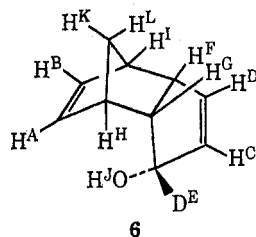cm^{-1}; nmr spectrum (CCl$_4$) an unsymmetrical doublet of doublets centered at -6.12 (1.1 H, H^A ^{or} ^{B}, J_{AB} = 5.7, $J_{AH or BI}$ = 2.2 cps), an unsymmetrical doublet of doublets centered at

6

-5.68 (H^B ^{or} ^{A}, J_{AB} = 5.7, $J_{BI or AH}$ = 3.0 cps) overlapping with a singlet at -5.51 (H^C, H^D) (2.8 H total), an unsymmetrical doublet of doublets centered at -3.24 (1.0 H, H^F, J_{FG} = 7.9, J_{FI} = 4.0 cps), a multiplet at -3.1 to -2.5 with a maximum at -2.91 (3.1 H, H^G, H^H, H^I), a singlet at -2.15 (0.9 H, H^J), and two overlapping unsymmetrical doublets of triplets centered at -1.55 (H^K ^{or} ^{L}, J_{KL} = 8.0, $J_{HK,IK or HL,IL}$ = 1.7 cps) and -1.36 ppm (H^L ^{or} ^{K}, J_{KL} = 8.1, $J_{HL,IL or HK,IK}$ = 1.4 cps) (2.1 H total), no absorption detected in the -5.0 to -4.0 ppm region for H^E; mass spectrum (200°) m/e 66 (100.0, base peak, C$_5$H$_6$$^+$), 83 (56.1, C$_5H_5DO^+$), 91 (0.72, C$_7H_7$$^+$), 92 (0.68, C$_7H_8D^+$), 117 (1.6, M$^+$ $-$ CH$_2$DO), 130 (1.3, M$^+$ $-$ HDO), 131 (2.5, M$^+$ $-$ H$_2$O), 149 (very weak, M$^+$) 150 (0.22, M$^+$ + H).

Anal. Calcd for C$_{10}$H$_{11}$DO: C, 80.50; H (D), 8.78. Found: C, 80.5; H (D), 8.31.

Stability of Dienol 2 to Lithium Aluminum Hydride.—The dienol 2 (50 mg) was added to a slurry of lithium aluminum hydride (100 mg) in 5 ml of dry ether and allowed to stand at *ca.* 25° for 18 hr. After hydrolysis with water and dilute hydrochloric acid, separation of the aqueous layer, washing with water, and concentration of the ether solution, gc analysis showed only starting material.

Chromic Acid Oxidation of Dihydro Alcohol 4.—To a cold (10–20°), stirred solution of 0.5 g (3.4 mmol) of alcohol 4 in 10 ml of redistilled acetone the Jones reagent[9] (2.7 *M* CrO$_3$ in H$_2$SO$_4$–H$_2$O) was added dropwise until an orange-brown coloration persisted. The acetone solution was then decanted from the chromium salts which were triturated with fresh acetone. The combined acetone solutions were concentrated under vacuum and the residue was taken up in 50 ml of ether. The organic layer was washed with two 20-ml portions of water and dried (MgSO$_4$). Evaporation of the ether and sublimation of the residue afforded 0.3 g (60%) of a waxy, white solid, mp 89–93°. Gc analysis of this material showed one compound with a retention time corresponding to that of the dihydro ketone 3. The infrared and nmr spectra of this material were identical with those of the authentic material.

Lithium Tri-*t*-butoxyaluminum Hydride Reduction of Dihydro Ketone 3.—A slurry of lithium tri-*t*-butoxyaluminum hydride was prepared by adding 2.3 g (31 mmol) of *t*-butyl alcohol to a solution of 0.38 g (10 mmol) of lithium aluminum hydride in 70 ml of dry ether. This mixture was stirred for 0.5 hr and 0.55 g (3.8 mmol) of ketone 3 in 5 ml of ether was added. The reaction mixture was stirred at *ca.* 25° for 5 hr and hydrolyzed by the addition of 10 ml of water, followed by 20 ml of 5 *N* hydrochloric acid. The ether layer was separated, washed with water, and dried (MgSO$_4$). Evaporation of the solvent and sublimation of the residue at 100° (0.5 mm) afforded 0.4 g (73%) of a white solid, mp 125–134°, mmp 128–134°, whose infrared spectrum was identical with that of the dihydro alcohol 4 described above. Analysis by gc showed only one product having a retention time identical with that of 4.

