

Anal. Calcd. for $C_{14}H_{19}BrO_3S$: C, 48.40; H, 5.53. Found: C, 48.64; H, 5.63.

cis-Hexahydro-*o*-tolualdehyde.—*cis*-2-Methylcyclohexanemethyl brosylate (0.25 g.) was dissolved in 5 ml. of dimethyl sulfoxide. Sodium bicarbonate (0.73 g.) was added and the mixture was immersed in a bath at 150° for 5 min. under a nitrogen atmosphere. After cooling in ice, water and pentane were added, and the water layer was extracted with pentane. The pentane layer was washed with water and dried over magnesium sulfate. The ether was evaporated and the product was collected from a TCEP column at 140°.

Hydroboration of 1-Methylcycloheptene.²⁷—1-Methylcycloheptene (11.0 g.) was treated with diborane at 0° and the product was oxidized with alkaline hydrogen peroxide giving 6.8 g. (53%) of a mixture of alcohols, b.p. 56–57° (1.0 mm.). Analysis of this mixture (TCEP, 140°) showed two major peaks of approximately equal amounts. These compounds were collected and identified as *trans*-2-methylcycloheptanol and *trans*-3-methylcycloheptanol by comparison of their infrared spectra with those of authentic samples.²⁸ The formation of *trans*-3-methylcycloheptanol was unexpected. However, a similar rearrangement has been observed in the case of hydroboration of 1-methylcyclooctene.²⁷

2-Methylcycloheptanone and 3-Methylcycloheptanone.—A solution of 1.27 g. of the above mixture of alcohols in 10 ml. of acetone was titrated to an orange-brown end-point with an 8 *N* solution of chromic anhydride in 30% sulfuric acid. The reaction was exothermic, causing the acetone to reflux gently. The acetone solution was decanted from the chromic salts and the product was isolated by adding 30 ml. of water, extracting with three 10-ml. portions of ether, washing the ether extracts with saturated sodium bicarbonate solution and water, and drying over magnesium sulfate. Distillation through a semi-micro column gave 0.86 g. (69%) of ketones, b.p. 79–80° (19 mm.), which were separated by gas chromatography (TCEP, 120°) and identified as 2-methylcycloheptanone (51%) and 3-methylcycloheptanone (49%) by the melting points of their 2,4-dinitrophenylhydrazones. 2-Methylcycloheptanone 2,4-dinitrophenylhydrazone had m.p. 119.2–120.3° (lit.^{29,30}

m.p. 121–122°). 3-Methylcycloheptanone 2,4-dinitrophenylhydrazone had m.p. 127.3–129.0° (lit.³¹ m.p. 130.5–131.0°). Both derivatives were recrystallized from aqueous ethanol.

Purification and Identification of 1-Methylcyclohexanecarboxaldehyde.—The peak containing the aldehyde was collected from a TCEP column at 120° and injected onto a silicone oil column at 110°. The two peaks which separated were collected. The first compound (47%) was identified as 1-methylcyclohexanecarboxaldehyde by comparison of its infrared spectrum and retention time (TCEP, 120°) with those of an authentic sample. An infrared spectrum of the second peak (53%) contained no hydroxyl or carbonyl absorption, but showed strong ether absorption between 900 and 1200 cm^{-1} .

1-Methylcyclohexanemethyl Brosylate.—1-Methylcyclohexanemethanol³² (0.45 g.) was converted in 48% yield to the brosylate (0.59 g.), m.p. 60.8–61.4°, after one recrystallization from pentane. An analytical sample had m.p. 61.0–61.5° after an additional recrystallization from pentane.

Anal. Calcd. for $C_{14}H_{19}BrO_3S$: C, 48.40; H, 5.53. Found: C, 48.43; H, 5.36.

1-Methylcyclohexanecarboxaldehyde.—A solution of 0.10 g. of 1-methylcyclohexanemethyl brosylate in 2 ml. of dimethyl sulfoxide was treated with 0.30 g. of sodium bicarbonate at 150°. The aldehyde was collected from a TCEP column at 140°.

Composition of the High-boiling (Bromohydrin) Fraction.—The fraction with b.p. 103–105° (1.5 mm.) was dark in color, gave a positive Beilstein test, showed hydroxyl absorption in the infrared, and had n_D^{20} 1.5205. Purification using activated charcoal and drying under reduced pressure gave an analytical sample.

Anal. Calcd. for $C_8H_{15}BrO$: Br, 38.59. Found: Br, 38.33.

The bromohydrin fraction failed to give a crystalline 3,5-dinitrobenzoate.

(30) M. Mousseron, R. Jacquier and H. Christol, *Bull. soc. chim. France*, 346 (1957).

(31) T. Nozoe, T. Mukai and S. Matsumoto, *Proc. Japan Acad.*, **27**, 110 (1951); *C.A.*, **46**, 5034 (1952).

(32) 1-Methylcyclohexanemethanol was obtained by lithium aluminum hydride reduction of 1-methylcyclohexanecarboxylic acid. The acid was prepared from 2-methylcyclohexanol by the procedure of H. Koch and W. Haaf, *Ann.*, **618**, 251 (1958).

(27) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961); A. C. Cope and G. L. Woo, to be published.

(28) A. C. Cope, S. Moon and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4843 (1962).

(29) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 181 (1939).

[A JOINT CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, MURRAY HILL, N. J., AND THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, NEW HAVEN, CONN.]

Structure of the 7-Norbornadienyl Carbonium Ion¹

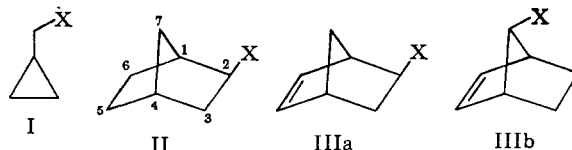
BY PAUL R. STORY^{2a} AND MARTIN SAUNDERS^{2b}

RECEIVED JUNE 29, 1962

The first direct and detailed physical evidence for the structure of an aliphatic non-classical carbonium ion has been obtained from the nuclear magnetic resonance spectrum of 7-norbornadienyl fluoroborate. The spectrum in liquid sulfur dioxide and in nitromethane indicates an unsymmetrical structure. Rearrangement of the bicyclic skeleton is ruled out by conversion of the fluoroborate to the corresponding acetate and to the corresponding methyl ether.

