

TABLE V
 CRYOSCOPIC MOLECULAR WEIGHT DETERMINATIONS

Compound	State	Solvent	Wt. of compd., g.	Wt. of solvent, g.	F.p. depression, °C.	Molecular weight	Av. mol. wt.	Degree of polymn.
Aluminum	Solid	<i>t</i> -Butyl	0.8733	19.72	0.698	523		
<i>t</i> -butoxide		alcohol	.7209	19.72	.605	506	524	2.14
			.7695	19.72	.60	544		
Aluminum	Solid	Benzene	1.9737	21.96	.56	823	820	4.20
isopropoxide			1.3505	21.70	.39	817		
Aluminum	Melt	Benzene	0.7007	8.039	.767	582	578	2.83
isopropoxide			0.6719	8.094	.741	574		

Cryoscopic constant of *t*-butyl alcohol = 8.37; cryoscopic constant of benzene = 5.12.

azobenzene as standard. Values of 477 and 483 were obtained, the average corresponding to a degree of polymerization of 1.95.

To prepare the supercooled melt solution, approximately 1 g. of aluminum isopropoxide was sealed in a Pyrex tube, heated to 200° for 5 minutes in an oil-bath, then removed, opened, and the contents immediately dissolved in benzene. In this way, rearrangement of the melt was kept to a minimum.

Preparation of Materials.—Commercial samples of aluminum isopropoxide were purified by distillation under reduced pressure; aluminum *t*-butoxide was prepared as described by Wayne and Adkins,¹⁸ and purified by recrystallization from benzene.

Nuclear Magnetic Resonance Spectroscopy.—All nuclear magnetic resonance spectra were measured on either a Varian A-60 or a Varian DP-60 nuclear magnetic resonance spectrometer. Measurements involving temperature effects, spin decoupling or integration of aluminum isopropoxide spectra were carried out on the DP-60 spectrometer, others on the A-60.

All samples, except melt solutions, were made up in a drybox, and used either tetramethylsilane or hexamethylbenzene as internal references for measurement of peak positions. Saturated solutions of aluminum *t*-butoxide in *t*-butyl alcohol and of tetrameric aluminum isopropoxide in dioxane and isopropyl alcohol were used. Other solutions contained 15–20% of the alkoxide. All peak positions are in cycles per second (at 60 Mc.) from internal tetramethylsilane reference. Peak positions quoted are considered accurate to ± 1 cycle per second, except for peaks of spin decoupled spectra.

Spin decoupling of the methyl protons from the single proton of the isopropoxide group in aluminum isopropoxide dissolved in carbon tetrachloride was achieved by generating a side band at 185 cycles per second from the main band, then scanning the methyl frequencies with the side-band generator on. Decoupling the single proton of the isopropoxide group from the methyl protons was achieved in the same way, but because of the difficulty of saturating six protons with a side band generated on the signal from one proton, decoupling was not quite complete,

(18) W. Wayne and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 48.

and the results are less accurate. Peak positions of spin decoupled peaks were measured by extrapolation from the known positions of other peaks in the spectrum, since the side band generator, normally used for measuring peak positions, was already in use. Peak positions quoted for spin decoupled peaks are probably accurate to ± 3 c.p.s.

Solutions of the supercooled melt of aluminum isopropoxide were prepared as described above. Supercooled molten aluminum isopropoxide is considerably more soluble than the tetramer in all solvents used in this work and is readily soluble in a good many solvents such as pyridine in which the tetramer is almost insoluble.

The solubilities of the two forms in a number of solvents were determined by removal of solvent from a weighed quantity of the saturated solution, and are given in Table VI.

 TABLE VI
 SOLUBILITIES OF TRIMERIC AND TETRAMERIC ALUMINUM ISOPROPOXIDE AT 22°

Solvent	Solubility, g. per 100 g. of solv.	
	Trimer	Tetramer
Carbon tetrachloride	Miscible	65.3
Benzene	Miscible	66.8
Cyclohexane	Miscible	109.7
Dioxane	Miscible	2.52
Isopropyl alcohol	Miscible	4.92

Acknowledgments.—The authors wish to thank Mr. A. Clouse for operating the Varian DP-60 spectrometer throughout this work. This study was supported by grant RG-8502 from the National Institutes of Health, Department of Health, Education and Welfare. The authors are indebted to Mr. J. S. Humphrey for drawing the figure.

