

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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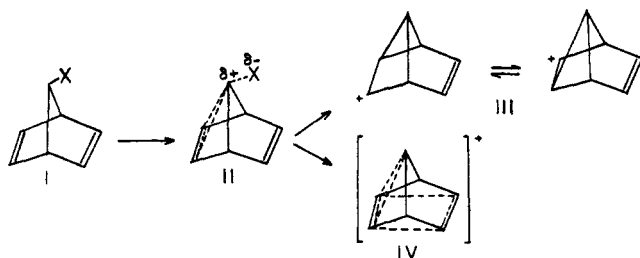
HERBERT C. BROWN
FRANK J. CHLOUPEK

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:

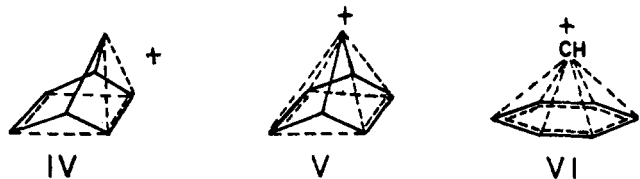
The marked rate enhancements observed in the solvolysis of 7-chloronorbornadiene and anti-7-dehydronorbornyl tosylate relative to the corresponding saturated derivatives reveal that the reactions must proceed with participation of the double bond in the transition state^{1,2} II. The question arises 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).

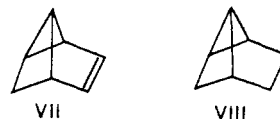
(2) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

(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

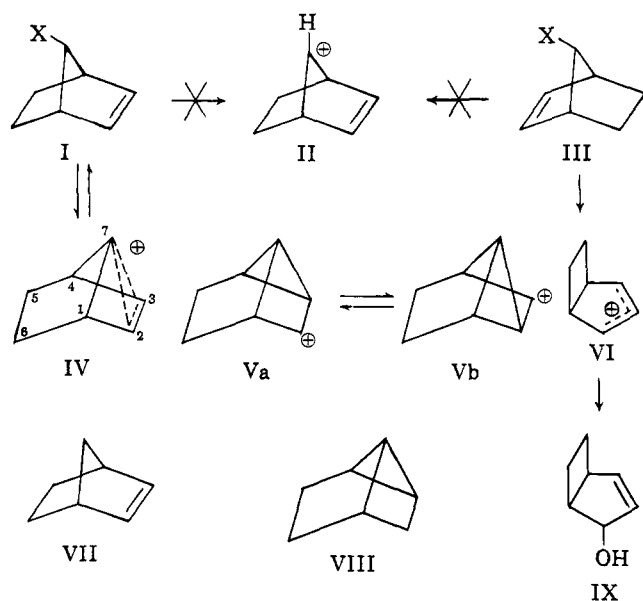
Sir:

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).

anti-7-norbornenyl *p*-toluenesulfonate² (I-OTs) have been accounted for on the basis of an intermediate non-classical "bishomocyclopropenyl" cation² IV. This interpretation has been questioned seriously by Brown.³ From comparing the reactivity of I with that of the 5-norbornenyl instead of the more logical 7-norbornenyl analog, he has questioned the evidence for anchimeric acceleration of ionization of I, thus suggesting classical 7-ion II for reconsideration.^{3a} Alternatively, he has formulated the intermediate more recently^{3b,c} as a rapidly equilibrating pair of tricyclic classical ions Va, b. We now report pertinent results of our more recent further investigation of the solvolysis of I-OTs and I-Cl.

Hydrolysis of I-OTs, m.p. 60.5–60.9°, in 50% aqueous acetone at room temperature in the presence of sodium bicarbonate gives rise to an alcohol which, even as a crude product, m.p. 113.0–113.3°, is pure I-OH, mixture m.p. and infrared spectrum identical with those of authentic I-OH (m.p. 113.0–113.5°). Vapor phase chromatographic analysis, a technique unavailable for our previous work,^{2a,b} indicated the presence of only I-OH, any contamination by the *syn*-epimer⁴ III-OH or the ring-contracted allylic isomer⁴ IX being definitely



below 0.1% for each of them. No sign of the presently unknown tricyclic alcohol X was observed. This material has been suggested^{3b,c} by Brown as the possible chief kinetic control product, but not isolated because of instability to the reaction conditions. However, the solvolytic, work-up and v.p.c. conditions in our present work were shown to permit survival of the most reactive alcohols ever encountered in these Laboratories, e.g., dienol^{5a} XI and the unsaturated *endo-endo* alcohol^{5b} XII. On this basis, it is doubtful that tricyclic alcohol X is an important product of kinetic control.

