

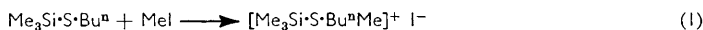
**461.** *The Reactions of Alkylthiotrimethylsilanes, Hexamethyldisilthiane, and Hexamethylcyclotrisilthiane with Some Organic Halides.*

By E. W. ABEL, D. A. ARMITAGE, and R. P. BUSH.

A number of alkyl halides and  $\alpha\omega$ -dihalogenoalkanes react with n-alkylthiotrimethylsilanes, hexamethyldisilthiane, and hexamethylcyclotrisilthiane to give alkylhalogenosilanes and a variety of linear and cyclic organic sulphides.

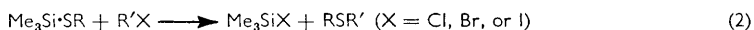
DISILYL and dimethylsilyl sulphides were reported not to react with iodomethane,<sup>1</sup> but it was observed that n-butylthiotrimethylsilane does react with n-butyl iodide to give trimethyliodosilane and di-n-butyl sulphide.<sup>2</sup> We have now extended this to the reaction of alkylthiotrimethylsilanes, hexamethyldisilthiane, and hexamethylcyclotrisilthiane with various organic halides.

It was suggested<sup>2</sup> that the reaction proceeds by way of a sulphonium salt. This view now receives some support from the reaction of iodomethane with n-butylthiotrimethylsilane. If these two compounds are mixed and allowed to stand in the dark for some days in a stoppered vessel, fine white crystals are formed. These are extremely hygroscopic and unstable. They do, however, give a melting point (with decomposition) and analyse quite well for n-butylmethyltrimethylsilylsulphonium iodide.



The salt is insoluble in light petroleum and is completely decomposed by water. Ethylthiotrimethylsilane reacted similarly with methyl iodide, but the white crystals obtained were too unstable to give good analysis figures.

Alkylthiotrimethylsilanes react with alkyl halides, on heating, to release the corresponding trimethylhalogenosilane, which is continuously removed by fractional distillation, to leave the unsymmetrical dialkyl sulphide.



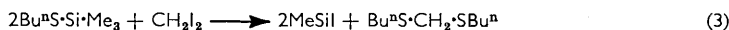
This reaction is fastest for iodide and very slow for chloride (see Table). An effort to use a more reactive alkyl chloride, 3-chloro-3-ethylpentane, with n-butylthiotrimethylsilane did not give the expected n-butyl 1,1-diethylpropyl sulphide, but instead a mixture of trimethylchlorosilane, 3-ethylpent-2-ene, and n-butanethiol. This was presumably due to the elimination of hydrogen chloride from the 3-chloro-3-ethylpentane on prolonged heating, and subsequent fission of the silicon-sulphur bond in the alkylthiotrimethylsilane by the hydrogen chloride. A similar elimination reaction occurred between cyclohexyl iodide and ethylthiotrimethylsilane, to give cyclohexene, ethanethiol, and trimethyliodosilane. Cyclohexyl bromide, however, reacted smoothly with n-butylthiotrimethylsilane to produce cyclohexyl n-butyl sulphide. Iodobenzene did not react with n-butylthiotrimethylsilane, despite prolonged heating.

<sup>1</sup> Emel us, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194; Emel us and Onyszchuk, *J.*, 1958, 604.

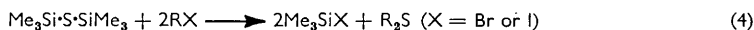
<sup>2</sup> Abel, *J.*, 1960, 4406.

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Both of the halogen atoms in di-iodomethane were replaced by alkythio-groups in its reaction with *n*-butylthiotrimethylsilane:



Hexamethyldisilthiane reacted with both *n*-heptyl iodide and *n*-octyl bromide, producing the appropriate trimethylhalogenosilane and dialkyl sulphide:

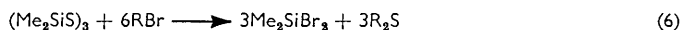


The corresponding reaction of hexamethyldisilthiane and 1,4-dibromobutane gave a 36% yield of tetrahydrothiophen:

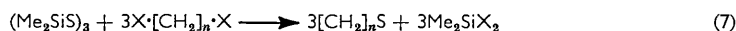


In this reaction considerable polymerisation appeared to have taken place, leaving an intractable solid; in the same reaction with 1,3-dibromopropane, despite considerable evolution of trimethylbromosilane, no thiacyclobutane was detected, and only polymer appeared to have been formed.