Introduction

The solvolyses of certain related carbocyclic molecules including cyclopropyl carbinyl (I), norbornyl (II) and norbornenyl derivatives (III) have provided a fund of information concerning the nature of the carbonium ion intermediates and the subject of non-classical structures and charge delocalization in general.³ Structures involving



non-classical delocalization of electrons have been proposed for the intermediate carbonium ions hypothesized in these and other systems in order to explain remarkably enhanced rates of solvolysis of certain derivatives. The information obtained

(1) A portion of this work has been reported in preliminary form; P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **82**, 6199 (1960).

(2) (a) Bell Telephone Laboratories, Murray Hill, N. J. (b) Department of Chemistry, Yale University, New Haven, Conn.

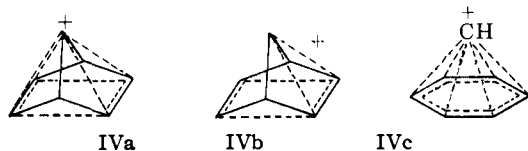
(3) For comprehensive discussions see: (a) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959); (b) R. H. Mazur,

W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

thus far consists chiefly of analysis of the products and rates of the solvolysis reactions. However, the precise structure or structures involved in each case are not obtainable from such indirect information. Ultraviolet spectra of a presumed non-classical species have been obtained in one system confirming the presence of the intermediate ion, but yielding no specific structural information.⁴

The problem has been one of obtaining some direct structural information concerning these non-classical carbonium ion intermediates. Nuclear magnetic resonance (n.m.r.) spectroscopy has been shown to be a very powerful structural tool and has been effectively used on the relatively stable heptamethylbenzeneonium⁵ and triphenylmethyl carbonium ions.⁶ It was, therefore, considered likely that similar useful information could be obtained regarding these bicyclic, aliphatic ions.

The 7-norbornadienyl system has been found to possess the necessary prerequisites to allow application of this technique to an aliphatic, non-classical system for the first time. This system was considered most advantageous because of the apparent stability of the C.7 carbonium ion as indicated by the remarkable rate enhancement observed in solvolysis of 7-norbornadienyl chloride⁷ and because several useful derivatives were readily available.⁸ The system was further made attractive by the very interesting non-classical structures possible for the 7-carbonium ion and because the principal structures already proposed (IV)⁷ could easily be distinguished by n.m.r. spectroscopy.



Results

7-Norbornadienyl Fluoborate.—Of the several possible ways in which the 7-norbornadienyl carbonium ion could be generated and presented for n.m.r. analysis, preparation of a salt from the corresponding chloride (7-chloronorbornadiene (VI)) was considered to be most promising. Acid generation of the ion from the alcohol or ether is considered risky because of the ease of protonation of the double bonds and subsequent rearrangement. Either of the two most commonly used reagents for salt preparation from halides, silver perchlorate or silver fluoborate at first appeared acceptable. The choice of liquid sulfur dioxide as the most satisfactory solvent, however, was found to dictate the use of silver fluoborate because of the limited solubility of silver perchlorate. Silver fluoborate was also preferred because of the explosive hazard of silver perchlorate and organic perchlorate salts.

(4) G. Leal and R. Pettit, *J. Am. Chem. Soc.*, **81**, 3160 (1959).

(5) W. v. E. Doering, M. Saunders, H. G. Boynten, H. W. Barhart, E. F. Wadley, W. R. Edwards and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(6) R. Dehl, W. R. Vaughan and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959); R. S. Berry, R. Dehl and W. R. Vaughan, *J. Chem. Phys.*, **34**, 1460 (1961).

(7) S. Winstein and C. Ordonneau, *J. Am. Chem. Soc.*, **83**, 2084 (1960).

(8) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

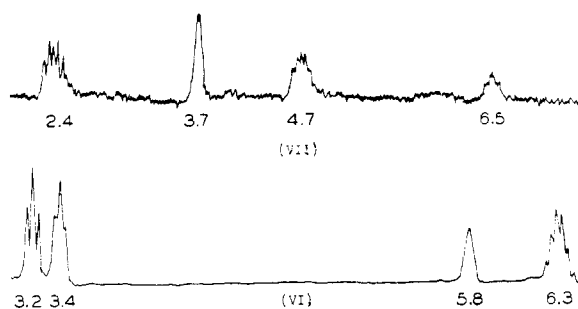
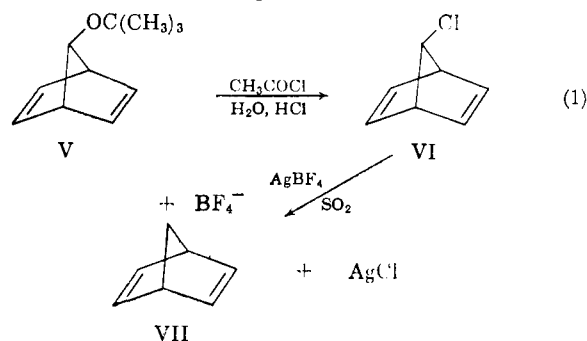


Fig. 1.—N.m.r. spectrum of 7-norbornadienyl fluoroborate and chloride in sulfur dioxide. Peak positions are given in p.p.m. relative to tetramethylsilane internal standard as 10 p.p.m.

