

- 1 H. GILMAN AND C. L. SMITH, *J. Am. Chem. Soc.*, 86 (1964) 1454.
- 2 C. L. SMITH AND R. L. HARRELL, unpublished studies.
- 3 H. GILMAN AND R. L. HARRELL, *J. Organometal. Chem.*, 5 (1966) 201.
- 4 H. GILMAN, W. ATWELL AND F. CARTLEDGE, in F. G. A. STONE AND R. WEST (Eds.), *Advances in Organometallic Chemistry*, Vol. IV, Academic Press, New York, in press.
- 5 M. KUMADA, M. ISHIKAWA AND M. SAJIRO, *J. Organometal. Chem.*, 2 (1964) 478.
- 6 D. R. WEYENBERG AND L. H. TOPORCER, *J. Am. Chem. Soc.*, 84 (1962) 2843.
- 7 D. R. WEYENBERG AND L. H. TOPORCER, *J. Org. Chem.*, 30 (1965) 943.
- 8 DOW CORNING CORP., *Brit.* 988,320 (Cl. CO7F), April 7, 1965; *Chem. Abstr.*, 63 (1965) 632c.
- 9 R. A. BENKESER, C. ARNOLD, JR., R. F. LAMBERT AND O. H. THOMAS, *J. Am. Chem. Soc.*, 77 (1956) 6042, and references cited therein.
- 10 D. R. WEYENBERG, L. H. TOPORCER AND A. E. BEY, *J. Org. Chem.*, 30 (1965) 4096.

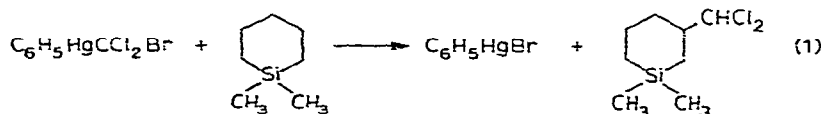
Received January 19th, 1966

J. Organometal. Chem., 5 (1966) 387-389

CCl₂ insertion into tetraalkyl-silicon and -tin compounds via phenyl (bromodichloromethyl)mercury

Recent studies have shown that CCl₂ insertion into benzylic C-H bonds of phenylalkanes can be effected with sodium trichloroacetate in 1,2-dimethoxyethane¹, or, in better yield, with phenyl(bromodichloromethyl)mercury². Use of the latter reagent even made possible the preparation of (dichloromethyl)cyclohexane from cyclohexane in 32% yield².

In a continuation of these studies we report here concerning surprisingly specific CCl₂ insertions into β C-H linkages of sila- and stanna-cyclohexanes and of the *n*-propyltrimethyl derivatives of silicon and tin. For example, when a solution of 0.03 mole of 1,1-dimethyl-1-silacyclohexane and 0.01 mole of phenyl(bromodichloromethyl)mercury in 20 ml of benzene was heated at reflux for 2 h, phenylmercuric bromide precipitated (92%), and fractional distillation gave as sole organosilicon product 3-dichloromethyl-1,1-dimethyl-1-silacyclohexane in 68% yield (eqn. 1). The product had a satisfactory combustion analysis; it was characterized by b.p. 81° (6 mm), *n*_D²⁵ 1.4878. Its NMR spectrum (CCl₄) showed a doublet (*J* = 3.5 c.p.s.) at 5.71 p.p.m. (1H), singlet at 0.07 p.p.m. (6H) and complex absorption (9H) in the region 0.3-2.1 p.p.m. downfield from TMS. The mass spectrum was consistent with this



structure. An unambiguous structure proof for this product was given by its reduction with sodium in liquid ammonia to 1,1,3-trimethyl-1-silacyclohexane, which was identical in all respects with authentic material prepared by reaction of the di-Grignard reagent from 1,5-dibromo-2-methylpentane with silicon tetrachloride, followed by methylation with methylmagnesium bromide.

