Chemistry of Certain Thiocyanates and Isothiocyanates Containing Silicon

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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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[2] A. A. Bugorkova, V. F. Mironov, and A. D. Petrov, *Izvest. Akad. Nauk, S.S.S.R., OKhN*, 474 (1960); English page 441.

[3] V. F. Mironov, Yu. P. Egorov, and A. D. Petrov, *Izvest. Akad. Nauk, S.S.S.R., OKhN*, 1400 (1959); English page 1351.

[4] A. D. Petrov, Yu. P. Egorov, V. F. Mironov, G. I. Nikishin, and A. A. Bugorkova, *Izvest. Akad. Nauk, S.S.S.R., OKhN*, 50 (1956); English page 49.

[5] G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **69**, 3049 (1947).

The Preparation of Certain Carbon-functional Silathiols and Silathio Esters

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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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[1] C. S. Marvel and H. Kripps, *J. Polymer Sci.*, **9**, 53 (1952).

[2] G. D. Cooper, *J. Am. Chem. Soc.*, **76**, 2500 (1954).

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[4] V. F. Mironov and N. A. Pogonkina, *Izvest. Akad. Nauk, U.S.S.R., Otdel. Khim. Nauk.*, 85 (1959).

[5] D. C. Noller and H. W. Post, *J. Org. Chem.*, **17**, 1393 (1952).

[6] L. D. Nasiak and H. W. Post, *J. Org. Chem.*, **24**, 489 (1959).

[7] R. Nagel and H. W. Post, *J. Org. Chem.*, **17**, 1379 (1952).

Petrov and Nikishin.[8] *Triethylvinylsilane* was synthesized by the method outlined by Nagel and Post.[7]

4,4-Dimethyl-4-sila-1,7-heptylene dithioacetate and *4,4-diphenyl-4-sila-1,7-heptylene dithioacetate* were prepared by the addition of thiolacetic acid to the proper olefinic silane but were not isolated. They were not distilled but converted to their respective dimercaptans immediately upon synthesis.

4-Methyl-4-phenyl-4-sila-1,7-heptylene dithioacetate. This compound was prepared by treating 40.47 g. (0.20 mole) of methylphenyl-diallylsilane in 75 cc. of cyclohexane, in a 200 cc. three necked flask with the usual stirrer, dropping funnel, and adapter, with 30.4 g. (0.40 mole) of redistilled thiolacetic acid in 25 cc. of cyclohexane, slowly added, with the temperature kept at about 65°. After two hours of refluxing, excess thiolacetic acid and cyclohexane were removed by distillation at reduced pressures. Above 200° at 1 mm. decomposition occurred. The pot material was dissolved in an equal volume of methyl alcohol, and the colored impurities removed by Norite. The organic products were then thrown out of solution by water, dried over anhydrous sodium sulfate, and analyzed, n_D^{25} 1.5480, d_4^{25} 1.0819. Purification was limited as distillation resulted in slight decomposition.

Anal. Calcd. for $C_{17}H_{26}O_2S_2Si$: Si, 7.91, M.R., 104.1. Found: Si, 8.21, 8.26, M.R., 102.9.

2,4,4-Trimethyl-4-silapentyl-1 thiolacetate. By a procedure similar to that used in the preceding preparation, this compound was prepared and isolated in 53% yield, b.p. 99°–100° (9 mm.), n_D^{25} 1.4664, d_4^{25} 0.9158.

Anal. Calcd. for $C_9H_{20}OSSi$: Si, 13.73, M.R., 61.28. Found: Si, 13.32, 13.50, M.R., 60.51.

3,3-Diethyl-3-silapentyl-1 thiolacetate. This compound was prepared as indicated above, yield 42%, b.p. 117°–119° (6.5 mm.) n_D^{25} 1.4779, d_4^{25} 0.9284. Infrared absorption occurred at 3.3, 5.8, 8.0, 11.8, and 14.3 μ.

Anal. Calcd. for $C_{10}H_{22}OSSi$: Si, 12.85, M.R., 66.91. Found: Si, 13.05, 13.11, 13.09, M.R., 66.57.

4,4-Dimethyl-4-silaheptylene-1,7 dimercaptan. As described for the thiolacetates, 75 cc. of purified cyclohexane and 33.6 g. (0.24 mole) of dimethyldiallylsilane were treated with 36.5 g. (0.48 mole) of redistilled thiolacetic acid at 55°. After two hours of refluxing, the mixture was hydrolyzed by the slow addition of 40 g. (1.0 mole) of sodium hydroxide in 100 cc. of distilled water and 40 cc. of 95% ethyl alcohol. The system was refluxed for 90 minutes, then neutralized with 6*N* hydrochloric acid. After cooling, the upper layer was separated and combined with two 50 cc. benzene extracts of the water layer. After drying over 10 g. of anhydrous sodium sulfate, the material was fractionated yielding 4,4-dimethyl-4-silaheptylene-1,7 dimercaptan, 25% yield, b.p. 119.0–119.5° (6 mm.), n_D^{25} 1.5034, d_4^{25} 0.9631. Infrared absorption was recorded at 3.3, 7.0, 8.0, 8.5, 10, 10.8, and 12–13 μ.

