780. *Alkyl Derivatives of Group I Metals. Part II.* Properties and Reactions of Methylcopper*(I)

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The reaction of cupric nitrate and sulphate with tetramethyl-lead in methanol and ethanol occurred thus:

$$Cu^{2+} + PbMe_4 \longrightarrow Cu^+ + PbMe_3^+ + Me$$
$$Cu^+ + PbMe_4 \longrightarrow CuMe + PbMe_3^+$$
$$CuMe + ROH \longrightarrow CuOR + CH_4$$

With cupric chloride the main product was methyl chloride:

$$2CuCl_2 + PbMe_4 \longrightarrow Cu_2Cl_2 + PbMe_3Cl + MeCl$$

In the presence of a large excess of the alkyl the following chain reaction was set up:

$$CuMe + MeOH \longrightarrow CuOMe + CH_4$$
$$CuOMe + PbMe_4 \longrightarrow PbMe_3{\cdot}OMe + CuMe$$

The failure to prepare alkyl coppers by normal methods of synthesis of alkyl metals has been attributed to their instability or to their reactivity with organic solvents. For instance, Buckton [1] failed to isolate an alkyl copper on reaction of cuprous chloride with diethylzinc. Wanklyn and Carius [2] noted that this reaction yielded ethane, butane, and ethylene. Reich [3] observed that adding cuprous iodide to ethereal ethylmagnesium bromide cooled in ice–salt led to the deposition of copper and evolution of a gas. He concluded that the intermediate CuEt was formed but was unstable at −18°. From studies of the same reaction at −80° Gilman and Straley [4] concluded (*a*) that a stable solution of ethylcopper(I) was formed that decomposed at higher temperatures, and (*b*) that a Grignard compound, reacting with a cupric salt, gave first a cuprous salt, which with excess of Grignard reagent formed the alkylcopper(I). They obtained no evidence of the existence of alkyl derivatives of copper(II). The formation of methylcopper(I) as a yellow precipitate was first observed by Gilman and Woods [5] when they treated methyl-lithium with cuprous iodide in dry ether at −15° and cupric nitrate with tetramethyl-lead at −70°. The gaseous products of the latter reaction contained ethane and methane, and the authors suggested that the former was the product of thermal decomposition of methylcopper(I) and that the methane arose from its partial hydrolysis.

The present work deals with the nature and mechanism of the tetramethyl-lead–cupric salt reaction in alcoholic solution and it is shown that the initial reaction is an electron-transfer between the cupric ion and the alkyl-lead with formation of a free radical. In

$$Cu^{2+} + PbR_4 \longrightarrow Cu^+ + PbR_3^+ + R\cdot$$

this respect the process is similar to that observed in the corresponding reaction of the silver nitrate with alkyl-leads.[6] Methylcopper(I) is formed by a secondary reaction of the cuprous ion with alkyl-lead:

$$Cu^+ + PbR_4 \longrightarrow CuR + PbR_3^+$$

Some of the properties and reactions of methylcopper(I) are reported. The following paper reports a detailed study of the corresponding reactions leading to ethylcopper(I).

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* Part I, preceding paper.

[1] Buckton, *Annalen*, 1859, **109**, 225.

[2] Wanklyn and Carius, *Annalen*, 1861, **120**, 69.

[3] Reich, *Compt. rend.*, 1923, **117**, 322.

[4] Gilman and Straley, *Rec. Trav. chim.*, 1936, **55**, 821.

[5] Gilman and Woods, *J. Amer. Chem. Soc.*, 1943, **65**, 435.

[6] Bawn and Whitby, *Discuss. Faraday Soc.*, 1947, **1**, 228; Glockling, *J.*, 1955, 716; Spice and Twist, *J.*, 1956, 3319.

EXPERIMENTAL

The reaction between cupric nitrate, sulphate, and chloride, and tetramethyl-lead in alcoholic solution was investigated by the use of the apparatus described by Bawn and Whitby.[6] Solutions were mixed in the absence of air and moisture. The gases evolved at various temperatures were removed by a Toepler pump and analysed for methane, ethane, and butane by methods previously described.

