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REACTIONS OF ORGANOALUMINUMS WITH COPPER(II) HALIDES. A CONVENIENT ROUTE TO ALKYL HALIDES FROM OLEFINS VIA HYDROALUMINATION

Fumie SATO, Yoshikuni MORI, and Masao SATO
Department of Chemical Engineering, Tokyo Institute of Technology,
Meguro, Tokyo 152

The reaction of lithium tetraalkylaluminums with copper(II) chloride or bromide gives the corresponding alkyl halides in good yield. The facile reaction offers a convenient method for the preparation of 1-haloalkanes or 1-haloalkenes from 1-alkenes or nonconjugated diolefins, respectively.

The facile addition of the aluminum hydrogen bond to olefinic double bonds in the presence of titanium tetrachloride makes organoaluminums as readily available as the corresponding organoboranes and renews interest in the organoaluminums as intermediates in organic syntheses.[1,2,3] In our continued efforts to apply these new hydroalumination reactions in organic syntheses, we have now found that hydroalumination of olefins followed by treatment with copper(II) chloride or copper(II) bromide affords the corresponding 1-haloalkanes in excellent yields as shown in the following general equation.[4,5]

$$\begin{tikzcd} \mathrm{LiAlH_4} + 4\ \mathrm{RCH{=}CH_2} \arrow[d, "\mathrm{TiCl_4}"] & \\ \mathrm{LiAl(CH_2CH_2R)_4} + 8\ \mathrm{CuX_2} \arrow[r] & 4\ \mathrm{RCH_2CH_2X} + 4\ \mathrm{Cu_2X_2} + \mathrm{LiX} + \mathrm{AlX_3} \end{tikzcd}$$

The following procedure for the preparation of 2-(4-cyclohexenyl)ethyl chloride is representative: After reaction of 4-vinyl-1-cyclohexene (3.53 g, 32.7 mmol) and $LiAlH_4$ (25 ml of 0.36 molar solution in THF, 9.0 mmol) in the presence of $TiCl_4$ (0.05 g, 0.27 mmol) for three hours at room temperature, the reaction mixture was cooled to -78°C and $CuCl_2$ (10.5 g, 78.1 mmol) was added. The mixture was gradually brought to room temperature over about two hours, diluted with addition of ether (10 ml), and then washed with 10 ml of dilute hydrochloric acid. GLC analysis indicated the presence of 2-(4-cyclohexenyl)ethyl bromide in 73% yield based on the olefin. By similar method, various halides were prepared in good yields as shown in the table.

Although hydroalumination of 1-olefins followed by treatment with Cl_2, Br_2 and I_2, or selective monohydroalumination of nonconjugated diolefins followed by treatment with N-chlorosuccinimide, N-bromosuccinimide or I_2 has been shown to provide valuable and useful synthetic procedures to 1-haloalkanes and 1-haloalkenes,[1] the present reaction is an attractive alternative, especially for the preparation of

1-haloalkenes from nonconjugated diolefins, because copper(II) halides are inexpensive and more readily available than N-halosuccinimides.

Table. Yields of alkylhalides

Olefin	Copper(II) halide	Product[a] (Yield,[b] %)
1-Hexene	$CuCl_2$	1-Chlorohexane (79)
	$CuBr_2$	1-Bromohexane (84)
1,4-Hexadiene	$CuCl_2$	6-Chloro-2-hexene (70)
	$CuBr_2$	6-Bromo-2-hexene (62)
2-Methyl-1,5-hexadiene	$CuCl_2$	6-Chloro-2-methyl-1-hexene (67)
	$CuBr_2$	6-Bromo-2-methyl-1-hexene (71)
4-Vinyl-1-cyclohexene	$CuCl_2$	2-(4-Cyclohexenyl)ethyl chloride (73)
	$CuBr_2$	2-(4-Cyclohexenyl)ethyl bromide (55)

[a] Identified by GLC and ^1H NMR. [b] By GLC analysis based on the olefin used.

No mechanistic investigation has been carried out for these reactions. However, it is assumed that the reaction involves two separate steps. The first step is believed to involve the formation of an alkyl radical either via direct electron-transfer oxidation of a carbon-aluminum bond by copper(II) halide or via homolytic decomposition of the alkylcopper intermediate produced by reaction of the alkylaluminum with copper(II) halide. This alkyl radical then reacts with a second equivalent of copper(II) halide by a ligand-transfer process, as it has been established that copper(II) halides are very effective ligand transfer oxidizing agents.[6)]

References and notes

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