Table I. Shifts and Coupling Constants for the Various Protons in Radical I

Spectral position	Assignment	Shift,[a] kHz	a_i, G
1	Phenoxy ring protons	13.75	+1.85
2	Methoxy protons, *anti* conformation	6.09	+0.82
3	Methoxy protons, *syn* conformation	2.90	+0.39
4	*t*-Butyl protons	0.54	+0.074
7	α-Cyclopropyl proton, *syn* conformation	5.43	−0.73
8	α-Cyclopropyl proton, *anti* conformation	14.98	−2.02

[a] The shifts are from the corresponding peak in the spectrum of the diamagnetic phenol.

The esr spectrum of radical I is given in Figure 2. This spectrum could be computer simulated with the proton coupling constants given in Table I and a nitrogen splitting of 3.78 G. This spectrum results from the isomer with the favored conformation. The spectrum from the other isomer has less than 10% of the intensity of this spectrum and cannot be observed.

Through the use of a free-radical solvent such as DBNO, one should be able to observe the nmr spectra of many organic radicals. With this technique one can unambiguously determine both the sign and magnitude of electron-nuclei coupling constants. Analysis of the nmr spectra is much simpler than analysis of the esr spectra. Couplings too small to be detected by esr may be observed and information about species in low concentration in mixtures of paramagnetic compounds may be obtained.

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Observation of Electron-Impact-Induced Anion of Dodecamethylcyclohexasilane

Sir:

The preparation of the radical anion of dodecamethylcyclohexasilane in a solution of tetrahydrofuran–1,2-dimethoxyethane has been described.[1] We wish to report that the negative ion mass spectrum of dodecamethylcyclohexasilane exhibits an ion which occurs at *m/e* 348[2] and which was shown to be $C_{12}H_{36}Si_6$ by examination of the ion abundance of *m/e* 349 and 350. This observation provides unequivocal evidence for the existence of the radical anion of dodecamethylcyclohexasilane as a stable species in the gas phase.

This ion must be formed by electron capture—as opposed to an ion pair or a dissociative attachment process—and hence the ion yield should be sensitive to the energy (velocity) of the electrons which produce it and should exhibit a maximum at relatively low electron energy.[3] This behavior is confirmed as shown in Figure 1, which indicates an approximately 20-fold increase in the *m/e* 348 ion signal at an electron bombardment energy of 4 V as compared to the 80 V usually used. We do not fix the position of maximum ion yield because of instrumental instability below 4 eV. Such a point does occur, however.

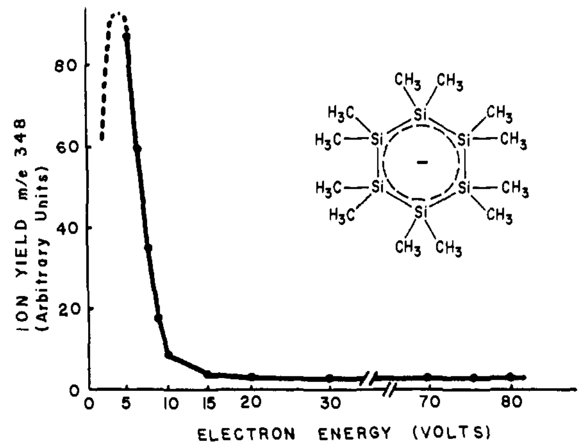

Figure 1. Effect of variation of electron energy on intensity of molecular anion of dodecamethylcyclohexasilane.

The existence of this species indicates that delocalization of the added electron (probably in the 3d orbitals of adjacent silicon atoms) imparts an unusual degree of stability to the radical anion. The negative ion mass spectrum of hexamethyldisilane also exhibits a molecular radical anion (*m/e* 146) which is produced by electron capture, although its abundance is approximately 100 times less than the molecular ion observed for dodecamethylcyclohexasilane. The mass spectrum of hexamethyldisiloxane, however, does not indicate a molecular anion under any conditions available to us. Stabilizing 3d orbital delocalization is, in this case, apparently prevented by the presence of the intervening oxygen atom, and only ion fragments are observed. The negative ion mass spectra of other polysilanes are being investigated.

