

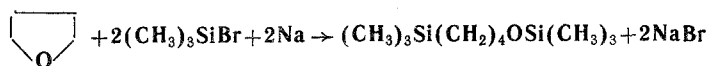
CLEAVAGE OF TETRAHYDROFURAN BY TRIMETHYLHALOSILANES
IN THE PRESENCE OF METALLIC SODIUM

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Tetrahydrofuran (THF) is cleaved by trialkylhalosilanes with the formation of trialkyl-4-halobutoxysilanes [1, 2]. The product of the reaction of trimethylchlorosilane with magnesium in THF medium, in the presence of iodine or C_2H_5I and with the solvent participating, is 1-(trimethylsilyl)-4-(trimethylsiloxy)butane (I) [3, 4].

We have found that, in the presence of excess metallic sodium, trimethylbromosilane cleaves THF even at room temperature according to the reaction



Thus, for example, when a mixture of the above components is mechanically shaken in the absence of atmospheric oxygen, the yield of I, bp 95°C (30 mm), n_D^{20} 1.4191 amounts to 20%. Found: C 53.91; H 11.87; Si 25.32%. Calculated for $C_{10}H_{26}OSi_2$: C 54.97; H 11.99; Si 25.71%. Literature data for I: bp 22°C (12 mm); n_D^{20} 1.4188 [3]; bp 134°C (78 mm) [4].

Prolonged shaking of a solution of trimethylchlorosilane in the THF with sodium wire also leads to cleavage of the tetrahydrofuran ring and the formation of I, bp $93^\circ\text{--}95^\circ\text{C}$ (30 mm), n_D^{20} 1.4191 (yield about 10%). Found: C 54.01; H 11.84; Si 25.29%.

When trimethylbromosilane is replaced by triethylbromosilane, hexaethyldisilane is formed in place of the expected THF cleavage product: bp $106^\circ\text{--}109^\circ\text{C}$ (6 mm), n_D^{20} 1.4750 (yield 42%). Found: C 61.05; H 13.27; Si 24.02%. Calculated for $C_{12}H_{30}Si_2$: C 62.52; H 13.12; Si 24.36%. Literature data: bp $87\text{--}89^\circ\text{C}$ (2.5 mm); n_D^{20} 1.4759 [5]; bp 251.7°C (760 mm); n_D^{20} 1.4790 [6].

The data which we have obtained give evidence that the reactions of organohalosilanes with alkali metals, which are often conducted in the THF medium, may be accompanied by the appearance of side products formed through solvent participation. We have observed this in a number of other examples as well.

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