Tetramethyl-lead was prepared by Calingaert's method [7] and was fractionally distilled (b. p. 26—28°/40 mm.).

Methyl and ethyl alcohol were purified as described by Walden, Ulich, and Laun.[8]

Salts used were of "AnalaR" grade. The salt $Cu(NO_3)_2,3H_2O$ was dehydrated by Ditte's method.[9]

RESULTS AND DISCUSSION

A primrose-yellow precipitate of methylcopper(I) is formed when alcoholic solutions of copper nitrate and tetramethyl-lead are mixed at temperatures (both solutions) from −78° to 30°. At room temperature the yellow solid slowly becomes orange, and finally orange-brown with gas evolution. The gaseous products (Table 1) consisted of ethane and methane in the ratio 1 : 2 and this ratio was not changed by small changes in (*a*) cupric-ion concentration, (*b*) tetramethyl-lead concentration, or (*c*) presence of water in the alcohol or complete removal of water. The primrose solid seems to be identical with the product obtained [5] by the action of methylmagnesium iodide on dry cuprous iodide at −20° and by the action of methyl-lithium on cuprous iodide at −15°. Results discussed below establish the formula CuMe, and no evidence was obtained in this work for the existence of methylcopper(II).

TABLE 1. *Reaction between* $Cu(NO_3)_2,3H_2O$ *and* $PbMe_4$ *in ethanol* (100 *ml.*).

		Initial concentrations					Carbon balance
Temp.	Conditions	$Cu(NO_3)_2,3H_2O$ 10^{-3}M	$PbMe_4$ 10^{-2}M	C_2H_6 (10^{-4} mole)	CH_4 (10^{-4} mole)	Ratio $C_2H_6 : CH_4$	(Cu^{2+} = 2Me)
15·0°	$Cu(NO_3)_2,3H_2O$. Dry EtOH	2·55	1·80	1·40	2·47	0·57	92·9
−40·0	,, ,,	2·55	1·80	1·45	2·46	0·59	100·8
8·5	,, ,,	2·55	1·43	1·32	2·83	0·47	103·0
18·0	$Cu(NO_3)_2$ (anhyd.). Dry EtOH		1·80	0·51	1·10	0·47	
16·0	$Cu(NO_3)_2,3H_2O$. 4·8% Aq. EtOH	2·55	1·43	1·10	2·40	0·46	87·1
14·5	$Cu(NO_3)_2,3H_2O$. 20% Aq. EtOH	2·55	1·80	1·50	2·59	0·58	105·5

* The low yield in this run was due to the fact that it was for only **3** hr. and reaction was not complete.

The experimental results can be explained in terms of the mechanism:

$$\begin{aligned} Cu^{2+} + PMe_4 &\longrightarrow Cu^+ + PbMe_3^+ + Me\cdot \quad \ldots\ldots\ldots \quad (1)\\ 2Me\cdot &\longrightarrow C_2H_6 \quad \ldots\ldots\ldots \quad (2)\\ Cu^+ + PbMe_4 &\longrightarrow CuMe + PbMe_3^+ \quad \ldots\ldots\ldots \quad (3)\\ CuMe + MeOH\ (EtOH) &\longrightarrow CuOMe\ (CuOEt) + CH_4 \quad \ldots\ldots \quad (4) \end{aligned}$$

Reactions (2) and (3) are analogous to the reaction of silver ion with lead alkyls:

$$Ag^+ + PbMe_4 \longrightarrow AgMe + PbMe_3^+ \longrightarrow Ag + C_2H_6$$

The methylsilver is unstable in alcoholic solution and decomposes rapidly above −20° to give a quantitative yield of ethane.[6]

The proof of the proposed scheme was provided by the separate investigation of reactions (1), (3), and (4).

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[7] Calingaert, *Chem. Reviews*, 1926, **2**, 55.

[8] Walden, Ulich, and Laun, *Z. phys. Chem.*, 1924, **114**, 275.