Experimental Conditions. Mass spectrometer Type MS-12, manufactured by Associated Electrical Industries, Ltd., was used in this investigation. The ion source and analyzer pressure were 1×10^{-6} torr and 2×10^{-7} torr, respectively. The width of the collector slit and the ion source slit was 0.020 in. The temperature of the sample reservoir was 85 ± 2°, the leak line was 100 ± 5°, and the ion source was 140 ± 10°. An all-glass (Pyrex) inlet system was employed. An electron multiplier containing 11 Cu–Be dynodes operated at an estimated gain of 10^5 (3000-V potential difference across dynodes) was used as the ion detector. The absolute magnitude of the ion current was not determined. The signal:noise ratio was, in the worst case, better than 100:1. The electron beam current was 20 μA (trap regulated) for a filament (tungsten) current which ranged between 3.2 and 4.4 A. The ion accelerating potential was 6000 V. The mass spectrometer was electrically refocused (ion repeller, beam centering, Y deflection) at each experimental point to ensure that the

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(1) G. R. Husk and R. West, *J. Amer. Chem. Soc.*, **87**, 3993 (1965).

(2) Verification of mass was carried out by using previously characterized perfluorokerosene as an internal mass standard in mixture with the dodecamethylcyclohexasilane.

(3) C. E. Melton in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 4, provides a good general discussion on negative ion mass spectrometry.

signal maximum was being observed. The magnet position was not changed.

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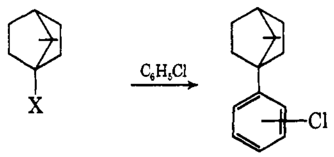
Cationic Aromatic Substitution at the Bridgehead of 1-Substituted Apocamphanes

Sir:

Studies of reactions at the bridgehead of bicyclo-[2.2.1]heptanes have been remarkably informative about structure–reactivity relationships.[1] The classic case is the seminal work of Bartlett and Knox,[2] which established both the inertness of 1-chloroapocamphane to ionization and the reactivity of 1-aminoapocamphane in deamination, and thus has proven important to the understanding of carbonium ion structure[1] and to the formulation of intermediates in the deamination of amines.[3] We wish to report that reactions which formally could produce the 1-apocamphyl cation by loss of different stable nonnucleophilic leaving groups lead to the same 1-arylapocamphanes.

Reaction of 1-chloroformylapocamphane (**1**) with silver fluoroborate or silver hexafluoroantimonate in chlorobenzene initially at ambient temperature gives the same ratio of 1-chlorophenylapocamphane isomers (**2**) in 24 and 81% yields.[4] The product ratio obtained for **2** is *ortho* 40%, *meta* 32%, and *para* 28%.[5] The same ratio[5] of isomers **2** was obtained from the reaction of 1-aminoapocamphane (**3**) with nitrosyl chloride or nitrosyl hexafluoroantimonate in chlorobenzene at ambient temperature in 15 and 9% yields[6] and from reaction of 1-chlorosulfinylapocamphane (**4**)[7] with silver fluoroborate in 19% yield. The indistinguishable ratio of products[5] strongly suggests that these aromatic substitutions at the bridgehead position proceed *via* a common intermediate.[8,9]

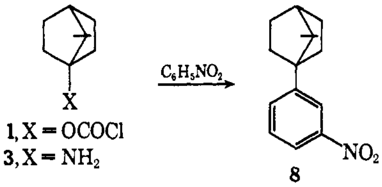


1, X = OCOCl
3, X = NH_2
4, X = OSOCl

2, *o*, 40%
m, 32%
p, 28%

The aromatic substitution reactions of **1**, **3**, and **4** to give isomers **2** may be formulated by analogy with deaminative substitutions at bridgehead positions as a radical,[13] cation,[3] or front-side displacement[3,14] process.

Apocamphyl free radical (**5**) may be ruled out as an intermediate by two observations. Generation of **5** in chlorobenzene, achieved by heating a solution of 1-acylperoxyapocamphane to 125°,[15,16] leads to 23% of the 1-chlorophenylapocamphane isomers (**2**), giving *ortho* 13%, *meta* 60%, and *para* 27%.[5] On the other hand, reaction of the chloroformate **1** with silver fluoroborate at 125° gives 21% of these isomers in a different ratio, *ortho* 35%, *meta* 32%, and *para* 33%,[5] implying a different mechanism for these reactions. In another test for the intermediacy of **5**, 1-chloroformylapocamphane (**1**) was treated with silver hexafluoroantimonate, and 1-aminoapocamphane (**3**) was allowed to react with nitrosyl chloride in separate experiments in nitrobenzene at ambient temperature. The product of these reactions is 1-*m*-nitrophenylapocamphane[17] (**8**) in 24 and 4% yields.



