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

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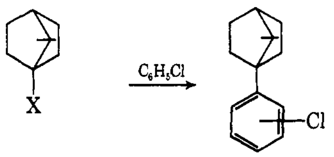
Cationic Aromatic Substitution at the Bridgehead of 1-Substituted Apocamphanes

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.

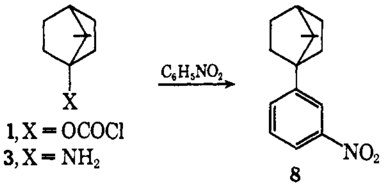
Reaction of 1-chloroformylapocamphane (**1**) with silver fluoroborate or silver hexafluoroantimonate in chlorobenzene initially at ambient temperature gives the same ratio of 1-chlorophenylapocamphane isomers (**2**) in 24 and 81% yields.[4] The product ratio obtained for **2** is *ortho* 40%, *meta* 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 **2**, *o*, 40%
3, X = NH_2 *m*, 32%
4, X = OSOCl *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.

The formation of only the *meta* isomer is diagnostic of reaction *via* a cationic species.[13,18,19] The potent reactivity of this species is illustrated by the high ratio of the *meta* isomer of 2[20] as well as by the alkylation of nitrobenzene.[21]

The reactivity of **1**, **3**, and **4** in aromatic substitution is accommodated by the correlation of relatively low energies of activation with the loss of stable leaving groups.[3,14b,22] The present evidence that substitution at the bridgehead position of apocamphane derivatives occurs by a cationic process is consistent with previous suggestions in this[1,3] and related systems.[23,24] The common isomer ratio obtained in the different alkylations of chlorobenzene cannot be taken as favoring reaction *via* the 1-apocamphyl cation since reaction could occur through front-side displacement to π complexes,[25] equilibrating σ complexes, or other species such that product sensitivity to the nature of the leaving group would not be observed.

We wish to call attention to the fact that a family of reactions suitable for the formal production of highly reactive cations may be envisioned in which reaction is facilitated by the loss of a stable, nonnucleophilic leaving group.[4] Diazonium ions,[3] isocarboxonium ions,[26] and carboxylium ions[4] are members of this family, and other potential members can be imagined.[27] Regardless of whether or not such ions are truly reaction intermediates, the postulation of these species may prove useful in designing synthetic routes for substitution at positions of low incipient carbonium ion stability and for the generation of other highly reactive species.

Acknowledgment. We are grateful to the Public Health Service (GM-12595) and to the Alfred P. Sloan Foundation for support.

(18) (a) G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1964, pp 1362, 1467, 1548; (b) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford, England, 1960, pp 77, 106.

(19) The formation of carbonium ions by the action of antimony pentafluoride on chloroformates and chlorosulfites has been reported by G. A. Olah, J. M. Bollinger, C. A. Cupas, N. Friedman, and J. Lukas, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract 56U.

(20) The previously reported alkylations of chlorobenzene[4a] showed only minor amounts of *meta* products.

(21) This appears to be the first cationic alkylation of nitrobenzene: G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p 34.

(22) (a) A. Streitwieser, *J. Org. Chem.*, **22**, 861 (1957); (b) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(23) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964).

(24) M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta*, **40**, 2129 (1957).

(25) (a) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962); (b) ref 21, pp 921–926.

(26) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

(27) For example, the reactions of sulfinylamines and isocyanates with nitrosonium salts reported by G. A. Olah, N. Friedman, J. M. Bolinger, and J. Lukas, *ibid.*, **88**, 5328 (1966).

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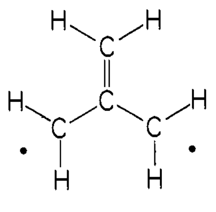
Trimethylenemethane. Proton Hyperfine Splitting

Sir:

Trimethylenemethane (I) has been postulated to be the central, stable intermediate in the low-temperature photochemical decomposition of 4-methylene-Δ^1-pyrazoline[1] and 3-methylenecyclobutanone.[2] The basis for this hypothesis lies in the detection of this ground-state triplet by electron spin resonance spectroscopy.[1,2] The observation that the same esr spectrum may be obtained from two independent precursors and the general agreement between the observed spectrum and that expected for such a symmetric diradical have been cited in support of the above hypothesis.[3]



I

The purpose of this communication is to present a striking new epr spectrum which not only establishes the skeletal structure of trimethylenemethane beyond question, but also affords a direct quantitative comparison with theoretical predictions of the ground electronic state of this molecule. This has been accomplished through the observation of the proton hyperfine splitting of trimethylenemethane in a single crystal. The new spectrum is essential to the structure proof in view of the special assumptions of bond length and spin density which were demanded in the comparison of the randomly oriented spectrum with theoretical expectation. In addition to being a stringent test of structure, the hyperfine splitting is of considerable theoretical interest as a direct measure of the electron spin density on the peripheral carbon atoms of the molecule.

The precursor to trimethylenemethane used in these experiments was 3-methylenecyclobutanone. A liquid at ambient temperatures, this material melts at −20°. Following a preliminary, but unsuccessful, search for a suitable crystalline host, it was decided to attempt to grow a single crystal of the pure starting ketone.[4–6] This attempt was successful. The crystal obtained was irradiated at −196° for 2 hr, giving rise in the esr to two major lines each of which was split into a number of hyperfine components. By suitable adjustment of the sample and rotation of the magnetic field, a maximum splitting of 525 G was reached.[7] This maximum corre-

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(1) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).

(2) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967).

(3) Evidence for the thermal production of trimethylenemethane in the gas phase has been presented recently by R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966); R. G. Doerr and P. S. Skell, *ibid.*, **89**, 3062 (1967); P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967); and J.-P. Schirmann and F. Weiss, *Tetrahedron Letters*, 5163 (1967).

(4) We are very much indebted to Professor Melvyn R. Churchill and Dr. Peter Bird for their generous assistance in the early stages of crystal growing.

(5) Crystal growth was carried out in a sealed quartz capillary 1 mm in diameter which was scored 4 mm from the end. The use of a controlled stream of cold nitrogen ensured a slow rate of crystal growth. When crystal growth was complete, the capillary was immersed in liquid nitrogen and broken off at the scored point. It was then fastened horizontally to a ceramic rod. Adjustment of sample position and magnetic field then yielded reproducible spectra. The reproducibility depended critically on the appearance of the crystal during growth. Those crystals which grew as long thin rods running the length of the capillary were completely satisfactory. A second form which appeared as cubes during crystal growth could not be satisfactorily oriented in the magnetic field with the equipment at hand.

(6) C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **34**, 908 (1961); R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, *ibid.*, **43**, 2006 (1965); R. M. Moriarty, M. Rahman, and G. J. King, *J. Am. Chem. Soc.*, **88**, 842 (1966).

(7) The randomly oriented spectra previously obtained[1,2] were most