

SOLID STATE REACTIONS OF ORGANOPENTAFLUOROSILICATES WITH COPPER(I) AND COPPER(II) SALTS¹

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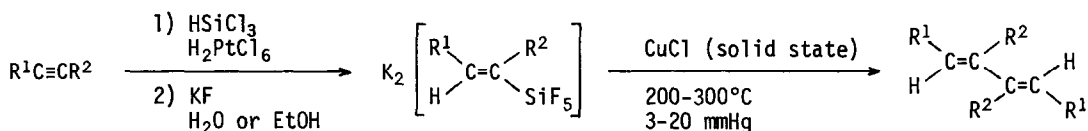
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Summary: Two types of solid state reaction of $K_2[RSiF_5]$ have been developed: (1) CuCl promoted homo coupling of alkenyl- and phenyl-silicates, and (2) formation of RH from alkyl- and alkenyl-silicates by heating with $CuF_2 \cdot 2H_2O$.

Recently we have shown that organopentafluorosilicates react with various electrophiles such as halogens,² NBS,² MCPBA,³ CuX_2 ,⁴ PdX_2 ,^{5,6} and AgX .⁷ These reactions all proceed apparently heterogeneously, since dipotassium organopentafluorosilicates are virtually insoluble in common organic solvents, and this property constitutes one of the advantages of the reactions of silicates in that the organic products can easily be separated by simple filtration. Possibly these reactions may take place at the solid surface of the silicate. Therefore it seems to be quite interesting to investigate the solid state reactions of silicates, which may not only be useful in organic synthesis but also contribute to the study of solid state organic chemistry.⁸







We have now found two types of solid state reaction of organopentafluorosilicates: (1) copper(I) promoted homo coupling of alkenylsilicates and (2) "protonolysis" of alkyl- and alkenyl-silicates by heating with copper(II) fluoride dihydrate.

Reactions with copper(I) chloride: (*E*)-Alkenylpentafluorosilicates were heated with copper(I) chloride^{9,10} under reduced pressure to give symmetrical (*E,E*)-1,3-dienes.¹¹ The isomeric purity of the (*E,E*)-isomer is higher than 92%, but the products were contaminated with substantial amounts of dialkenyldifluorosilanes¹² in some cases. Representative results are summarized in Table I.



A typical procedure is as follows. In the bottom bulb of a bulb-to-bulb distillation apparatus was placed a finely powdered mixture of (*E*)-1-octenylpentafluorosilicate (312 mg; 1.0 mmol) and copper(I) chloride (99 mg; 1.0 mmol). The apparatus was evacuated to 3 mmHg and the bottom bulb was heated at 250°C. A colorless liquid (71 mg) came out during 1 h from the solid mixture which turned to dark brown in the course of the reaction. GLC analysis of the product showed that (*E,E*)-7,9-hexadecadiene was formed in 56% yield (*E,E* 95%), together with ca. 8% yield of dioctenyldifluorosilane. The diene could be purified by passing through basic alumina (eluent: pentane) (35% yield).

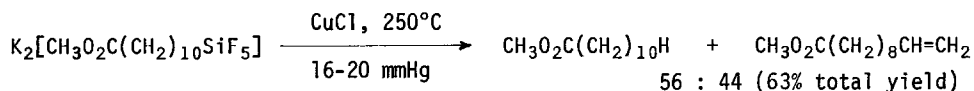
Table I. Solid State Reaction of Alkenyl- and Phenyl-pentafluorosilicates with CuCl to Give Homo Coupling Products.^a

R in K ₂ [RSiF ₅]	Temp. (°C)	Pressure (mmHg)	Yield (%) of R-R ^b	(E,E %) ^c
<i>n</i> -C ₄ H ₉ 	200	20	30 (46) ^d	(96)
<i>n</i> -C ₆ H ₁₃ 	250	3	35 (56) ^e	(95)
CH ₃ OCH ₂ 	250	20	(65) ^f	(97)
C ₆ H ₅ 	300	3	64 ^g	(>99)
<i>n</i> -C ₄ H ₉  <i>n</i> -C ₄ H ₉	200	3	43 ^g	(92)
C ₆ H ₅ - 	300	20	53 ^g	

^a Carried out on a 1-mmol scale as described in the text. ^b Isolated yield. GLC yields are given in parentheses. ^c Determined by GLC. ^d R₂SiF₂ 15%. ^e R₂SiF₂ 8%. ^f R₂SiF₂ 5%. ^g Purity is higher than 99%.




