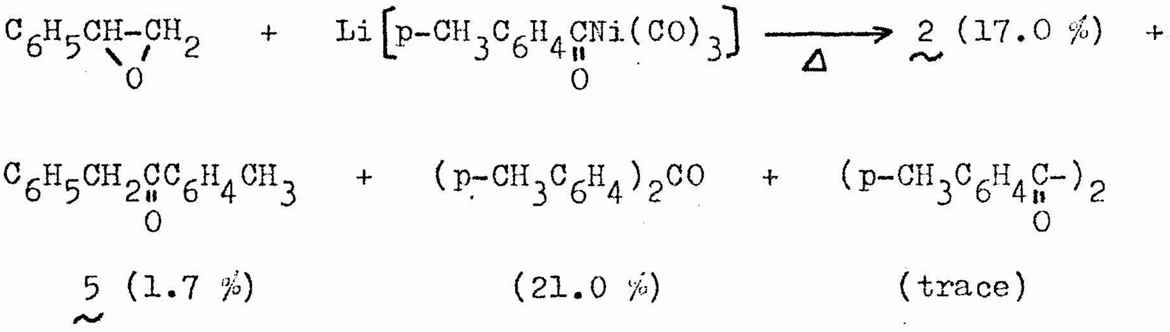
1

2 (19.3 %)

3 (trace) (23.5 %) (9.0 %)

(21)

The formation of **2** was not explained by the combination of benzoyl group in **1** with styrene oxide; so, in order to clarify whether the phenyl group in **2** came from styrene oxide or **1**, an analogous reaction was carried out using lithium p-toluoylnickel carbonylate (**4**) instead of **1** (eq 22). (Lithium aroylnickel carbonylate is simplified as **1** or **4**.) Then, **2** was obtained in a similar yield to that from reaction (21), and the formation of benzyl p-tolyl ketone (**5**) corresponded to the formation of **3**. Di-p-tolyl ketone and p,p'-bitolyl are the products formed by thermal decomposition of **4**.[1b]

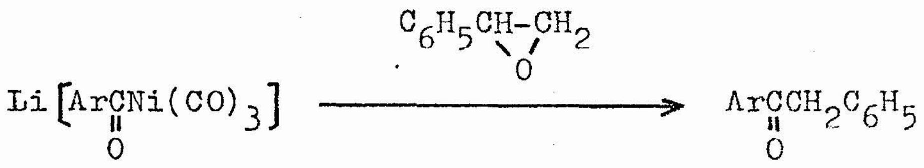


$$C_6H_5\underset{\diagdown O \diagup}{CH-CH_2} + Li\left[p\text{-}CH_3C_6H_4\underset{\|}{\overset{}{C}}\!\!\underset{O}{}Ni(CO)_3\right] \xrightarrow[\Delta]{} \mathbf{2}\ (17.0\ \%) +$$

$$\underset{\mathbf{5}\ (1.7\ \%)}{C_6H_5CH_2\underset{O}{\overset{}{C}}C_6H_4CH_3} + \underset{(21.0\ \%)}{(p\text{-}CH_3C_6H_4)_2CO} + \underset{(trace)}{(p\text{-}CH_3C_6H_4\underset{O}{C}\text{-})_2}$$

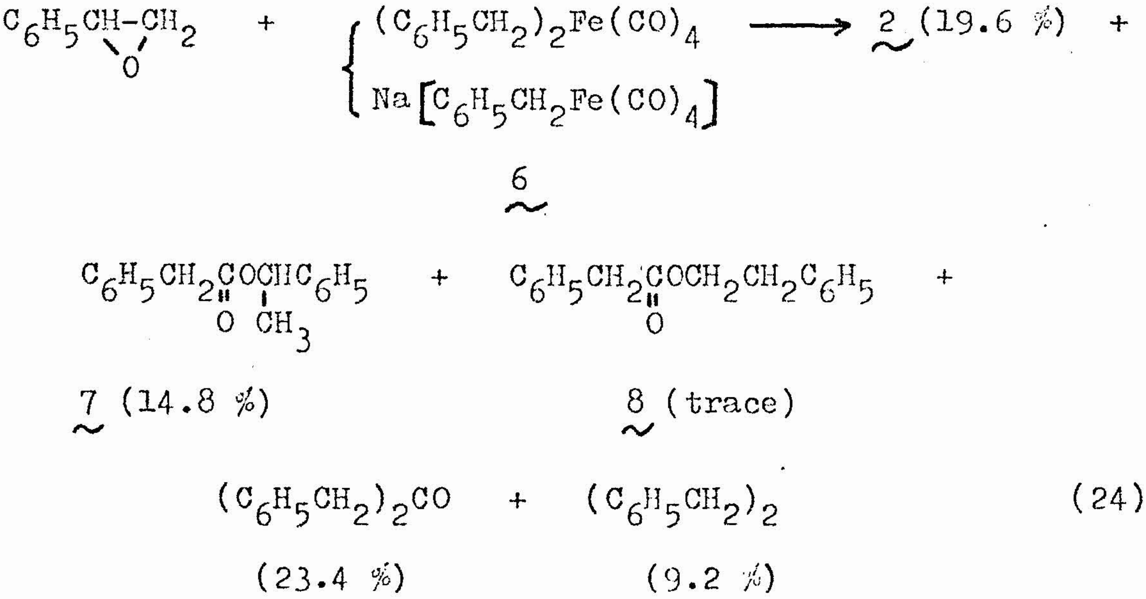
(22)