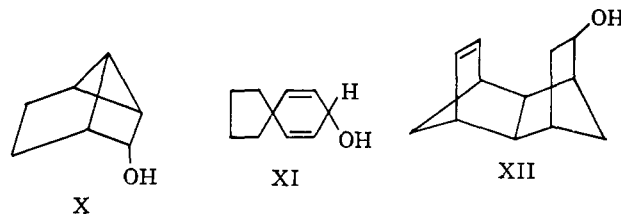
The hydrolysis of I-Cl and I-OTs may be largely diverted to hydrocarbon formation by inclusion of

sodium borohydride in the hydrolysis medium.⁶ Thus, from I-Cl and I-OTs at 50° in 65% aqueous diglyme containing 1.8 M sodium borohydride, only ca. 7% I-OH is formed, the rest of the product being hydrocarbon. When the sodium borohydride concentration was 0.5 M, the quantity of I-OH observed was several times as large. In 65% diglyme at 50°, I-Cl hydrolyzes with a rate constant of 1.1×10^{-4} sec.⁻¹. The reaction in the presence of 0.48 M sodium borohydride and 0.1 M sodium hydroxide occurs with a rate constant roughly equal to 1×10^{-4} sec.⁻¹. It is thus evident that borohydride is trapping the intermediate carbonium ion in the fashion illustrated recently by Brown and Bell⁶ for the benzhydryl and other systems and even more recently applied to I-OTs and 7-norbornadienyl chloride.^{8c}

The hydrocarbon product from the borohydride trapping consists of norbornene VII and the saturated tricyclic isomer⁷ VIII in the ratio⁸ of ca. 4:1. The tricyclic isomer was identified by hydrogenation to norbornane and by infrared and v.p.c. comparison with an authentic specimen kindly provided by Dr. W. R. Moore.

Regarding the structure of the carbonium ion from *anti*-7-norbornenyl derivatives, the classical 7-ion II would appear to us to be excluded by the high rate and stereospecificity of the solvolysis and the absence of leakage into the carbonium ion system derived from *syn*-7-norbornenyl derivatives.⁴ Product formation involving reaction exclusively at C₇ with water and quite predominantly at C₇ with borohydride is very difficult to rationalize on the basis of the classical tricyclic ion V. On the other hand, all of the facts are well accounted for on the basis of the non-classical cation IV with the C₇:C₂ reactivity ratio quite dependent on the nature of the nucleophile when it is varied so widely.⁹

Our early attempts to reduce I-Cl to the hydrocarbon were with lithium aluminum hydride in anhydrous ether. The rate was prohibitively slow compared to that of the analogous reduction of 7-norbornadienyl



chloride¹⁰ reported by Story.^{10b} From Story's work it was not clear whether the reaction of 7-norbornadienyl chloride involved prior ionization or was more concerted. However, the present rate comparison suggests 7-norbornadienyl chloride is reacting by prior ionization^{10a} and Story's observed 12:88 ratio of norbornene and tricyclic isomer is the ratio of C₇-attack to stereospecific *endo*-attack at C₂ of the non-classical intermediate. From the reaction of *anti*-7-norbornenyl chloride (I-Cl) with lithium aluminum hydride in refluxing tetrahydrofuran for 13 days there was obtained ca. 30% of unreacted chloride and a 37:63 mixture of norbornene and tricyclic hydrocarbon VIII, contaminated by ca. 3% of a material with the same retention time as norbornane. From I-OTs and sodium borohydride in dry diglyme at

(2) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

(3) (a) H. C. Brown, "Strained Carbonium Ions," Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 21–30, 1961, p. 2-O; (b) H. C. Brown, "Non-Classical Intermediates," Organic Reaction Mechanisms Conference, Brookhaven, New York, N. Y., September 5–8, 1962; (c) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963).

(4) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

(5) (a) E. C. Friedrich and S. Winstein, *Tetrahedron Letters*, No. 11, 475 (1962); (b) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).

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

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

(8) The accuracy may be low because of possible fractionation due to losses in concentrating dilute solutions of the reaction products.

(9) We differ markedly on this point with H. C. Brown and H. M. Bell,^{8c} who seem to feel that the formation of tricyclic hydrocarbon is difficult to rationalize on the basis of a non-classical intermediate.

(10) (a) S. Winstein and C. Ordonneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960); (b) P. R. Story, *ibid.*, **83**, 3347 (1961).

