acetoxy steroids were subjected to hydrogen abstraction by photochemically generated CCl_3 and C_6H_5ICl radicals. The products from these reactions were $\Delta^{9(11)}$- and $\Delta^{14(15)}$-olefins reflecting attack at C-9 and C-14 only. Their failure to obtain attack at C-5 was attributed to polar effects. In contrast we obtained attack at C-5 to approximately the same extent in the presence or absence of a 3-acetoxy function. In further contrast we found no evidence for attack at C-9.

The equal reactivity at C-5 and C-14 which we observed in these experiments would not have been predicted from our bromine radical epimerization studies, where reactivity at C-14 was very much greater than at C-5;[1] this may be attributed to the greater selectivity of bromine atom as compared to methyl radical.[5]

We are developing this reaction to provide synthetic access to the difficultly available cardenolides, all of which possess 14β-hydroxy functions.[6]

Acknowledgment. We would like to thank Professor Samuel Levine for helpful discussions during the course of this work.

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(5) William A. Pryor in "Introduction to Free Radical Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1966, p 56.

(6) (a) F. Sondheimer, *Chem. Brit.*, **1**, 454 (1965); (b) R. Deghenghi, *Pure Appl. Chem.*, 21, 153 (1970).

(7) This work forms part of the Ph.D. Dissertation of A. Rotman to be submitted in partial fulfillment of the requirements of the Feinberg Graduate School, The Weizmann Institute of Science.

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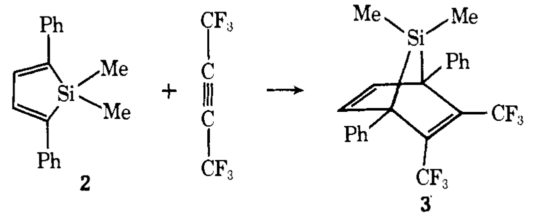
Thermal Decomposition of 1,4-Diphenyl-2,3-bis-(trifluoromethyl)-7-dimethylsilabicyclo[2.2.1]heptadiene

Sir:

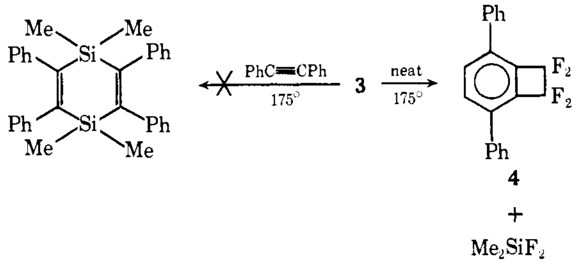
While it is well established that the thermal decomposition of 7-silanorbornadienes cleanly affords silylenes *via* bridge extrusion,[1] this work has been largely limited to those adducts derived from the Diels–Alder reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**) and various acetylenes. Recently Maruca has reported that 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**2**) reacts with diphenylacetylene to afford a crystalline material for which the 7-silanorbornadiene structure was suggested.[2] While X-ray diffraction studies have shown that this material is actually a crystal complex,[3] it does appear that at much higher temperatures the adduct is formed and dimethylsilylene is extruded. Even more recently it has been shown that silole **2** reacts with ethynyltrichlorogermane to provide the 4 + 2 adduct which thermally extrudes dimethylsilylene.[4] These reports prompt us to reveal the results of initial studies on the remarkable thermal behavior of the 1,4-diphenyl-2,3-bis(trifluoromethyl)-7-dimethylsilabicyclo[2.2.1]heptadiene (**3**).

The addition of perfluoro-2-butyne to **2** proceeds cleanly at room temperature (4 days, sealed tube, $MeCl_2$) to afford adduct **3**[5] [80%; mp 100–104°; m/e 424.110438, calcd m/e 424.108085; nmr (CCl_4) δ 0.12 (s, 3 H, $SiCH_3$), 0.64 (s, 3 H, $SiCH_3$), 6.82 (s, 2 H, vinyl), 7.11 (s, 10 H, phenyl)].



Upon heating **3** above 170° in an evacuated, sealed tube dimethyldifluorosilane was evolved as the sole gaseous component and identified by mass spectrometry. This surprising result was precedented by the report of Hota and Willis that the 7-silanorbornadiene derived from tetraphenylsilole (**1**) and perfluoro-2-butyne thermally decomposed to Me_2SiF_2 and polymer.[6] However, we find that from the nonvolatile material from the pyrolysis of **3** can be isolated the benzocyclobutene (**4**)[5] (45%; mp 161.0–162.5°; M^+ m/e 328; ^{19}F nmr singlet at 103.2 ppm downfield from $FCCl_3$).