Hexamethylcyclotrisilthiane reacted similarly with *n*-octyl bromide (reaction 6), to give dimethyldibromosilane and the dialkyl sulphide.



The reaction between hexamethylcyclotrisilthiane and  $\alpha\omega$ -dihalogenoalkanes has been carried out for compounds with  $n = 2, 3,$  and  $4$ :



In the case of 1,4-dibromobutane, a mixture of dimethyldibromosilane and tetrahydrothiophen was evolved, but subsequent hydrolysis allowed the isolation of the tetrahydrothiophen in good yield. With 1,3-dibromopropane, however, the corresponding hydrolysis of what is believed (from the range of boiling point) to have been a mixture of thiacyclobutane and dimethyldibromosilane did not permit the isolation of the thiacyclobutane. This was due to the polymerisation of the thia-alkane, which has been reported<sup>3</sup> to take place rapidly under these conditions. As thiacyclopropane has by far the lower boiling point of the products of the reaction between 1,2-dibromoethane and hexamethylcyclotrisilthiane (reaction 7,  $n = 2$ ), this was removed smoothly from the mixture by distillation, and no subsequent hydrolysis extraction was necessary.

### EXPERIMENTAL

The alkylthiotrimethylsilanes, hexamethyldisilthiane, and hexamethylcyclotrisilthiane were prepared as previously described.<sup>2,4,5</sup> Organic halides were dried and distilled before use, and precautions were taken to ensure that experiments were carried out under anhydrous conditions.

*Interaction of n-Butylthiotrimethylsilane and Iodomethane.*—An excess of iodomethane was added to the thiosilane (6.10 g.), and the mixture was set aside in darkness in a stoppered flask. After 15 hr. white crystals began to form. After 2 weeks they were removed by filtration, and rapidly washed with carefully dried light petroleum (b. p. 40–60°). Removal of the excess of solvent at 20°/0.01 mm. gave very pale yellow *n*-butylmethyltrimethylsilylsulphonium iodide (1.9 g., 17%), m. p. 58–62° (decomp.) (Found: C, 28.25; H, 6.2.  $\text{C}_8\text{H}_{21}\text{ISSi}$  requires C, 31.6; H, 6.9%). The salt was very hygroscopic, and was rapidly decomposed by water.

A similar reaction took place between ethylthiotrimethylsilane and iodomethane. The ethylmethyltrimethylsilylsulphonium iodide crystals, m. p. ca. 85° (decomp.), did not give a satisfactory analysis (Found: C, 21.6; H, 5.3. Calc. for  $\text{C}_7\text{H}_{17}\text{ISiS}$ : C, 26.1; H, 6.2%) owing to the rapid uptake of moisture and difficulty of handling.

<sup>3</sup> Bost and Conn, *Ind. Eng. Chem.*, 1933, **25**, 526.

<sup>4</sup> Abel, *J.*, 1961, 4933.

<sup>5</sup> Nomura, Yokoi, and Yamasaki, *Proc. Japan Acad.*, 1953, **29**, 342; *J. Amer. Chem. Soc.*, 1955, **77**, 4484.

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*Interaction of n-Butylthiotrimethylsilane and Alkyl Halides.*—These reactions were conducted on an approximately 0.05 molar scale. No heat was observed upon mixing the reactants. Subsequent heating caused evolution of trialkylhalogenosilane which was distilled off as formed. The residual liquid was distilled to give the dialkyl sulphides, RSBu<sup>n</sup> (see Table).

Products of reaction of alkyl halides, RX, with n-butylthiotrimethylsilane.