[9] Ditte, *Compt. rend.*, 1879, **89**, 576, 641.

In the presence of excess of Cu^{2+} the alkyl-lead would be consumed largely by reaction (1) unless reaction (3) was extremely fast compared with (1). In the presence of a 1·5 to 3-fold excess of Cu^{2+} the colour of the cupric ion was not discharged, no yellow precipitate formed, and the gaseous product was almost entirely ethane (Table 2). The low carbon yields (63·8%, 77·4% calculated on the initial alkyl added) on the cleavage of the methyl group were due to considerable loss of alkyl-lead on initial evacuation of the system.

On reaction in ethanol at −40° the only gaseous product was ethane [reactions (1) and (2)] but at room temperature the yellow precipitate formed reacted with the ethanol to give methane exclusively (Table 2). The results were the same for methanol solutions (Table 3) and it is apparent that the carbon yield (as gas) was approximately equivalent to three methyl groups per cupric ion, and not two as in ethyl alcohol. This is shown below to be the result of a chain reaction, but it will be noted that the yield of ethane is just that required by reactions (1) and (2).

TABLE 2. *The* $Cu(NO_3)_2,3H_2O$–$PbMe_4$ *reaction in ethanol* (100 *ml.*).

Temp. at stage 1	Temp. at stage 2	$Cu(NO_3)_2,3H_2O$ (10^{-3}M)	$PbMe_4$ (10^{-3}M)	CH_4 (c.c. at N.T.P.)	C_2H_6 (c.c. at N.T.P.)	Ratio $C_2H_6 : CH_4$	Carbon yield (%) (Cu^{2+} = 2Me)
−40·0°		2·55	3·73	0·00	1·91	0·46	110·0
	+20·0°			6·83	1·24		
−35·0		2·55	1·87	0·32	3·04	0·50	110·6
	+20·0			6·23	0·26		
−3·0		2·55	1·87	4·08	3·01	0·59	100·8
	+20·0			1·42	0·24		
−40·0		2·52	0·45	3·11	0·15		63·8
24·0	—	5·03	0·45	3·80	0·13		77·4

TABLE 3. *The copper salt–tetramethyl-lead reaction in methanol.*

$PbMe_4$ = 1·87 × 10^{-3}M; $Cu(NO_3)_2,3H_2O$ = 1·91 × 10^{-4}M (results 1—2). $Cu(SO_4)_3,5H_2O$ = 1·92 × 10^{-4}M (results 3 & 5).

No.	Temp. at stage 1	Temp. at stage 2	CH_4 (c.c. at N.T.P.)	C_2H_6 (c.c. at N.T.P.)	Ratio $C_2H_6 : CH_4$	Carbon yield (%) (Cu^{2+} = 3Me)
1	−45°		0·00	2·14	0·27	107·0
		+18°	9·25	0·40		
2	−45		0·00	2·24	0·29	114·8
		+18	9·66	0·61		
3	−40	—	0·00	2·11		
4	−45 *	—	0·00	2·15		
5	−50	—	0·00	1·84		

* Anhydrous copper sulphate (1·92 × 10^{-4}M).

Analogous results were obtained when cupric sulphate was used (Table 3), ethane being the sole gaseous product at −45°. When the reaction mixture warmed to room temperature, methane was evolved (Table 4). The high yield was shown to be the result of a chain reaction which occurs in the presence of excess of alkyl-lead.

TABLE 4. *The cupric sulphate–tetramethyl-lead reaction in dry methanol.*

Cu^{2+} (10^{-4}M)	$PbMe_4$ (10^{-3}M)	Temp.	Duration (hr.)	CH_4 (10^{-4}M)	C_2H_6 (10^{-4}M)	Ratio $C_2H_6 : CH_4$	Carbon yield (%) (Cu^{2+} = 2Me)
1·92	1·87	−40° +18°	8 12	0·76	2·63	3·46	156
—	1·87	−45 +20	8 12	0·27	2·72	10·24	—
1·92	3·73	−45 +20	6·5 16	1·32	1·86	1·41	130
1·92	1·87	−50 +20	19 6	2·12	1·53	0·72	135
1·92	4·48	−40 +18	3 90	14·95	1·78	0·12	482

Total vol. of solvent = 105 ml. except in the second (85 ml.) and fourth experiment (49 ml.). $CuSO_4,5H_2O$ was used in all runs except the second, where the anhydrous salt was used.