1, X = OCOCl
3, X = NH_2

8

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[1] (a) R. C. Fort and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 284 (1966); (b) U. Schöllkopf, *Angew. Chem.*, 72, 147 (1960); (c) D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954).

[2] P. D. Bartlett and L. H. Knox, *J. Am. Chem. Soc.*, **61**, 3184 (1939).

[3] H. E. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, pp 126–128.

[4] (a) P. Beak, R. J. Trancik, J. B. Mooberry, and P. Y. Johnson, *J. Am. Chem. Soc.*, **88**, 4288 (1966); (b) R. J. Trancik and P. Beak, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract 164S.

[5] Within an experimental error of ±4%.

[6] Alkylations of aromatics by deamination of other amines have been reported: G. A. Olah, N. A. Overchuck, and J. C. Lapierre, *J. Am. Chem. Soc.*, **87**, 5785 (1965); A. T. Jurewicz, J. H. Bayless, and L. Friedman, *ibid.*, **87**, 5788 (1965).

[7] This was contaminated by about 25% of 1-apocamphane sulfite: W. E. Bissinger and F. E. Kung, *ibid.*, **69**, 2158 (1947).

[8] Control experiments established that the *meta* isomer and a mixture of the *ortho* and *para* isomers were not interconverted in the presence of the reaction of **1** or in the work-up. The bridgehead chloroformate was stable in chlorobenzene in the presence of boron trifluoride at room temperature although partial conversion to the bridgehead chloride and a small amount of the 1-chlorophenylapocamphane isomers occurred on heating at 50–60° for 1–4 hr. The bridgehead chloride was stable to silver fluoroborate and boron trifluoride in chlorobenzene at room temperature.

[9] The structural assignments to the isomers **2** were made on the basis of analytical data, the established gross structure,[4] and infrared[10,11] and nmr spectral correlations. The liquid *meta* isomer, separated from the *ortho* and *para* compounds by preparative glpc, has a pmr spectrum showing a singlet for the *gem*-dimethyl group at δ 0.93 ppm and exhibits infrared absorptions at 688 and 771 cm^{-1} in carbon disulfide. The assignment of a mixture of *ortho* and *para* isomers for the other material purified by preparative glpc is confirmed by the appearance of infrared bands at 742 (*ortho*) and 812 (*para*) cm^{-1} and a pmr spectrum with two singlets for the two different *gem*-dimethyl groups at δ 1.29 (*ortho*)[12] and 0.85 (*para*) ppm. The ratio of *ortho* and *para* isomers determined by the relative areas of the different *gem*-dimethyl singlets is consistent with a glpc analysis using a 150-ft Golay capillary column.

[10] (a) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1964; (b) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, p 75; (c) J. R. Shelton and C. W. Uzelmeier, *J. Am. Chem. Soc.*, **88**, 5222 (1966); (d) G. A. Olah and N. A. Overchuk, *ibid.*, **87**, 5786 (1965).

[11] The isomers of cyclohexylchlorobenzene fit the infrared correlation. In this case, assignments to the *ortho* and *para* isomers could be confirmed by oxidation to the known corresponding chlorobenzoic acids.

[12] L. A. Paquette, J. H. Barrett, R. P. Spitz, and R. Pitcher, *J. Am. Chem. Soc.*, **87**, 3417 (1965), discuss the potentially variable effect of chlorine on the chemical shift of neighboring protons.

[13] (a) K. V. Scherer, Jr., and R. S. Lunt, III, *ibid.*, **88**, 2860 (1966); (b) K. V. Scherer, Jr., and R. S. Lunt, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract 102S.

[14] (a) J. A. Mills, *J. Chem. Soc.*, 260 (1953); (b) R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1 (1956).

[15] M. S. Kharasch, F. Engelmann, and W. H. Urry, *J. Am. Chem. Soc.*, **65**, 2428 (1943).

[16] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 467–511.

[17] The liquid *meta* isomer was purified by preparative glpc and the structure was assigned on the basis of a satisfactory microanalysis and mass spectral molecular weight, infrared absorptions at 680 and 795 cm^{-1},[10] and a proton magnetic resonance spectrum showing a singlet due to the *gem*-dimethyl at δ 0.95 ppm and two complex (non-AA′BB′) multiplets of equal area centered at δ 7.34 and 7.92 ppm. The pattern for the aromatic protons was shown to be characteristic of substitution type by comparison with the spectra of the known nitrotoluenes.