OXIDATION OF ORGANOMERCURY COMPOUNDS BY COPPER SALTS

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Summary

The products, and ease, of oxidation of organomercury compounds (R_2Hg or $RHgX$) by copper salts in DMF solution, under mild conditions, is shown to depend on the nature of R and the copper salt used. Some possible oxidation reaction mechanisms are considered.

Reactions of organometallic and, generally, organoelement compounds, organoboron compounds included, with copper(I) and copper(II) salts are wide-ly known*. This is especially true of organolithium and organomagnesium compounds used in the synthesis of organic derivatives of univalent copper [1]. In the case of Cu^{II} salts these reactions are undoubtedly of the redox type. Yet data on the systematic study of the nature of the organometallic compound, the anion in CuX_2, and of the solvent, allowing definite conclusions to be made as to the nature of every separate step of the progress, have been unavailable so far. The existing data indicate a strong dependence of product composition of such reactions [RX, RH, R_2, R(-H)] on the above factors. As the first step to the solution of this problem we have studied the interaction of a number of organomercury compounds with copper salts. The main task was to study the effect of the nature of the organic group R within the series of derivatives of the same metal, the nature of the group being widely varied (R = C_6H_5, C_6F_5, $C_6H_5CH_2$, $C_6F_5CH_2$, p-$CH_3OC_6H_4CH_2$, n-C_4H_9, CCl_3, $(CF_3)_2CH$, $C_6H_5CHCO_2C_2H_5$, $C_6H_5COCH_2$). There exist literature data on a number of reactions between R_2Hg or $RHgX$ and $CuHal_2$ (R = C_6H_5, $C_6H_5CH_2$, $ClCH=CH_2$, ferrocenyl) [2-5]. Although all the reactions went under fairly vigorous conditions the yields of

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* In recent years copper salts have been used not only for oxidation of organoelement compounds but also for oxidation of hydrocarbons, such as RC≡CH, phenols, as well as for introduction of halogen into ketones that can undergo enolization, etc.

products (RHal or solvolysis products, ROS) were, as a rule, far less than quantitative. Unfortunately, no complete analysis of all the reaction products has been carried out.

In the present paper it is shown that reactions between $CuBr_2$ and any of the organomercury compounds investigated, those containing strong electron-acceptor groups among them, can be carried out in dimethyl formamide (DMF) under extremely mild conditions to give nearly quantitative yields of RBr (in some cases oxygen-free conditions and an excess of $CuBr_2$ is required). About 0.03 mol l^{-1} concentrations were used and products were analysed by G.L.C.

The results obtained are summarized in Table 1. When R = Ph (in case of PhHgBr and Ph_2Hg) bromobenzene is the only reaction product obtained in a quantitative yield. In the case of benzyl derivatives of mercury when the reaction is carried out in air, with quantities of reagents corresponding to the stoichiometry ratio of the process, considerable quantities of benzaldehyde and benzyl alcohol are yielded along with benzylbromide:

$$R_2Hg + 4CuBr_2 \rightarrow 2RBr + 2Cu_2Br_2 + HgBr_2$$

The yield of benzyl bromide in vacuo is practically quantitative. The introduction of electron-acceptor substitutes (R = $C_6F_5CH_2$) sharply decreases the fraction of oxygen-containing products while electron-donor substituents (R = p-$CH_3OC_6H_4CH_2$) cause an increase.

A quantitative yield of butyl bromide in reactions with n-Bu_2Hg or n-BuHgBr was obtained only with a double excess of $CuBr_2$. With stoichiometry concentrations the yield of n-BuBr even in vacuo is 65-67% though butane and butene are obtained only in trace amounts while octane is not detected in the reaction mixture.

