hexanes); 300-MHz ¹H NMR (CDCl₃) δ 9.78 (s, 1 H), 5.43 (m, 1 H), 5.01 (m, 3 H), 2.42 (m, 2 H), 1.0–2.15 (m, 10 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 0.85 (2 doublets, 3 H); IR (neat) 3040, 2921, 2720, 1732, 1455, 1385, 927 cm⁻¹; mass spectrum (EI) 222 (M⁺, 0.7), 109 (13.5), 69 (46), 55 (20), 41 (34); exact mass calculated for C₁₅H₂₆O 222.1983, found 222.1987.

(±)-6,6-Diphenyl-3-hydroxy-1,5-hexadiene (28): R_f 0.46 (30% ether-hexanes); 300-MHz ¹H NMR (CDCl₃) δ 7.35 (m, 10 H), 6.25 (t, J = 7 Hz, 1 H), 5.83 (m, 1 H), 5.40 (d, J = 17 Hz, 1 H), 5.09 (d, J = 7 Hz, 1 H), 4.18 (m, 1 H), 2.39 (t, J = 6 Hz, 2 H), 2.10 (s, br, 1 H); 75-MHz ¹³C NMR (CDCl₃) δ 144.0, 143.9, 142.4, 140.4, 139.8, 129.8, 128.2, 128.0, 127.2, 127.0, 124.6, 114.8, 72.7, 37.2; IR (neat) 3370, 2920, 2808, 758, 696 cm⁻¹; mass spectrum (neat) no M⁺ observed, 194 (17.7), 193 (96.8), 178 (17.6), 115 (100.0); exact mass calculated for C₁₈H₁₈O₁ 250.1358, found 250.1379.

4,4-Diphenyl-5-hexenal (36): $R_f 0.34$ (20% ether-hexanes); 300-MHz ¹H NMR (CDCl₃) δ 9.61 (s, 1 H), 7.32 (m, 10 H), 6.38 (dd, J = 17, 11 Hz, 1 H), 5.23 (dd, J = 11, 1 Hz, 1 H), 4.85 (d, J = 17, 1 Hz, 1 H), 2.60 (dd, J = 8.4, 6 Hz, 2 H), 2.30 (m, 2 H); 75-MHz ¹³C NMR (CDCl₃) δ 201.6, 145.9, 143.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.7, 126.2, 114.4, 52.7, 40.1, 30.0; IR (neat) 1715, 695 cm⁻¹; mass spectrum (EI) 250 (M⁺, 8.5), 207 (17.0), 206 (68.5), 193 (88.2), 180 (15.3), 178 (37.4), 115 (100); exact mass calculated for $C_{18}H_{18}O$ 250.1360, found 250.1358.

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Generation and Reactions of Novel Copper Carbenoids through a Stoichiometric Reaction of Copper Metal with *gem*-Dichlorides in Dimethyl Sulfoxide

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Copper metal and such gem-dichlorides as α,α -dichloro acid esters, 1a–e, diphenyldichloromethane, 2, benzal chloride, 3, 1,1-dichloroacetone, 4, 1,1-dichloro-2-butene, 5, and carbon tetrachloride, 6, were found to undergo a stoichiometric reaction in dimethyl sulfoxide (DMSO) under a mild condition to produce copper carbenoid intermediates via α,α -elimination of dichlorides along with the formation of CuCl₂(DMSO)₂. Thus, 1 and 2 gave substituted olefins via a carbenoid coupling reaction. From 5 and 6, reaction products via the oxygen abstraction from DMSO were produced together with dimethyl sulfice; 3 and 4 were found to cause both types of reactions. The carbenoid intermediates formed from 1 did not cause cyclopropanation reaction with cyclohexene in contrast to the conventional carbalkoxy carbenoid generated by a decomposition reaction of ethyl diazoacetate. Also the carbenoid coupling reaction was completely inhibited by the addition of triphenylphosphine, which was contrastive to the formation of phosphonium ylide with a carbenoid from ethyl diazoacetate.

Introduction

Copper metal and its salts have been known to promote decomposition reactions of organic halides to generate copper carbenoid or radical intermediates, and these reactions have been utilized for versatile synthetic methods involving a carbon-carbon bond formation.¹ We report here unusual and novel stoichiometric reactions between copper metal and a number of organic halides, in particular gem-dichlorides, to form copper carbenoid intermediates under a mild condition. Also we focus on the unique reactivity of carbalkoxy carbenoids generated from α, α -dichloro acid esters in the present system by comparing with conventional ones produced through photodecomposition or thermal decomposition of diazoacetic acid esters.