Since the inorganic solid residue could not be fully characterized,¹³ the mechanism is not clear yet, but, speculatively, the present reaction might proceed through the intermediacy of an alkenylcopper species which thermally decomposes to give the diene product, being analogous to the copper-promoted homo coupling reactions of other alkenylmetallics.¹⁵ Thus the initial step must involve the transfer of an alkenyl group from silicon to copper. The high degree of retention of configuration must exclude a free radical mechanism.

While the phenylsilicate also gave a coupling product, biphenyl, similar solid state reaction of *alkyl*silicates with copper(I) chloride gave an almost 1 : 1 mixture of alkane, the protonolysis product, and 1-alkene, the β-elimination product, rather than the homo coupling product. This observation also seems to be compatible with the mechanism involving an alkyl-copper intermediate which undergoes disproportionation reaction.^{15a} *E.g.*

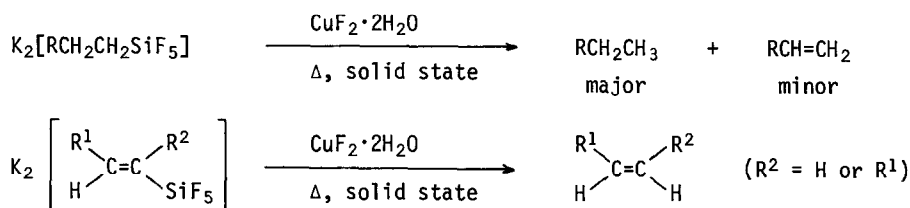


Reactions with copper(II) fluoride dihydrate: In contrast to the copper(I) salts, copper(II) salts, especially copper(II) fluoride dihydrate, gave almost exclusively "protonolysis products" both from alkyl- and alkenyl-silicates¹⁶ (Table II). While the action of protic acids on alkyl-pentafluorosilicates causes dissociation of the ate complex giving alkyltrifluorosilanes rather than protonolysis of the carbon-silicon bond, the present reaction provides a convenient route to the protonolysis products from organosilicates.

Table II. Solid State Reaction of Alkyl- and Alkenyl-pentafluorosilicates with Copper(II) Salts to Give "Protonolysis Products"^a

R in K ₂ [RSiF ₅]	CuX ₂ (equiv.)	Yield (%) ^b	RH/R(-H) ^c
<i>n</i> -C ₁₂ H ₂₅ -	none	3	79/21
	CuF ₂ ·2H ₂ O (1.00)	85	95/5
<i>n</i> -C ₁₈ H ₃₇ -	CuF ₂ ·2H ₂ O (0.50)	69	92/8
	CuF ₂ ·2H ₂ O (1.00)	94	86/14
CH ₃ O ₂ C(CH ₂) ₁₀ -	CuF ₂ ·2H ₂ O (0.25)	50	99.7/0.3
	CuF ₂ ·2H ₂ O (0.50)	75	99.8/0.2
	CuF ₂ ·2H ₂ O (0.75)	79	99.8/0.2
	CuF ₂ ·2H ₂ O (1.00)	76	99.8/0.2
	CuF ₂ ·2H ₂ O (1.50)	66	99.6/0.4
<i>n</i> -C ₁₆ H ₃₃ 	none	49	<i>d</i>
	CuF ₂ ·2H ₂ O (1.00)	90	<i>d</i>
	CuCl ₂ ·2H ₂ O (1.00)	66	<i>d</i>
	CuCl ₂ · <i>n</i> D ₂ O (ca. 1.0)	71 ^e	<i>d</i>
CH ₃ O ₂ C(CH ₂) ₈ 	CuF ₂ ·2H ₂ O (1.00)	74	<i>d</i>
<i>n</i> -C ₆ H ₁₃  <i>n</i> -C ₆ H ₁₃	CuF ₂ ·2H ₂ O (1.00)	78	<i>d</i>