The fact that organomercury compounds containing strong electron-acceptor groups enter into the reaction with $CuBr_2$ is of interest (Nos 10-15, Table 1). We ascribe the ease of oxidation to the ionization ability of these compounds. The oxidation of $(CCl_3)_2Hg$ and $[(CF_3)_2CH]_2Hg$ gives practically a quantitative yield of bromides, yet in the reaction of $PhCH(HgBr)CO_2Et$ and $(PhC\equiv C)_2Hg$ dimer products R_2* are formed along with bromides and in the case of $(PhCOCH_2)_2$·Hg hydrocarbon RH is formed. Nevertheless, the increase in $CuBr_2$ concentration in excess of that required by stoichiometry in these cases gives RBr as the only reaction product.

The nature of anion X in CuX_2 is an important factor in the process of oxidation. We have shown that no interaction takes place between $Cu(OAc)_2$ and diphenyl- and dibenzyl-mercury in DMF even at 60-70°C. However, compounds containing electron-acceptor groups enter into the reaction with $Cu(OAc)_2$ in DMF at room temperature, although the rate of the reaction is slower than with $CuBr_2$. This result may be considered as evidence in favor of ion-pair R^-Hg^+X participation in reactions.

It is obvious that the rate of the reaction and the product composition are strongly affected by nature of the solvent, although the problem has not been

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* The yield of the dimer depends on the order of mixing the reagents, on slow addition of $CuBr_2$ to the solution of RHgBr or R_2Hg the yield of R_2 as compared to RBr sharply increases. Usually the solutions were poured together.

TABLE 1

YIELDS (MOLAR %) OF THE PRODUCTS OF OXIDATION OF ORGANOMERCURY COMPOUNDS BY $CuBr_2$ IN DMF (concentration of RHgX = concentration of R_2Hg = 0.03 mol l⁻¹)

Reaction No.	R_2Hg or RHgX	Reaction conditions	Reaction products					
			RBr	R'CHO	ROH	ROCHO	RH	RR
1	$(C_6H_5)_2Hg$ or C_6H_5HgBr	in air or vacuo, 10 min	98-99					
2	$(C_6F_5)_2Hg$ or C_6F_5HgBr	in air or vacuo, 10 min	98-99					
3	$(C_6H_5CH_2)_2Hg$ or $C_6H_5CH_2HgBr$	in vacuo, 15 min	90-97	1-3		3-3.5[a]		
4		in air, 15 min	60-75	14-25	14-30	1[a]		
5	$(C_6F_5CH_2)_2Hg$ or $C_6F_5CH_2HgBr$	in air, 1 h	95-98	1-2				
6	$p\text{-}CH_3OC_6H_4CH_2HgCl$	in air	b	40.0	b			
7	$(n\text{-}C_4H_9)_2Hg$ or $n\text{-}C_4H_9HgBr$	in air, 2.5 h	46-47	4-5			traces of n-butane on 1-butene	
8	$(n\text{-}C_4H_9)_2Hg$ or $n\text{-}C_4H_9HgBr$	in vacuo, 2.5 h	65-67					
9	$(n\text{-}C_4H_9)_2Hg$ or $n\text{-}C_4H_9HgBr$	in vacuo, 2.5 h double excess of $CuBr_2$	99.0					
10	$(CCl_3)_2Hg$	in vacuo, 1.5 h	95-97					
11	$[(CF_3)_2CH]_2Hg$	in vacuo, 2 h	80-83					
12[c]	$(C_6H_5COCH_2)_2Hg$	in vacuo, 10-15 min	40-42				10-12	traces
13[c]	$C_6H_5CH(HgBr)CO_2C_2H_5$	in vacuo, 10-15 min	45-50				1-2	25-30
14	$C_6H_5CH(HgBr)CO_2C_2H_5$	the same with double excess of $CuBr_2$	95-97					2-2.5
15	$(C_6H_5C{=}O)_2Hg$		40-45				traces	40-50

[a] It was shown by reference experiments that benzyl formate originates from a secondary transformation of benzyl bromide in the presence of copper and mercury salts. Its quantity rapidly increases with time, whereas that of benzyl bromide decreases. [b] Identified qualitatively. [c] Considerable amounts of unidentified products were formed.

