CLEAVAGE OF TETRAHYDROFURAN BY TRIMETHYLIODOSILANE

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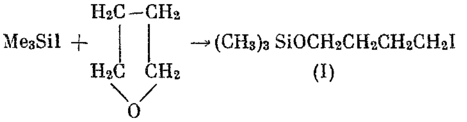
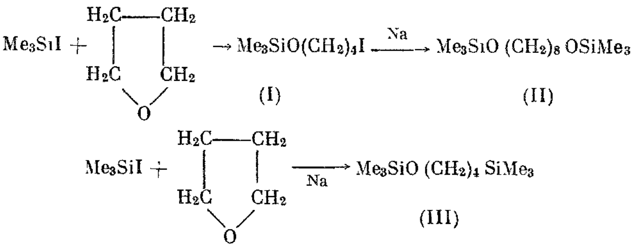
The reaction of halosilanes with THF has been studied quite well. Under fairly drastic conditions both Me_3SiCl and Me_3SiBr cleave THF to give the corresponding trimethyl-(4-halobutoxy)silanes [1]. When pyridine hydrobromide is used as catalyst the alkylbromo- and alkylchlorosilanes react with THF to give 1,4-dihalobutanes [2]. It is also possible for THF to react with Me_3SiI [3], but the trimethyl-(4-iodobutoxy)silane formed here was not characterized. In the presence of Na metal both Me_3SiCl and Me_3SiBr react with THF to give 1-trimethylsilyl-4-trimethylsiloxybutane [4].

We studied the cleavage of THF by Me_3SiI. Under mild conditions (60°C) it leads to the formation in quantitative yield of the unstable trimethyl-(4-iodobutoxy)silane (I).



The structure of (I) was confirmed by the NMR and IR spectral data. In the presence of Na, Me_3SiI reacts with THF to give in 50% yield the previously unknown 1,8-bis(trimethylsiloxy)octane (II) and a small amount (10%) of 1-trimethylsilyl-4-trimethylsiloxybutane (III).



Compound (II) was also obtained in 42% yield by the reaction of (I) with sodium in THF, which confirms the formation of (II) by the indicated scheme. This reaction can be recommended as a convenient method for the synthesis of (II) and its hydrolysis product, namely 1,8-octanediol (70% yield).

The attempted synthesis of (III) by reacting (I) with Me_3SiI and Na under various conditions ended in failure. The sodium failed to enter into the reaction and the only products were tars and hexamethyldisiloxane, the formation of which is due to cleavage of (I) by trimethyliodosilane according to the scheme:

$$Me_3SiI + \underset{(I)}{Me_3SiO(CH_2)_4I} \rightarrow Me_3SiOSiMe_3 + \underset{(IV)}{I(CH_2)_4I}$$

Here the yield of 1,4-diiodobutane (IV) reaches 85%.

EXPERIMENTAL METHOD

The NMR spectra were obtained on a Tesla BS-487C spectrometer (80 MHz). Here we used 20% solutions in CCl_4 [(II) and (III)] or in $HCCl_3$ (I), with C_6H_6 [(III) and (II)] or C_6H_{14} (I) as the internal standard. The IR spectra were taken on a UR-20 spectrometer as a microlayer.

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All of the reactions were run in a dry argon atmosphere. The trimethyliodosilane was obtained as described in [5]. The THF was purified by distillation over sodium.

Trimethyl-(4-iodobutoxy)silane (I). To 53.3 g (0.74 mole) of THF was added in drops 13.6 g (0.068 mole) of Me_3SiI, at such a rate that the temperature of the mixture did not exceed 60°. The mixture was carried for another hour at ~20°, the excess THF was distilled using a water-jet pump, and the residue was vacuum-distilled. We obtained 18.5 g (99%) of (I) with bp 93° (11 mm); n_D^{20} 1.4757; d_4^{20} 1.3347. Found: C 30.90; H 6.35; Si 10.69; I 46.48%; MR 57.44. $C_7H_{17}SiOI$. Calculated: C 30.90; H 6.25; Si 10.30; I 46.7%; MR 57.99. Infrared spectrum (ν, cm^{-1}): 510, 595 (CI), 1100 (SiOC), 830-870, 1256 (SiC), 2870-2955 (CH). NMR spectrum (τ, ppm): 9.88 [$(CH_3)_3Si$], 826 [$C(CH_2CH_2)C$], 6.79 (CH_2I), 6.44 (CH_2O).

1,8-Bis(trimethylsiloxy)octane (II). a) To 53.3 g (0.74 mole) of THF was added 5.0 g (0.217 g-atom) of Na, and then 14.7 g (0.0735 mole) of Me_3SiI was added at −20° in drops. The temperature of the mixture was raised slowly up to ~20°, and here a precipitate of NaI deposited. After stirring for 1 h the precipitate was filtered and the excess THF was distilled from the filtrate. Vacuum-distillation of the residue gave 0.8 g (10%) of (III) with bp 82° (12 mm) [6]; n_D^{20} 1.4188, and 5.27 g (50%) of (II) with bp 90° (1 mm); n_D^{20} 1.4230; d_4^{20} 0.8480. Found: C 58.22; H 11.79; Si 19.68%; MR 87.27. $C_{14}H_{34}Si_2O_2$. Calculated: C 58.00; H 11.71; Si 19.34%; MR 88.27. Infrared spectrum (ν, cm^{-1}): 850-880, 1255 (SiC), 1108 (SiOC), 2862-2931 (CH). NMR spectrum (τ, ppm): 9.33 [$(CH_3)_3SiO$], 8.69 [$C(CH_2)_6C$], 6.50 (OCH_2).

b) A mixture of 20 ml of THF, 11.9 g (0.0438 mole) of (I), and 1.6 g (0.0695 g-atom) of Na was heated up slowly to 50° and kept at this temperature for 4 h. The obtained precipitate of NaI was filtered, and the excess THF was distilled off. Vacuum-distillation of the residue gave 2.66 g (42%) of (II) with bp 102° (2 mm).

1,4-Diiodobutane (IV). A mixture of 11.62 g (0.0427 mole) of (I) and 9.85 g (0.049 mole) of Me_3SiI was heated at 70° for 4 h. Vacuum-distillation gave 11.26 g (95%) of 1,4-diiodobutane [7] with bp 88° (3 mm).

Hydrolysis of 1,8-Bis(trimethylsiloxy)octane. A mixture of 4.24 g (0.0146 mole) of 1,8-bis(trimethylsiloxy)octane and 14 ml of 2% NaOH solution was kept at ~20° for 48 h, and then it was refluxed for 4 h. The upper layer of hexamethyldisiloxane (1.8 g, 76.2%) was separated, and the residue was extracted with benzene. After removal of the benzene we obtained 1.47 g (70%) of 1,8-octanediol [8] with mp 60°.

CONCLUSIONS

The reaction of tetrahydrofuran with trimethyliodosilane under mild conditions gives trimethyl-(4-iodobutoxy)silane in quantitative yield. 1-Trimethylsilyl-4-trimethylsiloxybutane (10% yield) and the previously unknown 1,8-bis(trimethylsiloxy)octane (50% yield) are formed in the presence of sodium metal. The reaction of trimethyliodosilane with trimethyl-(4-iodobutoxy)silane gives 1,4-diiodobutane and hexamethyldisiloxane in high yield.

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