COMMUNICATIONS TO THE EDITOR

Rates of Ethanolsis of Camphene Hydrochloride and Related Alpha Methyl Substituted 1-Chloro-1-methylcyclopentanes—the Question of a Non-classical Camphenylyl Cation

Sir:

We wish to report that the rate of ethanolsis of camphene hydrochloride is comparable in magnitude to those exhibited by representative model compounds derived from 1-chloro-1-methylcyclopentane. Consequently, the fast rate of solvolysis of the bicyclic chloride cannot be utilized as an argument for the formation of a stabilized synartetic (mesomeric, non-classical) ion in its solvolysis.¹

It was originally suggested by Wilson and his co-workers that the camphene hydrochloride-isobornyl chloride rearrangement might involve a mesomeric

cation² instead of the classical ions considered by Meerwein.³ The very fast rate of ethanolsis of camphene hydrochloride (6000 times greater than that of *t*-butyl chloride¹) was considered to provide strong support for its ionization to such a stabilized mesomeric intermediate.¹

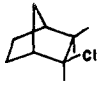
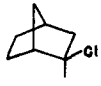




It would be of considerable interest to possess an estimate of the driving force afforded by the formation of the stabilized mesomeric intermediate. Such an estimate could be realized by comparing the observed rate of ionization with that of a comparable model compound which does not ionize to form a mesomeric species. It is evident that acyclic derivatives, such as *t*-butyl chloride, with their ability to minimize non-bonded interactions, cannot be satisfactory model systems. It would appear that 1-chloro-1-methylcyclopentane and its methyl derivatives, with bond

(1) F. Brown, E. D. Hughes, C. K. Ingold and J. F. Smith, *Nature* **168**, 65 (1951).

(2) T. P. Neville, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(3) H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922).

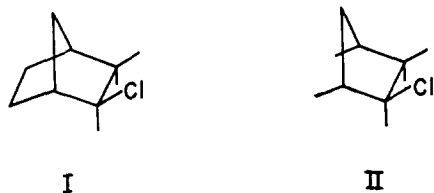
TABLE I
RATES OF ETHANOLYSIS AT 25° OF CAMPHENE HYDROCHLORIDE, *exo*-2-CHLORO-2-METHYLNORBORNANE AND RELATED α -METHYL-SUBSTITUTED 1-CHLORO-1-METHYLCYCLOPENTANES

Compound	k_{25}° sec. ⁻¹ × 10 ⁶	Relative rates			
<i>t</i> -Butyl chloride	0.85	1.00			
I 	1160	13600 ^a	206	5.7	
III 	30.2	355	5.4		2.1
IV 	5.62	66	1.00		
V 	14.5 ^b 10.6 ^c	171 125	2.6 1.9		1.00
VI 	202	2380	36		1.00
VII 	458	5390	82		

^a Our rate constant at 0°, 37.2×10^{-6} sec.⁻¹, is in reasonable agreement with the earlier value (ref. 1). The discrepancy in the relative rate must arise from the rate constant for *t*-butyl chloride, which was not given explicitly (ref. 1). ^b Chloride from *cis*-1,2-dimethylcyclopentanol. ^c Chloride from *trans*-1,2-dimethylcyclopentanol.

oppositions that can be partially relieved by ionization,^{4,5} should provide more satisfactory models.⁶

The ideal model compound for camphene hydrochloride (I) would appear to be 1-chloro-1,2,2-*cis*-3-*cis*-5-pentamethylcyclopentane (II), realized formally by opening the bicyclic ring system of camphene hydrochloride.



Unfortunately, the difficulties involved in the synthesis of this particular structure led us to examine somewhat simpler model compounds (III-VII).

The rate of ethanolysis of camphene hydrochloride at 25° proved to be 13,600 times greater than *t*-butyl chloride, but only 206 times greater than 1-chloro-1-methylcyclopentane (IV). Indeed, *exo*-2-chloro-2-methylnorbornane⁷ (III), without the two methyl substituents in the 3-position, undergoes solvolysis only 5.4 times faster than 1-chlorocyclopentane. The introduction of a methyl group in the α -position of 1-chloro-1-methylcyclopentane increases the rate by a

factor of approximately two. The introduction of two additional methyl groups in the other α -position results in a sharp increase. A fourth α -methyl substituent results in an additional increase. These increases would appear to be explicable in terms of the effect of increased steric strain. In each case it was demonstrated that the structure was maintained during the conversion of the tertiary alcohol into the chloride and subsequent solvolysis of the latter in weakly alkaline aqueous acetone.