50°, the isolated hydrocarbon product is nearly pure VIII (>95%). While this represents a useful synthetic method for preparation of VIII, it is not yet clear to what extent these reductions in the anhydrous media, which result in higher yields of tricyclic hydrocarbon, involve concerted reactions or prior ionizations.

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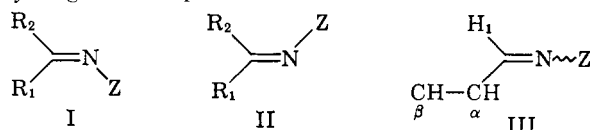
RECEIVED JUNE 21, 1963

Structural Studies by Nuclear Magnetic Resonance.

III. *syn-anti* Assignments from Solvent Effects

Sir:

N.m.r. is becoming progressively more important in the elucidation of structural problems arising from restricted rotation around double bonds. We can assign structures to I and II provided, when R₁ is methyl or hydrogen the equilibrium ratio I/II increases as R₂



changes from methyl to ethyl to isopropyl to *t*-butyl.¹

Table I summarizes results pertinent to *syn-anti* structural assignment. The notation H₁, H_α, H_β is shown in III. Shielded (+) means that hydrogens when *cis* to Z resonate at higher magnetic fields than when *trans*; deshielded (−) denotes the reverse. All spectra were taken with an A-60 Varian Associates n.m.r. spectrometer.

TABLE I

Z	Solvent	H ₁	H _α ^o	H _β
−NH ₂	<i>a, b</i>	−	+	−
−NHCH ₃	<i>a, b, i</i>	−	+	+
−NHC ₆ H ₄ X (<i>p</i>)	<i>a, b, c, f</i>	−	+	+
X=H, Cl, CH ₃				
−NHC ₆ H ₄ NO ₂ (<i>o</i>)	<i>f, i</i>	−	+	−
−NHC ₆ H ₄ NO ₂ (<i>p</i>)	<i>f, i</i>	−	+	<i>l</i>
−NHC ₆ H ₃ (NO ₂) ₂	<i>d, e, f, g, h, i, j, k</i>	−	+	−
−NHCONH ₂	<i>e, f</i>	−	+	<i>l</i>
−NHCSNH ₂	<i>e, f</i>	−	+	−
−OH ^m	<i>a, b, c, f, g</i>	−	−	+
−OTs	<i>b, c</i>	−	−	+
−N(CH ₃) ₂	<i>a, b, i</i>	<i>n</i>	−	+
−NCH ₂ C ₆ H ₅	<i>a, b, c</i>	<i>n</i>	+	+
Nitrosamines	<i>a, b, c, f</i>	+	+	+

^a Neat. ^b Carbon tetrachloride. ^c Benzene. ^d Methylene chloride. ^e Chloroform. ^f Methylene bromide. ^g Nitrobenzene. ^h Pyridine. ⁱ Dimethyl sulfoxide. ^j Dimethylformamide. ^k Tetramethylurea. ^l In most unsymmetrical compounds Δ*ν* is zero. ^m W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958); E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961), and observations from our Laboratories. ⁿ Only one aldehyde derivative isomer. ^o Values computed from α-methyl and α-methylene hydrogens.

Regardless of solvent used, H₁ is strongly deshielded (Δ*ν* = 15–60 c.p.s.) and it can be confidently used to assign *syn* and *anti* structures. Assignments from H_α and H_β are complicated because structural changes in R₁ and R₂, or changes in solvent, frequently reverse the resonances of *cis* and *trans* hydrogens, e.g., α-methine hydrogens are deshielded; benzyl (H_α) hydrogens of nitrophenylhydrazones are deshielded; H_α of acetaldehyde 2,4-dinitrophenylhydrazone and thiosemicarbazone is deshielded in dimethyl sulfoxide, dimethylformamide, acetone, and tetramethylurea; in benzene H_β's

(1) For equilibrium values see G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Am. Chem. Soc.*, **84**, 753 (1962); G. J. Karabatsos, B. A. Shapiro, F. M. Vane, J. S. Fleming, and J. S. Ratka, *ibid.*, in press.

are always shielded. Assignments, therefore, based on arguments from analogy must be made cautiously. The nitrosamine assignments² should be reversed.

