Silylation of Organic Halides. A New Method of Forming the Carbon–Silicon Bond

Sir:

In a previous communication[1] we reported the efficacy of the trichlorosilane–tertiary amine combination in the selective reduction of polyhalo compounds. The isolation of trichloromethyltrichlorosilane led us to propose that the amine-catalyzed reduction of carbon tetrachloride by trichlorosilane may well proceed *via* the formation and subsequent cleavage of the carbon–silicon bonded species. Reported here is a series of reactions that, beyond supporting this mechanistic contention, exemplify a novel method of forming stable carbon–silicon bonds. The general process, the silylation of organic halides, is represented in eq 1. Thus, refluxing

$$RX + HSiCl_3 + R'_3N \longrightarrow RSiCl_3 + R'_3N \cdot HX \qquad (1)$$

a mixture of 25.3 g of benzyl chloride (200 mmol), 40.8 g of trichlorosilane (300 mmol), and 28.7 g of tri-*n*-propylamine (200 mmol) at 56–90° for 20 hr afforded on work-up (ether precipitation of the amine hydrochloride, filtration, and fractionation of the filtrate) 27.1 g (60%) of benzyltrichlorosilane, bp 100–102° (15 mm) (lit.[2] bp 95.8° (10 mm)).

Data for the silylation of a series of halides are summarized in Table I.

Table I. Silylation of Organic Halides by Trichlorosilane–Tri-*n*-propylamine

Entry	Reactants (mole ratios) (halide : $HSiCl_3$: $(n\text{-}C_3H_7)_3N$)	Conditions	Products[a,b] (%)
1	$C_6H_5CH_2Cl$ (1:1.5:1)	Neat, 20 hr, 56–90°	$C_6H_5CH_2SiCl_3$ (66)
2	p-$CH_3C_6H_4CH_2Cl$ (1:1.5:1)	Neat, 20 hr, 57–143°	p-$CH_3C_6H_4CH_2SiCl_3$ (52)
3	p-$ClC_6H_4CH_2Cl$ (1:1.5:1)	Neat, 20 hr, 62–153°	p-$ClC_6H_4CH_2SiCl_3$ (78)
4	m-$CF_3C_6H_4CH_2Cl$ (1:1.5:1)	Neat, 20 hr, 60–152°	m-$CF_3C_6H_4CH_2SiCl_3$ (70)
5	$C_6H_5CHCl_2$ (1:1.25:1)	Neat, 1 hr, 97–100° 12 hr, 30°	$C_6H_5CH(SiCl_3)_2$ (59)
6	$C_6H_5CHCl_2$ (1:3:2)	CH_3CN, 14 hr, 35°	$C_6H_5CH(SiCl_3)_2$ (64)
7	$C_6H_5CHCl_2$ (1:4:2.5)	CH_3CN, 14 hr, 35°	$C_6H_5CH(SiCl_3)_2$ (66) $C_6H_5CH_2SiCl_3$ (34)
8	CH_3CHBr_2 (1:5:2)	CH_3CN, 18 hr, 43–44°	$CH_3CH(SiCl_3)_2$ (28)
9	CH_3CCl_3 (1:4.5:3)	CH_3CN, 16 hr, 58–67°	$CH_3CH(SiCl_3)_2$ (56)
10	$CHCl_3$ (1:4.5:3)	CH_3CN, 16 hr, 56–65°	$CH_2(SiCl_3)_2$ (60)

[a] Satisfactory elemental analyses and spectral data (ir and nmr) were obtained for all silanes reported. [b] In every case the tri-*n*-propylamine hydrohalide was isolated in addition to the silicon compounds listed.

When a mixture of *n*-butyl chloride, trichlorosilane, and tri-*n*-butylamine (1:1:0.8) was heated at reflux for 2 hr, noxious vapors were evolved[3] but neither *n*-butyltrichlorosilane nor the amine hydrochloride was produced. It may be construed from this finding and from the nature of the halides transformed (Table I) that electron withdrawal from the reaction center is likely of paramount importance. The process may be dependent on the qualities of R (eq 1) as a potential carbanion. Some substantiation of this postulate is provided by the relative rates of silylation of the various benzyl chlorides (Table I, entries 1–4), which increase in the order p-$CH_3C_6H_4CH_2Cl < C_6H_5CH_2Cl < p$-$ClC_6H_4CH_2Cl \approx m$-$CF_3C_6H_4CH_2Cl$.