Results and Discussion

Copper is traditionally known as a coinage metal because of its resistance to corrosion under ordinary atmospheric conditions. However, we found recently² that copper metal reacted in dimethyl sulfoxide (DMSO) with some organic halides under an extremely mild condition. For example, copper powder (250 or 40 mesh) was suspended in DMSO

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Cu/hal-

Table I. Reactions of Copper Metal with gem-Dichlorides in DMSO

	halide	ide ratio,					
run	(mmol)	mol/mol	DMSO, mL	temp, °C	time, h	conv, %	products and yields, ^a %
1	1a (40)	1.0	20	25	5	64	H ₃ COOCHC=CHCOOCH ₃ , 73 (70)
2	la (40)	1.0	20	50	3	68	$H_3COOCHC = CHCOOCH_3, 77 (82)$
3	1a (40)	1.0	20	80	0.5	68	$H_3COOCHC = CHCOOCH_3, 64 (77)$
4	1a (40)	3.0	20	25	5	100	$H_3COOCHC = CHCOOCH_3, 81 (52)$
5	1b (40)	1.0	20	25	5	59	$C_2H_5OOCHC = CHCOOC_2H_5, 92 (75)$
6 ^b	1 b (40)	1.0	20	25	5	64	$C_2H_5OOCHC = CHCOOC_2H_5, 88 (76)$
7°	1b (40)	1.0	20	25	5	61	$C_2H_5OOCHC = CHCOOC_2H_5, 93 (78)$
8	1b (40)	3.0	20	25	5	100	$C_2H_5OOCHC = CHCOOC_2H_5, 98 (67)$
9 ^d	1 b (20)	1.0	10	25	5	37	$C_2H_5OOCHC = CHCOOC_2H_5, 81 (77)$
10	1c (40)	1.0	20	50	5	70	$(t-C_4H_9)OOCHC = CHCOO(t-C_4H_9), 58 (90)$
11	1c (40)	3.0	20	50	5	100	$(t-C_4H_9)OOCHC = CHCOO(t-C_4H_9), 77$ (86)
12	1d (40)	1.0	20	25	1	73	$(C_6H_5)OOCHC = CHCOO(C_6H_5), 67 (76)$
13	1d (40)	3.0	20	25	1	100	$(C_{6}H_{5})OOCHC = CHCOO(C_{6}H_{5}), 65 (74)$
14	1e (20)	1.0	10	25	5	96	$C_2H_5OOCCH_3C=CCH_3COOC_2H_5, 30(0)$
15	1e (20)	3.0	10	25	5	100	$C_2H_5OOCCH_3C=CCH_3COOC_2H_5, 56$ (0)
16	1f (8.1)	2.2	3	65	5	100	CH ₃ OOCHC=CHCOOCH ₃ , 46 (54)
17	2 (10)	1.0	20	24	1.5	26	$(C_6H_5)_2C = C(C_6H_5)_2, 96$
18	2(10)	3.0	20	24	1.5	35	$(C_{e}H_{s})_{2}C = C(C_{e}H_{5})_{2}, 97$
19	3 (20)	1.0	10	25	20	87	$(C_{e}H_{s})HC = CH(C_{e}H_{s}), 36 (100); C_{e}H_{5}CHO, 5; CH_{3}SCH_{3}, 2$
20	3 (20)	1.0	10	50	2	83	$(C_{6}H_{5})HC = CH(C_{6}H_{5}), 41 (100); C_{6}H_{5}CHO, 12; CH_{3}SCH_{3}, 8$
21	3 (20)	3.0	10	50	2	100	$(C_{6}H_{5})HC = CH(C_{6}H_{5}), 41 (100); C_{6}H_{5}CHO, 9; CH_{3}SCH_{3}, 7$
22e	4 (20)	1.0	20	25	5	96	CH ₃ COCH=CHCOCH ₃ , 3 (100); CH ₃ SCH ₃ , 3
23e	4 (20)	1.0	20	50	2	97	CH ₂ COCH=CHCOCH ₂ , 5 (100); CH ₂ SCH ₃ , 5
24 ^e	4 (20)	3.0	20	50	2	97	CH ₃ COCH=CHCOCH ₃ , 20 (100); CH ₃ SCH ₃ , 4
25	5 (20)	1.0	20	25	0.5	86	CH ₂ CH=CHCHO, 99; CH ₂ SCH ₃ , 86
26	5 (20)	3.0	20	25	0.5	97	$CH_{3}CH = CHCHO, 98; CH_{3}SCH_{3}, 73$
27	6 (2.5)	1.0	5	15	50	48	CH ₃ SCH ₃ , 86
28	6 (2.5)	3.0	5	15	50	100	CH ₃ SCH ₃ , 97

