Tetrahedron Letters Vol. 21, pp 4105 - 4108 0040-4039/80/1015-4105$02.00/0

SOLVOLYTIC CLEAVAGE OF ALKENYLPENTAFLUOROSILICATES CATALYZED BY COPPER(II) ACETATE. A STEREOSELECTIVE SYNTHESIS OF (*E*)-ALKENYL ETHERS FROM ALKYNES[1]

Kohei Tamao, Toshio Kakui, and Makoto Kumada*

Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

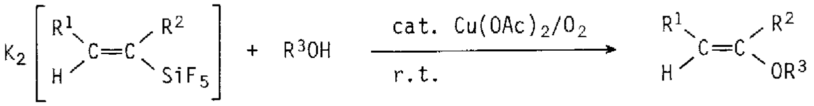
Summary: (*E*)-Alkenylpentafluorosilicates, obtainable from acetylenes via hydrosilylation-silicate formation, react with alcohols in the presence of a catalytic amount of copper(II) acetate under an atmosphere of air (oxygen) at room temperature to form (*E*)-alkenyl ethers stereoselectively in satisfactory yields. Similar reaction with water gives aldehydes.

We describe here a new efficient regio- and stereoselective transformation of acetylenes to (*E*)-alkenyl ethers.

(R^2 = H or R^1)

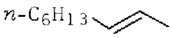
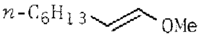
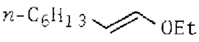
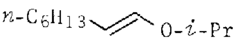
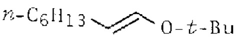
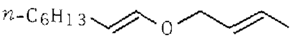
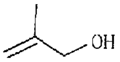
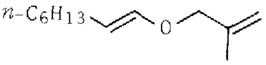
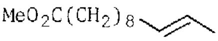
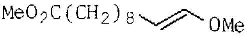
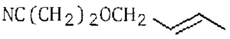
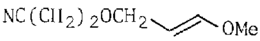
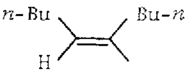
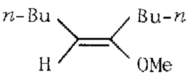
While alkenyl ethers have been prepared mainly from the corresponding carbonyl compounds, there have also been a few methods for their preparation from acetylenes.[2] They involve solvomercuration-demercuration of terminal acetylenes producing 2-alkoxy-1-alkenes,[2c] addition of alcohols to certain electron-withdrawing group substituted acetylenes,[2b] and acidic solvolysis of α,β-epoxysilanes,[2a,3] the last being probably the most general method so far developed.

We find that isomerically pure (*E*)-alkenyl ethers are obtained from (*E*)-alkenylpentafluorosilicates by treatment with a catalytic amount of copper(II) acetate in alcohol under an oxygen atmosphere. The starting silicates are readily obtained from acetylenes via hydrosilylation.



The simplicity of the reaction is demonstrated by the following typical procedure. A mixture of $K_2[MeO_2C(CH_2)_8CH{=}CHSiF_5]$ (1.19 g; 3.0 mmol), anhydrous copper(II) acetate (138 mg; 0.75 mmol), and dry methanol (10 mL) was stirred at room temperature (around 25°C) for 21 h under air to maintain the color of the mixture blue throughout the reaction. Ether was added and the mixture filtered. The filtrate was washed with water (once) and 10% brine (twice), and dried over magnesium sulfate. After evaporation of the solvent the residue was subjected to column chromatography (silica gel, eluent: pentane/benzene (1 : 1)) to give, along with the protonoly-

Table 1. Alcoholysis of $K_2[RSiF_5]$ Catalyzed by $Cu(OAc)_2$[a]

R in $K_2[RSiF_5]$	Alcohol	Product	Yield (%)[b]
	MeOH		56 (66)
	EtOH		(64)[c]
	i-PrOH		(23)[c]
	t-BuOH		(0)[c]
			50 (62)
			55
			31
	MeOH		51 (55)
	MeOH		67[e]
	MeOH		55
	MeOH		52[f]

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[a] Unless otherwise noted, a mixture of $K_2[RSiF_5]$ (3 mmol), dry alcohol (10 mL), and $Cu(OAc)_2$ (0.75 mmol, 25 mol%) was stirred at room temperature for 21 h under air to maintain the blue color of the reaction mixture. [b] Isolated yield based on the silicate (column chromatography, silica gel, pentane or pentane/benzene). GLC yields are given in parentheses. [c] As by-products, *n*-$C_6H_{13}CH{=}CHOAc$ (2-8%) and octanal (2-23%) were formed. [d] In these reactions, 5 mL of alcohol was used. [e] As a by-product, $MeO_2C(CH_2)_8CH{=}CH_2$ was isolated in 16% yield. [f] Isolated by distillation. GLC purification caused partial *cis/trans* isomerization of the product.

sis by-product $MeO_2C(CH_2)_8CH{=}CH_2$ in 16% yield, (*E*)-$MeO_2C(CH_2)_8CH{=}CHOMe$ (454 mg; 67% yield): n_D^{20} 1.4509; ^1H NMR (100 MHz, CCl_4, Me_4Si) δ 1.38 (br. s, 10H), 1.4-1.7 (m, 2H), 1.7-2.0 (m, 2H), 2.20 (t, *J* = 7 Hz, 2H), 3.42 (s, 3H), 3.59 (s, 3H), 4.56 (d, t, *J* = 13 Hz and 7 Hz, 1H), 6.17 (br. d, *J* = 13 Hz, 1H) ppm; IR (neat) 1744, 1675, 1657, 1207, 1173, 1130, 935 cm^{-1}.