Reaction of Cupric Alkoxide and Carbon Monoxide

TAKEO SAEGUSA, TETSUO TSUDA, AND KATSUHIKO ISAYAMA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

The reaction of cupric alkoxide with carbon monoxide was investigated. Cupric dimethoxide [Cu(OCH$_3$)$_2$], cupric dialkoxide of allyl alcohol [Cu(OC$_3$H$_5$)$_2$], cupric chloride methoxide [Cu(OCH$_3$)Cl], and cupric acetylacetonate methoxide [Cu(acac)(OCH$_3$)] were easily carbonylated to produce dialkyl carbonates. Carbonylation of cupric alkoxide in the presence of a secondary amine gave the corresponding carbamate. In the reaction, copper(II) was reduced to copper(I) and the extent of reduction was in good agreement with the yields of carbonylated products. The suggested reaction path involves the intermediate formation of carbomethoxycupric species by the insertion of carbon monoxide into the copper–oxygen bond of cupric alkoxide.

In our previous study,[1] the carbonylation of a ternary mixture of cupric acetate, methanol, and piperidine produced the corresponding carbamate. This finding suggested an intermediate carbomethoxycupric species which was formulated as being a product of the insertion of carbon monoxide into the copper–oxygen bond of cupric methoxide. In the present study, the reaction of cupric alkoxide with carbon monoxide was examined.

Studies of the carbonylation have hitherto been focused upon the insertion of carbon monoxide between carbon and metal of the groups VI to VIII. The carbonyl insertion into metal–oxygen and metal–nitrogen bonds has been little studied.[2] The present study opens up a new field of carbonylation which involves copper(II) as the metal component and alkoxyl group as the ligand component.

Carbonate Formation from Cupric Methoxide and Carbon Monoxide.—Cupric dimethoxide was readily carbonylated to produce dimethyl carbonate in high yields (Table I). Pyridine was a preferable reaction solvent, in which the carbonylation proceeded even at room temperature. Reactions in other solvents required higher reaction temperatures. Other cupric methoxide compounds such as Cu(OCH$_3$)Cl and Cu(acac)(OCH$_3$) were also effectively carbonylated to produce dimethyl carbonate. In the carbonylation of cupric dialkoxide of allyl alcohol, the olefinic group was not involved in the reaction and the product was diallyl carbonate. This finding provides an interesting contrast to the carbonylation of allyl alcohol in the presence of cobalt and rhodium carbonyl in which the olefinic

(1) T. Saegusa, T. Tsuda, K. Isayama, and K. Nishijima, *Tetrahedron Lett.*, 4123 (1967).

(2) J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition-Metal Complexes," Elsevier, Amsterdam, 1968, p 135.

TABLE I

CARBONYLATION OF CUPRIC METHOXIDES

Cupric methoxide	Amount, mmol	CO, kg/cm²	Solvent	Amount, mmol	Temp, °C	Time, hr	Yield of (CH₃O)₂CO, %
Cu(OCH₃)₂	7.9	80	Py[a]	79	0	20	16
	8.6	80	Py	86	Room temp	48	62
	3.9	75	Py	39	35	5	78
	7.5	10	Py	150	35	20	78
	8.2	80	Py	82	70	20	84
	4.9	80	Py	49	110	23	28
	6.4	60	DMSO	64	70	20	44
	5.5	80	DMSO	110	110	39	82
	6.0	60	NEt₃	60	70	20	6
	5.8	80	NEt₃	116	110	39	48
	6.8	60	THF	68	70	20	20
	5.7	80	THF	114	110	39	78
Cu(OCH₃)Cl	7.9	90	THF	79	115	19	89
Cu(acac)(OCH₃)	7.9	80	Py	79	100	13	51
Cu(OC₃H₅)₂[b]	7.9	85	Py	79	70	29	44

[a] Py = pyridine. [b] Cupric dialkoxide of allyl alcohol.