Sulfur dioxide was chosen as the best solvent to prepare and display the carbonium ion salt because it is transparent, readily obtainable in a pure, dry state and remains liquid at temperatures down to -75° . Also, it has been used previously as a solvent for conductivity measurements of stable carbonium ion salts.⁹

Silver fluoborate has been found to react quantitatively with 7-norbornadienyl chloride (VI) to yield 7-norbornadienyl fluoborate (VII). The chloride VI was prepared directly from 7-*t*-butoxynorbornadiene (V)⁸ by treatment with acetyl chloride as illustrated in eq. 1. The fluoborate VII was



also prepared in nitromethane, but less satisfactorily because of the higher freezing point of this solvent. The fluoborate VII did, however, appear to be slightly more stable at higher temperatures in nitromethane than in sulfur dioxide.

The N.m.r. Spectra.—The n.m.r. spectra of the fluoborate VII reaction solutions, after removal of silver chloride by centrifugation or filtration, were determined at temperatures ranging from -50° to about $+50^{\circ}$ with no apparent temperature effects, except that the solutions rapidly decomposed at temperatures over about 0° . The salient features of the spectra were not affected, however, until decomposition was nearly complete; the decomposition products merely added to the baseline noise. The n.m.r. spectrum of 7-norbornadienyl fluoborate (VII) in sulfur dioxide at -10° is recorded in Fig. 1. For comparison, the spectrum of the chloride precursor VI in sulfur dioxide is also shown.

The n.m.r. of the fluoborate VII in nitromethane was essentially identical to that in sulfur dioxide, except for a slight downfield shift in all the peak

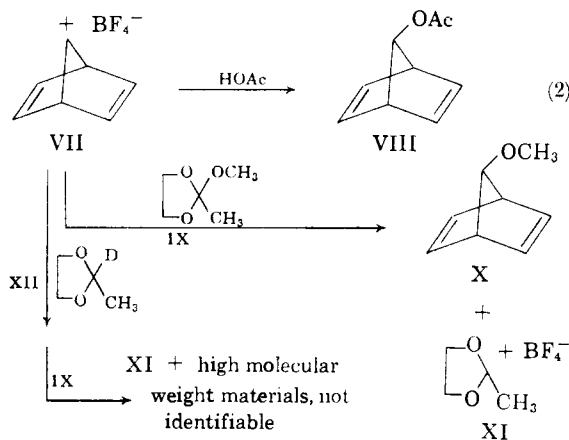
(9) H. P. Leftin and N. N. Lichtin, *J. Am. Chem. Soc.*, **79**, 4275 (1957).

positions, the absorptions occurring at $\tau = 2.30$, 3.60, 4.64, 6.30. The peak at $\tau = 2.30$ had the same fine structure as in sulfur dioxide. The general shape of the other peaks was also unchanged. The n.m.r. spectrum of the chloride VI in nitromethane was also unchanged with absorptions at $\tau = 3.25$, 3.41, 5.8, 6.40. Quite fortuitously, nitromethane absorption at $\tau = 5.6$ did not interfere with the spectrum.

The addition of tetramethylsilane had no effect on the spectra of any of the samples. The ultraviolet spectra of the relatively concentrated solutions prepared for n.m.r. spectral analysis showed no absorption above $330\text{ m}\mu$, the cutoff wave length of liquid sulfur dioxide, as might be expected.¹⁰

Reactions of the Fluoborate VII.—Treatment of a sulfur dioxide solution of the fluoborate VII with acetic acid, after removal of a near quantitative yield of silver chloride (>96%), gave 7-norbornadienyl acetate (VIII)⁸ exclusively in 50% yield (isolable).

The fluoborate VII was also converted exclusively to 7-methoxynorbornadiene (X) by treatment of the sulfur dioxide solution with 2-methoxy-2-methyl-1,3-dioxolane (IX). These reactions are shown in eq. 3. The reaction of the fluoborate VII with 2-deuterio-2-methyl-1,3-dioxolane (XII), which was worked-up by adding the methoxy-dioxolane IX, gave only high molecular weight materials distilling with difficulty over a wide temperature range. Furthermore, the fluoborate



VII did not react with deuteriotriphenylmethane over a four-hour period at low temperature in sulfur dioxide. This reaction was also worked up by the addition of IX to yield, in this case, 7-methoxynorbornadiene (X) containing no deuterium as determined by n.m.r.

Discussion

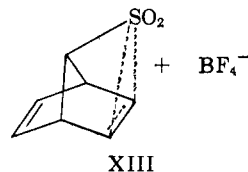
Structure of the Non-classical Ion.¹¹—It is immediately obvious from its n.m.r. spectra that the

(10) If we are permitted to compare this ion to the cyclopropenyl carbonium ion, with which it is formally analogous, we see that the dipropylcyclopropenium ion has only end absorption in the ultraviolet; R. Breslow and H. Höver, *J. Am. Chem. Soc.*, **82**, 2644 (1960).

(11) The information presented here will not, of course, differentiate between a non-classical ion or a mixture of rapidly equilibrating classical structures. However, since the only evidence published thus far (ref. 3a, 7) favors the non-classical structure, we shall argue in terms of this concept. This footnote was prompted by statements of one of the referees.

fluoborate VII is unsymmetrical, thereby eliminating structures IVa and IVc and implying IVb. We have assigned the peaks, which have areas in the ratio 1:2:2:2, to the 7-hydrogen, the bridgehead (1,4)-hydrogens and two different pairs of olefinic hydrogens. The peak at $\tau = 2.42$ is most reasonably interpreted as two overlapping triplets, strongly suggesting that the usual norbornadiene olefinic hydrogen triplet,¹² as seen in the chloride VI, is split by coupling of the olefinic hydrogens with one additional hydrogen with a coupling constant of about 5 c.p.s. The other peaks of the spectrum, at 3.74, 4.73 and 6.52, can be reasonably assigned to: remaining olefin (5,6), bridgehead (1,4) and bridge (7) hydrogens, respectively.

Since the spectrum of the fluoborate VII is unchanged in nitromethane, the possibility that the ion is a solvent adduct such as XIII is excluded.



