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ORGANOFLUOROSILICATES IN ORGANIC SYNTHESIS. 3. COPPER(II) OXIDATION OF ORGANOPENTAFLUOROSILICATES. SYNTHETIC UTILITY AND MECHANISTIC IMPLICATIONS[1]

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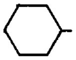
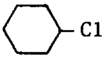
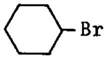
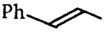
Organopentafluorosilicates, $M_2[RSiF_5]$, have recently been shown to be useful intermediates in the transformation of, particularly, olefins to primary alkyl halides[2] and alcohols.[1] We now find that carbon-silicon bonds in organopentafluorosilicates are easily cleaved by copper(II) chloride and bromide to form the corresponding organic halides in high yields, providing another synthetically useful route to 1-haloalkanes from olefins. This is the first case of the copper(II) cleavage of the silicon-carbon bond involving a ligand transfer from copper to the organic group.[3]

$$RCH{=}CH_2 \quad + \quad HSiCl_3 \longrightarrow RCH_2CH_2SiCl_3 \xrightarrow{KF} K_2[RCH_2CH_2SiF_5] \xrightarrow{CuX_2} \underset{(X\,=\,Cl,\ Br)}{RCH_2CH_2X} \qquad (1)$$

When a mixture of an organopentafluorosilicate and anhydrous copper(II) chloride or bromide was stirred in dry ether at room temperature, the color gradually faded out, possibly indicating the reduction of copper(II) to copper(I).[4] The mixture was filtered and analyzed by GLC, or distilled after washing with water and drying over sodium sulfate. As shown by the representative results summarized in Table I, the chlorine and bromine transfer occurred efficiently to primary alkyl and aryl groups, while with rather low efficiency to secondary alkyl and alkenyl groups. Since alkyl chlorides are not obtained by reactions of organosilicates with N-chlorosuccinimide,[2] the present procedure provides a new route to anti-Markownikoff hydrochlorination of olefins. Yields are greatly dependent upon the nature of solvent as shown in Table I and

Table I. Oxidation Reaction of $K_2[RSiF_5]$ by $Cu(II)X_2$[a]

$K_2[RSiF_5]$	(mmole)	CuX_2	(mmole)	Solvent	Time (h)	Product	Yield[b] (%)
R=n-C_8H_{17}-	1.0	X=Cl	1.0	Et_2O	2	n-$C_8H_{17}Cl$	58
			1.3	Et_2O	2		65
			1.9	Et_2O	2		70[c]
			3.9	Et_2O	1		73[d]
			1.0	THF	2		54
				MeCN	17		56
				MeOH	2		19
				C_6H_6	2		trace
				CCl_4	2		0
	1.0	X=Br	2.0	Et_2O	5	n-$C_8H_{17}Br$	70
	1.0		2.0	THF	20		88
R=$MeO_2C(CH_2)_{10}$-	2.0	X=Cl	4.0	Et_2O	1	$MeO_2C(CH_2)_{10}Cl$	70[e]
R=C_6H_5-	1.0	X=Cl	2.0	THF	14	C_6H_5Cl	75
	1.0	X=Br	1.8	THF	14	C_6H_5Br	79
R= 	1.0	X=Cl	2.0	Et_2O	54		58
	1.0	X=Br	2.0	THF	26		48
R=	1.0	X=Cl	2.0	THF	2		46
	4.5	X=Br	8.4	THF	2		47[e]

[a] Reactions were carried out at room temperature. [b] Yields were determined by GLC and are based on $K_2[RSiF_5]$. [c] n-$C_8H_{17}SiF_3$ was formed as a by-product in about 3% yield. [d] n-$C_8H_{17}SiF_3$ was formed in about 30% yield. [e] Isolated yield.

ether or THF is the most suitable one. The reaction can be accomplished even in the presence of certain functional groups. Other copper(II) salts, acetate, thiocyanate, and triflate, did not undergo similar ligand transfer reactions.

Although the mechanism has not yet been fully clarified, the following observations may be helpful to elucidate it. Copper(II) salt was reduced to copper(I) with no formation of copper metal.[5] In the reaction of the octylsilicate with copper(II) chloride in acetonitrile, the amount of the resulting soluble copper(I) chloride was determined by titration,[6] and was found to be equal to twice the yield of octyl chloride. Thus, the reaction obeys a stoichiometry (eq

2) analogous to that previously reported for the oxidation of other organometallic compounds by copper(II) salts.[7]

$$K_2[RSiF_5] + 2CuX_2 \longrightarrow RX + 2CuX + \{K_2[XSiF_5]\} \qquad (2)$$

It is also noteworthy here that octanal appeared as a by-product.[8] When the reaction was carried out under an atmospheric pressure of oxygen in the presence of copper(II) chloride in methanol, the chlorine transfer was greatly retarded and the oxygenation became the major course of reaction to form, for example, octanal in 30% yield. This is the first example of the metal-assisted oxygenation of an alkyl-silicon bond and the overall reaction corresponds to the conversion of an olefin to a terminal aldehyde.