TABLE II

CARBONYLATION OF CUPRIC DIMETHOXIDE IN THE PRESENCE OF PIPERIDINE[a]

Cu(OCH₃)₂, mmol	⬡NH, mmol	Pyridine (solvent), mmol	Temp, °C	Time, hr	Yield of ⬡NCO₂CH₃[b], %
4.3	4.3	43	0	20	54
13.6	13.6	136	Room temp	43	46
6.4	6.4	64	60	20	96
4.6	4.6	46	110	23	72

[a] Carbonylation was carried out under a CO pressure of 80 kg/cm². [b] Based on Cu(OCH₃)₂.

group is also involved to form a lactone.[3] Cupric acetylacetonate was not carbonylated under the conditions of the present study. No reaction was observed in the attempted carbonylation of the alkoxides of cobalt(II) and iron(III) in pyridine at 120–150° under carbon monoxide pressure of 80 kg/cm². Thus, the carbonylation of metal alkoxide appears to be restricted to cupric alkoxide.

Carbamate Formation from Cupric Methoxide, Secondary Amine and Carbon Monoxide.—Interestingly enough, the reaction of cupric dimethoxide and carbon monoxide carried out in the presence of secondary amine gave the corresponding carbamate (eq 1).

$$Cu(OCH_3)_2 + R_2NH \xrightarrow{CO} R_2\underset{\underset{O}{\|}}{N}COCH_3 \quad (1)$$
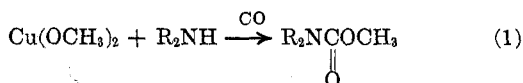
The results of the carbonylation of cupric dimethoxide in the presence of piperidine are given in Table II. Similarly, cupric chloride methoxide was also carbonylated to produce carbamate.

Reduction of Cu^II to Cu^I in Carbonylation.—Examination of the change of valence of copper in carbonylation is essential for the reaction stoichiometry and is informative to the reaction mechanism. Cu^II and Cu^I were analyzed separately by iodometry and thiocyanate method (see Experimental Section). The extent of reduction of Cu^II to Cu^I in the carbonylations of Cu(OCH₃)₂ and Cu(OCH₃)Cl with or without diethylamine is shown in Table III. The distillation residues of the mixtures of these reactions were all soluble in dilute hydrochloric acid. This observation indicates the absence of metallic copper in the reaction

(3) J. Falbe, *Chem. Ber.*, **98**, 886 (1965).

TABLE III

CARBONYLATION OF CUPRIC METHOXIDES.
ANALYSIS OF VALENCE OF COPPER

Cupric methoxide	Yield, % (CH₃O)₂CO	Et₂NCO₂CH₃	Cu^{I}, [a] %
Carbonylation in the Absence of Piperidine			
Cu(OCH₃)₂[b]	51		54
Cu(OCH₃)Cl[c]	89		83
Carbonylation in the Presence of Diethylamine			
Cu(OCH₃)₂[d]	7	54	58
Cu(OCH₃)Cl[e]	3	73	79

[a] The yield of Cu^I was calculated based on the initial amount of cupric methoxide. [b] Carbonylation in pyridine at 35° for 15 hr under 90 kg/cm² of CO. [c] The reaction conditions are given in Table I. Carbonylation in THF at 115° for 19 hr under 90 kg/cm² of CO. [d] A mixture of Cu(OCH₃)₂ (8.3 mmol), Et₂NH (8.3 mmol), and pyridine (83 mmol), was subjected to carbonylation with CO (90 kg/cm²) at 35° for 15 hr. [e] A mixture of Cu(OCH₃)Cl (11.2 mmol), Et₂NH (11.2 mmol), and tetrahydrofuran (112 mmol) was subjected to carbonylation with CO (90 kg/cm²) at 115° for 19 hr.
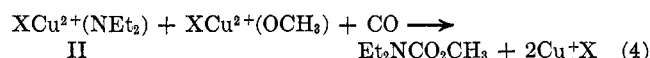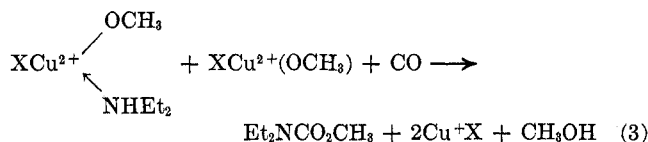
system. In the absence of diethylamine, the per cent reduction of Cu^II to Cu^I was in good agreement with the yield of dimethyl carbonate. This finding substantiates the over-all stoichiometry in eq 2.

$$2XCu^{2+}(OCH_3) + CO \longrightarrow (CH_3O)_2CO + 2Cu^+X \quad (2)$$
$$(X = -OCH_3 \text{ and } Cl)$$
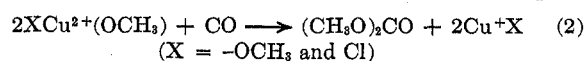
Cuprous methoxide is reasonably assumed to be the reduced species of cupric dimethoxide. The absence of metallic copper in the reaction mixture shows that cuprous methoxide is not active for carbonylation in the presence of pyridine at 35°.