Anal. Calcd. for $C_8H_{20}S_2Si$: Si, 13.46, M.R., 64.24. Found: Si, 13.06, 13.51, M.R., 64.01.

4-Methyl-4-phenyl-4-silaheptylene-1,7 dimercaptan was prepared in the same manner, yield 25%, b.p. 161–162° (2.5 mm.), n_D^{25} 1.5580, d_4^{25} 1.0396. Infrared absorption appeared at 3.4, 6.9, 7.8, 8.7, 9.7, 12.2, 13, and 13.6 μ.

Anal. Calcd. for $C_{12}H_{22}S_2Si$: Si, 10.38, C, 57.7, H, 8.17, M.R., 84.07. Found: Si, 10.58, 10.66, C, 56.5, H, 7.69, M.R., 83.87.

2,4,4,6-Tetramethyl-4-silaheptylene-1,7 dimercaptan. This compound was also prepared as described above, 22% yield, b.p. 147–148° (8 mm.), n_D^{25} 1.5031 d_4^{25} 0.9534.

Anal. Calcd. for $C_{10}H_{24}S_2Si$: Si, 11.87, C, 50.79, H, 10.2, M.R., 73.50. Found: Si, 11.65, 11.73, C, 50.53, H, 9.6, M.R., 72.36.

2,4,4-Trimethyl-4-silapentyl-1-mercaptan. In a similar apparatus, 40.0 g. (0.19 mole) of 4,4-dimethyl-4-silapentyl-1 thiolacetate in 80 cc. of purified cyclohexane was treated with 24.0 g. (0.60 mole) of sodium hydroxide in 100 cc. of water and 50 cc. of ethyl alcohol at 45–50°. The mixture was refluxed for five hours, then cooled and acidified with 6N hydrochloric acid. The product was worked up as in the cases described above, giving a 9% yield, b.p. 69.5–70.5° (16 mm.), n_D^{25} 1.4576, d_4^{25} 0.8597. Infrared absorption was recorded at 3.3, 5.1, 6.1, 6.8, 7.0, 8.1, 9.4, 9.8, 11.4–12.7, 13.1, and 14.0 μ.

Anal. Calcd. for C_7H_8SSi: C, 51.79, H, 11.17, M.R., 51.88. Found: C, 51.70, H, 11.41, M.R., 51.48.

β-Triethylsilylethyl mercaptan. Similarly, this compound was prepared in 50% yield by the hydrolysis of the corresponding thiolacetate, b.p. 113° (23 mm.), n_D^{25} 1.4730, d_4^{25} 0.8789. Infrared absorption occurred at 3.3, 6.8, 7.0, 7.8, and 9.8 μ.

Anal. Calcd. for $C_8H_{20}SSi$: Si, 15.91, M.R., 56.52. Found: C, 15.94, 16.01, M.R., 56.30.

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The γ-Ionones

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The base catalyzed condensation of citral with acetone, followed by acid cyclization, leads to a mixture of α- and β-ionones[1]; the ratio of the isomers formed is related to the acid used.[2] Similarly, methyl ethyl ketone has been shown to condense with citral to form on cyclization the *n*-methylionones (α and β) and the isomethylionones (α and β).[3] The γ-isomers (exocyclic methylene) have not previously been reported as products of these reactions, nor have they hitherto been characterized.[4]

We wish to report the isolation and characterization of pure γ-ionone and γ-*n*-methylionone from commercial products.

The formation of the exocyclic methylene isomer is not unexpected, as the intermediate II, prob-

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(2) H. Hibbert and L. T. Cannon, *J. Am. Chem. Soc.*, 119 (1924); *Org. Syntheses*, **23**, 78 (1943).

(3) M. G. J. Beets and H. van Essen, *Rec. trav. chim.*, **77**, 1138 (1958), and references therein.

(4) Two reports of a derivative of γ-ionone have appeared: (a) B. Willhalm, V. Steiner, and H. Schinz, *Helv. Chim. Acta*, **41**, 1359 (1958) have reported the semicarbazone of this isomer (column chromatographed), originally thought to be present as a mixture of β- and γ-ionone. More recently, D. Szabo, *Chem. Abstr.*, **54**, 19748 (1960) has indicated the presence of γ-ionone in the phosphoric acid cyclization of pseudo ionone by conducting the cyclization in the presence of 2,4-dinitrophenylhydrazine. Thus far, our efforts to form derivatives of both pure new compounds reported here have led to viscous, intractable oils with semicarbazide, 2,4-dinitrophenylhydrazine and thiosemicarbazide, due to apparent product instability.