The apparent coupling between the 7-hydrogen and the olefinic hydrogens (2,3) also argues against XIII as a possible structure.

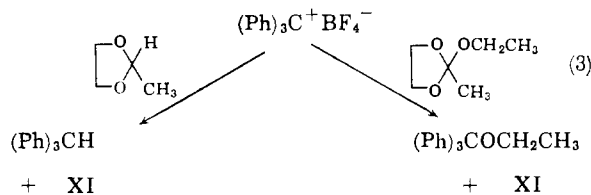
It is interesting that the hydrogens on the three carbons presumed to carry the positive charge are all at higher field than might be expected. The 7 proton is upfield from its counterpart in the chloride, although below norbornadiene, and the two olefin hydrogens, while shifted downfield from their positions in the chloride, are not as low as some examples (tropylium, cyclopropenium) might lead one to predict. However, in these examples the protons considered lie in the plane of the carbocyclic ring and thus are shifted downfield by the diamagnetic anisotropy of the distributed charge as well as by the charge itself. In the norbornadienyl ion, however, the hydrogens considered are substantially out of the plane of the carbons. Thus, the geometry is closer to that of cyclopropane than cyclopropenium. The same diamagnetic anisotropy effect which causes cyclopropane to appear at abnormally high field may be involved in determining the positions of the hydrogens in norbornadienyl.

Chemical Evidence.—The structure IVb deduced from the n.m.r. spectra is consistent with all the chemical facts so far available. While this evidence will not distinguish between IVa, b or c or even show that the ion is non-classical, it does demonstrate that rearrangement has not occurred and implies interaction between C.7 and at least one pair of olefinic carbons.

The fluoborate VII was found to be converted exclusively to 7-norbornadienyl acetate (VIII)⁸ in about 50% yield. The acetate VIII could not be obtained in a quantitative yield, but this was attributed to the rather inefficient isolation procedure and the necessary small scale of the reaction since no other products could be detected by G.P.C. or infrared analysis of the crude product.

(12) F. S. Mortimer, *J. Mol. Spect.*, **3**, 528 (1959).

Meerwein¹³ has shown that several carbonium ion salts, including triphenylmethyl fluoborate, will abstract alkoxy groups from 2-alkoxy-1,3-dioxolanes to yield 1,3-dioxolenium salts as shown in eq. 3. Triphenylmethyl fluoborate has also been shown to abstract hydrogen from 1,3-dioxolanes.



In similar fashion, 7-norbornadienyl fluoborate (VII) was converted to 7-methoxynorbornadiene (X) in 57% yield by the addition of 2-methoxy-2-methyl-1,3-dioxolane (IX) to a sulfur dioxide solution of the fluoborate VII at low temperature (eq. 2). The reaction appeared to be rapid and complete since the solution was quite stable on immediate warming to room temperature. The crude methyl ether X was found to be at least 95% pure by G.P.C. analysis. Claisen distillation gave essentially no residue. The 2-methyl-1,3-dioxolenium fluoborate (XI) was obtained in 53% yield, m.p. 172–175°. Authentic dioxolenium fluoborate (XI) melts at 164–166° dec. Examination of the apparently impure salt revealed that it was not quite completely soluble in sulfur dioxide. The n.m.r. spectrum of the sulfur dioxide solution was identical with authentic dioxolenium fluoborate (XI) except that it contained a trace of impurity (5%). The sulfur dioxide-insoluble material was probably silver chloride or silver fluoborate carried along as the acetonitrile complex.¹⁴

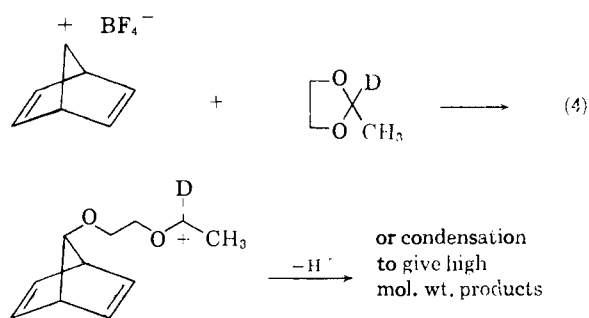
In order to obtain a rough estimate of the acidity of the carbonium ion and to check for any non-observable carbon skeleton rearrangement or equilibria which could incorporate deuterium but not be evidenced by reaction products, the fluoborate VII was treated with 2-deuterio-2-methyl-1,3-dioxolane (XII); g.p.c. analysis of the product which was isolated by treating the reaction mixture with the methoxydioxolane (IX) showed no norbornadiene and only a very slight trace of a material with the same retention time as 7-methoxynorbornadiene (X). There were no volatile products. However, impure 2-methyl-1,3-dioxolenium fluoborate (XI) was isolated from the reaction in 48% yield. Examination of the n.m.r. spectrum of the sulfur dioxide solution revealed about 7% impurity. Otherwise the product was identical with authentic XI.

There appear to be two reasonable explanations for these unexpected results. The fluoborate may have reacted as anticipated to give 7-deuterionorbornadiene or the tricyclic olefin, 2-deuteriotricyclo[4.1.0.0^{3,7}]heptene-4 (XV), which did not survive the reaction conditions. Alternatively, the dioxolane XII may have been attacked at one of

(13) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert and K. Wunderlich, *Ann.*, **632**, 38 (1960); H. Meerwein, V. Hederich, H. Morschel and K. Wunderlich, *ibid.*, **638**, 1 (1960).