The carbonylation in the presence of diethylamine produced methyl N,N-diethylcarbamate as the major

product and dimethyl carbonate as the minor product. In this case, the per cent reduction of Cu^{II} approximately agreed with the combined yield of the two carbonylated products. The production of carbamate may be explained by the carbonylation of cupric methoxide together with the coordinated amine ligand (eq 3) or with the aminocopper compounds (eq 4). The

$$XCu^{2+}\begin{smallmatrix}OCH_3\\ \\ NHEt_2\end{smallmatrix} + XCu^{2+}(OCH_3) + CO \longrightarrow$$

$$Et_2NCO_2CH_3 + 2Cu^+X + CH_3OH \quad (3)$$

$$XCu^{2+}(NEt_2) + XCu^{2+}(OCH_3) + CO \longrightarrow$$
$$\quad\quad II \quad\quad\quad\quad\quad Et_2NCO_2CH_3 + 2Cu^+X \quad (4)$$

diethylaminocopper compound (II) is formed by the substitution of methoxyl group by diethylamino group as follows. Methanol was actually formed in an

$$XCu^{2+}(OCH_3) + Et_2NH \longrightarrow XCu^{2+}(NEt_2) + CH_3OH \quad (5)$$
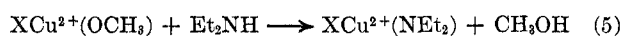
amount corresponding to the yield of carbamate. The stoichiometry of the carbonylation in the presence of dimethylamine is accounted for by the combination of two equations, eq 2 and 3 or eq 2 and 4.

Reaction Mechanism.—The results are explained by the insertion of carbon monoxide into the copper-oxygen bond of cupric methoxide to generate carbomethoxycupric species which then undergoes coupling with an adjacent methoxyl group. The reaction will proceed in aggregate form. The aggregation has been


$$2 \; {>}Cu^+ \; + \; CH_3OCOCH_3 \quad (6)$$
$$\quad\quad\quad\quad\quad\quad\quad\; \underset{O}{\|}$$
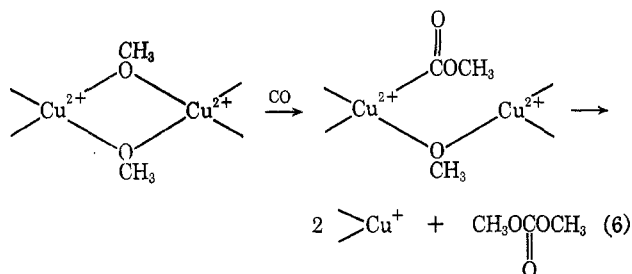
demonstrated in the three species of cupric methoxide of the present study.[4–6] $Cu(OCH_3)_2$ and $Cu(OCH_3)Cl$ are known to be highly polymeric,[4] and $Cu(OCH_3)Cl$ is in dimeric form in pyridine.[5] $Cu(acac)(OCH_3)$ also has a dimeric structure with the methoxyl oxygen bridge and an outer bidentate ligand of acetylacetonate.[6] Therefore, the coupling between the carbomethoxy and methoxyl ligands producing the cuprous species is quite possible and is illustrated by eq 6. The reaction pattern of eq 6 satisfies the stoichiometry of eq 2. The coupling of two carbomethoxyl groups to produce dimethyl oxalate was not observed.

The carbamate formation in the carbonylation of a mixture of cupric methoxide and secondary amine is also explained by assuming an unstable intermediate of carbomethoxycupric species. Coupling of dicarbomethoxyl group with amide group or with the coordinated amine ligand leads to carbamate. This reaction resembles the reactions of carbomethoxymercuric compounds with secondary amine to produce carbamate (eq 7).[7–9]

(4) C. H. Brubaker, Jr., and M. Wicholas, *J. Inorg. Nucl. Chem.*, **27**, 59 (1965).

(5) H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).