^a Yield based on reacted halides. % of E isomer in parentheses. ^b40 mesh copper metal was used. ^cCopper metal was washed with 20% H₂SO₄. ^dCyclohexene (10 mL) was present in the reaction. ^eCH₂ClCOCH₃ was also obtained (yield 15% in run 22, 20% in run 23, and 16% in run 24).

at room temperature, and one of such gem-dichlorides as α, α -dichloro acid esters, **1a**-e, diphenyldichloromethane, **2**, benzal chloride, **3**, 1,1-dichloroacetone, **4**, 1,1-dichloro-2-butene, **5**, or carbon tetrachloride, **6**,² was added. The reaction took place either immediately or gradually, and copper metal was found to dissolve into a solution to give a light-green or dark-green almost homogeneous mixture. No rigorous purification of copper and other reagents was required for this reaction to occur.

		X ₂ CRR′	
	х	Ř	R′
la	Cl	н	CO_2CH_3
1b	Cl	н	$CO_2C_2H_5$
1c	Cl	Н	$CO_2 - t - C_4H_9$
1d	Cl	н	$CO_2C_6H_5$
1 e	Cl	CH_3	$CO_2C_2H_5$
1 f	Br	н	CO_2CH_3
2	Cl	C_6H_5	$C_6 H_5$
3	Cl	H	C_6H_5
4	Cl	н	COCH ₃
5	Cl	н	CH=CHCH ₃
6	Cl	Cl	Cl

On the other hand, such gem-dichlorides as dichloromethane, 1,1-dichloroethane, 2,2-dichloropropane, 1,1dichloroethyl methyl ether, (dichloromethyl)trimethylsilane and dichloronorcarane failed to react with copper metal at an ambient condition. Dichloromethyl methyl ether was found to react with DMSO even in the absence of copper at room temperature.

No other metals than copper like titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zinc, silver, gold, and platinum caused the reaction with these *gem*dichlorides under an ambient condition.

The reaction solution of gem-dichlorides, 1–6, with copper was then evacuated to separate into a volatile part and a residual solid. In the latter part, $CuCl_2(DMSO)_2$ was detected as a major product by means of an IR spectro-



Figure 1. Time-conversion profiles on the reaction of 1a with copper metal at various reaction temperatures and at various 1a/copper ratios. At 25 $(0, \bullet)$, 50 (Δ, \blacktriangle) and 80 (\Box, \blacksquare) °C. Copper metal; 120 mmol $(0, \Delta, \Box)$ or 40 mmol $(\bullet, \blacktriangle, \blacksquare)$ 1a; 40 mmol, DMSO; 20 mL.

scopic analysis. The volatile mixture was subjected to GLC-MS and ¹H NMR analyses. Identified reaction products between copper metal and a series of *gem*-dichlorides were listed in Table I.

1. Reactions with α,α -Dichloro Acid Esters. A series of dichloroacetic acid esters having methyl, 1a, ethyl, 1b, *tert*-butyl, 1c, and phenyl, 1d, groups were allowed to react with copper metal in DMSO to examine the effect of ester substituents. Also ethyl α,α -dichloropropionate, 1e, was synthesized and used for the reaction to observe the effect of substituents on the α -position. Figure 1 shows the time-conversion profile of the reaction between 1a and copper metal at various reaction temperatures and at various 1a/copper ratios. 1a was found to react quantitatively at examined temperatures (25–80 °C) when a three times excess molar amount of copper metal was charged, while the conversion of 1a was observed to level off at around 70% in the equimolar reaction between copper metal and 1a.

Results of the reaction between a series of α . α -dichloro acid esters and copper metal are summarized in runs 1–15 of Table I. The reaction proceeded smoothly to complete conversion when an excess molar amount of copper was used. It was observed that 1d reacted most rapidly, while 1a and 1b showed a similar reactivity against copper metal. 1c was found to react at 50 °C, while very sluggish at 25 °C. Major reaction products from 1a-d were always fumaric and maleic acid esters. The formation of fumarate and maleate esters can be best accounted for by the generation and the subsequent coupling reaction of a carbalkoxy carbenoid as an intermediate. The yield of fumarate and maleate esters based on the conversion of starting dichloroacetic acid esters appeared to be affected by the type of ester substituents and was almost quantitative in case of 1b. The copper/halide ratio did not influence significantly on the product yield based on the amount of reacted dichloroacetic acid esters.

