Table I. Distribution of $C_3(H,D)_5^+$ Ions from $CD_3CH_2CHCH_2$

m/e	Ion	% expected from 1,3 shift	% expected, random	% observed at nominal ionizing voltage[a] 9.9 V	10.5 V	11.1 V	11.5 V	13.1 V[b]	13.0 V[c]
41	$C_3H_5^+$	12.5	1.8	5.5	6.3	7.3	8.1	12.4	9.1
42	$C_3H_4D^+$	37.5	26.8	26.9	26.3	25.7	25.5	25.3	27.3
43	$C_3H_3D_2^+$	. .	53.6	48.5	47.9	46.8	45.9	40.9	45.3
44	$C_3H_2D_3^+$	50.0	17.8	19.1	19.7	20.2	20.5	21.4	18.1

[a] Calibration of the energy scale with Xe indicates that these voltages differ less than 0.3 V from the most probable value of the electron energy distribution. [b] At this energy unlabeled 1-butene shows 5.9% of the ions in this group to be $C_3H_3^+$ and $C_3H_4^+$. [c] Reference 3.

be almost entirely associated with $C_3(H,D)_5^+$ ions since the mass spectra of unlabeled 1-butene show that the intensities of neighboring mass peaks are less than 5% of that at m/e 41 at nominal energies less than 11.5 eV. Formation of the $C_3H_5^+$ ion at these energies is observed even though its appearance potential is 11.4 eV[6] because of the exponential high-energy tail of the electron energy distribution, whose width at half-height was 0.65 eV.

The participation of skeletal rearrangement in the randomization would lead to a loss of carbon identity as well. When 1-butene-4-^{13}C with an isotopic purity of 38.5% was subjected to electron bombardment, the resultant $C_3H_5^+$ ion contained 28.5% ^{13}C at ionizing voltages where other fragment ions did not contribute materially. This abundance corresponds to 75% retention of the ^{13}C label in the allyl ion, demonstrating loss of carbon identity and rearrangement of the carbon skeleton. Methyl loss involving solely the terminal carbons would lead to a retention of only 50% of the label in the $C_3H_5^+$ ion.

The early work of Rylander and Meyerson[6] suggests the methylcyclopropane cation as the intermediate responsible for the skeletal randomization. Thermodynamic arguments would also lead one to prefer this entity since rearrangement of 1-butene ion to that structure requires only 0.83 eV while formation of the cyclobutane ion demands 1.2 eV.[7] Wagner[8] suggested a substituted cyclopropane ion structure to account for the radiation-induced skeletal isomerization of solid pentenes and hexenes at 77 °K. Lastly, fragmentation of propene-1-^{13}C to $C_2H_3^+$ induced by 75-eV electrons is preceded by ca. 25% skeletal isomerization.[9] This evidence strongly supports a sequence of 1,3 ring closures to methylcyclopropane ion and reopenings as the mechanism for loss of carbon atom identity and much of the hydrogen atom randomization. It obviates the necessity to invoke an unattractive series of 1,2 hydrogen atom or hydride shifts.

The tendency toward decreasing deuterium randomization with increasing electron energy suggested by Bryce and Kebarle[3] appears to be supported by the data in Table I, whose trend could not be materially affected by any plausible correction for labeled $C_3H_3^+$ and $C_3H_4^+$.[10] Similarly, ^{13}C retention in the $C_3H_5^+$ ion from butene-1-^{13}C is decreased to 69% at a nominal ionizing voltage of 15.1 V. Even the maximum reasonable correction for contributions of labeled $C_3H_4^+$ to the peak at m/e 41 leads to a calculated retention of only 70% at that energy. The rate of fragmentation thus appears to become competitive not only with that of deuterium atom migration but also with that of skeletal rearrangement at higher excitation energies of the precursor ion.

Acknowledgment. We are indebted to the U. S. Atomic Energy Commission for their support of this investigation.

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Received December 16, 1968

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(7) G. G. Meisels, J. Y. Park, and B. G. Giessner, 16th Annual Meeting on Mass Spectrometry, Pittsburgh, Pa., May 1968.