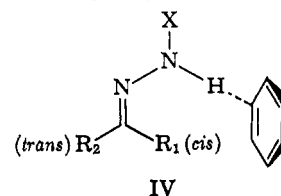
We wish to present a general method for assigning *syn* and *anti* structures, and to comment on the structure of some substrate-solvent association complexes. In aromatic solvents *cis* and *trans* hydrogens resonate at higher fields than they do in aliphatic solvents. From the fact that the degree of upfield shift differs for *cis* and *trans* hydrogens we can assign *syn-anti* structures. Table II summarizes Δ*ν* values (Δ*ν* = *ν* in aromatic solvent − *ν* in aliphatic solvent) compiled from derivatives of three aliphatic aldehydes, six aliphatic ketones, and acetophenone. We have used benzene, chlorobenzene, and alkylbenzenes as aromatic solvents, and acetone, dimethyl sulfoxide, carbon tetrachloride, chloroform, methylene bromide, and methylene chloride as aliphatic solvents.

TABLE II^a

Z	Δ <i>ν</i> (α-CH ₃)		Δ <i>ν</i> (α-CH ₂)		Δ <i>ν</i> (β-CH ₃)	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
−NHC ₆ H ₅ ^b	20–32	3–7	22–39	3.5–7	14–17	2.4–5
−NHC ₆ H ₄ CH ₃ (<i>p</i>) ^b	18–23	2–5			15.6 ^e	3.0 ^e
−NHC ₆ H ₄ Cl(<i>p</i>) ^b	22–38	7–13		7.2 ^e	15.6 ^e	4.2 ^e
−NHC ₆ H ₄ NO ₂ (<i>o</i>) ^c	28–38	5–21	34.8 ^f	18.6 ^f	22.8 ^e	12–14
−NHC ₆ H ₄ NO ₂ (<i>m</i>) ^c	38–47	15–16			24.0 ^e	7.8 ^e
−NHC ₆ H ₄ NO ₂ (<i>p</i>) ^c	43–55	16–23	27.0 ^f	15–18	27.6 ^e	9.6 ^e
−NHC ₆ H ₃ (NO ₂) ₂ ^c	38–60	24–38	37.8 ^f	25.2 ^f	27–36	10–19
−NHC ₆ H ₄ CO ₂ H(<i>o</i>) ^c	24–32	11–26				
−NHC ₆ H ₄ CO ₂ H(<i>p</i>) ^{c,e}	38.8	8.4				
−NHCH ₃ ^{b,g}	21.6	4.2				
−NHCSNH ₂ ^d	42.5	29.4	70.8	36.0	37.2	21.0
−N(CH ₃) ₂ ^{b,h}	3.0	1.2				
−NCH ₂ C ₆ H ₅ ^{b,c}	12.0	9.6				
−OH ^g	3–5	9.6–10.5	1.2 ^e	9.0 ^e	11–26	11–26
Nitrosamines ^b	18–28	29–41	22.8 ⁱ	34.8 ⁱ	24–35	28–36

^a All Δ*ν* values are in c.p.s. Sample concentrations varied from 5–10%. Wherever a range for Δ*ν* is given, the low Δ*ν* (*cis*) values correspond to the low Δ*ν* (*trans*) values. ^b Δ*ν* values were computed from spectra in benzene and carbon tetrachloride. ^c Δ*ν* values were computed from spectra in benzene and methylene bromide. ^d Δ*ν* values were computed from spectra of butanone thiosemicarbazone in benzene and chloroform. ^e Values from butanone derivative. ^f Values from phenylacetone derivative. ^g Values from acetaldehyde derivative. ^h Values from methyl isopropyl ketone derivative. ⁱ Values from N-nitrosomethyl-ethylamine.

Compounds of the structure =NNHX have Δ*ν* (*cis*) > Δ*ν* (*trans*). Increase in the acidity of the NH, or decrease in R₁ and R₂ size, results in larger Δ*ν* values. In the absence of the NH hydrogen (Z = −N(CH₃)₂, −NCH₂C₆H₅) Δ*ν*'s are small and the difference between Δ*ν* (*cis*) and Δ*ν* (*trans*) negligible. We interpret the results in terms of the hydrogen-bonded complex IV. Nitrobenzene behaves as acetone and dimethyl sulfoxide do; apparently the NH hydrogen bonds with the nitro group and not with the phenyl ring.



For nitrosamines Δ*ν* (*cis*) < Δ*ν* (*trans*). We propose an unsymmetrical association complex (V) analogous to the one suggested for amides.³ Repulsions between oxygen and benzene force the ring closer to R₂ than R₁. We predict that alkyl nitrites will behave similarly.

For oximes Δ*ν*'s are small and Δ*ν* (*cis*) < Δ*ν* (*trans*). This striking difference between oximes and compounds

(2) C. E. Looney, W. D. Phillips, and E. L. Reilly, *ibid.*, **79**, 6136 (1957).

(3) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960); **5**, 139, 153 (1962).