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Preliminary communication

Chemical diversion of radical-anion intermediates in the metal cleavage of carbon–silicon bonds: coupling of cyclopropyl(triphenyl)silane

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The cleavage of carbon–silicon bonds by alkali metals represents an important, broadly applicable route to the preparation of synthetically useful silylmetallic reagents (R_3SiM)[1], as well as a means of degrading organosilanes in a selective fashion (eq. 1)[2]:

$$R_nSiR'_{4-n} + 2M \xrightarrow[\text{-R'M}]{\text{solvent}} R_nR'_{3-n}SiM \xrightarrow{H_3O^+} R_nR'_{3-n}SiH \qquad (1)$$

We now wish to report the chemical diversion, in high yield, of a radical-anion intermediate formed in the metal cleavage reaction of cyclopropyl(triphenyl)silane (I). Depending upon temperature, I was shown to undergo exclusively either the expected carbon–silicon bond cleavage or the novel reductive coupling of the phenylsilane moiety. This observed reduction, shown to be rather general for phenyl-, vinyl- and alkinyl-silanes, constitutes a unique synthetic route to previously inaccessible silanes and, at the same time, offers strong chemical evidence for the crucial role of radical-anions in carbon–silicon bond cleavage by alkali metals.★

In an attempt to learn whether the cyclopropylsilyl group could form a radical-anion by virtue of cyclopropyl p_π–silicon d_π conjugation,★★ cyclopropyl(triphenyl)silane (I)★★★ was treated with potassium metal in 1,2-dimethoxyethane at –40° or with lithium metal in tetrahydrofuran at –70°. In both cases, hydrolytic work-up (H_2O or D_2O) gave 4,4'-bis[cyclopropyl(diphenyl)silyl]-1,1',4,4'-tetrahydrobiphenyl (IIa or IIb) in yields of 50% and 80% respectively; the products possessed the following properties: (a) m.p. 149–150°; (b) NMR of IIa (CS_2, δ): multiplets centered at 0.17 (3H), 0.70 (2H), 2.17 (1H, broad doublet), 2.95 (1H, br.d.) and 7.47 (10H); and two broad doublets of doublets

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★Although radical-anions of organosilanes have often been observed at the low concentrations detectible by ESR spectroscopy ($10^{-8}M$; *cf.* ref.3), the present trapping work makes the actual role of such radical-anions in metal cleavages much more manifest. Furthermore, although the formation of biphenyl traces from the action of metals on phenyl derivatives has been observed in ESR measurements, this report describes the first phenyl group reductive coupling of preparative significance.

★★*Cf.* J.J. Eisch and R.J. Beuhler, *J. Org. Chem.*, 28 (1963) 2876, for the lithium metal reductive coupling of triphenylvinylsilane. The formation of a radical-anion by a vinyl group enjoying no formal p_π–p_π conjugation with adjacent atoms supports the operation of p_π–d_π vinyl–silicon interaction.

★★★Satisfactory elemental analyses and concordant infrared and NMR data were obtained for all new organosilicon compounds herein reported.

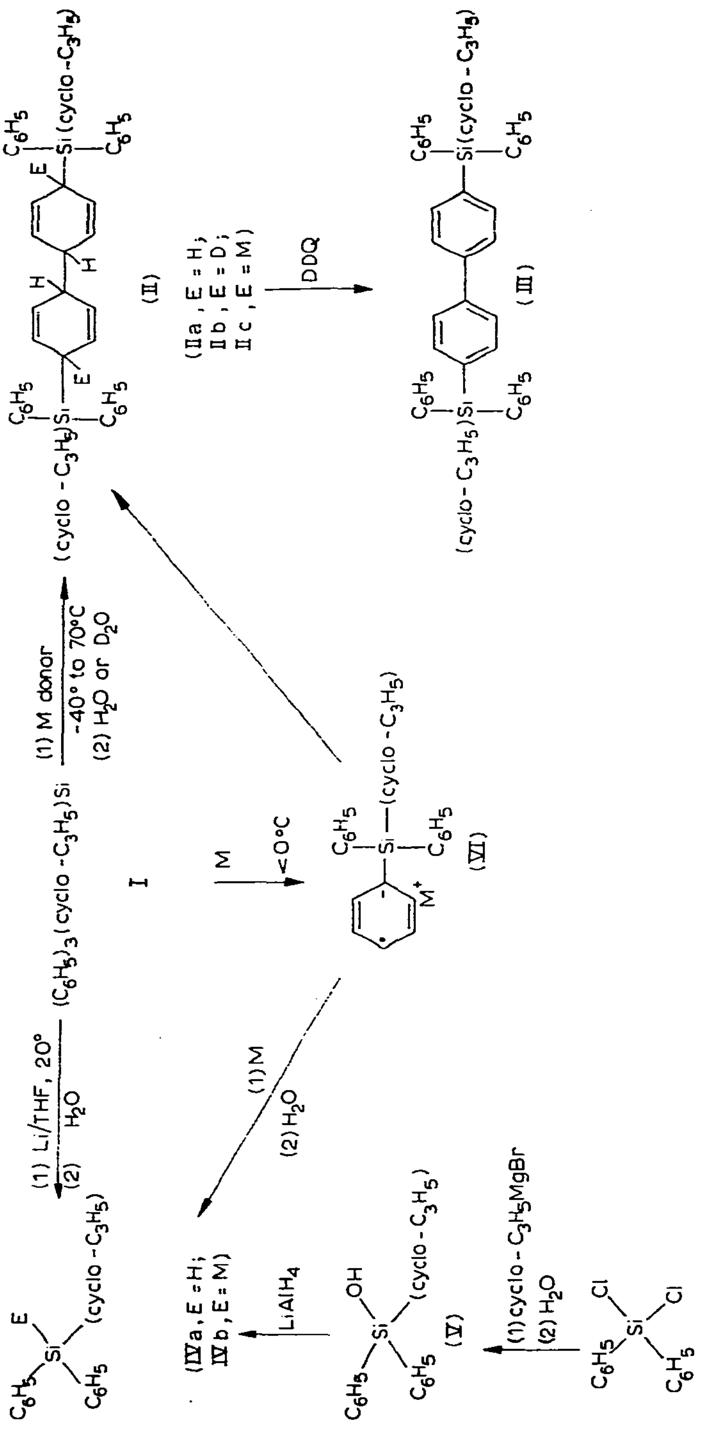
(1) Li/THF, 20°
(2) H2O
(C6H5)3(cyclo-C3H5)Si
I
(1) M donor
-40° to 70°C
(2) H2O or D2O
(II)
(IIa, E = H; IIb, E = D; IIc, E = M)
DDQ
(III)
M
<0°C
M+
(VI)
(1) M
(2) H2O
(IVa, E = H; IVb, E = M)
LiAlH4
(V)
(1) cyclo-C3H5MgBr
(2) H2O
Si
E
OH
Cl