sufficiently studied. In recent papers [6-8] it has been shown that the composition of products obtained in the reaction of CuX_2 with ArTlYZ [6,7] and Et_4Pb [8] varies over a very wide range of dependence on solvent (cf. ref. 9). The importance of the nature of the solvent in oxidation of radicals by copper salts has also been noted [10]. We have shown that $Cu(OAc)_2$ can react with dibenzylmercury if acetic acid is used as a solvent ($t = 60°C$) with benzaldehyde (40%), benzyl alcohol (18%) and benzyl-acetate (38%) formed in the process. On the other hand, the oxidizing power of $CuBr_2$ appears to increase sharply when passing from DMF to acetonitrile since stoichiometry oxidation of $C_6H_5CH(HgBr)CO_2C_2H_5$ results in a high yield of RBr and only trace amounts of R_2 (irrespective of the order of mixing the reagents). In the case of $R = PhC\equiv C$ the yield of RBr also increased.

At present it seems difficult to propose a unified mechanism of oxidation by copper salts for organomercury compounds, let alone all organometallic compounds. Let us consider some possible mechanisms of reaction.

1. Formally, under the action of salts of bivalent copper- on organo-mercury compounds two-electron oxidation of carbanion R^- takes place, hence a two-step redox process is a possibility:

$$R^- \xrightarrow{CuX_2} R^{\cdot} \xrightarrow{CuX_2} R^+ \tag{1}$$

It should be noted that it was from this particular point of view that the interaction of organolithium [11] and organolead compounds [12] with Cu^{II} salts was regarded:

$$RMX_{n-1} + CuX_2 \rightarrow R^{\cdot} + MX_n + CuX \tag{2}$$

The appearance of radicals has been proved by use of diphenylpicrylhydrazyl radical traps [13] and by polymerization of monomers introduced into the reaction mixture [12]. Comparatively recently this mechanism was used to explain the results of oxidation of organoboron compounds by copper salts [9]. It is of interest that along with n-BuBr the formation of small amount of s-BuBr has been observed in the reaction of n-Bu_3B with $CuBr_2$ in THF, which is indicative of cationic butyl formation as kinetically independent particle. The formation of isomers has also been observed in reactions of other R_3B compounds [9]. However, with an equimolar ratio of reagents, especially in the case of $CuSO_4$ or $Cu(OAc)_2$, the main reaction products were R_2 and RH, which can be regarded as products of R transformation [9,14-16] (See below on the possibility of the formation of $R^{\cdot}$ via RCuX decomposition).

It is unlikely, however, that such a redox mechanism is valid for organomercury compounds, at any rate, for those not liable to preliminary ionization if we take into account that Cu^{II} salts are rather weak single-electron oxidants*. This point of view is confirmed by the fact that organomercury compounds (with the exception of those with sufficiently strong corresponding acid hydrocarbons RH) do not react with univalent copper salts which are stronger oxidants than Cu^{II} salts (in DMF or CH_3CN, 20°C). Unfortunately, at present there are

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* However, surprisingly copper(II) is often a very much more efficient oxidant than cobalt(III) or lead(IV) even though it has a lower oxidation potential [40].

practically no available data on the electrochemical behaviour which would allow a quantitative estimation of the feasibility of redox in a system. Judging by ionization potentials in the gaseous phase the direct oxidation of organoboron as well as of organomercury compounds by copper salts is also impossible since ionization potentials of R_3B and R_2Hg are too close [17]. Clinton and Kochi [8] consider the direct oxidation of tetraethyllead by Cu^{II} salts impossible as well (Et_4Pb I.P. 12.5 eV in the gaseous phase, Cu^{II} complexes 1.2 eV). However, from general considerations one may expect that the redox process may take place in the case of organoelement compounds with sufficiently ionic (C—E) bonds where oxidative dimerization is possible at equimolar ratio of reagents [18-21].