Fumarate esters, i.e. E isomers, were produced always predominantly among a series of dichloroacetic acid esters. The bulkiness of ester substituents was observed to scarcely influence on the E/Z ratio of products except for the case of 1d, where the ratio of E isomer was as high as 90% even though the position of a substituent was relatively remote from a reaction site of the α -position of carbonyl groups to cause the α,α -elimination of dichlorides. The E/Z isomer ratio of products was also influenced by the copper/halide ratio in the reaction and a slightly higher E selectivity was observed in equimolar reactions.

An α, α -dichloro acid ester possessing a methyl group at the α -position of the carbonyl group, namely 1e, was also subjected to react with copper metal to give α, α' -dimethyl fumaric and maleic acid esters. In contrast to a series of dichloroacetic acid esters, the product possessed exclusively the Z form. Thus, the type of substituents at α -position of carbonyl group (H or CH₃), where the elimination of dichlorides took place, affected remarkably the E/Z selectivity in the reaction. The product yield based on the reacted 1e was lower than those in dichloroacetic acid esters.

Methyl dibromoacetate, 1f, was also used to react with copper metal in DMSO to examine the effect of the type of halides. The formation of a carbalkoxy carbenoid was previously reported on the reaction of dibromoacetate in the presence of copper metal at an elevated temperature in benzene^{1f} to cause a cyclopropanation with cyclohexene. In the present system in DMSO, fumarate and maleate esters were obtained in a lower yield compared to the corresponding dichloro counterpart, 1a. It should be noted also that no cyclopropanation was observed in DMSO even in the presence of cyclohexene.

2. Reactions with Other gem-Dichlorides. Copper metal was found to undergo a stoichiometric reaction with a number of other gem-dichlorides in DMSO under a mild condition. Results are given in runs 17-28 of Table I. 2 was previously reported to decompose in the presence of copper metal at reflux temperature in benzene to give tetraphenylethylene, and a diphenyl carbenoid was postulated as an intermediate.^{1d} In the present reaction in DMSO, an instantaneous exothermic reaction took place to give tetraphenylethylene. The conversion of 2 remained lower than 40% even when an excess molar amount of copper was used. On the other hand, the reacted 2 was selectively converted to tetraphenylethylene. When tetraphenylethylene was added in advance to start the reaction, the conversion of 2 was completely inhibited. This indicates that tetraphenylethylene formed in the reaction mixture prevents the further progress of the reaction between 2 and copper metal.

The reaction of 3 with copper metal was found to give stilbene as a major reaction product. The produced stilbene was exclusively the E isomer. Benzaldehyde and dimethyl sulfide were also observed as minor products with almost equal amount each other. The product ratio between stilbene and benzaldehyde was not affected either by reaction temperatures (25 or 50 °C) or by reactant ratios. Stilbene was thought to be produced through the coupling reaction of a benzal carbenoid as an intermediate while benzaldehyde and dimethyl sulfide were thought to be formed through the oxygen abstraction reaction from DMSO by the benzal carbenoid.

With 4, 1,2-diacetylethylene was observed but in a modest yield. The produced 1,2-diacetylethylene was exclusively the *E* isomer. Dimethyl sulfide was also detected, but α -keto aldehyde, which might be produced by the oxygen abstraction from DMSO with an acetonyl carbenoid intermediate, was not observed. Alternatively, monochloroacetone was observed in a comparable amount. Although an acetonyl carbenoid is most probably involved in this reaction, an alternative stepwise mechanism may not be excluded by considering the formation of monochloroacetone with a notable yield.

In contrast to these halides, 5 failed to give any olefinic products in the reaction with copper metal in DMSO. Instead, crotonaldehyde and dimethyl sulfide were obtained in a high yield based on the reacted 5. The molar amount of both products was nearly equal each other. The formation of these two products was best accounted for by the oxygen abstraction from DMSO with a carbenoid intermediate formed through α,α -elimination of dichlorides from 5. The reaction of 5 with cyclohexene in the presence of a copper isonitrile complex was studied previously, and cyclopropane derivatives were observed in high yields.³ On the contrary, no cyclopropane derivative was observed in the reaction of 5 with copper metal in DMSO even in the presence of cyclohexene.

