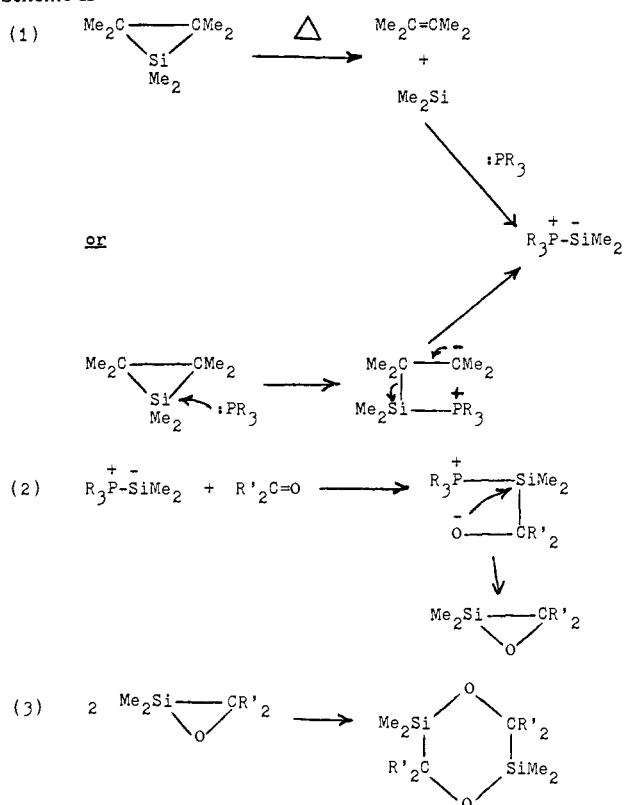Scheme II

A likely mechanism by which these 1,4-dioxa-2,5-disilacyclohexanes are formed is shown in Scheme II. The phosphine is essentially a catalyst in this process since it is recovered unchanged at the end of the reaction. However, it does appear to be intimately involved in this reaction. No 1,4-dioxa-2,5-disilacyclohexane products were obtained when hexamethylsilirane and aliphatic ketones were heated together in the absence of a tertiary phosphine. The fact that the more nucleophilic dimethylphenylphosphine is much more effective in giving good product yields than is triphenylphosphine also speaks strongly for phosphine participation in this reaction. Moreover, Japanese workers have reported that reactions of silylenes (Me_2Si[4,5] and $Me_3SiSiPh$[6]) with the ketones used in this study in the absence of a tertiary phosphine give silyl enol ethers as products (eq 1), rather than 1,4-dioxa-2,5-disilacyclohexanes. Products of type **7** were obtained regardless of the

$$R_2Si: \; + \; (R'CH_2)_2C{=}O \; \longrightarrow \; R'CH_2\underset{\underset{\displaystyle 7}{OSiMe_2H}}{C}{=}CHR' \qquad (1)$$
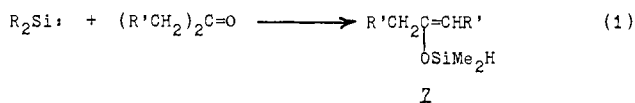
method of generation of the silylene: thermally, at 500 °C in the gas phase,[4] or photochemically in solution.[5,6] Only in the case of nonenolizable ketones such as 2-adamantanone and norbornone were 1,4-dioxa-2,5-disilacyclohexane-type products obtained when dimethylsilylene was generated by photolysis.[5]

It would seem then that the betaine formed by reaction of the dimethylsilylenephosphorane with the ketone (Scheme II) decomposes in a manner analogous to the decomposition of the betaine derived from reaction of a sulfur ylide with a carbonyl compound, a process which gives an oxirane and a sulfide.[7] The strong Si–O covalent bond energy and the reluctance of a silicon–carbon double bond to form very likely serve to steer the decomposition in the direction of oxasilirane formation so that a Wittig-type process does not occur.

Reduction of such 1,4-dioxa-2,5-disilacyclohexanes with lithium aluminum hydride results in formation of dimeth-

ylsilyl-substituted carbinols, $Me_2HSiC(OH)R_2$, so that the hexamethylsilirane–dimethylphenylphosphine–ketone reaction also is of preparative interest. More detailed studies of this new reaction are in progress and will be reported at a later date.

