Chemistry of Certain Thiocyanates and Isothiocyanates Containing Silicon

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Received April 4, 1961

Bugorkova, Petrova, and Radionov[1] as well as others[2-4] have reported the addition of thiocyanogen to several olefinic compounds including some organosilanes. It may be assumed that the SCN groups attached themselves to form $-SCN$ radicals. In reacting with silicon compounds however, there is always the possibility that rupture may take place between silicon and carbon. In fact, qualitative runs demonstrate this in the treatment of *p*-trimethylsilylphenol with thiocyanogen. On the basis of other work[5] the isothiocyanate structure is assigned to the products of certain syntheses described below.

EXPERIMENTAL

2,3-Dithiocyanopropyltrimethylsilane. To 10.0 g. (0.087 mole) of trimethylallylsilane in 150 cc. of anhydrous ether, in a flask equipped with stirrer, etc., fresh thiocyanogen solution was added, containing 0.09 mole in 100 cc. of anhydrous ether. During the addition, the system was stirred vigorously and kept immersed in water at 10°. Three days later polymerized thiocyanogen was removed by filtration, the ether was distilled and the products fractionated giving 2,3-dithiocyanopropyltrimethylsilane, 6.5 g., 34% yield, b.p. 127–131°, $n_D^{27.5}$ 1.4965. Infrared absorption was recorded at 2970, 2180, 2080, 1260, and 1415 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{14}N_2S_2Si$: C, 41.70; H, 6.06; N, 12.10; Si, 12.18. Found: C, 41.14; H, 5.76; N, 12.20; Si, 11.80.

1,2-Dithiocyanoethyltrimethylsilane. In similar manner, this compound was prepared and isolated in 1.6% yield, m.p. 72–74°, and showing infrared absorption at 2970, 2180, 1260, and 1415 cm.$^{-1}$.

Allylsilyl triisothiocyanate. To 90.0 g. (1.1 mole) of dry sodium thiocyanate in 500 cc. flask was added 176 g. (1.0 mole) of allyltrichlorosilane, freshly distilled. The flask, equipped now with calcium chloride tube and reflux condenser, was immersed in cold water at first, then the cooling was discontinued and refluxing was permitted. About 20 minutes later, refluxing was continued by heating, this time for 90 minutes. The cooled mixture was filtered through glass wool. Distillation gave allylsilyl triisothiocyanate, yield 70%, b.p. 126–128° (2.5 mm), n_D^{26} 1.6140, with infrared absorption showing at 3080, 2090, 1995, 1635, and 1055 cm.$^{-1}$.

Anal. Calcd. for $C_6H_5N_3S_3Si$: C, 29.60; H, 2.06; N, 17.30; S, 39.50; Si, 11.50. Found: C, 29.34, 29.31; H, 1.98, 2.06; N, 17.20; S, 38.54; Si, 11.28.

Vinylsilyl triisothiocyanate. Similarly to the above, vinylsilyl triisothiocyanate was synthesized in 82% yield, b.p. 134–138° (3.0 mm.), n_D^{26} 1.6350. Infrared absorption appeared at 3070, 2090, 2000, 1600, 1410, and 1055 cm.$^{-1}$.

Anal. Calcd. for $C_5H_3N_3S_3Si$: C, 26.20; H, 1.31; N, 18.30; S, 41.90; Si, 12.25. Found: C, 26.04, 25.75; H, 1.33, 1.40; N, 17.84.

p-Tolylsilyl triisothiocyanate. This compound was also prepared similarly to the above but using ammonium thiocyanate, in 57% yield, b.p. 182–185° (3.5 mm.), n_D^{26} 1.6490. Infrared absorption was recorded at 3030, 2940, 2090, 2020, 1605 and 1130 cm.$^{-1}$.

Anal., Calcd. for $C_{10}H_7N_3S_3Si$: C, 41.00; H, 2.40; N, 14.30; S, 32.80; Si, 9.59. Found: C, 39.50; H, 2.38; N, 14.12; S, 27.80; Si, 9.61.

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The Preparation of Certain Carbon-functional Silathiols and Silathio Esters

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Received April 19, 1961

Marvel and Kripps[1] have reported the addition of thiolacetic acid to dimethyldiallylsilane to form dimethylbis-(3-mercaptopropyl)silane diacetate. Hydrolysis of this diester gave the corresponding dimercaptan. Cooper[2] obtained trimethylsilylmethyl mercaptan by treating trimethylchloromethylsilane with potassium hydrosulfide. Mironov and Pogonkina,[3,4] prepared a series of carbon functional mercaptans of organosilicon compounds from the corresponding thiocyanates. Other methods already in the literature, were used herein.[5-8]

Saponification of these thiol esters, followed by their acidification yielded the corresponding mono- or dimercaptans. Infrared data are included. The formulas of the addition products are written to indicate that addition had taken place in a manner known as "anti-Markownikoff." The conclusion to this effect was reached on the basis of the results from analogous work by others.[1,3,4]

EXPERIMENTAL

Dimethyldiallylsilane, methylphenyldiallylsilane, diphenyldiallylsilane, and dimethylbis-β-methallylsilane were prepared by the methods outlined by Nasiak and Post.[6] *Trimethyl-β-methallylsilane* was prepared by the procedure given by

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