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THE CUPROUS CHLORIDE CATALYZED ADDITION OF HALOGEN COMPOUNDS TO OLEFINS UNDER PHOTO-IRRADIATION

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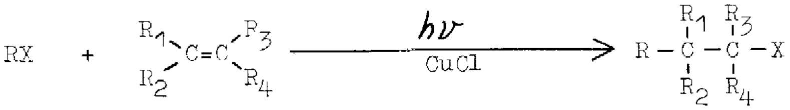
Summary: The addition of organic halogen compounds to olefins in the presence of cuprous chloride under U.V. irradiation gave 1:1 adducts.

Some transition metal salts or complexes such as Cu(I), Fe(II), Ru(II), as well as $Co_2(CO)_8$ and $Mo_2(CO)_{10}$ have been known to be effective catalysts in addition of polyhalogen compounds to olefins.[1] Unfortunately, the reactions are limited to rather strongly activated halogen compounds (or those having relatively weak halogen-carbon bonds) such as CCl_4, $CHCl_3$, $CHCl_2CN$ etc. A notable exception is the addition of dichloromethane catalyzed by $NiCl_2(PPh_3)_2$, although the yields of 1:1 adducts are low.[2]

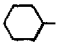
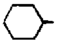
In this paper we report a new methodology for the addition of organic halides to olefins. We used cuprous chloride in combination with U.V. irradiation so that the reducing ability of the copper salt could be enhanced. By employing this new system, the addition of unactivated halogen compounds such as dichloromethane and even bromobenzene to olefins has been realized. The results are listed in the Table[3] and the reaction conditions are given in the footnote of the Table.



$$RX + \begin{matrix} R_1 & & R_3 \\ & C=C & \\ R_2 & & R_4 \end{matrix} \xrightarrow[CuCl]{h\nu} R-\overset{R_1}{\underset{R_2}{C}}-\overset{R_3}{\underset{R_4}{C}}-X$$

Thus, chloroform reacted with acrylonitrile in the presence of a catalytic amount of cuprous chloride under U.V. irradiation for 30 hr using

Table. Photo-assisted addition of halogen compounds to olefins[a]

Run	Halogen compound	Olefin	PTC[b] and(or) solvent[c]	Adduct	Yield[d] (%)
1	$CHCl_3$	acrylonitrile		$CHCl_2CH_2CHClCN$ **1**	75
2	$CHCl_3$	acrylonitrile	TBAB	**1**	91
3	CH_2Cl_2	acrylonitrile	TBAB	$CH_2ClCH_2CHClCN$ **2**	90
4	CH_2Cl_2	acrylonitrile	TEBAC	**2**	31
5	CH_2Cl_2	acrylonitrile	TPBPB	**2**	15
6	CH_2Cl_2	ethyl acrylate	TBAB	$CH_2ClCH_2CHClCOOEt$ **3**	93
7	PhBr	acrylonitrile	TBAB	$PhCH_2CHBrCN$ **4**	43
8	PhBr	acrylonitrile	THF/TBAB	**4**	23
9	PhBr	acrylonitrile	DGDM/TBAB	**4**	47
10	PhBr	acrylonitrile	DMSO	**4**	60
11	PhBr	ethyl acrylate	DMSO	$PhCH_2CHBrCOOEt$ **5**	77
12[e]	PhBr	diethyl fumarate	DMSO	$EtOOCCH(Ph)CHBrCOOEt$ **6**	75
13[e]	PhBr	ethyl crotonate	DMSO	$CH_3CH(Ph)CHBrCOOEt$ **7**	40
14	$CH_3(CH_2)_3Br$	acrylonitrile	DMSO	$CH_3(CH_2)_4CHBrCN$ **8**	20
15	 Br	ethyl acrylate	DMSO	 $CH_2CHBrCOOEt$ **9**	15
16[f]	PhBr	acrylonitrile	DMSO	**4**	94[g,h]
17[f]	PhBr	styrene	DMSO	$PhCH_2CHBrPh$ **10**	95[g,i]

[a] U.V. source; low-pressure Hg lamp, reaction time; 30 hr, CuCl (0.1 mmol) and an olefin (3 mmol). Run 1-7; a halogen compound (20 ml), run 8-17; a solvent (20 ml) and a halogen compound (9 mmol). [b] PTC:CuCl=4:1 (molar ratio). [c] Abbreviation; TBAB=$(n\text{-}Bu)_4N^+\cdot Br^-$, TEBAC=$PhCH_2N^+Et_3\cdot Cl^-$, TPBPB=$PhCH_2P^+Ph_3\cdot Br^-$ and DGDM=$(MeOCH_2CH_2)_2O$. [d] Based on charged olefins and determined by GLC. [e] Reaction time; 40 hr. [f] t-Butylcatechol (0.2 mmol) was added. [g] Based on consumed olefins. [h] Consumption of olefin; 52%. [i] Consumption of olefin; 38%.