RX	Reaction time	Yield (%)	B. p./mm.	$n_D^{20}$	Found (%)		Calc. (%)	
					C	H	C	H
n-C <sub>7</sub> H <sub>15</sub> I	15 hr.	68	122°/15	1.4581	70.6	13.0	70.3	12.8
n-C <sub>8</sub> H <sub>17</sub> Br *	60 hr.	64	94—96/1	1.4578	71.1	12.9	71.2	12.9
n-C <sub>8</sub> H <sub>17</sub> Cl *	4 weeks	48	248/760	1.4575				
Cyclo-C <sub>6</sub> H <sub>11</sub> Br	4 weeks	31	38/0.02	1.4879	67.4 †	11.4	69.7	11.7

\* The infrared spectra of the n-butyl n-octyl sulphide samples produced were identical.  
† Appears to decompose slightly upon distillation.

*Interaction of n-Butylthiotrimethylsilane and 3-Chloro-3-ethylpentane.*—The chloride (6.63 g., 1 mol.) and the thiosilane (7.99 g., 1 mol.) were heated together under reflux for 18 hr. Distillation then gave trimethylchlorosilane (4.10 g., 70%), b. p. 58°,  $n_D^{20}$  1.3910, and a fraction, b. p. 94—100°, shown by gas chromatography to contain 3-ethylpent-2-ene and n-butanethiol.

*Interaction of Ethylthiotrimethylsilane and Cyclohexyl Iodide.*—The iodide (6.11 g., 1 mol.) and the thiosilane (3.90 g., 1 mol.) were heated together under reflux for 18 hr., by which time the temperature of the condensing vapour had fallen to 107°. An effort at fractional distillation of the products resulted in a mixture, b. p. 107—130°, which contained cyclohexene, ethanethiol, trimethyliodosilane, and some unchanged ethylthiotrimethylsilane.

n-Butylthiotrimethylsilane and iodobenzene were heated under reflux for 100 hr. with no apparent reaction, and no evolution of trimethyliodosilane.

*Interaction of n-Butylthiotrimethylsilane and Di-iodomethane.*—The iodide (3.03 g., 1 mol.) and the thiosilane (3.67 g., 2 mol.) were heated under reflux for 12 hr., by which time the temperature of condensing vapour had fallen to 107°. Trimethyliodosilane (2.44 g., 54%) was distilled off during 48 hr. Distillation of the residue gave di-n-butylthiomethane (1.60 g., 70%), b. p. 62—64°/0.3 mm.,  $n_D^{20}$  1.4908 (Found: C, 56.45; H, 10.3. Calc. for C<sub>8</sub>H<sub>20</sub>S<sub>2</sub>: C, 56.3; H, 10.4%).

*Interaction of Hexamethyldisilthiane and n-Heptyl Iodide.*—The iodide (20.20 g., 2 mol.) and the disilthiane (7.93 g., 1 mol.) were heated at 160°. Slow evolution of trimethyliodosilane, b. p. 107°, (15.61 g., 88%) occurred during 100 hr. Distillation of the residue gave di-n-heptyl sulphide (9.88 g., 96.5%), b. p. 295°,  $n_D^{20}$  1.4600 (Found: C, 72.5; H, 12.9. C<sub>14</sub>H<sub>30</sub>S requires C, 72.9; H, 13.1%).

*Interaction of Hexamethyldisilthiane and n-Octyl Bromide.*—The bromide (10.95 g., 2 mol.) and the disilthiane (5.06 g., 1 mol.) were maintained at 160° for 100 hr. while trimethylbromosilane (6.25 g., 72%),  $n_D^{20}$  1.4208, was removed as formed. Distillation of the residue gave a small fraction, b. p. 160—180°, and then di-n-octyl sulphide (4.01 g., 55%), b. p. 315°,  $n_D^{20}$  1.4605 (Found: C, 74.0; H, 12.65. Calc. for C<sub>16</sub>H<sub>32</sub>S: C, 74.4; H, 13.2%).