The fact that **2** was obtained in both reactions (21) and (22) in similar yields shows that the aroyl group in **1** or **4** is not incorporated into the structure of **2**, and so 2 mol of styrene oxide is transformed to 1 mol of **2** with the aid of the aroylnickel carbonylate complex. As the reaction mixture before distillation (bath temp 200-250°) under reduced pressure does not show a peak due to the carbonyl group of the γ-lactone at 1780 cm^{-1}, heating is necessary for the formation of **2** in addition to the aroylnickel carbonylate complex. By column chromatographic separation of the residual oil after removal of the solvent, the crude material, which had a peak at 3600-3200 cm^{-1} and no peaks in the carbonyl region (2100-1630 cm^{-1}), was obtained from the methanol eluate, and this material, which could not be purified by recrystallization, was transformed to **2** by heating above 200°. This suggests that an alcoholic compound is formed prior to the formation of **2** and heating of the compound results in the formation of **2**. The formation of **3** in reaction (21) and 5 in reaction (22) is important in spite of the low yields, for they are the sole products, respectively, formed by the sddition of the aryl group in the nickel complex to styrene oxide, but the mechanism is still open to question.



$$\mathrm{Li}\left[\mathrm{Ar}\underset{O}{\underset{\|}{C}}\mathrm{Ni(CO)_3}\right] \xrightarrow{\mathrm{C_6H_5\underbrace{CH-CH_2}_{O}}} \mathrm{Ar}\underset{O}{\underset{\|}{C}}\mathrm{CH_2C_6H_5} \qquad (23)$$

Further, to establish the formation of γ-lactone from styrene oxide by the action of metal complexes, the reactions of styrene oxide with dibenzyliron tetracarbonyl (and sodium benzyliron tetracarbonylate), nickel carbonyl, disodium iron tetracarbonylate, and palladium dichloride were carried out. Styrene oxide gives 2 and α- and β-phenylethyl phenylacetate (7 and 8) by the reaction with dibenzyliron tetracarbonyl (and sodium benzyliron tetracarbonylate) (6) (eq 24).



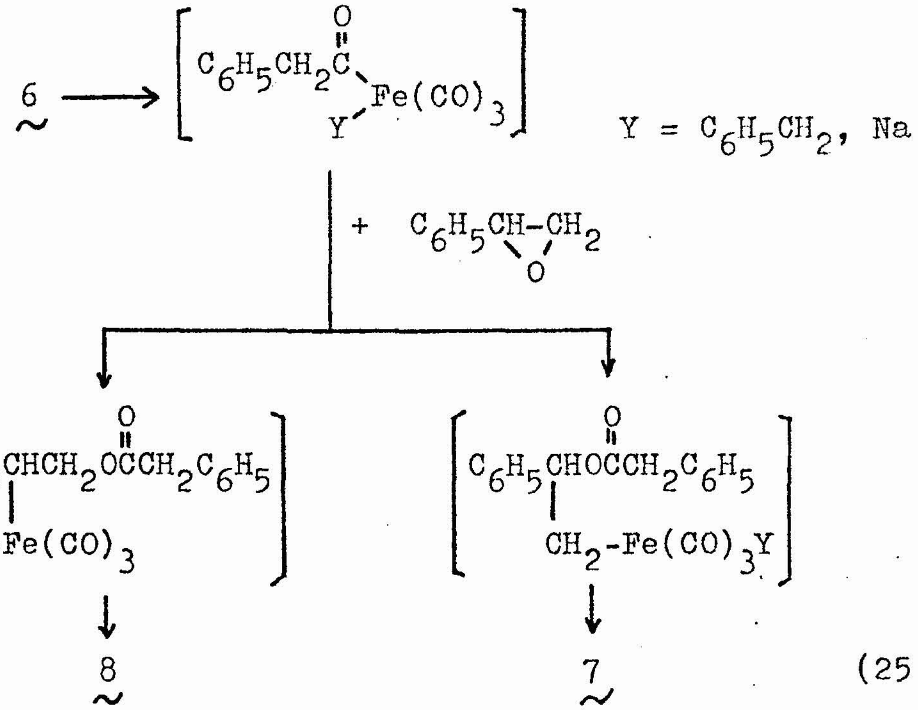
$$\mathrm{C_6H_5\underbrace{CH-CH_2}_{O}} + \left\{\begin{array}{l}\mathrm{(C_6H_5CH_2)_2Fe(CO)_4} \\ \mathrm{Na[C_6H_5CH_2Fe(CO)_4]}\end{array}\right. \longrightarrow 2\ (19.6\ \%) +$$