Fig.1.

centered at 5.2 (1H) and 5.69 (1H); (c) NMR of IIb (CS_2,δ): disappearance of broad doublet at 2.95 and coalescence of broad doublet at 2.17 into a broad singlet; narrowing of doublet at 5.69; (d) heating IIa or IIb with 2,3 -dichloro-5,6-dicyanobenzoquinone in benzene provided 4,4'-bis[cyclopropyl(diphenyl)silyl] biphenyl (III). The latter compound III possessed the following properties: (a) m.p. 159–160°; (b) mass spectrum parent peak at 598; and (c) NMR (CS_2,δ): multiplets at 0.1 (3H), 0.6 (2H), 6.8–7.5 (14H) (Fig.1).

Although no cleavage of the cyclopropyl ring or of carbon–silicon bonds in I was observed under the foregoing conditions, treatment of I with a fivefold excess of lithium metal in THF at 20° led only to phenyl–silicon bond scission. Cautious hydrolysis provided a 29% yield of cyclopropyldiphenylsilane (IV). The structure of the latter compound was established by independent synthesis via the sequence: (a) treatment of dichlorodiphenylsilane with one equivalent of cyclopropylmagnesium bromide and subsequent hydrolysis to afford cyclopropyldiphenylsilanol (V); and (b) reduction of V with $LiAlH_4$ (Fig.1).

The most cogent interpretation of these reductive dimerization and cleavage reactions of I is the formation of the radical-anion VI, which can couple (→IIc) or add another electron and then dissociate into $R_2R'SiM$ and C_6H_5M (→IVb). The cyclopropyl group I is unnecessary for such dimerization since a similar pattern of behavior is also observed for tetraphenylsilane. Exclusive coupling through the *para*-position of VI is consistent with previous ESR studies of the trimethyl(phenyl)silane radical-anion[3], where the magnitudes of the ring proton hyperfine constants were best explicable in terms of the added electron entering the symmetric anti-bonding M.O. The approximate free spin densities would accordingly be maximized at C_{para} and C_1 and be minimized at C_{ortho} and C_{meta}.

The significance of radical-anion intermediates, which at low temperatures are sufficiently stable to cause reduction in high yield and at higher temperatures lead to carbon–silicon bond rupture, is also apparent in the behavior of triphenyl(vinyl)silane (VII) and 1-propynyl(triphenyl)silane (VIII). At low temperatures, VII undergoes reductive coupling[4] and VIII is reduced to *trans*-1-propenyl(triphenyl)silane. At room temperature cleavage of the vinyl- and 1-propynyl groups, respectively, becomes the principal course.

The foregoing observations open up new synthetic methods for the monomolecular and bimolecular reduction of organosilanes, as well as providing important insight into the mechanisms of metal cleavages of carbon–silicon bonds. Electron spin resonance spectroscopic studies, currently underway in this Laboratory[5], are examining the hyperfine spectra of the radical-anions of I, VII and VIII, in order to attempt a correlation of electron density on the various organic groups around silicon with their chemical behavior.

Finally, the experimental observations as to the suitability of active alkali metals, high state of particle dispersion, donor solvents and temperature for the cleavage of organo-silanes and -polysilanes[1] can best be understood mechanistically in terms of a Born–Haber treatment for the formation of radical-anion intermediates[6].

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