In the reaction of copper metal with 6 in DMSO, dimethyl sulfide was detected as an only isolatable product. An expected oxidation product of dichlorocarbene by DMSO, phosgene, was not detected because a rapid reaction took place between phosgene and copper metal in DMSO as was confirmed by an separate experiment.² The oxygen abstraction reaction from DMSO by a dichlorocarbene was observed also in the reaction between DMSO and a conventional dichlorocarbene generated by an alkali treatment of ethyl trichloroacetate.⁴

Although an alternative path to explain the formation of oxidation products of *gem*-dichlorides 5 and 6 might be a Kornblum type stepwise reaction,⁵ *n*-butyl bromide, which is susceptible to the Kornblum type oxidation, failed to give butyraldehyde in the presence of copper metal at an ambient condition, and the observation of olefinic compounds together with oxidation products in cases of 3 and 4 favors carbenoids as intermediates in a series of present reactions.

3. Reactions with Other Copper Salts. Reactions of a series of gem-dichlorides with various copper salts

⁽³⁾ Ito, Y.; Yonezawa, K.; Saegusa, T. J. Org. Chem. 1974, 39, 1763. (4) Oda, R.; Mieno, M.; Hayashi, Y. Tetrahedron Lett. 1967, 2363. Authors also obtained the identical result in an alkaline treatment of chloroform in DMSO.

⁽⁵⁾ Kornblum, N.; Anderson, G. J.; Jones, W. T. J. Am. Chem. Soc. 1957, 79, 6562.

Table II. Reactions of Copper Compounds with gem-Dichlorides in Various Solvents

	nande	copper	Cu/nalide ratio,	solvent	temp,	time,	conv,	
run	(mmol)	compd	mol/mol	(mL)	°C	h	%	products and yields, ^a %
1	1a (40)	CuCl	2.0	DMSO (20)	25	5	30	CH ₃ OOCHC=CHCOOCH ₃ , 57 (70)
2	1a (40)	CuBr	2.0	DMSO (20)	25	5	25	$CH_3OOCHC = CHCOOCH_3, 69 (62)$
3	1 b (40)	CuCl	2.0	DMSO (20)	25	5	36	$C_2\dot{H}_5OOCHC = CHCOOC_2\dot{H}_5, 47 (78)$
4	1 b (40)	CuBr	2.0	DMSO (20)	25	5	24	$C_2H_5OOCHC = CHCOOC_2H_5, 61 (70)$
5	1c (40)	CuCl	2.0	DMSO (20)	50	5	27	$(t-C_4H_9)OOCHC=CHCOO(t-C_4H_9), 49 (86)$
6	1 d (40)	CuCl	2.0	DMSO (20)	25	1	38	$(C_6H_5)OOCHC = CHCOO(C_6H_5), 28 (64)$
7	1e (20)	CuCl	2.0	DMSO (10)	25	5	48	$C_2H_5OOCCH_3C = CCH_3COOC_2H_5$, 11 (0)
8	2 (10)	CuCl	2.2	DMSO (20)	24	1.5	8	$(C_6H_5)_2C = C(C_6H_5)_2, 89$
9	3 (20)	CuCl	2.0	DMSO (10)	50	2	39	$(C_6H_5)HC = CH(C_6H_5), 31 (100); C_6H_5CHO, 50; CH_3SCH_3, 34$
106	4 (10)	CuCl	2.0	DMSO (10)	50	2	67	CH ₃ COCH=CHCOCH ₃ , 3 (100); CH ₃ SCH ₃ , 13
11	5 (4)	CuCl	2.0	DMSO (5)	25	2	78	CH ₃ CH=CHCHO, 67; CH ₃ SCH ₃ , 57
12	6 (2.5)	CuCl	2.0	DMSO (5)	15	50	48	CH ₃ SCH ₃ , 83
13	6 (2.5)	CuCl	6.0	DMSO (5)	15	50	100	CH_3SCH_3 , 95
14	la (40)	Cu	1.0	DMAc (20)	25	5	17	$CH_3OOCHC = CHCOOCH_3, 40$ (65)
15	la (40)	Cu	1.0	DMAc (20)	25	50	75	$CH_3OOCHC = CHCOOCH_3, 52$ (62)
16	la (40)	Cu	1.0	HMPA (20)	25	5	80	$CH_3OOCHC = CHCOOCH_3, 37 (68)$
17	1b (40)	Cu	1.0	DMF (20)	25	20	31	$C_2H_5OOCHC = CHCOOC_2H_5, 56 (73)$
18	1 b (40)	Cu	1.0	DMF (20)	25	95	86	$C_2H_5OOCHC=CHCOOC_2H_5$, 58 (79)
19	5 (10)	Cu	3.0	DMF (10)	25	2	100	$CH_3CH=CHCHO, 23$

^a Yield based on reacted halides. % of E isomer in parentheses. ^bCH₂ClCOCH₃ was also obtained (yield 18%).

instead of copper metal were carried out in DMSO as for a comparison purpose. As shown in runs 1–13 of Table II, monovalent copper salts like CuCl and CuBr were found to cause relevant reactions to give products identical with those with copper metal. The product yield based on the reacted halide was, however, considerably lower than that with copper metal. The Z/E ratio of coupling products was, on the other hand, not significantly affected by copper metal or copper salts. Such a monovalent copper salt like CuI and a divalent copper salt like CuCl₂ failed to react with these gem-dichlorides. Also copper oxides like Cu₂O and CuO were inactive. Thus a possibility that the oxidized copper moiety at the surface of copper powder reagent might be an active site will be excluded.