$$6$$

$$\underset{7\ (14.8\ \%)}{\mathrm{C_6H_5CH_2\underset{O}{\underset{\|}{C}}O\underset{CH_3}{\underset{|}{C}H}C_6H_5}} + \underset{8\ (\text{trace})}{\mathrm{C_6H_5CH_2\underset{O}{\underset{\|}{C}}OCH_2CH_2C_6H_5}} +$$

$$\underset{(23.4\ \%)}{\mathrm{(C_6H_5CH_2)_2CO}} + \underset{(9.2\ \%)}{\mathrm{(C_6H_5CH_2)_2}} \qquad (24)$$

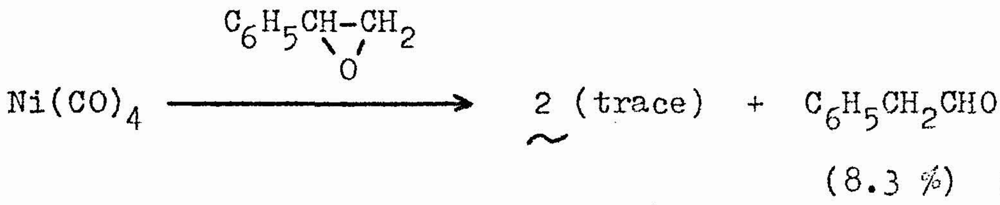
In the formation of the esters 7 and 8, the sequences shown in the following scheme seem to be probable (eq 25).



(25)

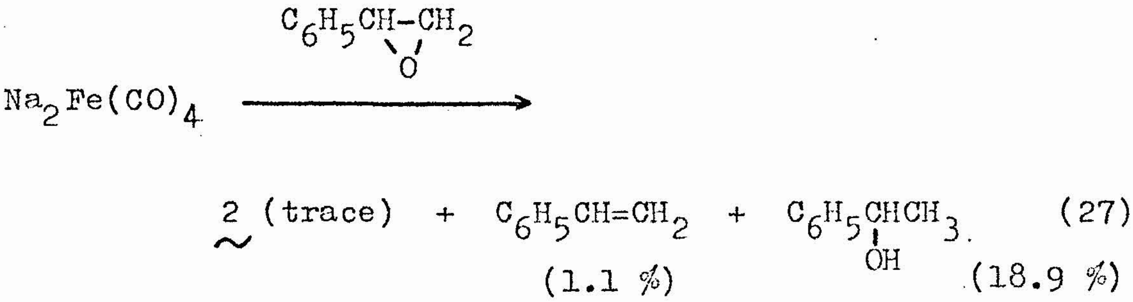
When propylene oxide was used instead of styrene oxide, isopropyl phenylacetate, and n-propyl phenylacetate were produced. The formation of the γ-lactone 2 was not explained in terms of the attack of the benzyl or the phenylacetyl group to styrene oxide, for in the analogous reaction using p-methylbenzyl bromide instead of benzyl halide as a partner in the reaction with disodium iron tetracarbonylate, 2 was also produced in a similar yield (14.9 %). Styrene oxide (2 mol) is transformed to 2 as well as in the case of reaction (21) or (22).

On the other hand, in the case of nickel carbonyl, styrene oxide was transformed to 2 (trace amount) and phenylacetaldehyde (8.3 %) but not to acetophenone (eq 26).



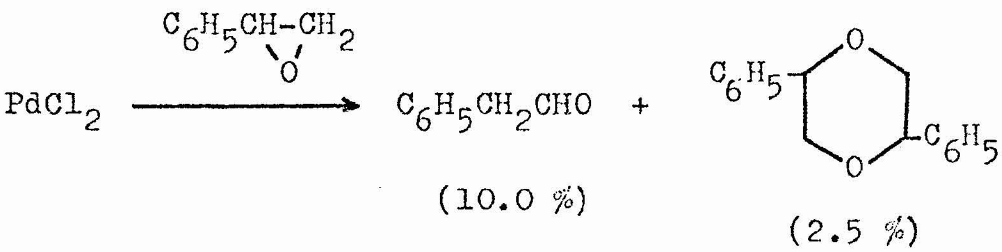
(26)

From the reaction of styrene oxide with disodium iron tetracarbonylate, 2 (trace amount), styrene (1.1 %), and α-phenylethyl alcohol (18.9 %) were obtained (eq 27).



