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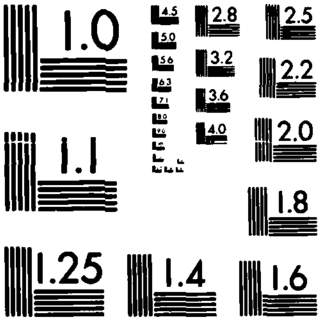

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SILYLATED TETRAHYDROFURAN DERIVATIVES

by
Curtis L. Schilling, Jr.

Prepared for Publication in
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Union Carbide Corporation
Tarrytown, New York 10591

3 December 1982

SILYLATED TETRAHYDROFURAN DERIVATIVES

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ABSTRACT

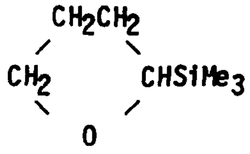
2-Trimethylsilyltetrahydrofuran and 2-(2-trimethylsilylethyl)tetrahydrofuran have been isolated from dechlorinations of mixtures of silane monomers by potassium metal in tetrahydrofuran solvent. These low yield products may involve the common intermediacy of the 2-tetrahydrofuryl anion or the 2-tetrahydrofuryl radical and its trapping by trimethylchlorosilane and vinyltrimethylsilane.

INTRODUCTION

Numerous reactions have been run in tetrahydrofuran (THF) solvent wherein products which arise by hydrogen abstraction from the solvent are isolated. For example, treatment of gem-dibromocyclopropanes with methylmagnesium bromide yields monobromocyclopropanes[1]. Grignard[2,3] or lithium[4] reactions of organopolyhalides with trimethylchlorosilane yield products in which halogens have been replaced by hydrogens. Triphenylsilyllithium[5] and α,ω-dilithioperphenylpolysilanes[6] react with dichloromethane to yield triphenylmethylsilane and α,ω-dimethylperphenylpolysilanes, respectively.

2-Lithiotetrahydrofuran is proposed as a product of the reaction of n-butyllithium with THF[7,8] with mass spectral evidence for monodeuterotetrahydrofuran when the reaction is quenched with D_2O[7]. Deprotonation of THF by a bicyclononadienyl anion has also been reported[9].

Active metal dechlorinations of mixtures of silane monomers, including chlorosilanes, vinylic silanes, and chloromethyl silanes have yielded polycarbosilane precursors for silicon carbide.[10]. Certain of these reactions, run using potassium metal in THF as the dechlorinating medium, have provided 2-trimethylsilyltetrahydrofuran (I) or 2-(2-trimethylsilyl)ethyltetrahydrofuran (II) in relatively low yields, in addition to the expected products.



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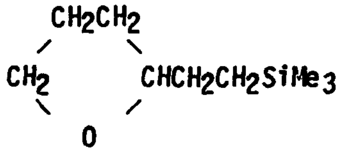

II

Isolable quantities of I were obtained from the reaction of trimethylchlorosilane with dichloromethane using K metal in THF. Addition of a mixture of Me_3SiCl/CH_2Cl_2 to refluxing THF/molten K metal suspension

$$2.1\ Me_3SiCl + CH_2Cl_2 + 2.2K \xrightarrow{THF} (Me_3Si)_2O + (Me_3Si)_2 + (Me_3Si)_2CH_2 + I + \text{higher boilers}$$

at a rate maintaining the reflux temperature above 64°, followed by cooling, cautious termination with aqueous THF, and neutralization with conc. HCl yielded a group of products including I (5.3% yield based on Me_3SiCl). Preparative gas chromatography yielded a pure sample with appropriate NMR/mass spectra and elemental analyses ($C_7H_{16}OSi$, Calc'd: % C, 58.33, % H, 11.11, % Si, 19.44; Found: % C, 58.39, % H, 11.15, % Si, 19.66).

Similarly, dechlorination of ethyltrichlorosilane in the presence of vinyltrimethylsilane

$$EtSiCl_3 + 1.2\ CH_2 = CHSiMe_3 + 1.6K \xrightarrow{THF} II + polymer$$

yields a branched polycarbosilane + II (0.12% yield). A purified sample provided correct NMR/mass spectra and elemental analyses ($C_9H_{20}OSi$, Calc'd: % C, 62.79, % H, 11.63, % Si, 16.28; Found: % C, 63.03, % H, 11.87, % Si, 16.04. Yields of II up to 2.9% have been obtained from other reactions.

The isolations of I and II support the intermediacy of the 2-tetrahydrofuryl anion or the 2-tetrahydrofuryl radical. The anionic intermediate is more likely in the formation of I via simple displacement of chloride from Me_3SiCl. Compound II could form via a free radical process, or by Michael addition of an anionic intermediate to CH_2=$CHSiMe_3$. Both radical and anionic intermediates may be involved in a common pathway with K metal transforming 2-tetrahydrofuryl radicals to 2-tetrahydrofuryl anions by electron transfer. Our attempts to prepare I by quenching an n-butyllithium/THF solution[7] with Me_3SiCl were unsuccessful, while treatment of a refluxing solution of THF/CH_2=$CHSiMe_3$ with benzoyl peroxide or azobisisobutyronitrile (method of reference 11) provided a very low yield of II.

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REFERENCES

1. D. Seyferth and B. Prokai, J. Org. Chem. 1966, 31, 1702.
2. R. L. Merker and M. J. Scott, J. Am. Chem. Soc. 1963, 85, 2243.
3. R. L. Merker and M. J. Scott, J. Org. Chem. 1964, 29, 953.
4. R. L. Merker and M. J. Scott, J. Organometal. Chem. 1965, 4, 98.
5. H. Gilman and D. Aoki, Chem. and Ind. (London) 1960, 1165.
6. P. K. Sen, T. B. Brennan, and H. Gilman, J. Indian Chem. Soc. 1974, 51, 561.
7. R. B. Bates, L. M. Kroposki, and D. E. Potter, J. Org. Chem. 1972, 37, 560.
8. R. J. Crawford, Diss. Abstr. Int. B 1971, 31, 5254.
9. M. V. Moncur and I. B. Grutzner, J. Am. Chem. Soc. 1973, 95, 6449.
10. C. L. Schilling, T. C. Williams, and J. P. Wesson, Report 1981, TR-80-1, Order No. AD-A099030; Chem. Abstr. 1982, 95, 170175q.
11. G. Ahlgren, J. Org. Chem. 1973, 38, 1369.

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