The composition and yield of the products from anhydrous cupric chloride were very different from those obtained from cupric nitrate and sulphate under similar conditions (Table 5). The main product was methyl chloride, formed by the reaction:

$$2CuCl_2 + PbMe_4 \longrightarrow 2CuCl + PbMe_3Cl + MeCl$$

The small yield of ethane came from reactions (1) and (2), and the cuprous chloride formed, being insoluble and un-ionised, did not undergo reaction (3).

In the presence of polymerisable monomers (styrene or acrylonitrile) the formation of gaseous hydrocarbons was very considerably reduced (Table 6) and polymer was precipitated. No methylcopper was formed and this was shown to be partly due to the complexing-formation by, or adsorption of, the cuprous ion with the monomer and polymer respectively. These results are in accordance with the formation of free radicals and this is substantiated by kinetic studies of the polymerisation of styrene and acrylonitrile to be described later.

The reason why the yield of methane in the copper nitrate–tetramethyl-lead reaction in methyl alcohol (but not in ethyl alcohol) was larger than required by the reactions (3) and (4) was elucidated by measurements of the yields of methane from solutions containing a large excess of tetramethyl-lead. The results (Table 7 and Figure) show that, other conditions being constant, the amount of methane increases with the amount of tetramethyl-lead and the time

TABLE 5. *Reaction between* $CuCl_2$ *and* $PbMe_4$ *in dry ethanol.*

Cu^{2+} (10^{-4}M)	$PbMe_4$ (10^{-5}M)	Temp.	Duration (hr.)	MeCl (10^{-4} mole)	C_2 hydrocarbon (10^{-5} mole)	Ratio $C_2 : C_1$	Carbon yield (%) (Cu^{2+} = 1Me)
—	1·87	+18°	—	1·14	0·92	0·081	—
3·75	1·87	−40	5	1·66	1·54	0·093	52·4
		+18	14				
3·52	1·87	−45	24	1·33	1·64	0·123	47·0
		+18	3				
6·09	2·98	−30	4	1·72	2·16	0·125	35·5
		+18	1				
3·75	1·87	−30	30	1·54	1·37	0·090	48·3
		+18	15				

In the first experiment the anhydrous salt was used. The total volume of ethanol was 105 ml. in all experiments, except the fourth where 40 ml. were used.

TABLE 6. *Reaction of* Cu^{2+} *with* $PbMe_4$ *in ethanol* (100 *ml.*) *in presence of styrene.*

Temp.	$CuNO_3,3H_2O$ (10^{-4}M)	Styrene (10^{-2}M)	C_2H_6 (10^{-6} mole)	CH_4 (10^{-5} mole)	Carbon yield (%) (Cu^{2+} = 2Me)
+18°	1·99	2·62	10·8	4·2	15·9
−20	2·36	15·60	0·89	5·8	12·6
+40	2·36	21·90	1·74	4·4	10·1

TABLE 7. *Reaction of* $Cu(NO_3)_2,3H_2O$ *with* $PbMe_4$ *in methanol at room temperature.*

$[Cu^{2+}] = 1·99 \times 10^{-4}$ M, and excess of $PbMe_4$.