The results are summarized in Table I. The data reveal that the rate of ethanolysis of *exo*-2-chloro-2-methylnorbornane (III) is only twice that of 1-chloro-1,2-dimethylcyclopentane (V), while the rate for camphene hydrochloride differs by only a factor of five from that of model compound, 1-chloro-2,2,5-trimethylcyclopentane (VI).

These results do not support the conclusion that the solvolyses of camphene hydrochloride and the related tertiary chloride, *exo*-2-chloro-2-methylnorbornane, exhibit marked rate enhancements anticipated for the postulated participation of the 1,6-bonding pair to form a stable mesomeric ion.¹ Moreover, it was recently concluded that the 1,2-dianisylnorbornyl cation exists in sulfuric acid as a rapidly equilibrating pair of classical ions, and not as a single mesomeric species.⁸ It may, of course, be argued that relatively stable tertiary ions, such as those present in the solvolysis of I and III, do not require participation of the 1,6-bonding pair.⁹ However, the fact is that non-classical ions have been utilized in the past to interpret the behavior of stabilized tertiary¹⁰ as well as the more usual secondary bicyclic

(8) P. von R. Schleyer, D. C. Kleinfelter and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963).

(9) S. Winstein, Reaction Mechanisms Conference at Brookhaven, September 5, 1962.

(10) P. D. Bartlett, E. R. Webster, C. E. Dills and H. G. Richey, Jr., *Ann.*, **623**, 217 (1959); P. D. Bartlett, C. E. Dills and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **82**, 5414 (1960).

(4) P. D. Bartlett, *Bull. soc. chim. France*, C100 (1951).

(5) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951).

(6) Cyclohexyl derivatives have frequently been utilized as standards against which the bicyclic derivatives have been compared. However, the normal strain-free conformation of the cyclohexane ring system, with its staggered bonds, would appear to bear little resemblance to the strained bicycloheptane system with its opposed bonds. This conclusion is supported by the observed magnitude of the carbonyl group stretching vibration (in cm.⁻¹): cyclopentanone, 1750; cyclohexanone, 1717; norcamphor, 1751 [R. Zbinden and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1215 (1960)].

(7) N. J. Toivonen, E. Siltanen and K. Ojala, *Ann. Acad. Sci. Fennicae, Ser. A II*, 64 (1955).

cations, without distinction.¹¹ Consequently, it appears desirable to subject the evidence which has been considered to require the participation of mesomeric intermediates in the solvolytic reactions of bicyclic systems to a critical re-examination.¹² We are presently examining the solvolytic behavior of a number of tertiary derivatives of representative bicyclic systems in an attempt to obtain definitive evidence as to the importance of non-classical intermediates in such systems.

Acknowledgment.—This study was made possible by the financial support provided by Project No. AT(11-1)-70 supported by the Atomic Energy Commission.

(11) For a summary of the data and their interpretation in terms of non-classical intermediates, see A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(12) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp. 140-158, 174-178.

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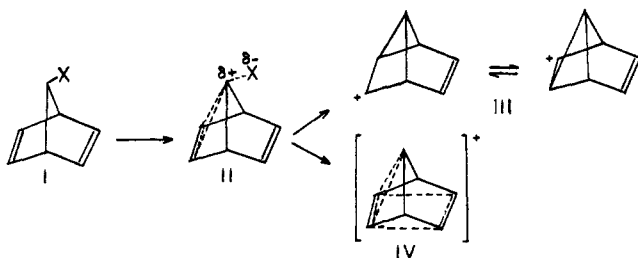
HERBERT C. BROWN
FRANK J. CHLOUPEK

RECEIVED MAY 18, 1963

The Reaction of 7-Norbornadienyl and 7-Dehydronorbornyl Derivatives with Borohydride under Solvolytic Conditions—Evidence for the Tricyclic Nature of the Corresponding Cations

Sir:

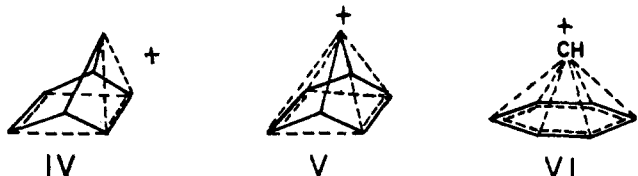
The marked rate enhancements observed in the solvolysis of 7-chloronorbornadiene and anti-7-dehydronorbornyl tosylate relative to the corresponding saturated derivatives reveal that the reactions must proceed with participation of the double bond in the transition state^{1,2} II. The question arises as to the precise nature of the cationic intermediate accompanying ionization. It has been generally assumed that this intermediate possesses a non-classical structure IV, although the possible existence of this intermediate as an equilibrating pair of classical tricyclic carbonium ions III cannot be excluded by the available data.³ In the latter event, the structure IV would represent the transition state between the two equilibrating ions III.