2. In the case of organomercury and other organometallic compounds with C—E covalent bonds the mechanism involving transmetallation and subsequent decomposition or oxidation of an unstable Cu^{II} derivative is more likely.

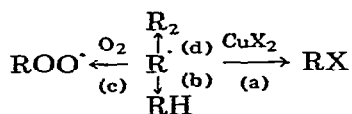$$RHgX(R_2Hg) + CuX_2 \rightarrow [RCuX] + HgX_2 \qquad (3)$$
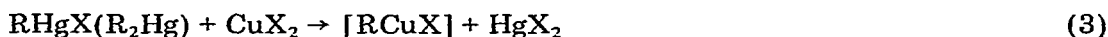
Besides the above considerations the possibility of such a mechanism is substantiated by the fact that the reaction goes instantaneously with aromatic derivatives of mercury, and at a slower rate with benzyl, and especially alkyl derivatives, i.e., the order of reactivity corresponds to that normally observed for the electrophilic substitutions (one may suppose that in this case it is this particular step that is rate-determining). A similar scheme was proposed for the reactions of organozinc [22] and organolead [8] compounds with CuX_2.

Thus, if the first step of the reaction with CuX_2 is transmetallation (eqn. 3), then the organocopper intermediate, being unstable, must obviously decompose with the formation of $R^{\cdot}$ radicals:
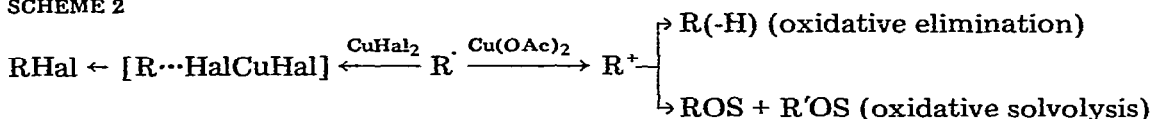
$$[RCuX] \rightarrow R^{\cdot} + CuX \qquad (4)$$

The radical formed may be oxidized by a Cu^{II} salt or by O_2, interact with a solvent or be dimerized depending on its structure, nature of the solvent, anion X in CuX_2, and on the concentration of CuX_2 (Scheme 1).

SCHEME 1

$$ROO^{\cdot} \underset{(c)}{\overset{O_2}{\longleftarrow}} \overset{\overset{\textstyle R_2}{\uparrow (d)}}{\underset{\underset{\textstyle RH}{\downarrow (b)}}{R^{\cdot}}} \overset{CuX_2}{\underset{(a)}{\longrightarrow}} RX$$

However, the ability of Cu^{II} salts to oxidize radicals is well known. In this connection Kochi's studies [10] are of special interest, demonstrating differences in the interaction of $R^{\cdot}$ with $CuHal_2$ (ligand transfer) and $Cu(OAc)_2$ (oxidation) (Scheme 2).

SCHEME 2

$$RHal \leftarrow [R\cdots HalCuHal] \overset{CuHal_2}{\longleftarrow} R^{\cdot} \overset{Cu(OAc)_2}{\longrightarrow} R^+ \Bigg\lbrace \begin{array}{l} R(-H) \text{ (oxidative elimination)} \\ \\ ROS + R'OS \text{ (oxidative solvolysis)} \end{array}$$