References and Notes

(1) (a) D. Seyferth and D. C. Annarelli, *J. Am. Chem. Soc.*, **97**, 2273 (1975); (b) D. Seyferth and D. C. Annarelli, *ibid.*, **97**, 7162 (1975); (c) D. Seyferth and D. C. Annarelli, *J. Organomet. Chem.*, **117**, C51 (1976); (d) D. Seyferth, D. P. Duncan, and S. C. Vick, *ibid.*, **125**, C5 (1977); (e) D. Seyferth and S. C. Vick, *ibid.*, **125** C11 (1977); (f) D. Seyferth, T. F. O. Lim, and D. P. Duncan, *J. Am. Chem. Soc.*, **100**, 1626 (1978).
(2) A C–Si–C bond angle of 49.2° was found in the X-ray crystal diffraction study of another compound containing a silacyclopropane ring: G. L. Delker, Y. Wang, G. D. Stucky, R. L. Lambert, Jr., C. K. Haas, and D. Seyferth, *J. Am. Chem. Soc.*, **98**, 1779 (1976).
(3) D. Seyferth, D. C. Annarelli, and S. C. Vick, *J. Am. Chem. Soc.*, **98**, 6382 (1976).
(4) W. Ando, M. Ikeno, and A. Sekiguchi, *J. Am. Chem. Soc.*, **99**, 6447 (1977).
(5) W. Ando, M. Ikeno, and A. Sekiguchi, *J. Am. Chem. Soc.*, **100**, 3613 (1978).
(6) M. Ishikawa, K. Nakagawa, and M. Kumada, *J. Organomet. Chem.*, **135**, C45 (1977).
(7) A. W. Johnson, "Ylid Chemistry", Academic Press, New York/London, 1966, Chapter 9.
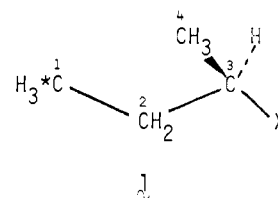
Dietmar Seyferth,* Thomas F. O. Lim
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received May 22, 1978

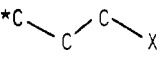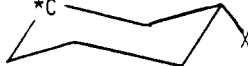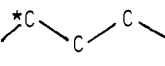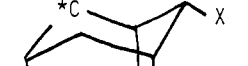## γ-Methyl Substituent Effect on Vicinal Coupling Constants Involving Carbon-13

Sir:
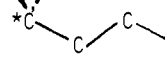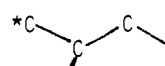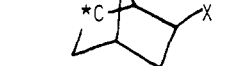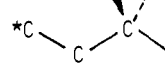
The γ effect on ^{13}C chemical shielding, which arises from gauche 1,4 carbon atoms,[1] has been used widely in ^{13}C chemical shift assignments. This effect has been interpreted[2] in terms of a model which emphasizes the steric interactions between the hydrogens on the C-1 and C-4 atoms in the arrangement **1**. In the present study, it is shown from both ex-

perimental and theoretical results that the γ-methyl or -methylene substituents on C-3 decrease the magnitude of the vicinal ^{13}C coupling constants ($^3J_{CX}(180°)$) between the C-1 atom and the trans oriented nuclear spin X in **1**. Moreover, it is essential to be aware of the γ-methyl effect in using vicinal coupling constants in molecular conformational studies as the effects are shown to be substantial and lead to results which would appear to be anomalous.

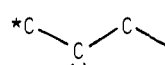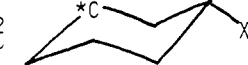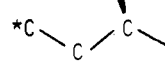In a previous study[3] it was found that vicinal ^{13}C–^{13}C coupling constants in a series of 1-substituted butyl compounds (for which conformational averaging is expected) were uniformly *greater* in magnitude than the $^3J_{CC}(180°)$ for a series of 11-substituted 1-methyladamantanes (one might expect these to conform to the largest values entering the averaged coupling constants in the butyl series). In the same study[3] it was shown that the Fermi-contact contributions (INDO-FPT[4,5]) to $^3J_{CC}(180°)$ in the series *trans*-butane, equatorial

Table I. INDO-FPT Results for Trans Vicinal Coupling Constants ($^3J_{CH}(180°)$, $^3J_{CC}(180°)$, and $^3J_{CF}(180°)$) in Propane (X = H), Butane (X = $^{13}CH_3$), and Fluoropropane (X = ^{19}F), as Well as Methyl-Substituted and Cyclic Compounds Exhibiting These Types of Coupling. Experimental Values Are in Parentheses.[a]