4. Reactions in Other Solvents. Since DMSO is known to readily form a complex with CuCl₂ to give $CuCl_2(DMSO)_{2,6}$ alternative solvents to give a relevant complex with $CuCl_2$, i.e. dimethylformamide, DMF, dimethylacetamide, DMAc, and hexamethylphosphoramide, HMPA, may replace DMSO. As shown in Runs 14-19 of Table II, fumarate and maleate esters were formed from 1 also in DMF, DMAc, and HMPA although the reaction was comparably slower in DMF and in DMAc and the product yield based on the reacted halide was markedly lower in HMPA. The E/Z ratio of products was, however, scarcely influenced by the type of solvents used. The reaction of 5 with copper metal in DMF was found to proceed to give crotonaldehyde as was in DMSO. In other conventional solvents like benzene, acetonitrile, THF, chloroform and methanol, the reaction between the above gem-dichlorides and copper metal did not take place at all in an ambient condition.

5. Reactivity of Carbenoids Formed in the Reaction of Copper Metal with gem-Dichlorides. Carbalkoxy carbenes and carbenoids were commonly generated by photodecomposition or thermal decomposition reactions of diazoacetic acid esters in the presence or absence of copper species as a catalyst.⁷ Thus it will be of interest to compare the reactivity of copper carbenoids generated in the present system with that from diazoacetate. Since carbalkoxy carbenoids produced from diazoacetic acid esters underwent an addition reaction to olefins to produce cyclopropane derivatives,⁸ the relevant reaction of 2 with copper metal was carried out in DMSO in the presence of cyclohexene. In contast to diazoacetates as a precursor, no cyclopropanation was observed, but fumarate and maleate esters were produced in almost identical yields as in the absence of cyclohexene.

Besides, when ethyl diazoacetate was decomposed in DMSO in the presence of copper metal, neither fumarate nor maleate esters were observed but dimethyl sulfide (16% yield) was detected. The formation of a sulfoxonium ylide was postulated as an intermediate.⁹

It was noticed also that the reaction of dichloroacetic acid ester with copper metal was completely inhibited by the addition of triphenylphosphine. No phosphonium ylide was observed in contrast to the reaction with conventional carbalkoxy carbenoids from diazoacetates.¹⁰ This may be accounted for by the competitive coordination of triphenylphosphine over DMSO and/or gem-dichloride on the active copper surface otherwise initiates the reaction. From these observations, it can be concluded that the reactivity of carbalkoxy carbenoids generated in the present system is remarkably different from that by the traditional procedure with diazoacetic acid esters.

Experimental Section

Gas-liquid chromatography (GLC) was performed on a Hitachi 260-10 equipped with a data processor Shimadzu C-R6A and with a thermal conducting detector. Columns were a $2 \text{ m} \times 3 \text{ mm}$ i.d. stainless steel containing either polyethylene glycol (PEG 20M, Gasukuro Kogyo) on 10% Uniport B 60/80 or silicone (SE 30, Gasukuro Kogyo) on 10% Uniport HP 60/80. Carrier gas was helium. The detailed conditions of GLC analysis were described in the each section below. Mass spectra (MS) were recorded on a Shimadzu AUTO GCMS-6020S high-resolution electron impact mass spectrometer. Proton magnetic resonance spectra (¹H NMR) were obtained at 270 MHz on a JEOL GX-270 instrument. Infrared spectra were taken on a Hitachi 260-10 spectrophotometer.