The possibility that **4** results from silylene abstraction of fluorine is made unlikely by the observation that decomposition of **3** in the presence of excess diphenylacetylene yields *no* 1,4-disilacyclohexadiene and essentially a quantitative recovery (>95%) of diphenylacetylene. Diphenylacetylene is known to be an excellent trap for dimethylsilylene generated in this fashion[7] and has been used previously as a negative test for silylene intermediacy.[8]



That decomposition of **3** does not initiate through loss of dimethylsilylene is quite surprising as this is clearly a symmetry-allowed, cheletropic fragmentation which should proceed in a concerted fashion.[9] A possible mechanism would involve initial homolytic cleavage of a Si–C bond to diradical **5** followed by fluorine atom transfer to yield **6**. This is formally a γ-halosilicon elimination and in contrast to the α-halosilicon[10] and β-halosilicon[11] eliminations may well proceed through a free-radical process.[10] Although it is

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(1) For a recent, general review on divalent silicon intermediates, silylenes, see W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(2) R. Maruca, *J. Org. Chem.* **36**, 1626 (1971).

(3) J. C. Clardy and T. J. Barton, *J. Chem. Soc., Chem. Commun.*, 690 (1972).

(4) A. Laporterie, J. Dubac, P. Mazerolles, and M. Lesbre, *Tetrahedron Lett.*, **48**, 4653 (1971).

(5) All new compounds gave satisfactory (±0.3%) elemental analyses.

(6) N. K. Hota and C. J. Willis, *J. Organometal. Chem.*, **15**, 89 (1968).

(7) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 1596 (1964).

(8) W. H. Atwell and D. R. Weyenberg, *ibid.*, **90**, 3438 (1968).

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinham/Bergstr., Germany, 1970, p 156.

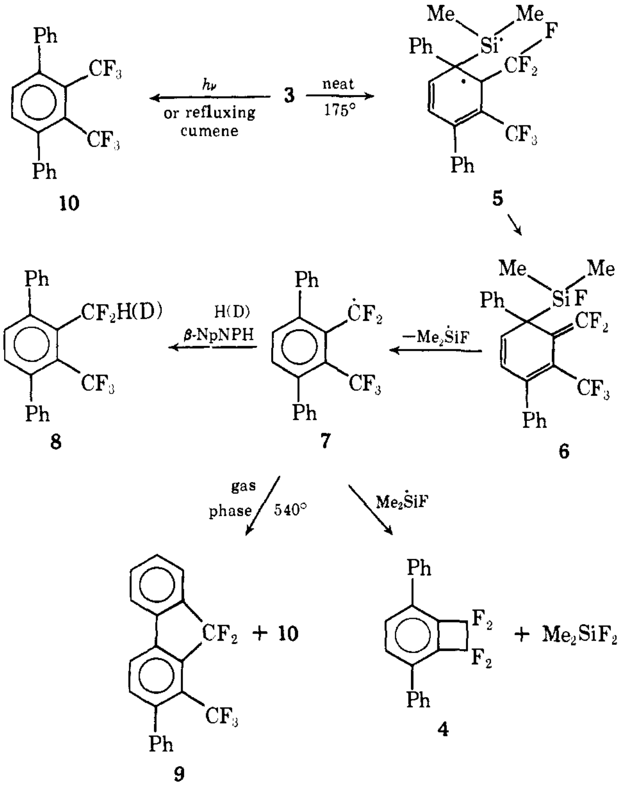
(10) G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Commun.*, 382 (1965).

(11) I. M. T. Davidson, C. Eaborn, and M. N. Lilly, *J. Chem. Soc.*, 2624 (1964).

tempting to assume loss of Me_2SiF_2 from **6** to proceed directly to **4**, further experiments make this route unlikely. When the neat pyrolysis of **3** is conducted in the presence of *N*-phenyl-2-naphthylamine, a hydrogen transfer agent,[12] the *p*-terphenyl **8**[5] [49%; mp 113–114°; ^{19}F nmr (*vs.* $FCCl_3$) δ +49.5 (t, J_{FF} = 15 Hz, CF_3), 106.2 and 107.1 ppm (nonoverlapping doublet of quartets, J_{HF} = 50.2 Hz); *m/e* 348.091802, calcd *m/e* 348.09181] is isolated and *no* **4**. Furthermore, when the pyrolysis of **3** is performed in the gas phase at 540° (flow system) an 87% overall yield of a *ca.* equal mixture of **9**[5] [mp 135–136°; ^{19}F nmr (*vs.* $FCCl_3$) $\delta\nu$ +57.7 (t, J_{FF} = 19 Hz, CF_3), +113 ppm (q, J_{FF} = 19 Hz, CF_2)] and **10** can be isolated and separated. Products **8** and **9** would seem to implicate the intermediacy of **7**.