Molecule	$^3J_{CH}$	$^3J_{CC}$	$^3J_{CF}$	Molecule	$^3J_{CH}$	$^3J_{CC}$	$^3J_{CF}$
2	8.78 (13±1)[b]	4.27	23.71	9	7.63 (8.12)[c]	3.72	17.38
3	8.74	4.26[d]	24.03	10	7.57	3.33[d] (3.44)[e]	15.39
4	8.62	4.12[d]	21.33	11	7.35	–	16.29[f] (9.8)
5	8.72	3.81	21.36	12	6.96	3.39	14.13 (11.5)[g]
6	8.74	3.44	19.24	13	6.82 (5.33)[h]	3.33[d] (3.2)[i]	13.08 (9.61)[j]
7	7.82	3.81	18.84				
8	7.07	3.44	15.02				

[a] All values are in hertz. [b] This is an estimated value from the experimental coupling constant of 5.7 ± 0.2 Hz reported for propane by R. E. Wasylishen and T. Schaefer, *Can. J. Chem.*, **52**, 3247–3250 (1974), and assuming a gauche coupling constant value of 2.0 ± 0.2 Hz, and also assuming that the experimental value is simply one third trans and two thirds gauche. [c] Low temperature value from V. A. Chertkov and N. M. Sergeyev, *J. Am. Chem. Soc.*, **99**, 6750–6752 (1977). [d] Value from ref 6. [e] This work. [f] J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107–7120 (1970). [g] O. A. Subbotin and N. M. Sergeyev, *ibid.*, **97**, 1080–1084 (1975), for conformationally frozen (low temperature) fluorocyclohexane. [h] This work; obtained from the d_{15} compound. [i] Reference 3. [j] This work; a value of 10 Hz was reported by T. Pehk, E. Lippmaa, V. V. Sevostjanova, M. M. Krayuschkin, and A. I. Tarasova, *Org. Magn. Reson.*, **3**, 783–790 (1971).

methylcyclohexane, and 1-methyladamantane are 4.27, 3.72, and 3.32 Hz, respectively. From these results it was proposed[3] that the decrease in the coupling constant in this series of molecules paralleled the increase in the number of carbon rear lobes impinging in the center of these cyclic structures. More recently, it has been suggested[6] that the latter effect is small, and that the calculated decrease in this series of compounds could be correlated with the increase in the number of β-methylene substituents. The recognition that there was some feature associated with these cyclic molecules leading to a decreased coupling was useful in removing a number of apparent anomalies in previous studies of $^{13}C-^{13}C$ coupling constants.[7,8] The ensuing discussion will show that these are actually γ-*substituent effects arising from the 1,4-type interactions* in **1**. This conclusion would not be apparent from the previous studies[3,6–8] of vicinal $^{13}C-^{13}C$ coupling because this corresponds to the special case in which the C-4 methyl group in **1** is *both* a β substituent (to X = $^{13}CH_3$) and a γ substituent (γ to the C-1 atom).

Selected results from a very large number of INDO-FPT calculations of vicinal $^{13}C-H$, $^{13}C-^{13}C$, and $^{13}C-^{19}F$ coupling constants are compiled in Table I. Experimental data from this study and available literature values are given in parentheses in the table. In addition to the calculated values for propane,[9] butane,[10] and 1-fluoropropane,[11] results are included for trans $^3J_{CX}$ (X = H, $^{13}CH_3$, and ^{19}F) in molecules, with one or two methyl groups at each of the carbons 1–3, and for a number of cyclic molecules.

The INDO-FPT results for vicinal $^{13}C-H$ coupling in Table 1 clearly indicate that the effects of β-methyl substituents are

small in comparison with γ-methyl substituents; methyl groups at either the C-1 or C-2 atoms in **3-6** (X = H) give calculated results which are not significantly different from the propane value (8.78 Hz for **2**), but successive methyl substitution at the γ carbon (C-3) decreases $^3J_{CH}(180°)$ by 1.0 and 1.7 Hz in **7** and **8**, respectively. Furthermore, for the series of cyclic molecules in Table 1 having single γ-methylene groups (**9-11**), the $^3J_{CH}$ is decreased by 1.2 to 1.4 Hz, whereas, with two γ-methylene substituents (**12** and **13**), the $^{13}C-H$ coupling is decreased by 1.8 to 2.0 Hz. It is important to note that the experimental results of ~13, 8.1, and 5.3 Hz for the molecules propane, cyclohexane, and adamantane, respectively, suggest that the actual γ-methyl substituent effect is at least twice as large as indicated by the calculated results.