Materials. Copper metal used in the present study was powder form (250 mesh) obtained from Merck. Copper metal of another particle size was obtained from Aldrich (40 mesh) and used as a comparison purpose to show no remarkable difference in the reaction. Surface purification of copper powder was carried out

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in one case with a 20% sulfuric acid followed by rinsing with water and acetone, but no remarkable influence was noticed. Thus copper metal was used as received. Other metals and copper salts were powder form reagent grade (Nacalai Tesque) and used as received. A series of gem-dichlorides, 1a-b, 2-4, and 6, were obtained from Nacalai Tesque and distilled under nitrogen atmosphere. 1c and 1d were synthesized by the reaction of dichloroacetyl chloride with tert-butyl alcohol¹¹ and with phenol,¹² respectively. 1e was synthesized by the reaction of α, α -dichloropropionyl chloride with ethanol.¹³ 1f was synthesized by the reaction of dibromoacetyl chloride with methanol.^{1f} 5 (100%) E isomer) was synthesized by the reaction of crotonaldehyde (100% E isomer) with phosphorous pentachloride.³ Ethyl diazoacetate was synthesized according to the standard procedure¹⁴ and stored in a refrigerator. DMSO and other solvents were used after distillation. Authentic samples such as methyl and ethyl esters of fumaric and maleic acids were obtained from Nacalai Tesque and used as received. Di-tert-butyl fumarate¹⁵ was synthesized by the reaction of fumaric dichlorides with tert-butyl alcohol. Diphenyl fumarate and maleate were prepared by the method described before.¹⁶ Diethyl dimethylmaleate was synthesized by the reaction of 2,3-dimethyl maleic anhydride with ethanol.¹⁷ (E)-¹⁸ and (Z)-¹⁹ 1,2-diacetoxyethylene were also synthesized. These reagents were then used for the assignment of reaction products by means of a GLC-MS technique. CuCl₂(DMSO)₂ was synthesized by the reaction of CuCl₂ with DMSO in ethanol.⁶ Other reagents were used after usual purification.

Reaction of gem-Dichlorides with Copper Metal in **DMSO.** The following is a typical example of a reaction procedure and GLC conditions for product analyses were described separately. To a mixture of 2.5-40 mmol of gem-dichlorides and 5-40 mL of DMSO in a round-bottom flask, a weighed amount of copper powder was added under stirring with a magnetic stirrer in a thermostatted bath at 25 °C. After the prescribed reaction time, a determined amount of an internal standard was added, and the reaction mixture was analyzed directly by GLC after filtration. In another run, the reaction mixture was subjected to a trap-to-trap procedure to divide into a volatile and a residual part for an NMR and an IR measurements. GLC conditions for a series of gem-dichlorides were as follows: (1) For 1a, ethylbenzene was used as an internal standard and a column was a PEG 20M at 70-150 °C (5 °C/min) with an injection and a detector kept at 190 °C. (2) For 1b, ethylbenzene was used as an internal standard and a column was a PEG 20M at 80-160 °C (5 °C/min) with an injection and a detector kept at 200 °C. (3) For 1c, ethylbenzene was used as an internal standard and a column was a PEG 20M at 120-200 °C (5 °C/min) with an injection and a detector kept at 230 °C. (4) For 1d, diphenyl was used as an internal standard and a column was a SE 30 at 150-250 $^{\circ}C$ (5 $^{\circ}C/min$) with an injection and a detector kept at 200 $^{\circ}C$. (5) For 1e, ethylbenzene was used as an internal standard and a column was a PEG 20M at 80-190 °C (5 °C/min) with an injection and a detector kept at 200 °C. (6) For 2, diphenyl was used as an internal standard and a column was a SE 30 at 200-300 °C (10 °C/min) with an injection and a detector kept at 330 °C.

(11) Yield 66%; bp 66.0-67.0 °C (17 mmHg); ¹H NMR (DMSO-d₆) δ 1.50 (s, 9 H), 6.65 (s, 1 H) ppm. (12) Kunckell, F.; Johannssen, F. Ber. 1898, 31, 169.

(13) Yield, 35%; bp 42.0–43.0 °C (10 mmHg); ¹H NMR (CDCl₃) δ 1.23 (t, 3 H), 2.15 (s, 1 H), 4.20 (q, 2 H) ppm. (14) Womach, E. B.; Nelson, A. B. Organic Syntheses; Wiley: New

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(7) For 3, the conversion of 3 and the product yield were determined separately due to the decomposition of 3 in a GLC column at high temperature. tert-Butyl benzene was used as a common internal standard. The conversion was determined with a column of a SE 30 at 50-150 °C (5 °C/min) with an injector and a detector kept at 80 °C, while the product yield was estimated with a column of a PEG 20M at 130-230 °C (5 °C/min) with an injection and a detector kept at 250 °C. (8) For 4, tert-butylbenzene was used as an internal standard and a column was a SE 30 at 80-140 °c (5 °C/min) with an injection and a detector kept at 150 °C. (9) For 5, due to the decomposition of 5 in a GLC column in the range of at most 10%, the conversion was estimated by the extraporation with a calibration obtained through GLC measurements of pure 5. tert-Butylbenzene was used as an internal standard and a column was a SE 30 at 65 °C with an injection and a detector kept at 120 °C. (10) For 6, a volatile fraction was recovered by a trap-to-trap technique. The conversion was determined by GLC with 1,2-dichloroethane as an internal standard and a column was a SE 30 at 100 °C with an injection and a detector kept at 190 °C. The product yield was estimated by means of a ¹H NMR analysis with 1,2-dichloroethane as an internal standard.