Evidence has recently been accumulating that the bridge elimination of carbenes from norbornadienes occurs through initial homolytic scission of a C–C bond to provide a diradical which may either close to a norcaradiene or aromatize through carbene extrusion.[13] The work reported here makes it quite likely that silylene extrusions from 7-silanorbornadienes generally proceed by this route.[14] It is only because of the favorable location of the trifluoromethyl groups and the great strength of the Si–F bond[16] that we are able to divert the normal reaction and thus be aware of the mode of initial cleavage.

Surprisingly we find that decomposition of **3** brought about either by ultraviolet irradiation or refluxing solvent (cumene) affords the expected thermal product **10**[5,17] [mp 130–132°; ^{19}F nmr (*vs.* $FCCl_3$) δ +51 ppm (s); *m/e* 366.083417, calcd *m/e* 366.084300]. The photochemical reaction provides a 61% yield of **10**, and Me_2Si has been trapped by tolan to give 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene in very low yield.



Acknowledgment. This work has been generously supported by the National Institutes of Health (GM 16689-03). One of us (C. L. M.) also thanks the National Science Foundation (GP 28152X).

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(12) R. F. Bridger, *J. Org. Chem.*, **35**, 1746 (1960).

(13) For a recent review of the evidence for this mechanism see: R. W. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).

(14) The possibility of **3** undergoing a 1,3-sigmatropic migration of silicon (ref 15) to form a silanorcaradiene which could open to **5** (or a similar diradical) is a mechanistic possibility which we tentatively exclude because of the great strain involved in the initial rearrangement.

(15) H. Kwart and J. Slutsky, *J. Amer. Chem. Soc.*, **94**, 2515 (1972).

(16) D(SiF) = 193 ± 10 kcal/mol (Me_3SiF): G. G. Hess, F. W. Lampe, and L. H. Sommer, *ibid.*, **87**, 5327 (1965).

(17) This compound was synthesized for comparison from the Diels–Alder reaction between 1,4-diphenylbutadiene and perfluoro-2-butyne followed by dehydrogenation with sulfur. Compound **8** was found to be thermally stable when heated neat at 170–180° and in the gas phase (flow system) at 540°, thus excluding that route to **4**.

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Reliability of Coupling Constants Obtained from Tris(dipivalomethanato)europium Shifted Proton Magnetic Resonance Spectra

Sir:

Pseudocontact nuclear magnetic resonance shift reagents have received considerable attention in molecular structure studies due to their ability to provide first-order spectra from which chemical shifts and coupling constants can be directly obtained.[1–3]

Chemical shifts are usually dealt with by comparing the experimentally found isotropic shift with that calculated from the pseudocontact shift equation.[4] Certain precautions regarding this approach have been recorded.[5–9]

Coupling constants obtained from shifted spectra have not received careful attention regarding their validity. However, claims have been made that coupling constants from shifted spectra of both σ[10] and π[11] systems are unaffected by the shift reagent.

We now wish to report a case where a shift reagent does affect the values of coupling constants. Tris(dipivalomethanato)europium, $Eu(dpm)_3$,[12] shifted spectra from benzocyclopenten-2-ol[13] (**1**) and benzocyclobuten-1-ol[14] (**2**) were obtained at 60 MHz[15] on 20% solutions of the solute in carbon tetrachloride at

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(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(2) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(3) W. DeW. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

(4) M. R. Willcott, III, R. E. Lenkinske, and R. E. Davis, *ibid.*, **94**, 1743 (1972).

(5) B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *ibid.*, **93**, 3281 (1971).

(6) S. B. Tjan and F. R. Visser, *Tetrahedron Lett.*, 2833 (1971).

(7) I. Fleming, S. W. Hanson, and J. K. M. Sanders, *ibid.*, 3733 (1971).

(8) I. Armitage and L. D. Hall, *Can. J. Chem.*, **49**, 2770 (1971).

(9) J. Goodisman and R. S. Matthews, *Chem. Commun.*, 127 (1972).

(10) I. Armitage and L. D. Hall, *Chem. Ind. (London)*, 1537 (1970).

(11) A. F. Bramwell, G. Riezebos, and R. D. Wells, *Tetrahedron Lett.*, 2488 (1971).

(12) Obtained from Alfa Inorganics, Inc., Beverly, Mass.; mp 189–191.5°.

(13) W. F. Whitmore and A. I. Gebhart, *J. Amer. Chem. Soc.*, **64**, 912 (1942); mp 66.5–68°.

(14) H. H. Wasserman and J. Solodar, *ibid.*, **87**, 4002 (1965); mp 60–61°.

(15) A Varian Model T-60 spectrometer was used. The probe temperature was 35°.