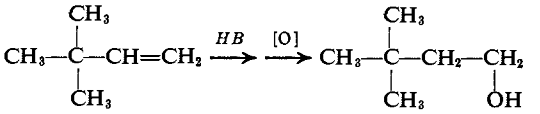
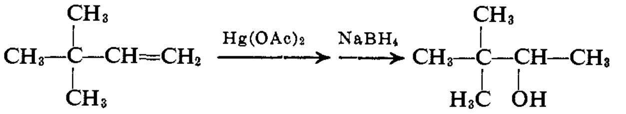


$$CH_3{-}C(CH_3)_2{-}CH{=}CH_2 \xrightarrow{HB} \xrightarrow{[O]} CH_3{-}C(CH_3)_2{-}CH_2{-}CH_2OH$$

I



$$CH_3{-}C(CH_3)_2{-}CH{=}CH_2 \xrightarrow{Hg(OAc)_2} \xrightarrow{NaBH_4} CH_3{-}C(CH_3)_2{-}CH(OH){-}CH_3$$

II

scope and range of applicability of this oxymercuration–demercuration procedure, comparable to the one we have been pursuing in the hydroboration area.

(9) National Defense Education Act Fellow (Title IV) at Purdue University.

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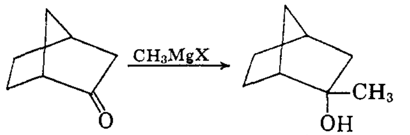
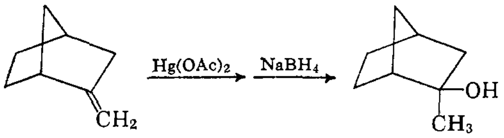
Stereoselectivity of the Hydration of Representative Cyclic and Bicyclic Olefins by the New Oxymercuration–Demercuration Procedure

Sir:

The addition of the methyl Grignard reagent to many bicyclic ketones results in the predominant, if not the exclusive, formation of the *endo* tertiary alcohol, involving addition of the methyl group from the less hindered side[1] (I). We wish to report that the hydration of related bicyclic olefins by the oxymercuration–demercuration procedure[2] results in the predominant, if not the exclusive, formation of the epimeric tertiary alcohol, involving addition of water to the tertiary center from the less hindered side (II). Consequently, the oxymercuration–demercuration procedure provides a highly convenient synthetic route to isomeric alcohols epimeric with those available *via* the Grignard synthesis.



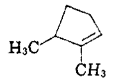
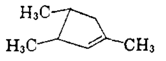
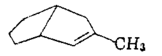
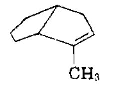
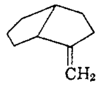
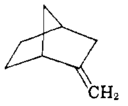
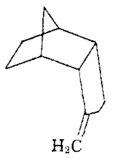
I



II

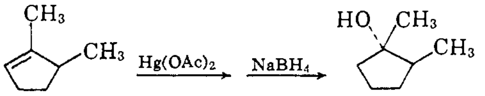
The procedure used is essentially identical with that described previously.[2] The data are summarized in Table I. In all cases we observed only the formation of the isomeric tertiary alcohols.

Table I. Results Realized for the Markovnikov Hydration of Representative Cyclic and Bicyclic Olefins by the Oxymercuration–Demercuration Procedure

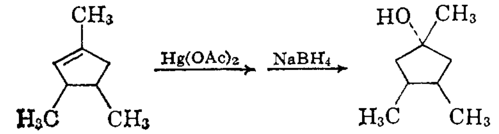
	Reaction time		
Olefin[a]	t_1[b]	t_2[c]	Products[d]
	30 sec	5 min	73% 1,*cis*-2-dimethyl- 27% 1,*trans*-2-dimethyl-cyclopentanol
	1 min	15 min	76% 1,*cis*-3,*cis*-4-trimethyl- 24% 1,*trans*-3,*trans*-4-trimethylcyclopentanol
	5 min	5 min	78% *exo* (*t*-OH) 22% *endo*
	5 min	5 min	84% *exo* 16% *endo*
	15 sec	5 min	89% *exo* 11% *endo*
	20 sec	5 min	99.5% *exo* 0.5% *endo*
	20 sec	1 min	100% *exo* 0% *endo*