^a A solid mixture of a silicate and CuX₂·*n*H₂O was heated at 250°C under reduced pressure (16-20 mmHg) for 1-2 h. ^b Isolated yield. ^c R(-H) stands for 1-alkenes from alkyl-silicates. Ratios were determined by GLC. ^d Only alkenes were formed. ^e Deuterium content 24% based on NMR and MS spectral data.



The following points should be noted. (1) A half equivalent of copper(II) salt seems to be enough for the protonolysis. (2) Reaction with copper(II) chloride containing D₂O instead of H₂O formed a deuterium incorporated product, the D-content being rather low (24%). (3) In the case of alkenylsilicates, the protonolysis occurred stereoselectively with retention of configuration as shown by the formation of (*Z*)-7-tetradecene.

Although the mechanism has not yet been clarified, it may be envisaged that the organo-copper(II) intermediate is hydrolyzed by water possibly contained in the copper salt and/or in the silicates.

While the elucidation of the mechanism of solid state reactions is quite difficult, the present development, from a synthetic point of view, may open a new field of solventless organic synthesis.¹⁸

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7. K. Tamao, H. Matsumoto, T. Kakui, and M. Kumada, *Tetrahedron Lett.*, submitted for publication.
8. For a pertinent review, see M. D. Cohen and B. S. Green, *Chem. Brit.*, 9 (1973).
9. While the homo coupling occurred most efficiently with CuCl, the yield of the coupling product was very low with CuBr (*e.g.*, 20% yield of 5,7-dodecadiene), and CuI did not induce the similar coupling reaction at all.
10. Mueller and his coworkers have reported that butadiene and perfluorobutadiene are formed by the action of AgNO₃ or CuSO₄ on the corresponding vinyl- and perfluorovinylpentafluorosilicates in water: R. Mueller, M. Dressler, and C. Dathe, *J. Prakt. Chem.*, **312**, 150 (1970).
11. For other methods for the preparation of symmetrical 1,3-dienes, see ref. 7 and references cited therein.
12. Tentatively characterized by IR, ¹H NMR, and MS spectral data. Such compounds may be formed by disproportionation between certain dissociated penta- or tetra-coordinate organofluoro-silicon species at high temperatures, but the mechanism is not clear.
13. IR analysis of the solid residue showed only characteristic bands of the hexafluorosilicate.¹⁴ Products arising from the copper salt could not be characterized.
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15. (a) Alkenyllithium: G. M. Whitesides and C. P. Casey, *J. Am. Chem. Soc.*, **88**, 4541 (1966); (b) alkenylmagnesium halide: T. Kaufmann, and W. Sahm, *Angew. Chem., Int. Ed. Engl.*, **6**, 85 (1967); (c) alkenylalane: G. Zweifel and R. L. Miller, *J. Am. Chem. Soc.*, **92**, 6678 (1970); (d) alkenylborane: Y. Yamamoto, H. Yatagai, K. Maruyama, A. Sonoda, and S. Murahashi, *ibid.*, **99**, 5652 (1977); (e) alkenylzirconium: M. Yoshifuji, M. J. Loots, and J. Schwartz, *Tetrahedron Lett.*, 1303 (1977).
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17. The stoichiometry might be represented by the following equation, but this is only speculation at the present time.

$$2 \text{RSiF}_5^{2-} + \text{CuF}_2 + \text{H}_2\text{O} \longrightarrow 2 \text{RH} + \text{CuO} + 2 \text{SiF}_5^{2-}$$
18. We thank the Grant-in-Aid for Scientific Research of the Ministry of Education (No. 303523), the Yamada Science Foundation, and Shin-etsu Chemical Co., Ltd. for support of the work.