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SILYL RADICALS V

NOVEL CYCLIZATION REACTIONS INVOLVING HOMOLYTIC AROMATIC SILYLATION

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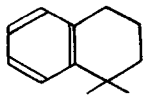
Cyclization reactions involving homolytic aromatic substitution by carbon radicals have been well known. For example, an interesting case is that reported by Winstein et al. involving both migration of the phenyl group and cyclization (1).

$$PhC(CH_3)_2CH_2CH_2CH_2\cdot \xrightarrow{RCHO} PhC(CH_3)_2CH_2CH_2CH_3 \quad +$$



$$+ \quad HC(CH_3)_2CH_2CH_2CH_2Ph$$

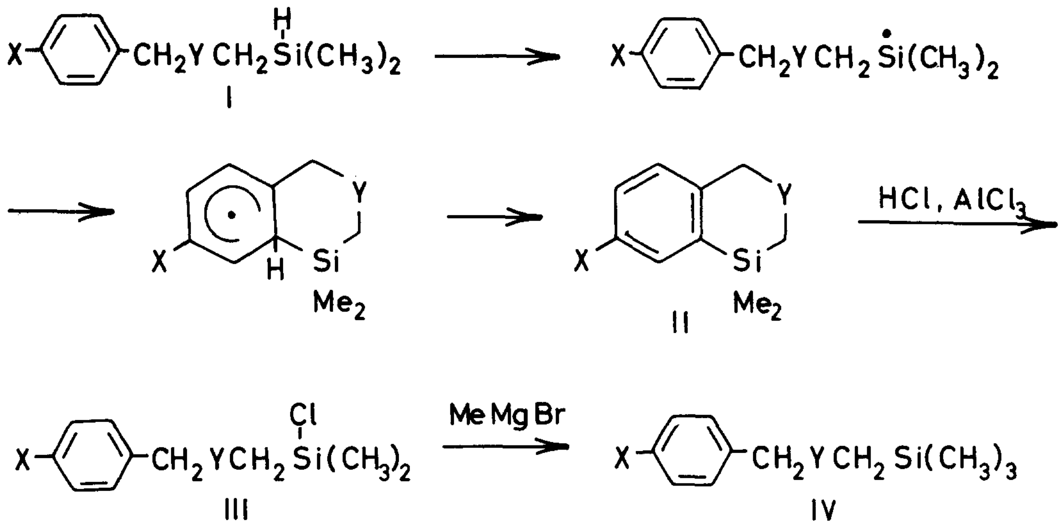
We report now a novel example of such a type of cyclization by radicals other than carbon; the homolytic cyclization by silyl radicals (2).

An equimolar mixture of (3-phenylpropyl)dimethylsilane (Ia) (0.64g, 3,56 m moles) and di-tert-butyl peroxide (DTBP, 0.53g, 3.63 m moles) was placed in a sealed tube with degassing, and allowed to react in a constant-temperature bath kept at 135° for 13 h. Examination of the mixture by glc revealed that only single volatile product was present in addition to the expected acetone and t-butyl alcohol and some polymeric substance. The product was isolated by glc and identified as 1,1-dimethyl-silatetralin (IIa, 0.089g, 0.51 m mole). Determination of the structure was based on ir and nmr (τ ppm, 9.63, s, 6H; 9.00, t, 2H; 7.96, m, 2H; 7.11, t, 2H; 2.30-2,70, m, 4H) spectra (3) and transformation to the authentic sample shown in chart 1.

Thus, protodesilylation of Ia with dry hydrogen chloride in the presence of a catalytic amount of aluminum chloride in chloroform afforded IIIa, that was identified by comparing with the authentic sample (4). IIIa was further converted to (3-phenylpropyl)trimethylsilane (IVa), bp 110° (20 mmHg), n_D^{20} 1.4918, d_4^{20} 0.8804.

Analogously, 2,4,4-trimethyl-5-phenyl-2,4-disilapentane (Ib), bp 111° (11 mmHg), n_D^{20} 1.5014, d_4^{20} 0.8898, gave a cyclization product, IIb, that was separated by preparative glc, n_D^{20} 1.5245, d_4^{20} 0.9365. Its structure was verified by elemental analysis and ir and nmr (τ ppm, 10.18, s, 2H; 9.98, s, 6H; 9.71, s, 6H; 7.96, s, 2H; 2.55-3.20, m, 4H) spectra. Furthermore, IIb was also converted to IIIb, bp 131° (11 mmHg), n_D^{20} 1.5120, d_4^{20} 0.9859, then to IVb, bp 127° (26 mmHg), n_D^{20} 1.4970, d_4^{20} 0.8841.