(1) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

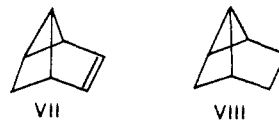
(2) S. Winstein and C. Ordonneau, *ibid.*, **82**, 2084 (1960).

(3) The authors (ref. 2) suggested three different non-classical structures for the cation from 7-chloronorbornadiene (IV-VI). However, from their



n.m.r. examination of the product produced by the reaction of the chloride with silver fluoroborate, P. R. Story and M. Saunders [*ibid.*, **84**, 4876 (1962)] concluded that their data required the first, unsymmetrical structure IV. The authors discussed their results only in terms of possible non-classical structures, although they stated that the n.m.r. data could not distinguish between the unsymmetrical non-classical ion IV and a rapidly equilibrating pair of classical tricyclic ions III.

Story observed that lithium aluminum hydride in refluxing ethyl ether reacts slowly with 7-chloronorbornadiene to yield 43% (isolated) of tricyclo[4.1.0.0^{3,7}]hept-4-ene VIII with the concomitant formation of 6% of norbornadiene.⁴



The predominant formation of the tricyclic hydrocarbon VII might be considered evidence for the existence of the tricyclic ion III. However, it can be argued that the slow reaction in ether proceeds by a path not involving an ionic species.

We recently reported that the solvolysis of secondary and tertiary derivatives in the presence of sodium borohydride provides a convenient means for trapping the carbonium ions formed in the solvolysis.⁵ Under these conditions (65% aqueous diglyme, 1.8 M sodium borohydride), the reaction of 7-chloronorbornadiene was very fast, complete in 15 min. at room temperature. An 83% yield of tricyclo[4.1.0.0^{3,7}]hept-4-ene VII was realized, with 12% norbornadiene.

The solvolysis of anti-7-dehydronorbornyl tosylate under the same conditions produced 15% of tricyclo[4.1.0.0^{3,7}]heptane⁶ VIII, along with 70% of norbornene and 6-7% of anti-7-dehydronorborneol. However, the relatively rapid reaction of the tosylate with lithium aluminum hydride in tetrahydrofuran or diglyme provided a 60% yield of tricyclo[4.1.0.0^{3,7}]heptane and a 34% yield of norbornene. This reaction offers a convenient route to this strained hydrocarbon.

Solvolysis of 7-chloronorbornadiene and anti-7-dehydronorbornyl tosylate under weakly alkaline conditions in the absence of sodium borohydride results in the formation of 7-norbornadienol and anti-7-dehydronorborneol. These results appear to support the nonclassical structures for the cations involved. However, it should be pointed out that the tricyclic derivatives containing oxygen substituents at the 2-position are currently unknown and they may turn out to be unstable relative to the 7-derivatives which are isolated.

On the other hand, the tricyclic hydrocarbons^{4,6} are stable to the reaction conditions. The very high yields of the tricyclic hydrocarbons which have been realized in the present experiments appear difficult to rationalize on the basis of the non-classical structures for the carbonium ion intermediates. Consequently, it appears desirable to reopen the question as to whether the cationic intermediates formed in the solvolysis of 7-norbornadienyl and 7-dehydronorbornyl derivatives are best represented as the classical tricyclic structures, such as III, or as the non-classical structures, such as IV.

Acknowledgment.—The assistance provided by an N.D.E.A. Fellowship to H. M. B. is gratefully acknowledged.

(4) P. R. Story, *ibid.*, **83**, 3347 (1961).

(5) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).

(6) W. R. Moore, H. R. Ward and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

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The Non-classical 7-Norbornenyl Cation¹

Sir:

The high rate (10¹¹ times 7-norbornyl) and over-all retention of structure and configuration in solvolysis of

(1) Research sponsored by the U. S. Army Research Office (Durham).