Kornblum Reaction Using Copper Metal. n-Butyl bromide (0.36 g, 2.6 mmol) and 0.18 g (2.8 mmol) of copper metal were mixed in 2.5 mL of DMSO in the presence of 0.03 g (0.3 mmol) of triethylamine and stirred at 25 °C for 24 h. The reaction mixture was separated into a volatile part and a residual solid. The volatile part was subjected to an NMR analysis to fail to detect n-butyraldehyde.

The Reaction in the Presence of Cyclohexene. In a 30-mL round-bottom flask, 3.14 g (20 mmol) of 1b, 10 mL of DMSO, and 10 mL of cyclohexene were mixed, and 1.27 g (20 mmol) of copper powder was added. The mixture was stirred for 5 h at 25 °C and was subjected to a GLC analysis after filtration.

The Decomposition Reaction of Ethyl Diazoacetate in DMSO. In a 30-mL round-bottom flask, 0.33 g (2.3 mmol) of ethyl diazoacetate, 2.5 mL of DMSO, and 0.01 g of copper powder were mixed and stirred for 13 h at 20 °C. The reaction mixture was evacuated by a trap-to-trap technique, and the volatile part was subjected to an NMR analysis after the addition of 1,2-dichloroethane as an internal standard.

The Reaction in the Presence of Triphenylphosphine. In a 100-mL round-bottom flask, 6.28 g (40 mmol) of 1b, 3.15 g (12 mmol) of triphenylphosphine, and 20 mL of DMSO were mixed. Thereupon 2.54 g (40 mmol) of copper powder was added and stirred for 5 h at 25 °C. An aliquot of the mixture was then subjected to a GLC analysis after filtration. GLC conditions were ethylbenzene as an internal standard with a column of a PEG 20 $m \tilde{M}$ at 100–180 °C (5 °C/min) with an injection and a detector temperature kept at 190 °C.

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Registry No. 1a, 116-54-1; 1b, 535-15-9; 1c, 49653-47-6; 1d, 10565-20-5; 1e, 17640-03-8; 1f, 6482-26-4; 2, 2051-90-3; 3, 98-87-3; 4, 513-88-2; 5, 56800-09-0; 6, 56-23-5; (E)-H₃CO₂CCH= CHCO₂CH₃, 624-49-7; (Z)-H₃CO₂CCH=CHCO₂CH₃, 624-48-6; (E)-C₂H₅O₂CCH=CHCO₂C₂H₅, 623-91-6; (Z)-C₂H₅O₂CCH=CHCO₂C₂H₅, 141-05-9; (E)-t-C₄H₉O₂CCH=CHCO₂C₄H₉-t, 7633-38-7; (Z)-t-C₄H₉O₂CCH=CHCŎ₂C₄H₉-t, 18305-60-7; (E)- $\begin{array}{l} C_{6}H_{5}O_{2}CCH = CHCO_{2}C_{6}H_{5}, \ 6338-19-8; \ (Z)-C_{6}H_{5}O_{2}CCH = \\ CHCO_{2}C_{6}H_{5}, \ 7242-17-3; \ (Z)-C_{2}H_{5}O_{2}CC(CH_{3}) = \\ C(CH_{3})CO_{2}C_{2}H_{5}, \ 22644-89-9; \ (C_{6}H_{5})_{2}C = \\ C(C_{6}H_{5})_{2}C = \\ C(C_{6}H_{5})_{3}C = \\ C(C_{$ 103-30-0; $C_{6}H_{5}CHO$, 100-52-7; $(CH_{3})_{2}S$, 75-18-3; (E)-CH₃COCH=CHCOCH₃, 4436-75-3; CH₃CH=CHCHO, 4170-30-3; CuCl, 7758-89-6; CuBr, 7787-70-4; CH₂ClCOCH₃, 78-95-5; DMSO, 67-68-5; cyclohexene, 110-83-8; copper, 7440-50-8; butyl bromide, 109-65-9; ethyl diazoacetate, 623-73-4.