(27)

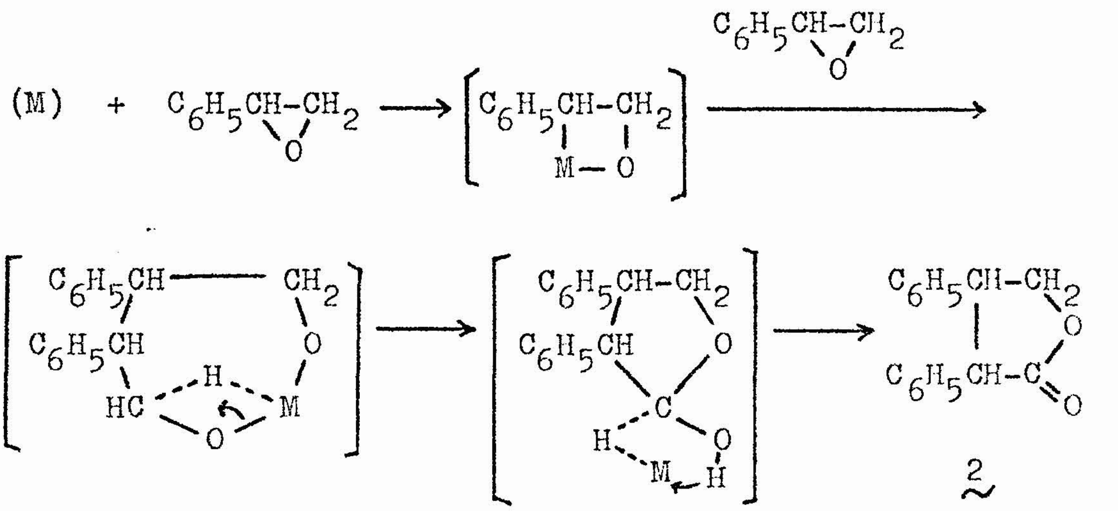
Therefore, nickel carbonyl or disodium iron tetracarbonylate is not effective for the transformation of styrene oxide to 2. As the formation of 2 from styrene oxide seems to involve the dimerization and the hydrogen abstraction processes, it is expected that palladium dichloride which causes easy hydrogen transfer may cause the analogous reaction behavior to occur, but the formation of 2 was not observed and the isolated products were phenylacetaldehyde and trans-2,5-diphenyl-1,4-dioxane[35] (eq 28).



(28)

It is interesting to note that styrene oxide is transformed to trans-α,β-diphenyl-γ-butyrolactone by the action of lithium aroylnickel carbonylate or dibenzyliron tetracarbonyl (and sodium iron tetracarbonylate) in contrast to the reaction of styrene oxide with π-methallylnickel bromide,[34]in which case the epoxide ring was cleaved as a result of the addition of the methallyl group to form 2-methyl-4-phenyl-5-hydrxypentene-1.

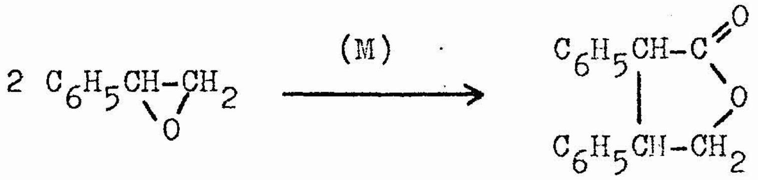
A possible mechanism for the formation of trans-α,β-diphenyl-γ-butyrolactone from styrene oxide by the action of lithium aroylnickel carbonylate or dibenzyliron tetracarbonyl (and sodium iron tetracarbonylate) is the following sequences via organometal hydridic complexes, for anionic organometal species are effective in this reaction (eq 29). (In eq 29, the complex used is illustrated as (M) and the other ligands are omitted.)



(29)

Table V shows the yields of **2** from a new type of reaction of styrene oxide in the presence of several organometal carbonyl complexes (M) derived from the reaction cited in the first column.