[a] All new compounds had microanalytical and spectral data consistent with their structures. In all cases but one we prepared or had available authentic samples of the two epimeric alcohols. The assignments for the two epimeric alcohols from 1,3-*cis*-4-trimethylcyclopentene (76% *cis* and 24% *trans*) and from the addition of methyl Grignard to *cis*-3,4-dimethylcyclopentanone (11% *cis*, 89% *trans*) were based on the nmr data. [b] Time for yellow color to disappear; see discussion in ref 2. [c] Complete reaction time for the oxymercuration stage, before addition of the 3.0 *M* sodium hydroxide. [d] In all cases only the corresponding tertiary alcohols were found in the gas chromatograms. The yields were essentially quantitative except for 2- and 3-methylbicyclo[3.3.0]-octene, where the reduction was carried out before the oxymercuration stage was complete in order to minimize the increasing appearance of the *endo* tertiary alcohols noted with increasing reaction times in these two cases.

The data clearly reveal that the hydration of the initial mercury intermediate, whatever its structure may be,[3] occurs predominantly from the less hindered side of the molecule. This results in the preferential formation of the *cis*-dimethyl- and *cis*-trimethylcyclopentanols, in the case of the two cyclopentenes examined (III, IV)



III, 73%



IV, 76%

and the *exo* alcohols in the case of the bicyclics (V, VI). It is interesting to note that as the molecular models indicate increasing steric hindrance for *endo* approach (2-methylenebicyclo[3.3.0]octene < 2-methylenenorbornane < 8-methylenetetrahydro-*endo*-dicyclopentadiene), there is observed an increasing preference for the formation of the *exo* isomer, *i.e.*, an increasing preference

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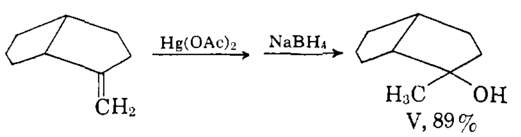
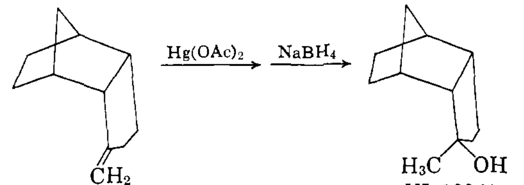
(1) For a review of pertinent data, with literature references, see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

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

(3) For a review of the stereochemistry of the oxymercuration reaction and the various conflicting proposals that have been advanced to account for the experimental results, see N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965).



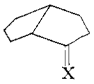
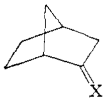
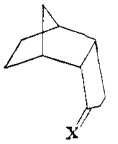
V, 89%



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

Substrate	*exo* attack, %	
	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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Received December 30, 1966

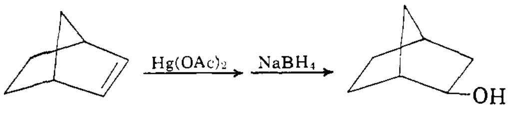
A Remarkable Stereoselectivity in the Oxymercuration–Demercuration of Norbornene, 7,7-Dimethylnorbornene, and Related Derivatives

Sir:

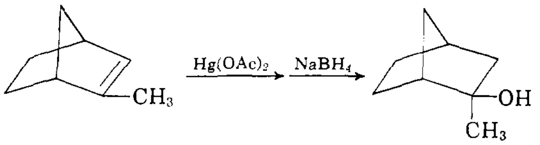
We report that the combined oxymercuration–demercuration reaction[1,2] converts norbornene, 7,7-dimethylnorbornene, and related derivatives to *exo* alcohols of remarkable isomeric purity, resembling that realized in solvolysis and previously interpreted in terms of the formation of σ-bridged nonclassical 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.