The product composition must be determined by reactions 3 and 4 and by the competitive reactions summarized in Scheme 1. The presence of aldehydes and alcohols ($R = XC_6H_4CH_2$, n-Bu) as well as hydrocarbons R_2 and RH [especially RH ($R = PhCOCH_2$, PhCHCOOEt, n-Bu)] in the reaction mixture testifies to the intermediate radical formation (see also ref. 9). Yet, there exists a possibility that organocopper intermediates [RCuX] are oxidized by CuX_2 and oxygen or decompose with the formation of R_2 dimers without the formation of the radical. It is known that the decomposition of Cu^I derivatives to R_2 [23] as well as oxidation of cuprates [24] may occur without the formation of free radicals.
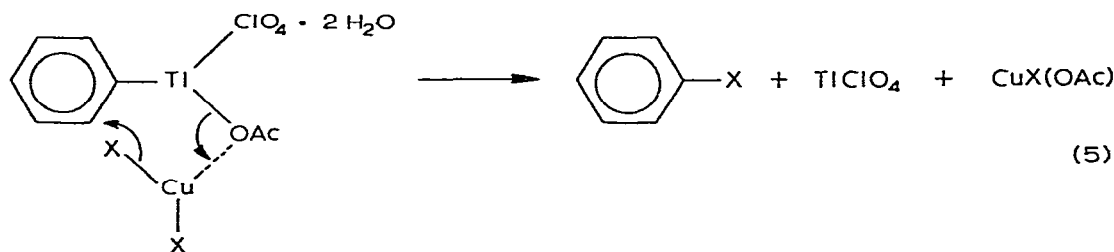
SCHEME 3

$$[RCuX] \quad \overbrace{\begin{array}{l} \xrightarrow{CuX_2} RX \\ \xrightarrow{O_2} ROO^{\cdot} \\ \longrightarrow R{-}R \end{array}}$$
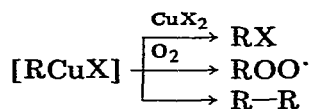
At present it is hardly possible to make an unambiguous choice between the pathways, eqn. 4, Scheme 1 and Scheme 3. It is likely that they are competing reactions one or the other prevailing depending on the $R^{\cdot}$ radical structure. Thus the formation of benzene or diphenyl has not been observed in the reaction of PhHgBr or Ph_2Hg with $CuBr_2$ whatever changes are made in concentrations and reaction conditions. It follows from this fact that no free radicals are formed in the reaction but that the oxidation of [PhCuX] takes place. However, the oxidation of Et_4Pb by Cu^{II} salts in acetic acid gives the same ratio of products as the oxidation of $Et^{\cdot}$ obtained by catalytic decomposition of valeryl peroxide under the same conditions. In both cases a quantitative yield of ethyl chloride is obtained under the action of $CuCl_2$ [8]. According to these authors the results favour the homolysis of [EtCuX] and subsequent oxidation of the radical.

As follows from the above facts, that the composition of products formed in the reactions of organometallic compounds with Cu^{II} salts is also determined by the relation of the rates of the transmetallation step and subsequent decomposition or oxidation of organocopper intermediates. Thus the results of the reactions of phenyl derivatives of mercury with CuX_2 may alternatively be explained by the fact that the oxidation of phenyl radical or [PhCuX] goes at a much faster rate than transmetallation. In the case of organometallic compounds more liable to ionization, to say nothing of ionic organometallic compounds, the reverse is possible which allows oxidation to RH or R_2 when reagents are present in a 1/1 ratio.

3. Another point of view is put forward by Ichikawa et al. [6,7] on the basis of results obtained from the study of the reactions of Tl^{III}—organic derivatives and CuX_2. He supposes the products of two-electron oxidation of RX to be formed via the heterolytic mechanism, i.e. (S_NC) mechanism essentially including the intramolecular two-electron transfer catalysed by a Cu^{II} salt with the reduction of Tl^{III} to Tl^I. What the driving force of such a process is remains unclear. It should be noted that along with RX the products of single-electron

$$\underset{\substack{\\ \text{X} \quad \text{Cu} \quad \text{OAc}}}{\text{Ph—Tl}\overset{ClO_4 \cdot 2 H_2O}{\diagup}} \longrightarrow \text{Ph—X} + TlClO_4 + CuX(OAc) \tag{5}$$

oxidation of ArH and Ar_2 are formed in the reaction with the ratio changing depending on the nature of Ar and anion X of the copper salt.