Table V



2

Reaction		(M)	% yield
C_6H_5Li	+ $Ni(CO)_4$	$Li[C_6H_5CONi(CO)_3]$	19.3
$p\text{-}CH_3C_6H_4Li$	+ $Ni(CO)_4$	$Li[p\text{-}CH_3C_6H_4CONi(CO)_3]$	17.0
$C_6H_5CH_2I$	+ $Na_2Fe(CO)_4$	$C_6H_5CH_2Fe(CO)_4Y$	16.1
$C_6H_5CH_2Br$	+ $Na_2Fe(CO)_4$	$C_6H_5CH_2Fe(CO)_4Y$	19.6
$p\text{-}CH_3C_6H_4CH_2Br$	+ $Na_2Fe(CO)_4$	$p\text{-}CH_3C_6H_4CH_2Fe(CO)_4Y'$	14.9

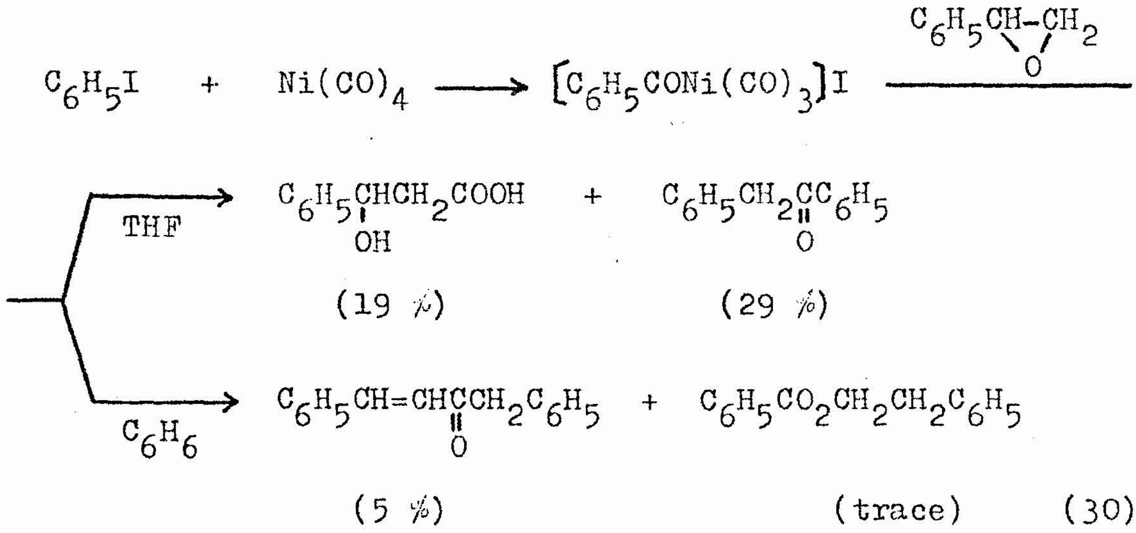
$Y = C_6H_5CH_2$, Na; $Y' = p\text{-}CH_3C_6H_4CH_2$, Na

3-2 Reaction of benzoylnickel carbonyl iodide with styrene oxide or with cyclohexene oxide.

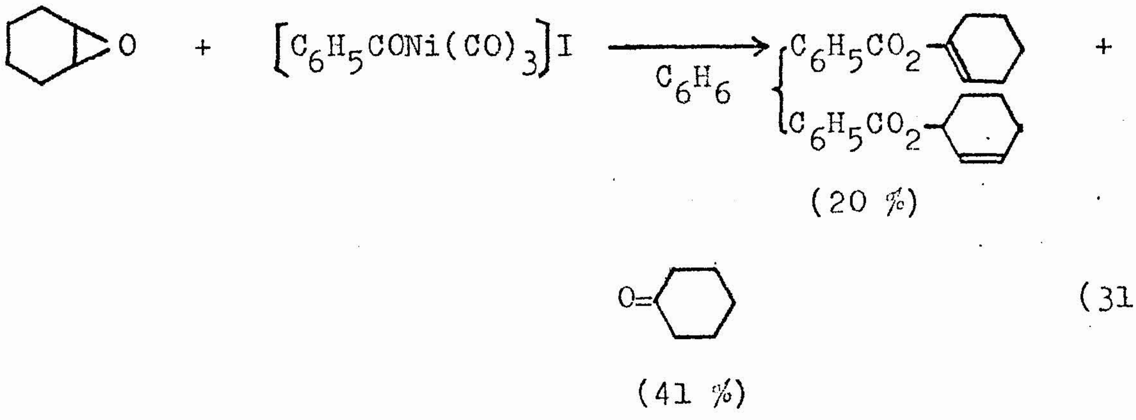
Results and Discussion

Treatment of styrene oxide with benzoylnickel carbonyl iodide derived from iodobenzene and nickel carbonyl [36] results in formation of 3-hydroxy-3-phenylpropionic acid and benzyl phenyl ketone in THF, and of benzyl styryl ketone and β-phenylethyl benzoate in benzene (eq 30).

Cyclohexene oxide reacts with benzoylnickel carbonyl iodide to give cyclohexene benzoate and cyclohexanone after treatment of the reaction mixture with triethylamine (eq 31).



(30)



(31)

3-3 Summary.

