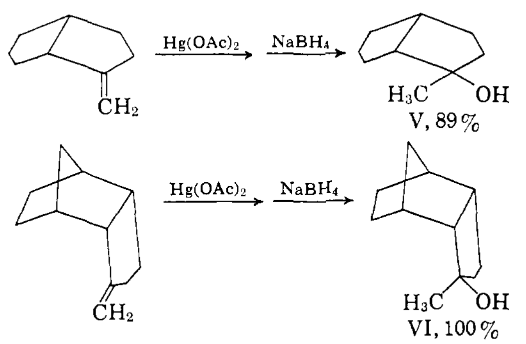
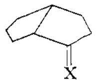
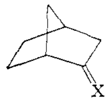
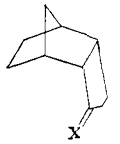


V, 89%

VI, 100%

for the addition of solvent to the intermediate to take place from the *exo* direction. A similar increasing preference for *exo* attack by lithium aluminum hydride is observed in the corresponding ketones (Table II).

Table II. Comparison of the Per Cent *exo* Attack in Reduction of Ketones by Lithium Aluminum Hydride and in the Hydration of the Corresponding Methyl Derivatives in the Oxymercuration–Demercuration Reaction

	exo attack, %	
Substrate	$LiAlH_4$[a]	$Hg(OAc)_2$-$NaBH_4$[b]
	75	89
	89[c]	99.5
	99[d]	100

[a] X = O. [b] X = CH_2. [c] H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965). [d] Unpublished results of Dr. I. Rothberg.

Prior to the development of this procedure we relied on epoxidation of the bicyclic olefin, followed by reduction with lithium aluminum hydride, to obtain the *exo* alcohol.[4] The present procedure exhibits both higher stereospecificity, in comparable cases, and higher yields, while utilizing a far simpler, briefer experimental procedure. Consequently, we believe it is the procedure of preference for such stereoselective hydrations.

(4) H. C. Brown and G. L. Tritle, *J. Am. Chem. Soc.*, **88**, 1320 (1966).

(5) Research assistant, 1964–1966, on a grant (G 19878) from the National Science Foundation. General Electric Company Fellow at Purdue University, 1966–1967.

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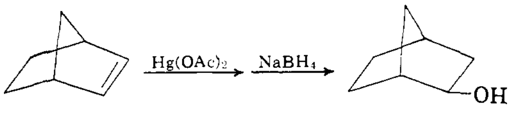
A Remarkable Stereoselectivity in the Oxymercuration–Demercuration of Norbornene, 7,7-Dimethylnorbornene, and Related Derivatives

Sir:

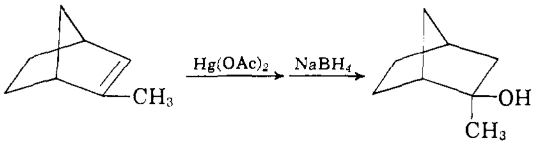
We report that the combined oxymercuration–demercuration reaction[1,2] converts norbornene, 7,7-dimethylnorbornene, and related derivatives to *exo* alcohols of remarkable isomeric purity, resembling that realized in solvolysis and previously interpreted in terms of the formation of σ-bridged nonclassical norbornyl cations as intermediates.[3,4] However, the oxymercuration–demercuration reaction fails to exhibit the facile rearrangements and scramblings required by such a bridged intermediate. Consequently, it no longer appears possible to take the position that the marked stereoselectivity exhibited by the norbornyl and the 7,7-dimethylnorbornyl cation is inexplicable without σ bridging to exercise control over the steric path taken by the entering nucleophile.

In the two accompanying communications, it was pointed out that oxymercuration–demercuration provides a convenient route for the Markovnikov hydration of double bonds.[1,2] The practically exclusive formation of 2-hexanol from 1-hexene[1], of 2-methyl-2-butanol from 2-methyl-2-butene,[1] and of 2-methyl-*exo*-norbornanol from 2-methylenenorbornane[2] represents an exceedingly powerful directive influence of the intermediate on the entering water molecule of the kind that we normally associate with a carbonium ion reaction. However, the oxymercuration–demercuration reaction appears to be free of the rapid rearrangements that are generally associated with reactions involving carbonium ion intermediates. Such rearrangements are exceedingly common in the bicyclo[2.2.1]heptane system. Accordingly, we decided to apply the oxymercuration–demercuration reaction to norbornene, 7,7-dimethylnorbornene, 2-methylnorbornene, 1-methylnorbornene, and bornylene in order to learn whether such rearrangements would be a significant factor in these labile derivatives.

