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(*E*)-ALKENYL THIOCYANATES FROM (*E*)-ALKENYLPENTAFLUOROSILICATES BY THE OXIDATIVE CLEAVAGE WITH COPPER(II) THIOCYANATE[1]

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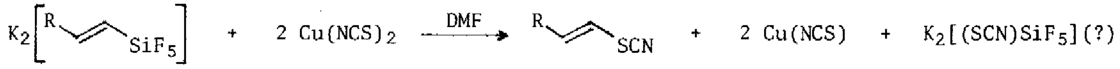
Summary: (*E*)-Alkenylpentafluorosilicates react with copper(II) thiocyanate in DMF at ambient temperature to give (*E*)-alkenyl thiocyanates stereoselectively in high yields.

As part of our current interest in the application of organopentafluorosilicates in organic synthesis,[2] we have recently reported that organopentafluorosilicates react with copper(II) chloride and bromide to give the corresponding organic halides.[3] We have now found that the thiocyanate group also transfers from copper(II) thiocyanate to alkenyl and phenyl groups in organopentafluorosilicates.



This reaction has opened up a simple and general method for the preparation of (*E*)-alkenyl thiocyanates. While there have been many methods for the preparation of alkyl and allyl thiocyanates, only a few methods have been developed for the preparation of alkenyl derivatives, in spite of their expectative versatility in synthetic organic chemistry.[4]

The nature of solvent influenced the yield of product. For example, the yield of (*E*)-1-octenyl thiocyanate in the reaction of (*E*)-1-octenylsilicate with two equiv. of $Cu(NCS)_2$[5] was 33% in benzene, 40-45% in EtOH, MeCN or ether, 51% in acetone, and 59% in DMF. The use of three equiv. of $Cu(NCS)_2$ improved the yield up to 74% in DMF. The silicate reacted also with a mixture of KSCN and $CuSO_4 \cdot 5H_2O$ (2:1) which should form $Cu(NCS)_2$ *in situ*, but the yield was not so high (60%). The addition of an excess of KSCN markedly decreased the yield (34%), suggesting that a cuprate such as $K_2Cu(NCS)_4$ might be less reactive than the neutral Cu(II) salt. The most satisfactory result has been obtained under conditions described in the following typical procedure.

A mixture of $K_2[(E)\text{-}C_6H_{13}CH=CHSiF_5]$ (936 mg; 3.0 mmol), copper(II) thiocyanate (1.620 g; 9.0 mmol), and dry DMF (10 mL) was stirred at room temperature for 3 h. The color of the reaction mixture changed from black to yellow-brown, indicative of the reduction of copper(II) to copper(I). Ether was added and the mixture was filtered. The filtrate was washed with water and 10% brine, and dried over magnesium sulfate. After evaporation of solvent, bulb-to-bulb distillation of the residue under reduced pressure gave 338 mg (67% yield) of (*E*)-1-octenyl thiocyanate as a colorless liquid.

Compounds listed in Table 1 were obtained under similar conditions. The reaction is highly stereoselective at least for terminal (*E*)-alkenylsilicates, giving isomerically pure (*E*)-alkenyl thiocyanates only. The product from 1-butyl-1-hexenylsilicate was also assigned analogously to the (*E*) isomer, which was contaminated with a small amount (ca. 7%) of the other isomer. The IR spectra of alkenyl thiocyanates exhibit, in addition to a sharp strong band at 2155 cm^{-1} due to thiocyanate, a weak to medium broad band in the 2100 cm^{-1} region, which is characteristic of isothiocyanate. However, GLC analysis, ^1H NMR and mass spectral data, and comparison with literature data of the known compound (PhCH=CHSCN)[6] were inconsistent with the presence of any isothiocyanate as an impurity. The phenylsilicate also formed phenyl thiocyanate in about 40% yield, but alkylsilicates gave only trace amounts of alkyl thiocyanates.