In the presence of organometal carbonyl complexes, several new types of reactions of olefin oxides were found. They may be classified to the following four types, although the mechanisms have not yet been clear.

(1) Isomerization to aldehyde or ketone: (27), (31).

(2) Dimerization accompanying with dehydrogenation or dehydration: (21), (22), (24).

(3) Insertion into carbon-metal bond: (23), (30), (esters).

(4) Carboxylation accompanying with ring cleavage: (30).

Experimental Section

General.—All reactions were carried out under nitrogen. All melting points and boiling points were uncorrected. Gas-liquid partition chromatographic analyses were performed on the same instruments mentioned in CHAPTER 1. The infrared, mass, and nmr spectra were also taken on the same instrments mentioned in CHAPTER 1.

Reaction of Styrene Oxide with Lithium Benzoylnickel Carbonylate.—The ether solution (50 ml) of nickel carbonyl (17.1 g, 0.1 mol) was added dropwise to the ether solution of phenyllithium prepared from bromobenzene (15.7 g, 0.1 mol) and lithium metal (1.5 g, 0.22 g-atom) at -70° to -60°, and the mixture was stirred for 2 hr at that temperature.[1b] Then styrene oxide (15 g, 0.13 mol) was added to this lithium benzoylnickel carbonylate solution and the mixture was stirred for 5 hr from -60° to room temperatures. Benzene (100 ml) was added to this solution and the mixture was stirred for 5 hr at 50-60°. After hydrolysis with 4 N hydrochloric acid (50 ml), the reaction mixture was extracted with ether, and this ether solution was separated by extraction with 5% aqueous sodium hydroxide to an acidic part and a neutral part. From the acidic part, benzoic acid (1.1 g, 9.0 % based on bromobenzene used) was obtained. The neutral part was distilled under reduced pressure after removal of the solvents to give the following fractions: (1) bp 50-100°/5 mm, 1.6 g; (2) bp 100-180°/5 mm, 9.4 g;

(3) bp 180-200°/5 mm, 6.6 g; and (4) bp 200-210°/5 mm, 2.4 g. Most of fraction (1) consisted of the recovered styrene oxide. Recrystallization of fractions (2) and (3) from petroleum ether (bp 30-60°)-benzene gave trans-α,β-diphenyl-γ-butyrolactone (2): mp 96-96.5°; white crystals; m/e 238, 193, 179, 116; $\nu_{C=O}$ 1780 cm^{-1}; nmr ($CDCl_3$) τ 6.05 (2H), 5.1-5.8 (2H), 2.75 (10H).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92; mol wt, 238. Found: C, 81.00; H, 5.90.

(3 g, 19.3 % based on styrene oxide used), and benzoin (2.5 g, 23.5 % based on bromobenzene used). Benzyl phenyl ketone (**3**, trace) was identified by glpc of fractions (2) and (3). Alkali hydrolysis (KOH-ethylene glycol) of **2** gave α,β-diphenyl-γ-hydroxybutyric acid: mp 147-148°; white crystals; m/e 256, 238, 179, 137; $\nu_{C=O}$ 1690 cm^{-1}, ν_{O-H} 3600-3300 cm^{-1}. Reduction of **2** with lithium aluminum hydride gave 2,3-diphenyl-1,4-butanediol: mp 102-102.5°; white crystals; m/e 242, 212, 194, 180, 165; ν_{O-H} 3400 cm^{-1}; nmr ($CDCl_3$) τ 7.25 (2H), 6.60 (2H), 6.10 (4H), 3.00 (10H). As fraction (4) had no peaks at the carbonyl region of the lactone, more purification was not carried out.

Reaction of Styrene Oxide with Lithium p-Toluoylnickel Carbonylate.—In place of bromobenzene, p-bromotoluene (17.1 g, 0.1 mol) was used, and an analogous reaction was carried out under the same conditions as those of above reaction. After reaction was over, the reaction mixture was extracted with hot benzene and the benzene-soluble part was ditilled under reduced pressure to give **2** (3.0 g, 17.0 % based on styrene oxide used), benzyl p-tolyl ketone **5** (0.5 g, 1.7 % based on styrene oxide used), di-p-tolyl ketone (4.4 g, 21.0 % based on p-bromotoluene used), and p,p′-bitolyl (trace). The identification and the calculation of yields of the products were carried out by glpc analysis. Instead of distillation under reduced pressure, the reaction mixture was separated by alumina column chromatography, and **5**, di-p-tolyl ketone, and p,p′-bitolyl were also obtained from a benzene or ether eluate. From the methanol eluate, a yellow solid (16.4 g) was obtained, and it showed a peak at 3600-3200 cm^{-1} but no peaks at the carbonyl region. Attempts to purify this yellow solid were unsuccessful but it was transformed to **2** (2 g) by distillation under reduced pressure above 200°.