The oxymercuration–demercuration of norbornene is an exceedingly fast reaction, resulting in a quantitative yield of norborneol (I) in approximately 30 sec for the oxymercuration stage.[1] The product was >99.8% *exo*-norborneol.[5] Similarly, 2-methylnorbornene underwent rapid conversion to the tertiary alcohol, also >99.8% *exo* (II).



I, yield 100%; >99.8% *exo*



II, yield 86%; >99.8% *exo*

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(1) H. C. Brown and P. Geoghegan, Jr., *J. Am. Chem. Soc.*, **89**, 1522 (1967).

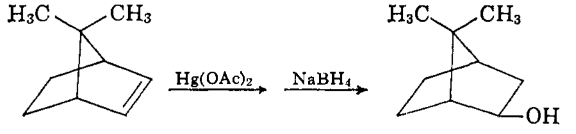
(2) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967).

(3) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(4) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 378 (1965); R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, **87**, 379 (1956).

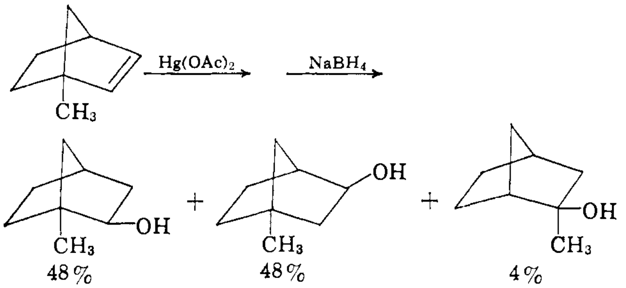
(5) T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963). As reported by these authors, the oxymercuration of norbornene and similar bicyclics with mercuric acetate is accompanied by the formation of moderate amounts (10–20%) of the corresponding acetate. Accordingly, after reduction, the tetrahydrofuran layer was separated, dried, and treated with a small quantity of lithium aluminum hydride to convert any acetate present to the alcohol, which constituted the predominant product.

An interesting result was encountered in the oxymercuration of 7,7-dimethylnorbornene (apobornylene). Here the reaction was considerably slower, requiring 15 min for the yellow color[1] to vanish. After a total reaction time of 73 min, there was obtained an 84% yield of alcohol, >99.8% apoisoborneol (III), with no indication of any rearranged product.[6]



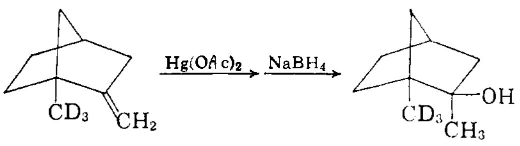
III, yield 84%; >99.8% *exo*

It might be tempting to attribute the marked stereoselectivity observed in these experiments to nonclassical σ bridging in the intermediate. However, this appears to be ruled out by the following results. First, 1-methyl-2-norbornene provides in 5 min a 100% yield of product (IV), analyzing for 48% 1-methyl-2-*exo*-norborneol, 48% 1-methyl-3-*exo*-norborneol, and 4% 2-methyl-*exo*-2-norborneol. Evidently, the small amount of tertiary alcohol is the result of the acid produced in the oxymercuration stage, rather than the result of the reaction itself, since oxymercuration–demercuration with added sodium acetate produces 93% product in 1.0 hr, analyzing for 46% 2-*exo*, 53.5% 3-*exo*, and only 0.5% tertiary. Similarly, bornylene forms roughly equal quantities of isoborneol and epiisoborneol.[7]



IV

Second, oxymercuration–demercuration of 1-methyl-d_3-2-methylenenorbornane[8] proceeds to give 1-methyl-d_3-2-methyl-*exo*-norbornanol without detectable scrambling (V).