To determine the importance of the enormous number of electronic interactions on the calculated vicinal coupling constants, a modified INDO-FPT procedure was adopted in this study.[12] Elements of the Fock matrices associated with orbitals centered on various atom pairs were set equal to zero in each SCF cycle, thereby preventing any "leakage" of unpaired spin density (and spin-spin coupling) between atoms along that path. For example, in the calculations of $^3J_{CH}$ for 2-methylbutane (**8**), the most important substituent interaction (−2.65 Hz) is that involving the hydrogen atoms on C-1 and the six hydrogen atoms of the two γ-methyl groups. This is partially offset by the next most important contribution (+1.24 Hz) arising from interactions between the valence atomic orbitals on the C-1 atom and the hydrogens of the two γ-methyl groups.

In the examples of vicinal $^{13}C-^{13}C$ coupling in Table 1,

methyl substitution at the C-1 atoms has little effect in **3** and **4** (X = $^{13}CH_3$), whereas substitution at the C-2 or C-3 atom decreases $^3J_{CC}(180°)$ by the same amount because of the equivalence of these positions. As a consequence, the equality of the calculated results and the near equality of the experimental results for 2-methyladamantane and 1-methyladamantane (**10** and **13**, respectively; X = $^{13}CH_3$) is a unique situation in which the two γ-methylenes give equal contributions to $^3J_{CC}(180°)$. Any change in the nature of X from a methyl or methylene group is expected to lead to different values of $^3J_{CX}(180°)$ for **10** and **13**. Because the interactions between hydrogens make negative contributions to the couplings, it is reasonable to expect that vicinal $^3J_{CX}$ for **10** would be consistently greater in magnitude than the values for **13**. This is the case for all of the experimental data obtained for the two compounds. For example, the vicinal $^{13}C-^{13}C$ coupling constants for **10** and **13** with X = $^{13}CO_2H$ are 4.2 and 3.6 Hz, respectively;[6,7] for X = $^{13}CH_2OH$ the values are 3.54 and 3.27 Hz, respectively.[13] In the more complex physical situation in which X = $^{119}Sn(CH_3)_3$ the experimental values are 60.0 and 51.1 Hz, respectively.[14] It seem likely that the recognition of the substituent γ-methyl effect will prove to be important in understanding other types of vicinal coupling involving ^{13}C.[15,16]

References and Notes

(1) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984–2990 (1964).
(2) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315–5318 (1967).
(3) M. Barfield, S. A. Conn, J. L. Marshall, and D. E. Miiller, *J. Am. Chem. Soc.*, **98**, 6253–6260 (1976).
(4) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960–2964, 2965–2970 (1968).
(5) Contributions to vicinal $^{13}C-H$ and $^{13}C-^{13}C$ coupling constants from orbital and spin-dipolar terms are thought to be quite small: A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950–963 (1971); see ref 6.
(6) V. Wray, *J. Am. Chem. Soc.*, **100**, 768–770 (1978).
(7) J. L. Marshall and D. E. Miiller, *J. Am. Chem. Soc.*, **95**, 8305–8308 (1973).
(8) M. Barfield, I. Burfitt, and D. Doddrell, *J. Am. Chem. Soc.*, **97**, 2631–2634 (1975).
(9) Conformational and substituent effects on $^3J_{CH}$ have been investigated by R. E. Wasylishen and T. Schaefer, *Can. J. Chem.*, **51**, 961–973 (1973).
(10) Conformational and substituent effects on $^3J_{CC}$ have been discussed in ref 3 and 8.
(11) Conformational and substituent effects on $^3J_{CF}$ have been discussed by V. Wray, *J. Chem. Soc.*, *Perkin Trans. 2*, 1598–1605 (1976).
(12) In previous studies, where coupling paths were of qualitative interest,[3] it was found to be sufficient to set the appropriate overlap integrals equal to zero; see J. L. Marshall, S. R. Walter, M. Barfield, A. P. Marchand, N. W. Marchand, and A. L. Segre, *Tetrahedron*, **32**, 537–542 (1976). However, because of the small effects of interest in this investigation, it seemed appropriate to eliminate the remaining terms as well; see V. Mamayev and Kh. Orazberdeiv, *Dokl. Akad. Nauk USSR*, **220**, 877–880 (1975).
(13) J. L. Marshall, S. A. Conn, and M. Barfield, *Org. Magn. Reson.*, **9**, 404–407 (1977).
(14) D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C.-H. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila, and R. H. Sarma, *J. Am. Chem. Soc.*, **96**, 1640–1642 (1974).
(15) W. Kitching, D. Praeger, D. Doddrell, F. A. L. Anet, and J. Krane, *Tetrahedron Lett.*, 759–762 (1975).
(16) G. E. Buchanan and C. Benezra, *Can. J. Chem.*, **54**, 231–237 (1976).