More striking, however, is the ready conversion of the polyhalides to polysilyl compounds.[4] In none of these cases (entries 5–10) was more than a trace of a partially substituted product detected. The high reactivity of such halotrichlorosilyl intermediates is especially well demonstrated in the reaction of trichlorosilane and tri-*n*-propylamine with excess benzal chloride (entry 5), from which α,α-bis(trichlorosilyl)toluene was obtained in 59% yield. In a simplified interpretation of this phenomenon, the intermediacy of carbanions stabilized by the trichlorosilyl moiety can be invoked.[5]

$$R\bar{C}HSiCl_3 \longleftrightarrow RCH{=}\bar{Si}Cl_3$$

If one employs this view, the over-all silylation process may be depicted[6] as in eq 2 and 3.

$$HSiCl_3 + R'_3N \rightleftharpoons R_3\overset{+}{N}H + {}^{-}SiCl_3 \qquad (2)$$

$$RX + {}^{-}SiCl_3 \longrightarrow [R^{-} + XSiCl_3] \longrightarrow RSiCl_3 + X^{-} \qquad (3)$$

The several reactions leading to replacement of halogen by hydrogen (Table I, entries 7, 9, 10) can be viewed as variants of the reduction process previously reported.[1] Whether such products result from cleavage of the carbon–silicon bond[7] or are formed in a more direct manner is a point currently being investigated.[8]

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(1) R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, **90**, 5307 (1968).

(2) M. G. Voronkov and B. N. Dolgov, *Zh. Obshch. Khim.*, **24**, 1082 (1954). Quantitative glpc analysis of the distillation forerun and cold-trap contents indicated the presence of another 2.5 g (6%) of benzyltrichlorosilane and 0.2 g (1%) of toluene.

(3) Catalysis by tetrabutylammonium chloride of the disproportionation of trichlorosilane to dichlorosilane and silicon tetrachloride has been amply demonstrated: D. R. Weyenberg, A. E. Bey, and P. J. Ellison, *J. Organometal. Chem.*, **3**, 489 (1965).

(4) To our knowledge, this represents an entirely new and certainly the most convenient method now available for preparing *gem*-disilyl compounds. Additional avenues for the synthesis of the latter compounds will be published shortly by us.

(5) C. Eaborn, "Organosilicon Compounds," Butterworth & Co. (Publishers), Ltd., London, 1960, pp 91–113, 348; F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

(6) In accord with the equilibrium represented in eq 2, we have observed a facile isotope exchange between trichlorosilane and tri-*n*-butylammonium deuteriochloride in the presence of tri-*n*-butylamine: R. A. Benkeser, S. Dunny, P. R. Jones, and W. E. Smith, in preparation.

(7) G. D. Cooper and A. R. Gilbert, *J. Amer. Chem. Soc.*, **82**, 5042 (1960).

(8) We wish to emphasize that the mechanisms we have presented here and in recent publications[1] dealing with the trichlorosilane–amine combinations are to be considered as purely working hypotheses. The main thrust of our program thus far has been to illustrate the synthetic utility of the silicon–amine systems. In this regard, the mechanisms we have *suggested* proved useful both in explaining the products observed and in pointing the way for new experiments. In no case do we consider these mechanisms as firmly established.

Acknowledgment. The authors are grateful to the Purdue Research Foundation whose financial assistance made this work possible.

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Stable Carbonium Ions. LXXXIX.[1]
The Tetramethylcyclobutenium Dication, an Aromatic 2 π-Electron System

Sir:

Simple molecular orbital theory predicts that the cyclobutenium dication should have aromatic resonance stabilization because it is a planar, monocyclic system containing $4n + 2$ ($n = 0$) π electrons.[2] A number of investigators have tried to prepare this dication or its derivatives but were unsuccessful.[3,4] The tetraphenylcyclobutenium dication was reported by Freedman, but X-ray crystallographic studies on an isolated crystalline salt showed the monocation monodonor–acceptor structure.[5,6] There is now the serious possibility that exchange phenomena involving the monocation monodonor–acceptor complex and not the dication are responsible for the observed apparent equivalence of the phenyl groups in pmr studies in solution.[5]

The preparation of the tetramethylchlorocyclobutenium cation **2** from tetramethylcyclobutenyl dichloride **1** and silver hexafluoroantimonate has been reported by Katz.[7] He and others have reported the preparation of other derivatives of this monocation.[8] Since the work of Breslow on cyclopropenium cations indicates that alkyl groups make an aromatic cation thermodynamically more stable than aryl groups[9] (the kinetic stability might, however, be decreased), we felt that the tetramethylcyclobutenium dication might be stable in SbF_5–SO_2 solution.

We wish now to report our success in preparing the tetramethylcyclobutenium dication, the first well-defined cyclobutenyl dication. When **1**[10] was added to SbF_5–SO_2 at −78°, a very pale yellow solution was formed whose nmr spectrum was identical with that previously reported by Katz for ion **2** in SO_2 solution.