V

Consequently, we appear to be faced by the following dilemma. Both the orientation taken by the entering hydroxyl group and the almost exclusive formation of *exo* derivatives, even in the case of apobornylene with its sterically demanding 7,7-dimethyl substituents, are identical with phenomena that in the past have been considered to require bridged nonclassical carbonium ions in this system. Yet the failure to observe either significant rearrangement or scrambling in this reaction does not appear to be compatible with the presence of such bridged intermediates in detectable amounts. Clearly we must now give careful reconsideration to the argument[3,4] that the high stereoselectivity exhibited by the norbornyl and apobornyl cations in solvolysis requires a σ-bridged formulation for these intermediates.

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(6) Prior to our development of the simple oxymercuration–demercuration procedure which is the subject of this group of communications, we learned from T. T. Tidwell and T. G. Traylor that they had oxymercurated 1,4,7,7-tetramethylnorbornene with mercuric acetate in acetic acid and had established the structure of the oxymercuration product. These results are now in the process of publication. Our work in developing the simple combined procedure described in the present communications was greatly facilitated by a full exchange of information with Professor T. G. Traylor, and we wish to acknowledge our debt to him. In turn, we were happy to make available our own unpublished data and procedures on the hydroboration of norbornenes containing sterically demanding and labilizing substituents and to assist Tidwell and Traylor in applying this reaction to 1,4,7,7-tetramethylnorbornene.

(7) P. von R. Schleyer has informed us that he had observed long ago that the addition of hydrogen chloride to 1-methylnorbornene also proceeds without significant discrimination between the 2 and 3 positions, a result that is difficult to rationalize in terms of the usual σ-bridged cationic intermediate. We are currently reexamining this observation by our new automatic hydrochlorination procedure[8] in collaboration with Professor Schleyer.

(8) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, 89, 466 (1967). We are indebted to Kwang-Ting Liu for this experiment.

(9) Research assistant, 1964–1967, on grants supported by the National Science Foundation (G 19878, GP 6492 X) and the National Institutes of Health (5 ROI-GM-10937).

(10) Postdoctorate research associate on a grant supported by the National Science Foundation (GP 6492 X).

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The Detection of Trapped Electrons in γ-Irradiated 3-Methylpentane Glasses by Electron Spin Resonance[1]

Sir:

Extensive optical studies by Hamill and his collaborators[2] have provided evidence that trapped electrons are produced by the γ radiolysis of 3-methylpentane (3-MP) glasses at 77°K. We now wish to report that trapped electrons can also be readily detected by electron spin resonance (esr) in irradiated 3-MP glasses containing ammonia or trimethylamine (TMA), additives which are capable of functioning as suitable proton acceptors in the radiolysis of hydrocarbons.[3] Because the glasses formed from 3-MP and TMA were transparent and homogeneous over the concentration range of interest (0–20 mole % TMA), this system has been studied in detail.

A narrow intense singlet ($g = 2.002 \pm 0.001$, $\Delta H_{ms} =$ 3.5 gauss) dominates the esr spectrum shown in Figure 1 against a background consisting of the much broader four center lines from the sextet spectrum of 3-MP. The measurements were made with a Varian-4502 9.5-GHz spectrometer employing a 100-kHz modulation frequency and a modulation amplitude of 1.7 gauss. The low-power arrangement of the microwave bridge was used with a total attenuation of 35 db. Repeated irradiations under the same conditions showed that the singlet was not saturated at 35 db, but drastic saturation did set in below 30 db. At any stage during its thermal decay at 77°K, the singlet could be obliterated by exposure to filtered light (saturated potassium dichromate, $\lambda > 540$ mμ) from a tungsten lamp.

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(1) This work was supported by the Atomic Energy Commission under Contract No. AT-(40-1)-2968. This is AEC Document No. ORO-2968-23.

(2) (a) J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, 86, 777 (1964); (b) J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, 44, 1279 (1966); (c) D. W. Skelly and W. H. Hamill, *ibid.*, 44, 2891 (1966).

(3) W. R. Busler, D. H. Martin, and F. Williams, *Discussions Faraday Soc.*, 36, 102 (1963).