*Interaction of Hexamethylcyclotrisilthiane and n-Octyl Bromide.*—The bromide (17.50 g., 6 mol.) and the disilthiane (4.08 g., 1 mol.) were heated together at 180° for 14 days while dimethyldibromosilane (5.45 g., 55%), b. p. 112°,  $n_D^{20}$  1.4590, was removed by distillation. Distillation of the residue gave a fraction, b. p. 160—170°, probably containing tetramethylcyclodisilthiane formed by rearrangement of the starting material, n-octyl bromide, b. p. 47°/0.5 mm.,  $n_D^{19}$  1.4523, and di-n-octyl sulphide (1.71 g., 15%), b. p. 133°/0.5 mm.,  $n_D^{19}$  1.4603.

*Interaction of Hexamethyldisilthiane and 1,4-Dibromobutane.*—The dibromide (6.85 g., 1 mol.) and the disilthiane (5.64 g., 1 mol.) were heated at 180° for 90 hr. during which time distillation of a mixture took place over the range 80—115°. Careful fractional distillation yielded trimethylbromosilane (6.05 g., 61%), b. p. 79—80°,  $n_D^{20}$  1.4208, and tetrahydrothiophen (1.0 g., 36%), b. p. 116°,  $n_D^{20}$  1.4961 (infrared spectrum identical with an authentic sample).

*Interaction of Hexamethyldisilthiane and 1,3-Dibromopropane.*—The dibromide (7.45 g., 1 mol.) and the disilthiane (6.57 g., 1 mol.) were heated together at 160°, and trimethylbromosilane (11.06 g., 98%), b. p. 82°,  $n_D^{20}$  1.4231, was removed during 14 days. Redistillation gave a pure sample, b. p. 79.5°,  $n_D^{20}$  1.4216. The only other product was an intractable charred solid in the reaction vessel; no sulphides of low molecular weight were detected.

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*Interaction of Hexamethylcyclotrisilthiane and 1,4-Dibromobutane.*—The dibromide (17.9 g., 3 mol.) and the disilthiane (7.44 g., 1 mol.) were heated at 170°. The combined products (24.33 g., 96%) distilled off at 112–119° during 48 hr. Fractional distillation of the mixture was not possible owing to the close proximity of the boiling points of the two products (dimethyldibromosilane 112°, and tetrahydrothiophen 119°). The mixture was hydrolysed with aqueous sodium hydroxide. The nonaqueous layer was separated, dried, and fractionally distilled, to give tetrahydrothiophen, b. p. 118°,  $n_D^{20}$  1.5016 (Found: C, 54.3; H, 9.2. Calc. for  $C_4H_8S$ : C, 54.5; H, 9.2%), infrared spectrum identical with that of an authentic sample. Our sample was further characterised as its mercuric chloride complex,  $C_4H_8S.HgCl_2$ , m. p. 128–129°.<sup>6</sup>

*Interaction of Hexamethylcyclotrisilthiane and 1,3-Dibromopropane.*—The dibromide (12.18 g., 3 mol.) and the silthiane (5.42 g., 1 mol.) were heated under reflux at 170° for 40 hr., during which time a colourless liquid (13.01 g.),  $n_D^{20}$  1.4745, distilled over the range 90–120°. This was thought to be a mixture of thiacyclobutane (b. p. 95°,  $n_D^{20}$  1.5059) and dimethyldibromosilane (b. p. 118°,  $n_D^{20}$  1.4590), but hydrolysis and subsequent work-up yielded no thiacyclobutane, only polymer.

*Interaction of Hexamethylcyclotrisilthiane and 1,2-Dibromoethane.*—The dibromide (19.13 g., 3 mol.) and the trisilthiane (9.15 g., 1 mol.) were heated together, and a colourless liquid (20.80 g.), b. p. 56–112°, was collected during 48 hr.; an intractable solid remained in the flask. Fractional distillation of the liquid product gave thiacyclopropane (1.00 g., 20%), b. p. 54°,  $n_D^{20}$  1.4963 (Found: C, 39.85; H, 6.65. Calc. for  $C_2H_4S$ : C, 39.9; H, 6.7%).

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<sup>6</sup> Whitehead, Dean, and Fidler, *J. Amer. Chem. Soc.*, 1951, **73**, 3632.