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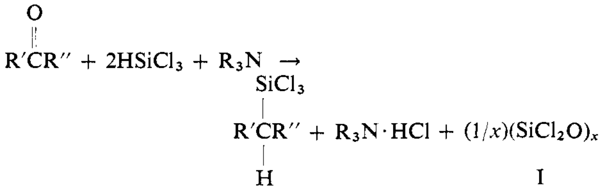
A New Method of Forming the Carbon–Silicon Bond. Reductive Silylation of Carbonyl Compounds

Sir:

In a previous communication[1] we described some aspects of the reducing power exhibited by the trichlorosilane–tertiary amine combination. In the course of further experiments with this reagent system, we have observed a novel reaction in which certain carbonyl compounds like aromatic ketones, aldehydes, and acid chlorides can be converted in excellent yields to organosilicon derivatives, *via* replacement of the carbonyl oxygen. One of the important aspects of this discovery is that it constitutes an entirely new preparative method for forming a carbon–silicon bond. The over-all process, "reductive silylation," can be represented by eq 1.



$$R'\overset{\overset{O}{\|}}{C}R'' + 2HSiCl_3 + R_3N \rightarrow R'\underset{\underset{H}{|}}{\overset{\overset{SiCl_3}{|}}{C}}R'' + R_3N\cdot HCl + (1/x)(SiCl_2O)_x \quad (1)$$

I

Thus, when equimolar quantities of benzophenone and tri-*n*-propylamine were combined with 3 equiv of trichlorosilane, a vigorously exothermic reaction ensued. After refluxing for 1 hr at 55–75° and treating the mixture with pentane, tri-*n*-propylamine hydrochloride (99%), melting at 136–138°, precipitated. Distillation of the filtrate afforded (95%) benzhydryltrichlorosilane (bp 141–145° (2.5 mm); mp 48–49°[2] after glpc purification). The distillation residue was a resinous material (suggesting

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

(2) This compound has been reported as melting at 55–56°. See E. A. Chernyshev and N. G. Tolstikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 7, 1223 (1962).

Table I. Reductive Silylation of Carbonyl Compounds by Trichlorosilane–Tri-*n*-propylamine

Run	Reactants (mole ratios) Carbonyl-$HSiCl_3$-$(n\text{-}C_3H_7)_3N$	Conditions	Products[a,e]
1	$(C_6H_5)_2CO$ (1:3:1)	Neat, 1 hr, 55–75°	$(C_6H_5)_2CHSiCl_3$ (95%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (99%)[b]
2	$p\text{-}ClC_6H_4COC_6H_5$ (1:3:1)	Neat, 1 hr, 52–77°	$p\text{-}ClC_6H_4CHSiCl_3C_6H_5$ (73%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (97%)[b]
3	$p\text{-}CH_3C_6H_4COC_6H_5$ (1:3:1.2)	CH_3CN (solvent), 24 hr, 60–67°	$p\text{-}CH_3C_6H_4CHSiCl_3C_6H_5$ (88%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (quantitative)[b]
4	C_6H_5CHO (1:3:1)	CH_3CN (solvent), 1 hr, 57–58°	$C_6H_5CH_2SiCl_3$ (5%)[c] $C_6H_5CHClSiCl_3$ (42%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (95%)[b]
5	2,6-$Cl_2C_6H_3CHO$ (1:3:1)	CH_3CN (solvent), 2 hr, 51–64°	2,6-$Cl_2C_6H_3CH_2SiCl_3$ (61%)[b] $(n\text{-}C_3H_7)_3N\cdot HCl$ (87%)[b]
6	C_6H_5COCl (1:1.25:1)	CH_3CN (solvent), 1 hr, 25°; 0.5 hr, 85°	$C_6H_5CHClSiCl_3$ (91%)[b,d] $(n\text{-}C_3H_7)_3N\cdot HCl$ (quantitative)[b,d]

[a] The distillation residues were resinous materials containing Si–O and Si–Cl linkages in accord with a structure like I. [b] Isolated yield. [c] Yield by glpc. [d] Yield based on $HSiCl_3$ and stoichiometry of eq 1. [e] Satisfactory elemental analyses and spectral data (nmr and ir) were obtained for all silicon compounds listed.

a polymeric structure similar to I[3]) whose ir spectrum was dominated by the Si–O absorption at 8.5–9.5 μ. Data for the transformation of a series of carbonyl compounds are summarized in Table I.