Thus mechanisms proposed for the reaction of organometallic compounds with copper salts are quite various. Yet the most likely is the mechanism including the transmetallation step, at least for covalent organometallic compounds. In this case the reaction exemplifies the redox process where radicals are partially formed not in the course of the main process but as a result of the homolysis of the organocopper intermediate.

It is known that some organoelement compounds (Li, Mg, Zn, Pb) may enter into the exchange reaction with Cu^I salts yielding organic derivatives of univalent copper [25-27] (eqn. 6). The same reaction seems responsible for RCu

$$RMX_{n-1} + CuX \rightarrow RCu + MX_n \tag{6}$$

in the reactions of RMX_{n-1} with CuX_2 as well [11,22,28]. We have shown that diphenylmercury in DMF at 20°C does not react with cuprous bromide, however, for compounds with electron-acceptor groups (R = PhCHCOOR, PhCOCH$_2$, PhC≡C) such a reaction goes rather readily yielding in the first two cases diphenylsuccinic ether and acetophenone respectively*, and in the case R = PhC≡C giving a phenylacetylenic derivative of Cu^I obtained in complex with Cu_2Br_2 (judging by the results of elementary analysis PhC≡CCuCu$_2$Br$_2$). Cu^I derivatives are probably formed in the case of R = PhCHCOOEt and PhCOCH$_2$ but are unstable and decompose. In the reaction of (PhC≡C)$_2$Hg with Cu_2Br_2 in the presence of bromophenylacetylene a quantitative yield of dimer (PhC≡C)$_2$ is observed. Thus, it is quite probable that under the action of Cu^{II} salts on organomercury compounds with electron-acceptor radicals R the reaction goes not only with CuX_2 but also with univalent copper formed in the course of the reaction. It is not excluded that the formation of dimers in the reaction of organomercury compounds with CuBr$_2$ (R = PhCHCO$_2$C$_2$H$_5$, PhC≡C) is in part explained by the interaction of RCu and RBr.

Oxidation of C—H bonds by CuX_2 salts constitutes a problem of its own. Only compounds containing "acid" hydrogen (i.e. those characterized by relatively low values of pK_A) are known to undergo such an oxidation. In this case a pre-equilibrium step giving rise to a carbanion or perhaps, cryptocarbanion may be assumed [29-31]. An increase in the rate of oxidation of substituted acetylenes in the presence of bases is evidence in favour of this assumption.

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* By GLC analysis unidentified products similar to those obtained in the reaction of these compounds with CuBr$_2$ were detected.

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An alternative mechanism of C—H bond oxidation without preliminary ioniza-
tion includes the formation of a cationic radical (eqn. 7).

$$(\equiv C\!-\!H) \rightarrow (\equiv C\!-\!H)^{\cdot} \rightarrow H^+ + \equiv C^{\cdot} \tag{7}$$

Ketones are rather readily oxidized by copper salts, $CuCl_2$ and $CuBr_2$,
though the yields of corresponding RHal compounds depend on the structure
of the ketone, and more often than not the reaction gives a rather complex mix-
ture of products [32-35]. The enol form is believed to undergo oxidation [36,
37] (eqn. 8). At the same time, if ionization of enols is assumed [32] the ambient

$$R\!-\!\underset{\underset{O}{\|}}{C}CH_2R \xrightarrow{CuX_2} R\!-\!\underset{\underset{OCuX}{|}}{C}\!=\!CHR \xrightarrow{CuX_2} R\underset{\underset{O}{\|}}{C}\overset{\overset{X}{|}}{C}HR + CuX \tag{8}$$

ion should be regarded as oxidized which brings the mechanism of enolizible
ketones oxidation to resemble more that of phenol oxidation [38,39]. It should
be noted, however, that such consideration is rather formal and that in every
particular case the mechanism may be quite complicated.

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