$PbMe_4$ (10^{-4}M)	Duration (hr.)	MeOH (ml.)	C_2H_6 (10^{-4} mole)	CH_4 (10^{-4} mole)	Ratio $C_2H_6 : CH_4$	Carbon yield (%) (Cu^{2+} = 2Me)
18·7	11	104	1·14	4·13	0·274	160·5
18·7	20	104	1·27	4·32	0·294	171·8
29·8	17	109	1·18	5·95	0·199	209·3
29·8	60	104	1·19	11·10	0·107	338·6
29·8	500	104	1·35	20·62	0·065	585·0
37·4	12	104	1·19	7·80	0·153	250·5
44·8	38	104	1·12	11·58	0·097	347·5
44·8	96	104	1·14	18·34	0·063	518·0
59·7	18	104	1·15	9·22	0·124	288·6
59·7	40	104	1·17	16·90	0·069	483·0
59·7	161	104	1·38	26·62	0·052	737·0
29·8	20	44	1·01	8·80	0·115	272·0

of reaction, and that the rate of methane production depends on the initial amount of alkylmetal. These facts accord with the occurrence of a chain reaction and evidence for the following sequence is discussed below:

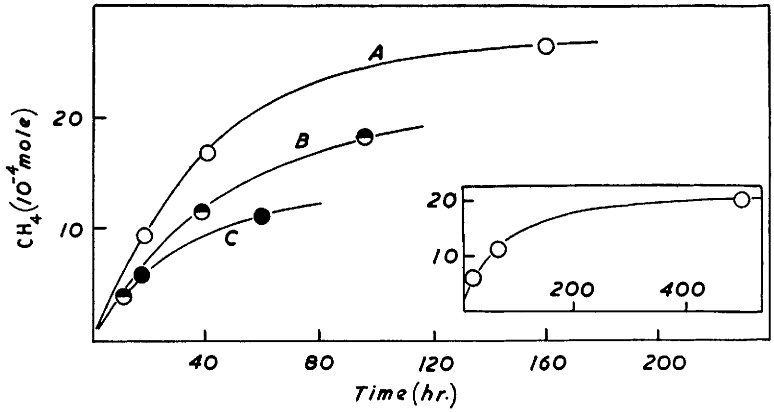
$$\text{CuMe} + \text{MeOH} \longrightarrow \text{CuOMe} + \text{CH}_4 \qquad (5)$$

$$\text{CuOMe} + \text{PbMe}_4 \longrightarrow \text{PbMe}_3\text{·OMe} + \text{CuMe} \qquad (6)$$

Although methylcopper(I) reacts with water the methane formed cannot be ascribed to the use of hydrated salts since as shown in Table 1 the ratio $C_2H_6 : CH_4$ is not dependent on the degree of hydration, nor could such a reaction explain the high yields of methane (Table 9). Further, the results reported in the following paper require the intermediate formation of cuprous ethoxide.

The experimental facts did not agree with an alternative scheme involving liberation of a free methyl radical as has been observed in the analogous reaction of isobut-1-enylsilver,[10] since under the same reaction conditions the yield of methane was not markedly increased when a large excess of tetramethyl-lead reacted with copper nitrate in ethanol (Table 8).

Dependence of yield of methane on amount of $PbMe_4$.



$[PbMe_4]$ = (*A*) 5·97, (*B*) 4·48, (*C*) 2·98 × 10^{-3}M. *Inset,* $[PbMe_4]$ = 2·98 × 10^{-3}M.

TABLE 8. *Reaction of* $Cu(NO_3)_2,3H_2O$ *with* $PbMe_4$ (*excess*) *in ethanol* (104 *ml.*).

Cu^{2+} (10^{-4}M)	$PbMe_4$ (10^{-4}M)	Temp.	Duration (hr.)	C_2H_6 (10^{-4} mole)	CH_4 (10^{-4} mole)	Ratio $C_2H_6 : CH_4$	Carbon yield (%) (Cu^{2+} = 2Me)
2·65	18·7	20°	22	1·45	2·46	0·590	100·8
2·65	18·7	20	40	1·47	2·92	0·504	110·6
2·65	37·4	18	12	1·41	3·05	0·462	110·0
1·99	44·8	18	18	1·06	2·96	0·359	127·5
1·99	37·4	18 40	60 10	0·97	3·26	0·297	133·0
1·99	37·4	18 40	40 20	1·01	3·24	0·313	132·1