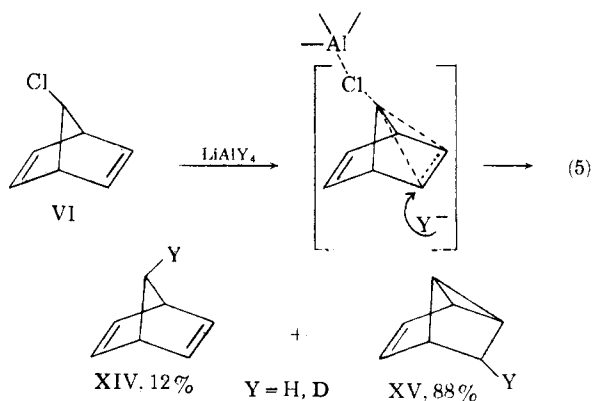
(14) H. Meerwein, V. Hederich and K. Wunderlich, *Arch. Pharm.*, **291**, 541 (1958).

the oxygens with subsequent ring opening as shown in eq. 4.



The fluoborate VII was found not to react with deuteriotriphenylmethane. There was no evidence of the characteristic yellow color of the trityl ion during the reaction. Furthermore, 7-methoxynorbornadiene (X), which was obtained as the only product (the reaction was not checked for trityl methyl ether) by working up the reaction as before with IX, contained no deuterium as demonstrated by its n.m.r. spectrum. This result should probably not be interpreted to mean that the 7-norbornadienyl carbonium ion (IVb) is less acidic than the trityl carbonium ion. It is, however, probably considerably more stable than its reactions and thermal instability would indicate. Because of the reactive double bonds it has more attractive decomposition paths open to it.

Convincing additional evidence for interaction of the *anti* double bond (C.2,3) and a developing carbonium ion at C.7 is provided by the lithium aluminum hydride reduction of 7-chloronorbornadiene (VI) which gave not only the expected norbornadiene (XIV) but also, quite remarkably, tricyclo[4.1.0.0^{3,7}]heptene-4 (XV) as the major product.¹⁵ The most probable reaction mechanism for the formation of XV is shown in eq. 5. The stereochemistry of the reduction at C.7 is unknown.



Ionization of the carbon-chlorine bond probably does not proceed to an appreciable extent before carbon-hydrogen bond formation begins. Moreover, the high degree of stereochemical control exerted by the non-classical ion thus indicates a high correspondence between carbon-chlorine bond breaking and electron transfer from the double

(15) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3347 (1961).

bond to C.7.¹⁶ Winstein's solvolysis of the chloride has led to the same conclusion.⁷

No previous reactions of 7-substituted norbornenes or norbornadienes have resulted in ring closure products such as XV because they were equilibrium processes and the strain involved in the tricyclic structure forced the equilibrium in favor of the bicyclic structure. Hydride reduction, on the other hand, is essentially irreversible and reaction at any carbon other than C.7 results in a ring-closed product.

While lithium aluminum hydride reduction of VI does not favor one non-classical cationic structure over another, it does provide the first direct chemical evidence of the type of transannular interaction proposed in the 7-norbornadienyl and *anti*-7-norbornenyl systems.

Extent of the Non-classical System.—All the available evidence is, therefore, consistent with IVb as the structure of the 7-norbornadienyl non-classical carbonium ion, with one reservation. It is not clear to what degree, if any, the *syn* double bond (5,6) participates in charge delocalization. The n.m.r. spectral evidence is probably best described as inconclusive regarding this point. However, the slight upfield shift of the 5,6-hydrogens in the carbonium ion compared to their position in the chloride VI probably indicates any interaction to be slight at most. Participation in charge delocalization by the *syn* double bond, as shown in IVb, is based solely on the fact that 7-chloronorbornadiene (VI) was observed⁷ to solvolyze *ca.* 800 × faster than *anti*-7-chloronorbornene (IIIb). This evidence must also be regarded as inconclusive, however, since it is in the realm of possibility that the rate difference is due largely to a ground state-transition state effect. Consequently, structure XVI must also be considered as a likely representation of the carbonium ion. For convenience, the carbonium ion will be



referred to henceforth as IVb with the tacit understanding that XVI is equally as likely a true representation.

Possible Interconversion of Non-classical Structures.—The evidence is thus strongly in favor of non-classical homoallylic stabilization of a cationic center at C.7. The n.m.r. evidence shows that this stabilization takes the form of the non-classical structure IVb in the fluoborate salt VII. Moreover, IVb is, *at least initially*, the expected structure. Because the double bond *syn* to the leaving group cannot participate *directly* at C.7 in the early stages of the formation of the non-classical ion, we see that structure IVb is exactly

(18) This is not too surprising, perhaps, considering the instability of the C.7 cation. For example, 7-norbornenyl tosylate solvolyzes 10⁴ slower than cyclohexyl tosylate. [S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955)]. The reduced bond angle at C.7 is presumably partly responsible, putting more s-character into the incipient empty p-orbital, thus making C.7 more electronegative. It may, in fact, be that the olefinic carbons have become positive relative to C.7 in the 7-norbornadienyl cation.

the structure one would, *a priori*, predict in every ionization at C.7 which is promoted by non-classical ion formation.

The observation that the olefin peaks are unchanged up to 50° indicates that the interconversion of the isomeric forms of IVb through the transition state IVa occurs slower than at twice per second in the range studied. This barrier may be rationalized by assuming that considerable energy is necessary to move the bridge away from one double bond before any benefit from interaction with the other double bond is felt. A considerable distortion from the symmetrical geometry as in IVa is therefore implied.

In view of the remarkable evidence of DePuy, *et al.*,¹⁷ it is not too surprising to find that interconversion if possible of the non-classical structures IV requires an activation energy. Reactions such as diazotization of the amine, 7-aminonorbornadiene, which will generate a positive charge at C.7 but are not primarily dependent on non-classical ion formation, may possibly yield one of the symmetrical structures (IVa, IVc) directly.

Acknowledgments.—We thank Mr. E. W. Anderson for determination of some of the n.m.r. spectra. P. R. S. is grateful for the many helpful suggestions and stimulating discussions provided by his colleagues in the Chemistry Department, Bell Telephone Laboratories.