The mechanism is not clear yet, but may be similar to that for the halogen transfer from copper(II) halides to organopentafluorosilicates[3] and other organometallics.[7] The reaction may obey the stoichiometry $RSiF_5^{2-}/Cu(NCS)_2 = 1/2$,[3] but an excess amount (3 equiv.) of the latter may be required owing to its great tendency to decomposition into Cu(NCS) and $(SCN)_2$.[5] The main difference from the halogen transfer reaction resides in that copper(II) thiocyanate does not react with alkyl silicates. Further mechanistic studies on copper(II)-oxidation reactions of organopentafluorosilicates are now in progress.

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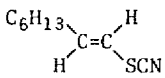
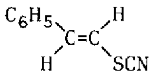
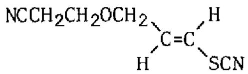
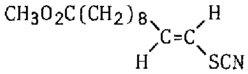
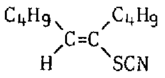
Table 1. Yield, Refractive Index, and Spectral Properties of Alkenyl and Phenyl Thiocyanates[a]

Product	Yield (%)[b]	n_D^{20}	^{1}H NMR[c], δ, ppm	IR[d], cm^{-1}	Mass[e] (rel. Int.)
	67[f] (74)[g]	1.4815	0.88 (t, 3H) 1.32 (br.s, 8H) 2.18 (q, *J*=6 Hz, 2H) 5.74 (q, *J*=16 Hz, 1H) 6.16 (d.t, *J*=16 Hz, 6 Hz, 1H)	2160 (s) 945 (m)	169 (M^+, 27.5) 99 (23) 86 (32) 83 (35) 68 (100)
	53[h]	1.6226[i]	6.43 (d, *J*=15 Hz, 1H)[i] 6.94 (d, *J*=15 Hz, 1H) 7.30 (s, 5H)	2155 (s)[i] 2100 (w, br) 947 (s) 738 (s) 670 (s)	161 (M^+, 100) 134 (48) 117 (41) 91 (23) 77 (22)
	49[f]	1.5106	2.63 (t, *J*=6 Hz, 2H) 3.22 (t, *J*=6 Hz, 2H) 4.15 (t, *J*=2 Hz, 2H) 6.22 (t, *J*=2 Hz, 2H)	2250 (m) 2155 (s) 2100 (w, br) 1113 (s) 938 (s)	168 (M^+, 1.7) 110 (100) 98 (34) 57 (57) 54 (39)
	70[j]	1.4851	1.15-1.7 (br, 12H) 2.1-2.35 (m, 4H) 3.61 (s, 3H) 5.82 (d, *J*=15 Hz, 1H) 6.15 (d.t, *J*=15 Hz, 7 Hz, 1H)	2155 (m) 2100 (w, br) 1738 (s) 1195 (m) 1170 (m) 945 (m)	255 (M^+, 34) 224 (52) 112 (85) 100 (58) 99 (100) 87 (48)
	78[f]	1.4368	0.8-1.1 (m, 6H) 1.1-1.7 (m, 8H) 1.9-2.3 (m, 2H) 2.40 (t, *J*=7 Hz, 2H) 5.90 (t, *J*=7 Hz, 1H)	2155 (s) 2080 (m, br) 1615 (s) 936 (m) 858 (m)	197 (M^+, 44) 99 (59) 98 (100) 95 (54) 83 (57) 55 (77)
C_6H_5SCN	42[f]	1.5685	7.3-7.6 (m, aromatic)	2145 (s) 1475 (s) 1440 (s) 740 (s) 685 (s)	135 (M^+, 100) 112 (14) 111 (25) 84 (11) 79 (26)

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[a] Satisfactory analytical data have been obtained. [b] Isolated yield based on silicate. [c] 100 MHz, CCl_4/TMS. [d] Liquid film. [e] 24 eV. [f] Isolated by distillation. [g] GLC Yield. [h] Silica gel, pentane/benzene (1:1). [i] Lit.[6]: n_D^{24} 1.6178. ^{1}H NMR ($CDCl_3$); 6.40 (d), 6.94 (d), 7.30 (s). IR; 2170 cm^{-1}. [j] Silica gel, benzene.

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