Chart 1

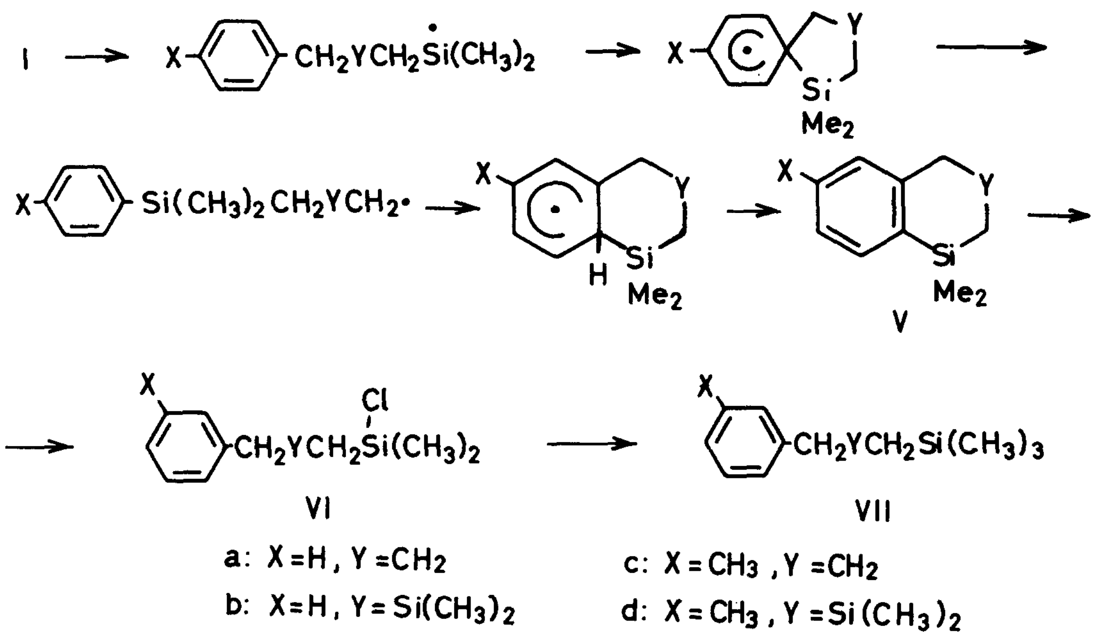


a: X = H, Y = CH_2
b: X = H, Y = $Si(CH_3)_2$
c: X = CH_3, Y = CH_2
d: X = CH_2, Y = $Si(CH_3)_2$

Now an interesting question may be raised whether the cyclization occurred actually by the silyl radical or by a carbon radical. Although homolytic aromatic silylations were demonstrated very recently (5,6), there may be another possibility that the phenyl group would migrate from carbon to silicon at the intermediate radical as depicted in the reaction of the carbon analog (1), and the resulting carbon radical would be responsible as the active species in the cyclization.

If this were the case, *para*-substituted I (Ic abd Id) would give cyclization products, V, instead of II, and then *meta*-substituted VI and VII would be obtained by further derivatization (chart 2).

Chart 2



However by the same procedure, Ic, bp 120° (17 mmHg), n_D^{20} 1.4966, d_4^{20} 0.8768, and Id, bp 133° (17 mmHg), n_D^{20} 1.5012, d_4^{20} 1.5012, afforded exclusively IIc and IId,, respectively. The structures of these compounds were verified unequivocally by leading to IIIc, bp 90° (2 mmHg), n_D^{20} 1.5040, d_4^{20} 1.0111, and IIId, bp 145° (10 mmHg), n_D^{20} 1.5085, d_4^{20} 0.9901, which were then converted to IVc, bp 116° (19 mmHg), n_D^{20} 1.4942, d_4^{20} 0.8716 and IVd, bp 140° (18 mmHg), n_D^{20} 1,4990, d_4^{20} 0.8845, respectively.

Hence, these results clearly demonstrate that cyclization occurred by the silyl radicals.

Furthermore, throughout the experiments, there is no indication of the formation of X-C_6H_4-$Si(CH_3)_2CH_2$-Y-CH_3 [Y = $(CH_2)_2$ and $Si(CH_3)_2$], which could arise from the rearranged radicals. Therefore, it may be concluded that the silyl radicals generated by hydrogen abstraction did not rearrange at least in the present reaction, but underwent facile cyclization (7).

REFERENCES

1 S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

2 For production of silyl radicals from hydrosilanes by hydrogen abstraction, see, H. Sakurai, M. Murakami, and M. Kumada, *J. Am. Chem. Soc.*, **91**, 519 (1969), and references cited therein.

3 Nmr spectra were determined as carbon tetrachloride solution using a Jeol model JNM-C-60H spectrometer. Cyclohexane or tetramethylsilane were used as internal standards and chemical shifts were converted to τ values taking 1.43 ppm as the signal difference between these standards throughout the study.

4 IIIa was conveniently prepared by the reaction of 3-phenylpropylmagnesium chloride and dimethyldichlorosilane, bp 121° (13 mmHg), n_D^{20} 1.5012, d_4^{20} 0.9959. Reduction of IIIa by $LiAlH_4$ gave Ia, bp 93° (11 mmHg), n_D^{20} 1.4940, d_4^{20} ÷ 0.8768.

5 H. Sakurai, A. Hosomi, and M. Kumada, *Tetrahedron Letters*, Preceding Paper.

6 C. Eaborn, R. A. Jackson, and R. Pearce, *Chem. Commun.*, 920 (1967), have reported possible homolytic aromatic substitution by the trimethylsilyl radical which was generated by photolysis of bis(trimethylsilyl)mercury.

7 All new compounds reported here had reasonable ir and nmr spectra and elemental analyses. Details will be reported later.