Experimental

N.m.r. spectra were determined on 60 mc. Varian Associates n.m.r. spectrometers. Peak positions are reported in p.p.m. relative to tetramethylsilane internal standard as 10 p.p.m.

Silver fluoborate was in part prepared by the method of Olah and Quinn¹⁸ and in part supplied by Chemical Procurement Laboratories. This material was dried over phosphorus pentoxide *in vacuo* before being stored, and warmed in a high vacuum just before use.

Sulfur dioxide was Matheson anhydrous grade and in several experiments was dried further by distillation from phosphorus pentoxide. The sulfur dioxide was, in every case, removed from the container in the vapor state.

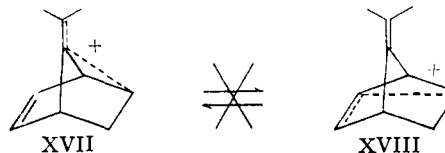
Nitromethane.—Eastman spectrograde was further rigorously purified by Pocker's method.¹⁹

Deuteriotriphenylmethane was prepared by the addition of 99.6% deuterium oxide to triphenylmethylsodium.²⁰ Recrystallization from ethanol and from benzene gave colorless crystals, m.p. 92.5–93.5. The n.m.r. spectrum in carbon tetrachloride showed no detectable aliphatic hydrogen.

7-*t*-Butoxynorbornadiene (V) was prepared as previously reported.⁸

2-Methoxy-2-methyl-1,3-dioxolane (IX) was prepared according to Meerwein's procedure¹⁴ for preparing the corresponding 2-ethoxy-2-methyl-1,3-dioxolane. These workers

(17) It was shown that the carbonium ions XVII and XVIII, derived from *endo*- and *exo*-7-isopropylidenedehydronorbornyl tosylates, respectively, were not interconvertible under the solvolysis



conditions; C. H. DePuy, I. A. Ogawa and J. C. McDaniels, *J. Am. Chem. Soc.*, **82**, 2398 (1960).

(18) G. A. Olah and H. W. Quinn, *J. Inorg. Nucl. Chem.*, **14**, 295 (1960).

(19) Y. Pocker, *J. Chem. Soc.*, 240 (1958).

(20) H. D. Zook and W. L. Relahan, *J. Am. Chem. Soc.*, **79**, 881 (1957).

employed the general method of Alexander and Busch,¹¹; b.p. 75° (105 mm.), infrared (neat): 3.35(m), 3.43(m), 7.20(s), 8.60(s), 9.43(s), 9.70(s), 10.46(m), 11.2(broad, s) μ ; n.m.r. (ca. 1 molar in carbon tetrachloride): 6.09(m), 6.85(s), 8.58(s).

2-Methyl-1,3-dioxolenium fluoborate (XI) was prepared according to Meerwein's method¹² from 2-methoxy-2-methyl-1,3-dioxolane (IX), m.p. 164–166° dec., n.m.r. (ca. 1 molar in sulfur dioxide): 4.64(s), 7.23(s).

7-Chloronorbornadiene (VI).—To a stirred solution of 61 g. (0.37 mole) of *t*-butyl ether (V) in 400 ml. of acetyl chloride (reagent grade), 0.5 ml. of water was added dropwise. Anhydrous hydrous hydrogen chloride was then bubbled in for about 5 minutes. Heating was begun and the mixture was refluxed for 1 hour. During this period, hydrogen chloride was bubbled in for two 5-minute periods. A nitrogen atmosphere was provided throughout the reaction time. The excess acetyl chloride was rapidly removed through a Claisen head at 70 mm. Immediate distillation through a spinning band column yielded 33 g. (70%) of 7-chloronorbornadiene (VI), b.p. 77° (55 mm.). This material was shown by infrared, n.m.r. and g.p.c. analysis to be identical to authentic chloride.¹³ It should be noted that on a few occasions yields were as low as 57% with only 22% conversion, the unreacted ether V being recovered.

7-Norbornadienyl Fluoborate (VII).—A solution of 0.254 g. (0.002 mole) of chloride VI, which was purified immediately before use by preparative scale g.p.c. using a 5' \times 5/8", 15% Apiezon-M column, in 2 ml. of sulfur dioxide was slowly added over 15 minutes to a stirred solution-suspension of 0.500 g. (0.0026 mole) of silver fluoborate in 2 ml. of sulfur dioxide. The silver fluoborate was incompletely soluble in this volume of sulfur dioxide. Silver chloride began to precipitate immediately upon addition of chloride VI. After addition was complete, the solution was stirred for an additional 15 minutes. The volume of the solution was then reduced to 2–3 ml. by application of a vacuum. After centrifugation, the solution was pipetted into an n.m.r. tube which was then sealed. Sealed tubes were stored in Dry Ice until used. Addition of tetramethylsilane had no effect on the n.m.r. spectrum.

The entire operation, except centrifugation, was conducted in either a nitrogen-atmosphere dry-box as described above or on a vacuum line using standard techniques. Cooling, which allowed the reaction to be conducted at various temperatures ranging from –80° to –15°, was effected by passing nitrogen through a copper tube immersed in liquid nitrogen or a Dry Ice-solvent-bath, then through the jacketed reaction apparatus. Solutions prepared at lower temperatures, below –30°, were discovered to be uniformly better. Solutions prepared above this temperature frequently were discolored when a portion of the solution inadvertently became too warm. Successful preparation always gave colorless solutions. Further, the relatively concentrated n.m.r. solutions showed no ultraviolet absorption above 330 μ at ca. –80°. Some preparations were carried out in liquid sulfur dioxide which had been distilled from phosphorus pentoxide, with no detectable improvement. Solutions of the fluoborate VII were stable for periods of at least one week, and possibly longer, at Dry Ice temperatures.

Nitromethane solutions of the fluoborate VII were prepared at –20° to –15° in exactly the same fashion. These solutions were, however, invariably discolored presumably due to the necessary higher temperature.

