Tetrahedron Letters No. 22 + 23, pp 1771 - 1772. 1975. Pergamon Press. Printed in Great Britain.

ISOLATION OF TRI-t-BUTYLSILANE

Edward M. Dexheimer and Leonard Spialter*
Chemistry Research Laboratory, Aerospace Research Laboratories,
Wright-Patterson Air Force Base, Ohio 45433

(Received in U.S.A. 3 February 1975; received in UK for publication 14 April 1975)

In the course of attempting to synthesize di-t-butyldichlorosilane (1)as an intermediate for the preparation of t-butylsilyl ketones, silicon tetrachloride was treated with t-butyllithium. However, in addition to the desired product, (1), and the expected byproduct[1] t-butyltrichlorosilane (2), there was also isolated, as the major product in 33% yield, di-t-butylchlorosilane[2] (3).

$$SiCl_4 + tBuLi \rightarrow \underset{1}{tBu_2SiCl_2} + \underset{2}{tBuSiCl_3} + \underset{3}{tBu_2SiClH}$$

This observation suggested that t-butyllithium could function as a reducing agent for halosilanes, in a manner similar to that known for hindered Grignard reagents.[3] To determine whether reduction occurred after formation of the monoalkylation product 2 or after formation of the more hindered product 1, both 1 and 2 were treated with excess t-butyllithium under the same conditions which had given 3. The result was that 1 was unreactive but 2 was observed to form 3.

During a repetition of the reaction of 2 with excess t-butyllithium, the solvent cyclohexane accidentally was lost while refluxing overnight and the reaction mixture was subjected to temperatures above 100°. Anhydrous workup gave as the only isolable products, di-t-butylsilane (4) and, surprisingly, tri-t-butylsilane[4](5). The formation of 5 is particularly remarkable since implications from the literature suggested that this molecule could not be prepared by conventional synthetic methods. All such attempts over the past 25 years had failed.[5]

$$2 + tBuLi \rightarrow \underset{4}{tBu_2SiH_2} + \underset{5}{tBu_3SiH}$$

Compound 5 is a colorless, crystalline solid with a melting point of 30°. The compound is stable and shows no decomposition even at 210° during gas chromatographic isolation. The proton nmr of 5 shows two sharp singlets, one at $\delta 3.36$ (1H,SiH) and one at $\delta 1.12$ (27H,CH_3). The ir spectrum shows the following absorptions: 3.42(s), 3.48(s), 3.52(s), 4.81(s), 6.81(s), 7.21(m), 7.34(m), 9.85(m), 10.49(w), 12.17(m), and 12.50(s)µ. (Found: C,71.96; H,14.00. $C_{12}H_{28}Si$ calcd.: C,71.91; H,14.08%).

The stability of 5 suggests that the failure of previous preparative efforts was likely due to improper reaction conditions or the wrong choice of reagents, rather than any inherent instability or extreme degree of steric hindrance. The availability now of this structurally unusual trialkylsilane[6] suggests a number of potentially interesting research studies. These include its behavior in hydrosilations of unsaturated compounds, coordination ability and non-bonded interactions, reactivity toward hydrosilane-reactive reagents (bases, ozone, trityl chloride, carbenes, nitrogen oxides, silver ion, perioxides, etc.) and the testing of various theoretical and empirical correlations, such as those between ν_{Si-H} and σ^* and others. Research results from some of these areas will be presented in larger expositions on this interesting silane.

Acknowledgement. This work was supported by a grant from the Air Force Systems Command, administered by the National Research Council, under which one of us, EMD, was a Resident Research Associate.

References and Notes

1. L. J. Tyler, L. H. Sommer, and F. C. Whitmore, J. Amer. Chem. Soc., 70, 2876 (1948).
2. Satisfactory analytical and spectral data were obtained for all new compounds.
3. M. B. Lacout-Loustalet, J. P. Dupin, F. Metras, and J. Valade, J, Organometal. Chem., 31, 337 (1971).
4. The yield was approximately 10%. Subsequent synthesis from SiF_4 raised the yield to 80%.
5. C. F. Shaw and A. L. Allred, Organometal. Chem. Rev. A, 5, 95 (1970) and references therein.
6. A Fischer-Herschfelder model of tri-t-butylsilane reveals that the back side of the molecule is completely shielded by methyl groups while the front side is left remarkably open to coordination or flank attack.