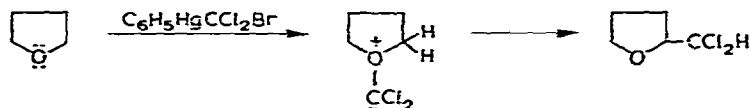
A similar reaction of phenyl(bromodichloromethyl)mercury with *n*-propyltrimethylsilane gave γ,γ -dichloroisobutyltrimethylsilane, *n*_D²⁵ 1.4561, but only in 15% yield. Its NMR spectrum unambiguously defined its structure as (CH₃)₃SiCH₂-

$\text{CH}(\text{CHCl}_2)\text{CH}_3$: $(\text{CH}_3)_3\text{Si}$ -, singlet at 0.06 p.p.m.; $-\text{CH}_2$ -, unsymmetrical triplet, 0.57-0.93 p.p.m., with additional splitting, AB pattern; CH_3 -, doublet ($J = 7$ c.p.s.) at 1.14 p.p.m.; $-\text{CH}_2-\text{CH}$ -, multiplet centered at 2.25 p.p.m.; Cl_2HC -, doublet ($J = 3.5$ c.p.s.) at 5.70 p.p.m. G.l.c. analysis of the reaction mixture failed to detect any other organosilicon products of comparable volatility, suggesting that this was the only product formed. Insertion of CCl_2 into the γ C-H bonds should give a stable product, while insertion into α C-H bonds of the propyl group or into methyl C-H linkages would give products that might possibly undergo β -elimination under the experimental conditions. However, fragmentation products from possible α C-H insertion-derived species were not observed.

Such insertion also occurs readily into the analogous organotin derivatives. Thus *n*-propyltrimethyltin (37 mmoles) reacted in benzene at reflux with phenyl(bromodichloromethyl)mercury (15.8 mmoles) during 2 h to give γ,γ -dichloroisobutyltrimethyltin in 70% yield, together with phenylmercuric bromide (93%). This product, n_D^{25} 1.5005, had an NMR spectrum (CCl_4) which confirmed the structure indicated: $(\text{CH}_3)_3\text{Sn}$ -, singlet at 0.04 p.p.m., with observable splitting due to ^{119}Sn and ^{117}Sn ; $-\text{CH}_2$ -, complex AB methylene pattern at 0.5-1.55 p.p.m.; CH_3 -, doublet ($J = 7$ c.p.s.) at 1.13 p.p.m.; $-\text{CH}_2-\text{CH}$ -, multiplet, 1.9-2.8 p.p.m.; Cl_2HC -, doublet ($J = 4$ c.p.s.) at 5.59 p.p.m. 1,1-Dimethyl-1-stannacyclohexane reacted with $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ under the same conditions to give 3-dichloromethyl-1,1-dimethyl-1-stannacyclohexane, n_D^{25} 1.5330, in 50% yield. In this case an unambiguous structure proof has not yet been possible, but the infrared spectrum of the product in the C-H region is very similar to the spectrum of the starting tin compound and in the fingerprint region is very similar to the infrared spectrum of the analogous organosilicon insertion product.

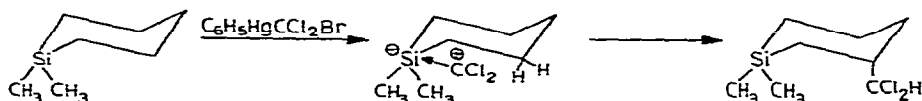
In contrast to CCl_2 insertion into the Si-H bond of triethylsilane^{2,3}, such insertion into C-H bonds of tetraalkyl-silanes and -tins does not compete favorably with CCl_2 addition to olefins. Thus when 0.03 mole each of cyclohexene and 1,1-dimethyl-1-silacyclohexane were allowed to compete for 0.01 mole of phenyl(bromodichloromethyl)mercury (in benzene at 80°), 7,7-dichloronorcarane was formed in 80% yield and 3-dichloromethyl-1,1-dimethyl-1-silacyclohexane in only 0.9% yield.