In contrast to the result described in entry 6 of Table I, benzoyl chloride, trichlorosilane, and tri-*n*-propylamine (mole ratio 1:3:1) combined in tetrahydrofuran (4 hr at −40 to +25°) produced, in addition to the amine hydrochloride (94%) and a small amount of α-chlorobenzyltrichlorosilane (II), a 59% yield of α-chlorobenzyltrichlorosilyloxydichlorosilane (III, $C_6H_5CHClSiCl_2OSiCl_3$): bp 110° (2 mm); nmr (CCl_4) δ 4.55 (s, 1), 7.35 (s, 5); ir band 9.0 μ. *Anal.* Calcd for $C_7H_6Si_2OCl_6$: C, 22.42; H, 1.61; Cl, 56.72; Si, 14.98. Found: C, 22.15; H, 1.74; Cl, 56.90; Si, 14.80. That III is a likely intermediate in the reductive silylation of benzoyl chloride was demonstrated by its rapid conversion to I and II on refluxing in acetonitrile in the presence of catalytic amounts of tri-*n*-propylamine.[4]

$$\text{III} \xrightarrow[\text{CH}_3\text{CN; 1 hr, 84°}]{0.1\text{ equiv of }(n\text{-C}_3\text{H}_7)_3\text{N}} \text{I} + \text{II}\ (85\%) \qquad (2)$$

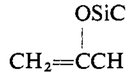
If one assumes the general intermediacy of trichlorosilyloxy compounds similar to III in reductive silylations, the over-all reaction sequence may be represented by eq 3.

$$\begin{aligned} &R'\overset{\overset{\displaystyle O}{\|}}{C}R'' + 2HSiCl_3 + R_3N \rightarrow R'\overset{\overset{\displaystyle SiCl_2OSiCl_3}{|}}{C}HR'' + R_3N\cdot HCl \qquad (3)\\ &R'CHSiCl_3R'' + \text{I} \xleftarrow{R_3N\text{ (catalyst)}} \end{aligned}$$

Based upon the reaction vigor, it appears that electron withdrawal from the carbonyl carbon facilitates the reductive silylation process. In substantiation of this premise, 2,4-dimethylbenzophenone was recovered virtually unchanged after refluxing for 4 hr with trichlorosilane and tri-*n*-propylamine.

Electronic and/or steric effects may be responsible for the rather anomalous behavior of benzaldehyde (entry 4 in Table I) compared to 2,6-dichlorobenzaldehyde (entry 5) and the other carbonyl compounds studied.

Acetophenone, cyclohexanone, and acetone each produced multicomponent mixtures when treated with the silane–amine combination, the last mentioned giving 2-trichlorosilyloxypropene[1] (IV) as the principal product



$$CH_2{=}\overset{\overset{\displaystyle OSiCl_3}{|}}{C}CH_3$$

IV

(45%). Whether other enolizable carbonyl compounds are unsuitable for reductive silylation is a point currently under investigation.

The general scope and mechanism of reductive silylations are under active investigation in our laboratory, since the reaction holds promise of becoming a powerful synthetic tool in both carbon and organosilicon chemistry.

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

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Received December 7, 1968

Total Synthesis of *dl*-Cedrene and *dl*-Cedrol

Sir:

Cation **1**, Y = +, as generated, for example, from the corresponding alcohol **1**, Y = OH, is potentially capable of cyclization *via* cations **2** and **3** to form cedrene (**4**)[1,2] in a

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(3) A similar (but phenyl-substituted) resinous substance was observed as the by-product in the high-temperature reduction of ketones by diphenylsilane. See H. Gilman and J. Diehl, *J. Org. Chem.*, **26**, 4817 (1961).

(4) This disproportionation can be regarded as a variant of that undergone by hexachlorodisiloxane, also with tertiary amine catalysis: G. D. Cooper and A. R. Gilbert, *J. Amer. Chem. Soc.*, **82**, 5042 (1960).

(1) Structure: (a) Pl. A. Plattner, A. Fürst, A. Eschenmoser, W. Keller, H. Kläui, St. Meyer, and M. Rosen, *Helv. Chim. Acta*, **36**, 1845 (1953); (b) G. Stork and R. Breslow, Jr., *J. Am. Chem. Soc.*, **75**, 3219 (1953).

(2) Absolute configuration: G. Büchi, R. E. Erickson, and N. Wakabayashi, *ibid.*, **83**, 927 (1961).