Reaction of Fluoborate VII with Acetic Acid.—A solution of the fluoborate VII was prepared in the usual way from 0.3844 g. (0.0030 mole) of chloride VI and 0.650 g. (0.0033 mole) of silver fluoborate in a total of 10 ml. of sulfur dioxide at –50°. The reaction mixture was allowed to stir for 30 minutes, whereupon it was centrifuged and decanted. The white precipitate was washed twice with sulfur dioxide. The washings were combined and added to 3 ml. of glacial acetic acid. The white precipitate, which was presumed to be silver chloride (soluble in concentrated ammonium hydroxide) was washed with distilled hot water and dried overnight at 140° to yield a constant weight of 0.4198 g. (96.4%) of silver chloride.

After 20 ml. of methylene chloride was added to the acetic acid-sulfur dioxide solution, the sulfur dioxide was

evaporated away at room temperature inside the dry-box. The methylene chloride solution was washed with water and sodium bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was then removed by slow Claisen distillation in an argon atmosphere. Isolation of the product by g.p.c. using a 40' \times 5/8" 10% Uconpolar on Fluoropak preparative scale column at 130° yielded 0.2290 g. (50%) of 7-norbornadienyl acetate (VIII) which was shown by infrared, n.m.r. and g.p.c. to be identical to authentic acetate VIII.⁸ No other products could be detected by g.p.c. analysis of the crude product. Neither did infrared and n.m.r. analysis of the crude product reveal other products.

Reaction of Fluoborate VII with 2-Methoxy-2-methyl-1,3-dioxolane (IX).—The fluoborate VII was prepared on a vacuum line, using standard techniques, from 2.00 g. (0.158 mole) of chloride VI and 3.11 g. (0.160 mole) of silver fluoborate in approximately 100 ml. of sulfur dioxide at –70°. To this stirred solution, 2.5 g. (0.21 mole) of methoxydioxolane IX was added over 15 minutes. The silver chloride was not removed prior to addition of the dioxolane IX. This solution was then stirred for 5 minutes, whereupon removal of the sulfur dioxide was begun at reduced pressure. Concomitantly, 50 ml. of methylene chloride was added in small portions. The reaction flask was removed to the dry-box and the contents filtered free of a white precipitate which was washed with two small portions of methylene chloride. The combined washings were washed with water and sodium bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was carefully removed and the product was distilled (Claisen-Vigreux) to yield 1.1 g. (57%) of 7-methoxynorbornadiene (X), b.p. 74–75° (56 mm.), infrared (neat): 3.21(w), 3.31(m), 3.42(m), 3.50(w), 6.42(w), 8.95(s), 13.6(s) μ ; n.m.r. (ca. 1 molar in carbon tetrachloride): 3.55(3), 3.65(m), 6.60(m), 7.00(s).

Anal. Calcd. for C₈H₁₀O: C, 78.65; H, 8.25. Found: C, 78.63; H, 8.44.

Examination of the distillation pot revealed very little residue and the distilled product was shown by g.p.c. to be at least 92% pure.

The white precipitate was washed with about 30–50 ml. of acetonitrile. The remaining silver chloride was washed with water and dried to constant weight to give 2.16 g. (95.2%). Anhydrous ether was added to the acetonitrile solution to precipitate a white solid which was filtered off and dried *in vacuo* at room temperature for 2 days to give 1.47 g. (53%) of apparently impure 2-methyl-1,3-dioxolenium fluoborate (XI), m.p. 172–175°. The melting point of authentic XI is reported,¹⁴ and has been observed in this Laboratory, as 164–166°. The fluoborate mI was dissolved in sulfur dioxide and found to be only about 90% soluble. The n.m.r. spectrum of this solution, except for a small amount of impurity (< 5%), was identical to that of the authentic fluoborate XI.

Reaction of the Fluoborate VII with Deuteriotriphenylmethane.—7-Norbornadienyl fluoborate (VII) was prepared in the usual way on the vacuum line from 2.00 g. (0.158 mole) of chloride VI and 3.11 g. (0.160 mole) of silver fluoborate in about 75 ml. of sulfur dioxide; 6.70 g. (0.273 mole) of deuteriotriphenylmethane was introduced into the mixture and stirred for 2 hours at –30° to –40° and 2.5 hours at –65°. The characteristic intense yellow color of the trityl carbonium ion was at no time apparent. A yellow color characteristic of the fluoborate VII reaction solutions which have been held at relatively high temperatures (–30°) was evident at the end of 2 hours. Consequently, the temperature was lowered to –65° for the remainder of the reaction time (2.5 hours); 2.50 g. (0.212 mole) of 2-methoxy-2-methyl-1,3-dioxolane (IX) was then introduced all at once with immediate dissipation of the yellow color. Solutions which were worked-up without addition of a quenching agent such as IX decomposed to give black intractable solids. This mixture was worked-up as described above and the crude product was examined by g.p.c. and found to contain no norbornadiene. Distillation through a small Claisen-Vigreux column yielded 0.95 g. (49%) of 7-methoxynorbornadiene (X), b.p. 70–71° (52 mm.). N.m.r. and infrared examination of this material revealed that it was identical to authentic ether X and contained no detectable deuterium as shown by careful integration. Triphenylmethane was also found to give no

(21) E. R. Alexander and H. M. Busch, *J. Am. Chem. Soc.*, **74**, 554 (1952).

visible reaction with the fluoborate VII prepared as above in nitromethane solution. This reaction was not examined further.