M. Barfield*
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

J. L. Marshall,* E. D. Canada
Department of Chemistry, North Texas State University
*Denton, Texas 76203*

M. R. Willcott, III
Department of Chemistry, University of Houston
*Houston, Texas 77004*
Received July 11, 1978

Tricoordinate Hypervalent Sulfur Species. Sulfuranide Anions[1]

Sir:

Over the past twenty years interest in trithiapentalene (6a-thiathiophthene) and its derivatives, a class of tricoordinate sulfur(IV) species, has continued at a high level,[2] primarily reflecting chemists' fascination with the unusual chemical bonding in these compounds. Recently, a series of tricoordinate sulfuranes with apical halogen and equatorial π-acceptor ligands has been prepared by Arduengo and Burgess.[3] We now report the synthesis of tricoordinate anionic sulfurane salts **1** and **2**, salts of fulfuranide anions, and their reactions with electrophiles.

1   **2a,** M = K   **3**
             b, M = $(Bu)_4N$
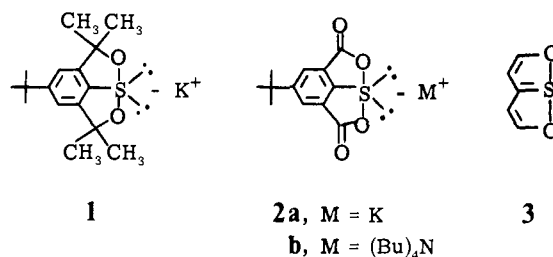
Compound **1**,[4] an anionic analogue of **3**[5] lacking its π-electron system, was obtained as a white precipitate by treatment of a THF solution of sultene **4**[6] with 1 equiv of KH.

4
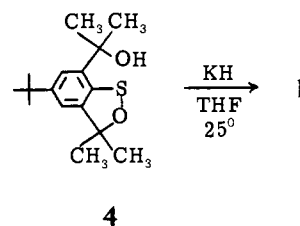
The structure of the anion of **1** may, a priori, be represented as a resonance hybrid of structures **1a**, **1b**, and **1c** or as an equilibrium mixture of structures of different geometries which may also be represented by **1a**, **1b**, and **1c**. Even at temperatures as low as −70 °C no evidence was seen in the ^{1}H NMR spectra of **1** for unsymmetrical structures such as **1b** or **1c**.

1a   **1b**   **1c**
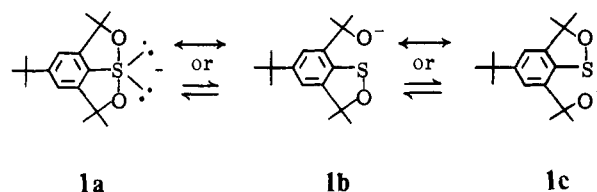
The ^{1}H NMR spectrum of **1** shows substantial upfield shifts of all peaks (δ (Me_2SO-d_6) 6.68 (s, 2, ArH), 1.25 (s, 9, *t*-C_4H_9), 1.20 (s, 12, $OCCH_3$)) when compared with that of **4** (δ (Me_2SO-d_6) 7.03–6.99 (m, AB pattern, 2, ArH), 5.70 (s, 1, OH), 1.48 (s, 6, $OCCH_3$), 1.41 (s, 6, $OCCH_3$), 1.31 (s, 9, *t*-C_4H_9)). This suggests negative charge delocalization into the benzene ring as well as the apical alkoxy ligands. The sharp singlet for the ring protons of **1** in THF solution, with 18-crown-6 as solubilizing agent, does not exhibit any sign of broadening even at −70 °C. In contrast, the aromatic ring protons of **4** have been found to be nonequivalent at room temperature.[6]

Reaction of a THF suspension of **1** with trimethylsilyl chloride or benzoyl chloride produces exclusively O-substituted products. Treatment with methyl fluorosulfonate or methyl iodide affords a mixture of sulfurane **5**[7] and sultene **6** (Scheme 1) in a ratio of 1:2 and 10:1, respectively. These results can be explained by applying the principle of hard and soft acids and