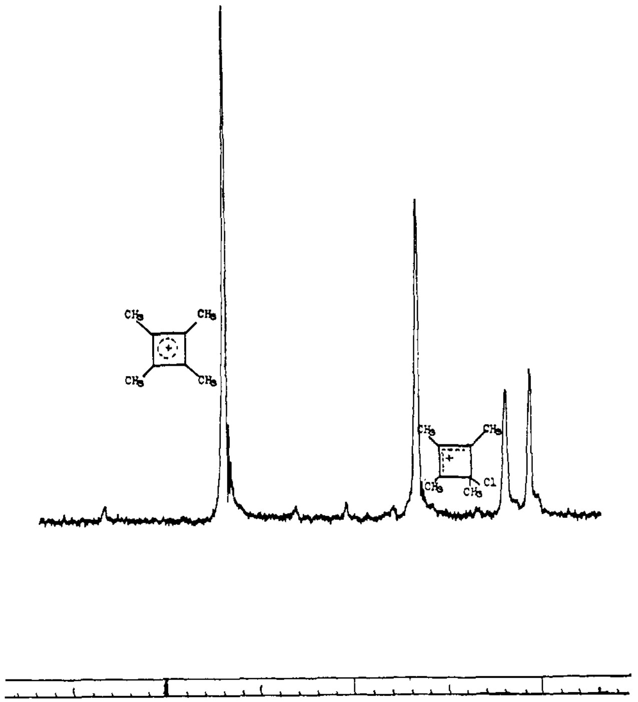
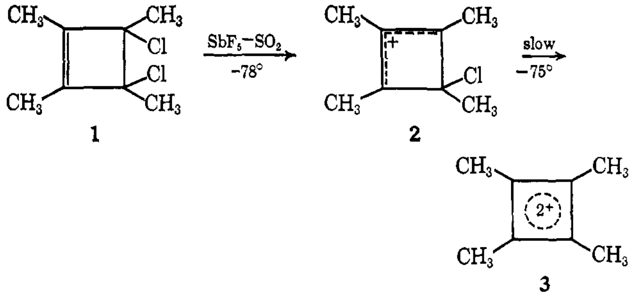


Figure 1. Nmr spectrum of tetramethylcyclobutene dichloride in SbF_5–SO_2 solution at −65°.



After several minutes at −75°, a single new absorption appeared as a sharp singlet at δ 3.68. The rate of appearance of the species giving this singlet increased with increasing temperature and was apparently formed irreversibly. In order to generate a maximum concentration of this ion (which we believe to be **3**) in SO_2 the temperature was maintained at or below about −65° because at higher temperatures absorptions characteristic of **2** disappeared but were not proportionately replaced by the single line of **3**. About 60% of **2** could be converted to **3** before appreciable decomposition took place at −65°. Figure 1 is a typical spectrum.

Solutions of ion **2** in FSO_3H–SO_2 are completely stable at −78° for at least 2 weeks. Solutions of **2** in SbF_5–SO_2 show a maximum concentration of **3** at −78° after approximately 24 hr, and, thereafter, decomposition takes place to another species whose structure we have been unable to determine. Solutions of **2** in 1:1 $HFSO_3$–SbF_5 in SO_2 are more than 80% decomposed after only 6 hr at −78°. Decomposition of these solutions can take place through the reaction of the dication **3** with the monocation **2**. The dimeric species can be quenched in methanol–sodium methoxide at −78° to a white crystalline solid containing chlorine but no methoxyl groups.[11] We have not yet been able to assign a

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[1] Part LXXXVIII: G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, in press.

[2] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, p 122. This book contains many other relevant references, and a complete discussion of cyclobutenium dications is recorded in Chapter 3.

[3] D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Amer. Chem. Soc.*, **86**, 673 (1964); *Tetrahedron Lett.*, 307 (1963).

[4] The 1,3-dihydroxydiphenylcyclobutenium dication (D. G. Farnum and B. Webster, *J. Am. Chem. Soc.*, **85**, 3502 (1963)) is apparently accepted as a cyclobutenium dication. However, G. A. Olah and A. M. White (*ibid.*, **87**, 4752 (1967)) have suggested that diprotonated squaric acid is better represented as a diprotonated diketone rather than as tetrahydroxycyclobutenium dication, based on the chemical shift of the protons on oxygen. A ^{13}C nmr study should, however, clarify this point.

[5] R. F. Bryan, *J. Amer. Chem. Soc.*, **86**, 733 (1964); H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

[6] H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964); H. H. Freedman, personal communication, Feb 1969.

[7] T. J. Katz and E. G. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964); T. J. Katz, J. R. Hall, and W. C. Neikam, *ibid.*, **84**, 3199 (1962).

[8] E. H. Gold and T. J. Katz, *J. Org. Chem.*, **31**, 372 (1966); C. F. Wilcox, Jr., and D. L. Nealy, *ibid.*, **39**, 3668 (1964); **28**, 3446 (1963).

[9] R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

[10] R. Criegee and A. Moschel, *Chem. Ber.*, **92**, 2181 (1959).