Representative results obtained under similar conditions are summarized in Table 1.

Several points deserve comments. (1) The transformation is highly stereoselective and gives (*E*)-alkenyl ethers in isomeric purities over 99%. (2) The reaction is sensitive to the steric bulkiness of alcohol. The yields of alkenyl ethers decrease in the order MeOH > EtOH > *i*-PrOH ≫ *t*-BuOH, with *t*-BuOH no alkenyl ether being fromed. (3) Allylic alcohols gave allyl alkenyl ethers, useful synthetic intermediates which undergo the Claisen rearrangement.[4] (4) Some functional groups such as ester and cyano groups are compatible with the present reaction. (5) An internal alkenyl ether is also prepared with comparable efficiency.

The present reaction is quite different from other copper(II)-cleavage reactions of alkenyl-silicates in that while copper(II) chloride,[5] bromide,[5] and thiocyanate[6] yield the ligand transfer products, copper(II) acetate induces a solvolytic cleavage of the carbon-silicon bond. Although the mechanism of the present novel solvolytic cleavage has not yet been fully clarified, several points should be mentioned. (1) If the reaction is carried out under an inert gas atmosphere copper(II) acetate is reduced to a copper(I) species. The stoichiometry could not be determined, but the formation of a Cu(I) species was confirmed by titration.[7] Under an oxygen atmosphere the resulting Cu(I) is oxidized to regenerate a copper(II) salt, making the reaction to proceed catalytically with respect to copper(II) acetate. (2) Since no alkenyl ether was formed when a mixture of alkenyl acetate, copper(II) acetate and methanol was stirred under similar conditions, the observed alkenyl ether is considered to be the direct reaction product, not via the ligand transfer product. (3) Reaction with CH_3OD gave no deuterium-incorporated product. The result may rule out, at the least, the mechanism involving the trans addition of alcohol-anti elimination of a silicon hydride species.

In the light of these observations, coupled with our previous mechanistic studies on the copper(II)-oxidation of organosilicates[5,8] and Kochi's works of the oxidative solvolysis of alkyl radicals by copper(II) salts,[7,9] the present reaction may be visualized by the following

$$\begin{array}{l}
RSiF_5^{2-} + Cu(OAc)_2 \longrightarrow RSiF_5^{-\bullet} + Cu(OAc) + OAc^- \\
RSiF_5^{-\bullet} + Cu(OAc)_2 \longrightarrow RCu(OAc)_2 + SiF_5^- \\
RCu(OAc)_2 + R'OH \longrightarrow ROR' + Cu(OAc) + AcOH \\
\hline
RSiF_5^{2-} + R'OH + 2Cu(OAc)_2 \longrightarrow ROR' + 2Cu(OAc) + AcOH + SiF_5(OAc)^{2-}
\end{array}$$

mechanism. Thus, the reaction may proceed through one-electron transfer from silicate to copper(II) species, followed by transfer of the organic group from silicon to copper forming an organocopper(III) species from which may be formed the observed solvolytic product together with the copper(I) species. Since the reaction is highly stereoselective, no free radical cannot be involved. The present oxidative solvolysis is observed only with alkenyl-silicates, but not with alkyl-silicates. Therefore, there may be an important interaction between the alkenyl group and a copper species throughout the reaction.

Oxidative-hydrolysis of alkenylsilicates has also been observed. Thus, in the presence of a catalytic amount of copper(II) acetate (25 mol%) an alkenyl-silicate reacted with water (100 μL) under an air atmosphere in acetonitrile (5 mL) at room temperature in 2 days to give an aldehyde in 50-52% yield. The reaction may apparently proceed through the formation of an enol

$$K_2[RCH{=}CHSiF_5] \quad + \quad H_2O \quad \xrightarrow[CH_3CN]{Cu(OAc)_2} \quad RCH_2CHO$$

$$(R = C_6H_{13} \text{ or } MeO_2C(CH_2)_8)$$

Acknowledgment We thank the Ministry of Education for the Grant-in-Aid for Scientific Research (No. 303523) and Shin-etsu Chemical Co., Ltd. for support of the work.

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(Received in Japan 21 July 1980)