$$K_2[n\text{-}C_8H_{17}SiF_5] + CuCl_2 + O_2 \xrightarrow{\text{MeOH, r.t.}} \underset{30\%}{n\text{-}C_7H_{15}CHO} + \underset{\text{trace}}{n\text{-}C_8H_{17}Cl} \qquad (3)$$

These results seem to be consistent with a two-step mechanism which involves the formation of an alkyl radical by alkyl transfer or electron transfer from silicate to copper(II) and the subsequent ligand transfer from another molecule of copper(II) halide producing an alkyl halide.[6b,9,10] Under an oxygen atmosphere the radical might be efficiently scavanged to form an alkanal ultimately. Stereochemical and further mechanistic studies in progress may hopefully delineate such a process.

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REFERENCES AND NOTES

1. Part 2. K. Tamao, T. Kakui and M. Kumada, *J. Am. Chem. Soc.*, in press.
2. K. Tamao, J. Yoshida, M. Takahashi, H. Yamamoto, T. Kakui, H. Matsumoto, A. Kurita and M. Kumada, *J. Am. Chem. Soc.*, 100, 290 (1978).

3. Cleavage of the silicon-hydrogen bond by copper(II) chloride producing hydrogen chloride and a chlorosilane is known: (a) R. F. Cunico and E. M. Dexheimer, *Syn. React. Inorg. Metal-org. Chem.*, 4, 23 (1974); (b) H. H. Anderson, *J. Am. Chem. Soc.*, 80, 5083 (1958). The silicon-aryl bond is also known to be cleaved by $CuCl_2$ at elevated temperatures; (c) I. S. Akhrem, R. S. Vartanyan, V. O. Topuzyan and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1387 (1975).
4. When one equivalent of $CuCl_2$ was used in ether, the reaction mixture changed to white completely, but with two equivalents of $CuCl_2$ the color remained brownish due to the unchanged $CuCl_2$.
5. The use of one equivalent of CuX_2 gave an organic halide in higher than 50% yield, possibly owing to reoxidation of Cu(I) to Cu(II) which might again react with the silicate. When the reaction was carried out under a nitrogen atmosphere using one equivalent of CuX_2, the yield was reduced to 50%.
6. (a) J. Knop, *J. Am. Chem. Soc.*, 46, 263 (1924); (b) C. L. Jenkins and J. K. Kochi, *ibid.*, 94, 856 (1972).
7. The oxidation of a variety of organometallic compounds by Cu(II) salts has been reported. E.g., organolead: (a) N. A. Clinton and J. K. Kochi, *J. Organometal. Chem.*, 42, 241 (1972); (b) *ibid.*, 56, 243 (1973); (c) J. K. Kochi, *Acc. Chem. Res.*, 7, 351 (1974). Organomercury: (d) I. P. Beletskaya, T. A. Artamkina and O. A. Reutov, *J. Organometal. Chem.*, 99, 343 (1975). Organoborane: (e) C. F. Lane, *ibid.*, 31, 421 (1971); (f) A. Arase, Y. Masuda and A. Suzuki, *Bull. Chem. Soc. Japan*, 47, 2511 (1974). Stereochemistry of the oxidation of organo-zirconium, mercury, and palladium compounds has been studied: (g) R. A. Budnik and J. K. Kochi, *J. Organometal. Chem.*, 116, C3 (1976).
8. Scavanging of alkyl radicals by molecular oxygen to form aldehydes and alcohols has been reported for the oxidation of organo-platinum and -mercury compounds by a hexachloroiridate(IV). (a) J. Y. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 99, 1450 (1977); (b) J. Y. Chen, H. C. Gardner and J. K. Kochi, *ibid.*, 98, 6150 (1976).
9. The sequence is essentially the same as a mechanism, proposed by Kochi et al. for other organometallic compounds, which involves initial alkyl transfer from an organometallic compound to a Cu(II) salt followed by spontaneous homolysis of a metastable alkylcopper(II) intermediate.[7a,b,c]

   $$\text{R-m} + \text{Cu(II)X}_2 \longrightarrow \text{R-CuX} + \text{m-X} \tag{4}$$

   $$\text{R-Cu-X} \longrightarrow \text{R}\cdot + \text{Cu(I)X} \tag{5}$$

   Ligand transfer from copper(II) salts to alkyl radicals has also been extensively studied by Kochi el al.[10]

   $$\text{R}\cdot + \text{Cu(II)X}_2 \longrightarrow \text{RX} + \text{Cu(I)X} \tag{6}$$

10. C. L. Jenkins and J. K. Kochi, *J. Org. Chem.*, 36, 3095, 3103 (1971); *J. Am. Chem. Soc.*, 94, 843 (1972).