

cations, without distinction.<sup>11</sup> 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.<sup>12</sup> 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.

R. B. WETHERILL LABORATORY  
PURDUE UNIVERSITY  
LAFAYETTE, INDIANA

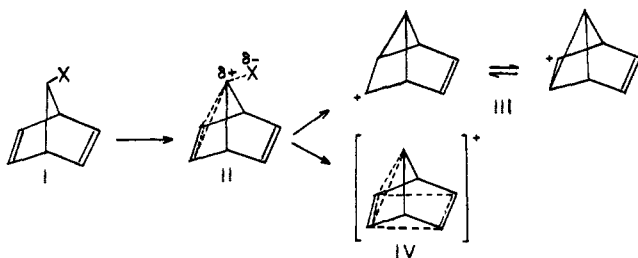
HERBERT C. BROWN  
FRANK J. CHLOUPEK

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:

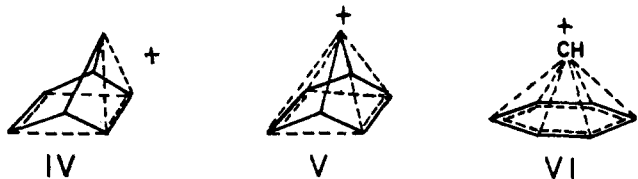
The marked rate enhancements observed in the solvolysis of 7-chloronorbornadiene and anti-7-dehydronorbornyl tosylate relative to the corresponding saturated derivatives reveal that the reactions must proceed with participation of the double bond in the transition state<sup>1,2</sup> II. The question 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.<sup>3</sup> 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).

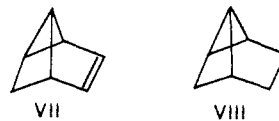
(2) S. Winstein and C. Ordonneau, *ibid.*, **82**, 2084 (1960).

(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<sup>3,7</sup>]hept-4-ene VIII with the concomitant formation of 6% of norbornadiene.<sup>4</sup>



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.<sup>5</sup> 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<sup>3,7</sup>]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<sup>3,7</sup>]heptane<sup>6</sup> 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<sup>3,7</sup>]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<sup>4,6</sup> 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).

R. B. WETHERILL LABORATORY  
PURDUE UNIVERSITY  
LAFAYETTE, INDIANA

HERBERT C. BROWN  
HAROLD M. BELL

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### The Non-classical 7-Norbornenyl Cation<sup>1</sup>

Sir:

The high rate (10<sup>11</sup> 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).