Reaction of Styrene Oxide with Dibenzyliron Tetracarbonyl (and Sodium Benzyliron Tetracarbonylate).—To the THF solution (150 ml) of disodium iron tetracarbonylate prepared from sodium dispersion (1.4 g, 0.06 g-atom) and triiron dodecacarbonyl (5 g, 0.01 mol), styrene oxide (15.5 g, 0.13 mol) was added at -40° to -30°. After stirring for 1-2 hr at that temperature, benzyl bromide (10.3 g, 0.06 mol) was added and the reaction mixture was stirred for 2 hr from -30° to room temperature and for 4 hr under refluxing THF. The solvent was removed by distillation and then the residue was extracted with hot benzene. The benzene-soluble part was distilled under reduced pressure after removal of benzene to give the following fractions: (1) bp 80-140°/0.4 mm, 2.0 g; (2) bp 140-200°/1 mm, 6.0 g. A glpc analysis of these fractions showed that fraction (1) consisted of dibenzyl ketone (1.5 g, 23.8 % based on benzyl bromide used) and bibenzyl (0.5 g, 9.2 % based on benzyl bromide used), and fraction (2) consisted of 2 (2.8 g, 19.6 % based on styrene oxide used), α-phenylethyl phenylacetate **7** (2.2 g, 14.8 % based on styrene oxide used), and β-phenylethyl phenyl acetate **8** (trace).. An analogous reaction using benzyl iodide (13.1 g, 0.06 mol) gave the same products: dibenzyl ketone (1.4 g, 22.2 %), bibenzyl (1.9 g, 35.0 %), **2** (2.3 g, 16.1 %), **7** (0.2 g, 1.4 %), and **8** (trace).

Reaction of Styrene Oxide with Di-(p-methylbenzyl)iron Tetracarbonyl (and Sodium p-Methylbenzyliron tetracarbonylate).—In place of benzyl halide, p-methylbenzyl bromide (11.1 g, 0.06 mol) was used and an analogous reaction was carried out under the same conditions as that in the above reaction. Products were α-phenylethyl alcohol (0.8 g, 11.1 % based on styrene oxide used), p,p'-dimethylbibenzyl (0.8 g, 13.2 % based on p-methylbenzyl bromide used), di-(p-methylbenzyl) ketone (1.9 g, 27.9 % based on p-methylbenzyl bromide used), and **2** (1.0 g, 14.9 %), which were identified by glpc analysis.

Reaction of Propyrene Oxide with Dibenzyliron Tetra-Carbonyl (and Sodium Benzyliron Tetracarbonylate).—Propyrene oxide (14.0 g, 0.24 mol) and benzyl iodide (13.1 g, 0.06 mol) were used and an analogous reaction was carried out under the same conditions as mentioned above, and isopropyl phenylacetate (0.18 g, 1.7 %), n-propyl phenylacetate (0.14 g, 1.3 %), dibenzyl ketone (1.5 g, 23.8 %), and bibenzyl (2.5 g, 45.6 %) were identified by glpc analysis.

Reaction of Styrene Oxide with Nickel Carbonyl.—A mixture of styrene oxide (2.4 g, 0.02 mol) and nickel carbonyl (3.5 g, 0.02 mol) in ether (10 ml) and benzene (10 ml) was stirred for 3 hr at 10° and for 5 hr at 50°. After removal of the solvents and the remaining nickel carbonyl, the residual oil was distilled under reduced pressure to give phenylacetaldehyde (0.2 g, 8.3 %) and **2** (trace), which were identified by glpc analysis. Phenylacetaldehyde was also confirmed by its infrared (2750, 1730 cm^{-1}) and nmr (τ 0.55) spectra. No acetophenone was detected by glpc.

Reaction of Styrene Oxide with Disodium Iron Tetracarbonylate.—Styrene oxide (1.56 g, 0.013 mol) was added to the THF solution of disodium iron tetracarbonylate, prepared from triiron dodecacarbonyl (1.7 g, 0.0034 mol) and sodium dispersion (0.7 g, 0.03 g-atom), and the mixture was stirred for 9 hr under refluxing THF. After removal of the solvent, the residue was filtered and the filtrate was distilled under reduced pressure to give styrene (0.015 g, 1.1 %), α-phenylethyl alcohol (0.3 g, 18.9 %), and **2** (trace), which were identified by glpc analysis.