The remarkable features of these reactions with tetraalkyl-silicon and -tin compounds are (1) the high yields in which the insertion products are formed (with the exception of the case of *n*-propyltrimethylsilane), and (2) the fact that CCl_2 insertion occurs exclusively into a C-H bond which is in β position with respect to the heteroatom. Specificity of CCl_2 insertion has been observed in the case of phenylalkanes^{1,2} and in the case of cyclic and acyclic ethers^{4,5}, e.g., tetrahydrofuran \rightarrow 2-dichloromethyltetrahydrofuran in 67% yield *via* $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ ⁵. In the case of ethers an ylid mechanism could be proposed to explain such specific insertion into the α C-H linkages:



In the case of the organosilicon and organotin compounds used in the present study it is tempting to consider an ylid mechanism with reversed polarity, *i.e.*, one in which the CCl_2 is the donor species and the substrate the electron acceptor, since tetraalkyl-

silanes and tetraalkyltin compounds have no Lewis base properties, but do have accessible vacant d orbitals. Here steric factors could serve to explain the observed specificity.



However, a radical pathway cannot be discounted. For instance, it is to be noted that in radical chlorination of 1,1-dichloro-1-silacyclopentane, substitution in the β position is favored by a factor of 4 (Ref. 6). However, in radical chlorination of tetraethylsilane, substitution in the α position is favored by a factor of 12, while the $\alpha:\beta:\gamma$ chlorination ratio in the case of sulfonyl chloride chlorination of n -propyltrichlorosilane was found to be 1.0:3.5:3.1 (Ref. 7). On this basis, the specificity observed by us in CCl_2 insertion is more compatible with a nonradical pathway, but the final answer to this problem must await further experimental results.

In any case, this novel insertion into the β C-H bonds of tetraalkyl-silicon and -tin compounds has unique preparative utility and should make possible the synthesis of new, organofunctional silicon and tin compounds by subsequent reactions of the β -dichloromethyl derivatives. Another promising synthetic application of these novel products is illustrated by the formation of a 3:1 mixture of *cis*-1-chloro-2-methylcyclopropane and methallyl chloride, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$, by zinc chloride-catalyzed γ -elimination of trimethyltin chloride from γ,γ -dichloroisobutyltrimethyltin.

It is to be expected that similar insertion reactions will be observed in the case of alkyl derivatives of other metals, and our current studies are directed toward this end.

The authors are grateful to the Air Force Office of Scientific Research for generous support of this Work.

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- 1 E. K. FIELDS, *J. Am. Chem. Soc.*, **84** (1962) 1744.
- 2 D. SEYFERTH AND J. M. BURLITCH, *J. Am. Chem. Soc.*, **85** (1963) 2667.
- 3 D. SEYFERTH, J. M. BURLITCH AND H. DERTOUZOS, report in preparation.
- 4 (a) J. C. ANDERSON AND C. B. REESE, *Chem. Ind. (London)*, (1963) 575;
(b) J. C. ANDERSON, D. G. LINDSAY AND C. B. REESE, *J. Chem. Soc.*, (1964) 4874.
- 5 D. SEYFERTH, J. M. BURLITCH, R. J. MINASZ, J. Y.-P. MUI, H. D. SIMMONS, JR., A. J.-H. TREIBER AND S. R. DOWD, *J. Am. Chem. Soc.*, **87** (1965) 4259.
- 6 R. A. BENKESER, Y. NAGAI, J. L. NOE, R. F. CUNICO AND P. H. GUND, *J. Am. Chem. Soc.*, **86** (1964) 2446.
- 7 Summarized in C. EABORN, *Organosilicon Compounds*, Butterworths, London, 1960, p. 381.

Received January 12th, 1966

* Alfred P. Sloan Foundation Fellow, 1962-1966.
** National Science Foundation Predoctoral Fellow.