Preparation of 2-Deuterio-2-methyl-1,3-dioxolane (XII).—A modified procedure of Claus and Morganthau²² for the reduction of *ortho* esters was used to reduce 2-methoxy-2-methyl-1,3-dioxolane (IX) with lithium aluminum deuteride. Benzene could not be used as Claus and Morganthau had done since it and the product XII boil at almost exactly the same point. Toluene was found to be unsatisfactory because it formed an azeotropic mixture (~ 1:1) with the product XII which could only be separated by g.p.c. Consequently, 2.36 g. (0.225 equiv. wt.) of lithium aluminum deuteride was added to 26 g. (0.22 mole) of IX in a small reaction flask equipped with stirrer and condenser and cooled in a Dry Ice-acetone-bath. If the mixture is not cooled it becomes violent after about 5 minutes. The cooled mixture is slowly warmed and finally refluxed for 3-4 hours. The product was distilled (Claisen) directly from this mixture to yield 6.0 g. (32%) of 2-deuterio-2-methyl-1,3-dioxolane (XII), b.p. 82-84°; g.p.c. analysis indicated a purity of 96%. The reported²³ boiling point of 2-methyl-1,3-dioxolane is 82°. Before use the deuterio-dioxolane XII was purified by preparative scale g.p.c. The n.m.r. was consistent with the assumed structure and no C-2 hydrogen could be detected. Reduction of the methoxydioxolane IX with lithium aluminum hydride gave

(22) C. J. Claus and J. L. Morganthau, *J. Am. Chem. Soc.*, **73**, 5095 (1951).

(23) H. J. Dauben, B. Loken and H. J. Ringold, *ibid.*, **76**, 1359 (1954).

authentic 2-methyl-1,3-dioxolane as indicated by its infrared, n.m.r. and boiling point; infrared (carbon tetrachloride): 3.31(m), 3.44(m), 4.70(m), 8.88(s), 9.47(s), 11.6(s) μ ; n.m.r. (carbon tetrachloride, 1 molar): 6.20 (10), 8.74 (s).

Reaction of Fluoborate VII with 2-Deuterio-2-methyl-1,3-dioxolane (XII).—The fluoroborate VII was prepared as usual on the vacuum line from 1.00 g. (0.008 mole) of silver fluoborate in about 40-50 ml. of sulfur dioxide at about -75°. To this stirred mixture, 1.20 g. (0.013 mole) of deuteriodioxolane (XII) was added all at once and stirring was continued for 4 hours. At the end of this period, 0.97 g. (0.008 mole) of methoxydioxolane (IX) was added and the reaction was worked-up as usual. Warming of the reaction mixture without addition of IX resulted in complete decomposition. Impure 2-methyl-1,3-dioxolenium fluoborate (XI) was obtained in 48% yield (0.67 g.), m.p. 174+° dec. As before, this salt was incompletely soluble in sulfur dioxide. The n.m.r. spectrum of the sulfur dioxide solution revealed about 7% impurity; otherwise, it was identical with authentic material.

Examination of the crude ether-soluble product by g.p.c. indicated the absence of norbornadiene or its possible isomers. Very little volatile material could be detected. However, two very small unresolved peaks appeared at approximately the retention time of 7-methoxynorbornadiene (X), but were insufficient to characterize. Excess dioxolanes IX and XII were, of course, removed in the water wash. The infrared of the crude product was inconclusive, except that the norbornadiene nucleus could not be detected. Claisen distillation gave a wide boiling point range, 100-150° (0.2 mm.), and no identifiable products.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Tribenzotalarene; an Unusual Polycyclic Organoboron Compound¹

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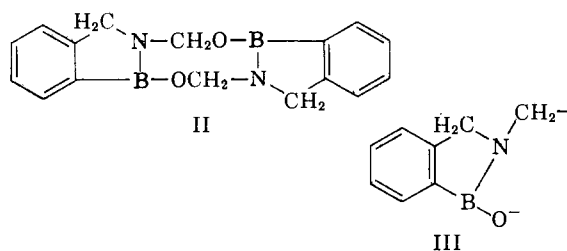
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We have shown that the product which Snyder, Reedy and Lennarz obtained by a Sommelet reaction on *o*-bromomethylbenzenboronic acid³ is a trimer with the probable structure IV, a tribenzo derivative of talarene (V). The mechanistic implications of the synthesis are discussed and possible use of IV as a clathrate is suggested.

In an attempt to prepare *o*-formylphenylboronic acid by application of the Sommelet synthesis to *o*-bromomethylbenzenboronic acid, Snyder, Reedy and Lennarz obtained a high melting substance,³ (C₉H₇BNO)_n (I). They suggested structure II for this compound because it dissolved in dilute acid and was apparently insoluble in water of dilute alkali. Since this structure involves an eight-membered ring which appears from models to be highly strained, and since the evidence for it was by no means conclusive, we decided to reinvestigate the compound.

The material obtained from the Sommelet process did indeed dissolve in dilute acids. However, the material did not dissolve in ethereal solutions of boron trifluoride etherate unless catalytic quantities of ethanol were added. It also dissolved in aqueous alkali if small amounts of ethanol were added to the solution. In several attempts we were unable to recover the original compound from any of the above solutions and changes in the ultraviolet and infrared spectra indicated that it had been destroyed. The solubility behavior of the

compound allows no immediate conclusions about the structure, however, since it would be impossible to assess the effect of B-N π -bonding on the donor-acceptor properties of the molecule.



There can be little doubt from analysis and the method of preparation that I contains the repeating unit III, (C₉H₇BNO). However, the material as obtained by the procedure of Snyder, Reedy and Lennarz analyzed as a monohydrate of the trimer of III, (C₉H₇BNO)₃·H₂O, suggesting that I is at least trimeric. The presence of water of crystallization was confirmed by a strong band in the infrared spectrum at 3655 cm.⁻¹ (Fig. 1) and by the fact that anhydrous I, free from this absorption, could be obtained by crystallization from anhydrous solvents or by heating to 150° in a vacuum.

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(2) Woodrow Wilson Fellow 1960-1961; National Science Foundation Pre-doctoral Fellow 1961-1963.

(3) H. R. Snyder, A. J. Reedy and W. J. Lennarz, *J. Am. Chem. Soc.*, **80**, 835 (1958).