Reaction of Styrene Oxide with Palladium Dichloride.—Styrene oxide (4.8 g, 0.04 mol) was added to a suspension of palladium dichloride in benzene (50 ml); the mixture was stirred for 27 hr under reflux of benzene. The mixture was filtered and the filtrate was distilled under reduced pressure after removal of benzene to give the following fractions: (1) bp 60-82°/12 mm, 0.62 g; (2) bp 100-134°/ 1.5 mm, 0.89 g; (3) bp 150-210°/1 mm, 1.0 g. A glpc analysis of fractions

(1) and (2) showed that the recovered styrene oxide (0.5 g, 10.4 %) and phenylacetaldehyde (0.48 g, 10.0 %) were contained in these fractions. Recrystallization of fraction (2) from petroleum ether gave trans-2,5-diphenyl-1,4-dioxane: mp 180-180.5° (lit.[35] 174-175°); white plates; m/e 240, 149, 120, 104, 91.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; mol wt, 240. Found: C, 80.69; H, 6.93.

As fraction (3) had no peaks at the carbonyl region of the lactone, more purification was not carried out.

Reaction of Styrene Oxide with Benzoylnickel Carbonyl Iodide.—A benzene (100 ml) solution of iodobenzene (12.2 g, 0.06 mol) and nickel carbonyl (12 ml, 0.09 mol) and styrene oxide (21.6 g, 0.18 mol) was stirred for 24 hr at 40-45°, then for 5 hr at 70-75°. After treatment of the reaction mixture with triethylamine (24.4 g, 0.24 mol) for 3 hr, the mixture was hydrolyzed with 2 N hydrochloric acid and extracted with ether. From the acidic part, benzoic acid (1.2 g, 16 %) was obtained. Benzyl styryl ketone (1.7 g, 5.0 %): mp 71°; $\nu_{C=O}$ 1695 cm^{-1}; m/e 222, 131, 103;(2,4-dinitrophenylhydrazone, mp 197°, m/e 402, 103, Anal. Calcd for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.28; H, 4.53; N, 13.69.), and β-phenylethyl benzoate (trace) were obtained from the neutral part.

The same reaction was carried out in THF, and 3-hydroxy-3-phenylpropionic acid (5.6 g, 19 %): mp 116-117°; ν_{O-H} 3410, $\nu_{C=O}$ 1720 cm^{-1}; m/e 148,103, 91; Anal. Calcd for $C_9H_{10}O_3$; C, 65.05; H, 6.07. Found: C, 65.03; H, 5.99., and benzyl phenyl ketone (3.4 g, 29 %), which is identified by glpc and irs comparison with an authentic sample, were obtained.

Reaction of Cyclohexene Oxide with Benzoylnickel Carbonyl Iodide.—Cyclohexene oxide (2.9 g, 0.03 mol) reacted with benzoylnickel carbonyl iodide prepared from iodobenzene (6.1 g, 0.03 mol) and nickel carbonyl (6 ml, 0.045 mol) in benzene (80 ml) under the same conditions as the above reaction to give benzoic acid (0.7 g, 19 %), cyclohexene benzoate (1- + 3-; 1.2 g, 20 %): bp 108-112°/0.35 mm, $\nu_{C=O}$ 1738 cm^{-1}, m/e 202, 105, 81, 77, and cyclohexanone (1.2 g, 41 %) after the same treatment.

Conclusion

This thesis is concerned with the organic reactions using some organometal carbonyls.

An air-sensitive anionic complex with a carbene type ligand, lithium dimethylcarbamoylnickel carbonylate, derived from the reaction of nickel carbonyl with lithium dimethylamide has been found to be an effective nucleophilic carbamoylating reagent under mild conditions and thus some new types of organic reactions has been explored:
a synthesis of succinamide and cinnamamide derivatives from an acetyrene compound; a synthesis of carboxylic acid amide derivatives from organic halides containing double bond at α,β- or β,γ-position. This complex has been also found to react with benzophenone yielding α-phenyl-N,N-dimethylmandelamide.

Furthermore, the structure and the reactivity of this carbamoyl complex has been compared with those of the analogous type of the anionic complexes, lithium acylnickel carbonylate, potassium t-butoxycarbonylnickel carbonylate.

The formation of urea derivatives from the reaction of nickel carbonyl with alkylmonochloroamines (or -amide) has been also described.

The reaction of organometal carbonyls with olefin oxides has been investigated and a new type of reaction of olefin oxide has been found: the formation of α,β-diphenyl-γ-butyrolactone or benzyl styryl ketone from two moles of styrene oxide by the action of organo transition metal complexes. Furthermore, olefin oxides have been also found to undergo several new types of reactions classfied as follows in the presence of organometal carbonyls: isomerization to aldehyde or ketone, dimerization accompanying with dehydrogenation or dehydration, insertion into carbon-metal bond, and carboxylation accompanying with epoxy ring cleavage.

The present studies have shown that an anionic carbamoylnickel complex can be used as an effective nucleophilic carbamoylating reagent in organic synthesis and a possibility of the utilization of olefin oxide which has been readily supplied in industrial scale has been opened.

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