It is therefore concluded that reaction (7) is slow compared with (6). This may be partly due to the much lower solubility of the copper ethoxide.

$$\text{CuOEt} + \text{PbMe}_4 \longrightarrow \text{CuMe} + \text{PbMe}_3\text{·OEt} \qquad (7)$$

Methylcopper(I), prepared by reaction of cupric nitrate and tetramethyl-lead at −35°, was separated by filtration at −78° under nitrogen. Suspensions in methanol and ethanol were decomposed at room temperature and the evolved gases and the residue were analysed. The

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[10] Glockling, *J.*, 1955, 716.

results summarised in Table 9 show that the yield of methane based on the amount of copper present was almost quantitatively in accordance with reaction (5). The departure from 100% was due to slight reaction with the alcohol during handling at −35°. The results show that composition of the methylcopper(I) was independent of the alcohol used.

TABLE 9. *Decomp. of* CuMe (*ca.* 4×10^{-4} *mole*) *in* MeOH *and* EtOH *at room temperature.*

Alcohol (14 ml.)	Time of decomp. (hr.)	Cu^{2+} in residue (10^{-4} g.-ion)	CH_4 (10^{-4} mole)	C_2H_6 (10^{-4} mole)	CH_4 yield (%) (Cu^{2+} = 1Me)
MeOH	40	4·76	4·10	0·214	86·2
,,	35	3·13	2·88	0·084	92·1
EtOH	16	5·00	4·48	0·364	89·7
,,	23	5·18	4·72	0·122	91·2

When methylcopper(I) was treated with methanol containing tetramethyl-lead, the vigorous alcoholysis at room temperature was followed by a slow formation of methane (many days). Although this reaction was never taken to completion, the balance between the alkyl-lead consumed (Table 10) and the methane produced [reactions (5) and (6)] was within the limits of experimental error. The corresponding reaction in ethanol gave only an 8—10% increase in yield of methane after 3 days, confirming the slowness of reaction (7).

TABLE 10. *Decomposition of* CuMe *in alcohols containing tetramethyl-lead.*

Solvent used for prep. at −35°	Details of decomp.			$PbMe_4$ added (10^{-4} mole)	$PbMe_4$ unused (10^{-4}M) *	CH_4 formed (10^{-4} mole)	Cu^{2+} in residue (10^{-4}M)	Moles of CH_4 formed per mole of $PbMe_4$ used †
	Alcohol	Alcohol (ml.)	Duration (hr.)					
MeOH	MeOH	25	72	17·16	5·66	19·68	6·01	1·19
,,	,,	20	81	14·93	7·13	13·89	5·76	1·04
EtOH	EtOH	20	74	14·93	12·40	3·43	3·45	99·4% carbon yield ‡
MeOH	EtOH	20	73	14·93	—	3·45	2·98	115·8% carbon yield ‡

All solvents were dry. Only traces of ethane were formed.

* Estimated by silver formed when alkyl-metal reacts with silver nitrate.

† The CH_4 produced from the alkyl-lead is calculated by assuming a 100% yield of CH_4 from the initial alcoholysis of methyl copper.

‡ Carbon yields are based on methane formed and copper in residue (Cu^{2+} = 1Me).

The orange-brown residue which remained after removal of all the solvent became deep brown on exposure to air or on addition of water. A similar product was obtained on adding water to methylcopper(I). It was soluble in hydrochloric or nitric acid, to form the characteristic blue copper salt solutions. These results suggest that the orange precipitate was cuprous alkoxide and that both this and methylcopper(I) were readily hydrolysed to cuprous oxide or hydroxide. No reference has been found to the previous preparation of cuprous alkoxides, but cupric methoxide and ethoxide have been prepared as blue or green precipitates on electrolysis of sodium methoxide at copper electrodes [11] and by the action of sodium alkoxides on cupric chloride.[12]

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[11] Szilard, *Z. Elektrochem.*, 1906, **12**, 393.

[12] German and Brandon, *J.*, 1942, 526.