chloroform itself as a solvent to give the 1:1 adduct (**1**) in 75% yield (Table run 1). The photochemical reaction of dichloromethane or bromobenzene in the presence of olefins and cuprous chloride gave only the telomers of the olefins. The failure of the photo-assisted addition reaction of these di- and mono-halogen compounds to olefins may be due to the poor solubility of cuprous chloride in these halogen compounds. We have overcome the solubility problem of the catalyst by using phase transfer catalysts (PTC).[4] We found that dichloromethane or bromobenzene reacted with olefins in the presence of cuprous chloride solubilized by PTC under U.V. irradiation to give 1:1 adducts. The organic halides were used in large excess in order to avoid telomerization of olefins in these reactions (Table runs 1-7). The possibility of addition reactions in other solvents was also investigated, and DMSO was found to be a good solvent for copper(I) catalyzed photo-assisted addition reactions. Besides the formation of 1:1 adducts with the halogen compounds, olefins were consumed in competing telomerization reactions (for example, Table run 10). When the photo-reaction was carried out in the presence of a radical inhibitor (e.g. t-butylcatechol) to suppress telomerization reactions, the olefins were consumed almost completely in 1:1 addition reactions (Table runs 16 and 17). An unactivated olefin gave a different product. For example, 1-octene reacted photochemically with chloroform in the presence of cuprous chloride to give a product (**11**) in 55% yield.

$$CHCl_3 \quad + \quad CH_3(CH_2)_5CH{=}CH_2 \xrightarrow[CuCl]{h\nu} CHCl_2(CH_2)_7CH_3 \qquad \mathbf{11}$$

Concerning the reaction mechanism, two possible pathways were considered; (1) a free radical chain pathway and (2) a photo-redox pathway. The former mechanism, however, seems unlikely because our addition products were not produced in the radical-induced reaction systems.

$$CHCl_3 \quad + \quad CH_2{=}CH\text{-}CN \quad \overset{h\nu}{\underset{Br_2}{\not\xrightarrow{\qquad\qquad}}} \quad \mathbf{1}$$

$$PhBr \quad + \quad CH_2{=}CH\text{-}CN \quad + \quad BPO \quad \overset{\Delta}{\not\xrightarrow{\qquad}} \quad \mathbf{4}$$

Thus, we prefer the photo-redox pathway to explain the photo-addition reactions

It is not certain which substrate cuprous chloride initially reduces photochemically, an olefin or a halogen compound. We prefer the pathway in which the halogen compound is initially reduced photochemically by cuprous chloride.[5] A mechanism in which the species derived from reduction of the olefin selectively abstracts halogen rather than hydrogen seems to be less plausible.

References and Notes

(1) M. Asscher and D. Vofsi, J. Chem. Soc., 1887 (1963); 3921 (1963); S. Murai and S. Tsutsumi, J. Org. Chem., 31, 3000 (1966); D. J. Burton and L. J. Kehoe, Tetrahedron Lett., 5163 (1966); J. Org. Chem., 35, 1339 (1970); 36, 2596 (1971); T. Susuki and J. Tsuji, Tetrahedron Lett., 913 (1968); J. Org. Chem., 35, 2982 (1970); Y. Mori and J. Tsuji, Tetrahedron, 28, 29 (1972); H. Matsumoto, T. Nikaido and Y. Nagai, J. Org. Chem., 41, 396 (1976); B. Boutevin and E. B. Dongala, Tetrahedron Lett., 4315 (1977).

(2) Y. Inoue, S. Ohno and H. Hashimoto, Chemstry Lett., 367 (1978).

(3) All products gave satisfactory spectral data (NMR, IR, MS). NMR data; (CCl_4) δ, **1**, 5.88(t, 1H), 4.68(t, 1H), 2.95(t, 2H), **2**, 4.68(t, 1H), 3.70 (t, 2H), 2.48(q, 2H), **3**, 4.45(t, 1H), 4.20(q, 2H), 3.68(t, 2H), 2.60-2.25 (m, 2H), 1.35(t, 3H), **4**, 7.45(s, 5H), 4.35(t, 1H), 3.38(d, 2H), **5**, 7.35 (s, 5H), 4.30(t, 1H), 4.15(q, 2H), 3.32(t, 2H), 1.20(t, 3H), **6**, 7.45(s, 5H), 4.85-3.78(m, 6H), 1.45-0.85(m, 6H), **7**, 7.35(s, 5H), 4.40-4.00(m,3H), 3.65-3.15(m, 1H), 1.50-1.08(m, 6H), **8**, 4.25(t, 1H), 2.15-1.15(m, 8H), 0.90 (t, 3H), **9**, 4.42-4.08(m, 3H), 2.10-1.50(m, 13H), 1.30(t, 3H), **10**, 7.40(s, 5H), 7.30(s, 5H), 5.00(t, 1H), 3.48(d, 2H).

(4) Phase transfer catalysts (PTC) such as ammonium or phosphonium salts have been known to solubilize cuprous chloride in the halogen compounds: O. J. Muscio Jr., Y. M. Yun and J. B. Philip Jr., Tetrahedron Lett., 2379 (1978).

(5) It is already suggested that the copper(I) catalyzed addition of polyhaloalkanes to olefins may be initiated by one-electron reduction of the formers by copper(I). See ref 1.

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