(6) J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, **4**, 1657 (1965).

$$AcOHgCO_2CH_3 + \bigcirc NH \longrightarrow$$
$$\bigcirc NCO_2CH_3 + Hg + AcOH \quad (7)$$
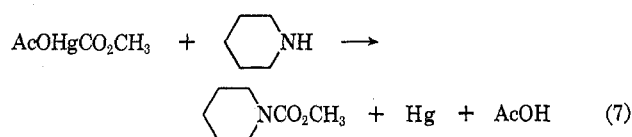
The $Cu(OCH_3)_2$–CO and $Cu(acac)(OCH_3)$–CO systems have been used as initiators of free-radical polymerization.[10] The active species are the reduced cuprous compounds of $Cu(OCH_3)$ and $Cu(acac)$, which undergo homolytic fission to produce methoxyl and acetylacetonyl radicals, respectively.

Experimental Section

Reagents.—$Cu(OCH_3)_2$ and $Cu(OCH_3)Cl$ were prepared from $CuCl_2$ and $LiOCH_3$,[4] and $Cu(acac)OCH_3$ was synthesized from $Cu(acac)_2$ and methanol in the presence of KOH.[6] $Cu(OCH_2-CH=CH_2)_2$ was prepared from $CH_2=CHCH_2OLi$ and $CuCl_2$ according to the procedure of the synthesis of $Cu(OCH_3)_2$. $Co(OCH_3)_2$ and $Fe(OCH_3)_3$ were prepared from the corresponding metallic chlorides and $LiOCH_3$.[11] Carbon monoxide was a commercial reagent. Pyridine was dried by refluxing over sodium hydroxide and calcium hydride, and fractionally distilled. Tetrahydrofuran was distilled twice from sodium wire. Dimethyl sulfoxide was distilled under reduced pressure and stored over molecular sieves. Triethylamine, diethylamine and piperidine were distilled over sodium hydroxide.

General Procedure of Carbonylation.—Cupric alkoxide, the amine if used, and the solvent were placed in a 50-ml stainless steel tube under nitrogen atmosphere, to which carbon monoxide gas was added under high pressure at room temperature. The tube was closed and was heated at a desired temperature. After reaction, the tube was cooled to $-78°$ and carbon monoxide was released. The reaction mixture was distilled at room temperature up to 200° under 1 mm of Hg. The distillate was collected and analyzed by glpc. Carbonates and carbamates were identified by comparison of ir and nmr spectra and glpc retention times with those of authentic samples. The authentic sample of dimethyl carbonate was a commercial reagent, and that of diallyl carbonate was prepared from phosgen and allyl alcohol in the presence of triethylamine. Authentic carbamates were synthesized from methyl chloroformate and the corresponding amine.

The Analysis of Valence of Copper.—The residue of reduced pressure distillation of the reaction mixture was analyzed for copper. Cu^{II} was determined by the ordinary iodometry.[12] Thus, acetic acid and potassium iodide was added to the aqueous suspension of the sample, and the liberated iodine was titrated with a standard 0.1 N $Na_2S_2O_3$ solution to the starch end point. The total copper was determined by the thiocyanate method[13] for Cu^I after Cu^{II} had been reduced to Cu^I by Na_2SO_3. Thus, a part of the distillation residue (about 0.1 g) was dissolved in a mixture of 20 ml of 5% Na_2SO_3 aqueous solution and 40 ml of 0.1 N HCl aqueous solution. Then, 1% KSCN aqueous solution was added slowly with magnetic stirring until no more precipitate was formed. The precipitate of CuSCN thus obtained was collected by filtration, dissolved in aqueous 6 N HCl, and titrated under nitrogen atmosphere with a standard 0.1 N KIO_3 aqueous solution to the chloroform end point (red to yellow). These two analytical procedures were verified by reference experiments using a definite amount of cupric chloride.

(7) W. Schoeller, W. Schrauth, and W. Essers, *Ber.*, **46**, 2864 (1913).

(8) F. E. Paulik and R. E. Dessy, *Chem. Ind.* (*London*), 1650 (1962).

(9) U. Schöllkopf and F. Gerhart, *Angew. Chem.*, **78**, 209 (1966).

(10) T. Saegusa, T. Tsuda, and K. Isayama, *J. Macromol. Sci. Chem.*, in press.

(11) R. W. Adams, E. Bishop, R. L. Martin, and G. Winter, *Aust. J. Chem.*, **19**, 207 (1966).

(12) For example, B. Park, *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931).

(13) F. P. Treadwell and W. T. Holl, "Analytical Chemistry," Vol. 2, Wiley, New York, N. Y., 1935, pp 617, 667.