

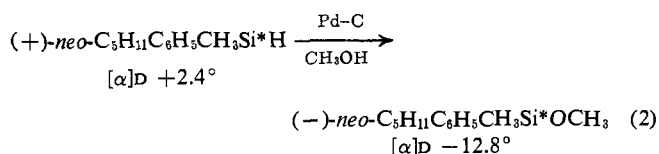
Table II. Raney Nickel^a Catalyzed Substitution Reactions of (+)-R₃Si*H^b

Reactant	Solvent	Product	Yield, %	[α] _D ^c	Stereospecificity ^d
Water	CH ₂ Cl ₂	(-)-R ₃ Si*OH	97	-17	94% invn
Methanol	<i>p</i> -Xylene	(-)-R ₃ Si*OCH ₃	94	-16.6	99% invn
Cyclohexanol	CH ₂ Cl ₂	(+)-R ₃ Si*OC ₆ H ₁₁	98	+7.1	95% invn
Cyclohexanol	<i>p</i> -Xylene	(+)-R ₃ Si*OC ₆ H ₁₁	95	+7.9	99% invn
<i>t</i> -Butyl alcohol	CH ₂ Cl ₂	(+)-R ₃ Si*OC(CH ₃) ₃	91	+21	88% invn
<i>t</i> -Butyl alcohol	<i>p</i> -Xylene	(+)-R ₃ Si*OC(CH ₃) ₃	93	+22	90% invn
Phenol	CH ₂ Cl ₂	(-)-R ₃ Si*OPh	97	-8.7	92% invn
Acetic acid	CH ₂ Cl ₂	(-)-R ₃ Si*OOCCH ₃	84	-12	83% invn
Benzoic acid	CH ₂ Cl ₂	(-)-R ₃ Si*OOCPh	85	-12	83% invn

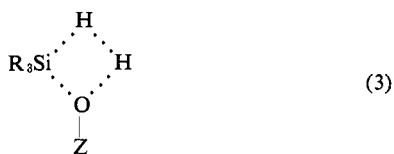
^a No. 28 Raney Active Nickel Catalyst in Water, Raney Catalyst Division, W. R. Grace & Co. (water removed at reduced pressure and stored under xylene). ^b The α-NpPh.MeSi*H used for this series was optically pure. ^c Rotation (in degrees) taken in the solvent as reported in the literature.^{10a-d} ^d A stereospecificity of 90%, for example, refers to a product which is 80% optically pure (20% racemic). ^e Based on a value of [α]_D +9.5° for optically pure R₃Si*OPh from unpublished results of R. Mason.

ally better with nickel than with palladium on carbon, and reaction rates are not greatly different.

The stereochemical paths of reactions 1 are not altered by a change in the structure of R₃SiH. Thus, when optically active neopentylphenylmethylsilane was treated with methanol in xylene using 10% palladium on carbon, the product¹¹ was formed with 98% in-



version of configuration. Although a four-center mechanism such as (3) with the catalyst surface activating the silicon-hydrogen bond and perhaps also the oxygen-hydrogen bond would appear to be very attractive for reactions 1, on the basis of its simplicity, the present finding of *inversion* shows that the mechanism is more complex.¹²



It is interesting to note that certain hydrogenolysis reactions at asymmetric carbon centers proceed with inversion of configuration in the presence of heterogeneous catalysts.^{13a-c} However, reactions involving cleavage of the carbon-hydrogen bond on the surface of group VIII metals generally lead to racemic prod-

(9) Unpublished work of L. H. Sommer and R. Mason.

(10) (a) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964); (b) L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964); (c) L. H. Sommer, G. A. Parker, and C. L. Frye, *ibid.*, **86**, 3280 (1964).

(11) (a) L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, **85**, 371 (1963); (b) L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, **89**, 868 (1967). These references report syntheses and correlations of configuration.

(12) Lukevics and Voronkov^{4e} have proposed a four-center mechanism similar to (3) for the reactions of alcohols with triethylsilane in the presence of chloroplatinic acid which is reduced to platinum during the reaction.

(13) (a) S. Mitsui, Y. Senda, and K. Konno, *Chem. Ind. (London)*, 1354 (1963); (b) S. Mitsui and Y. Kato, *ibid.*, 381 (1965); (c) S. Mitsui and Y. Nagahisa, *ibid.*, 1975 (1965); (d) A. M. Khan, I. J. McQuillan, and I. Jardine, *Tetrahedron Letters*, **24**, 2649 (1966); (e) W. A. Bonner, *J. Am. Chem. Soc.*, **74**, 1033 (1952).

ucts.^{7,14} Our results show that reactions 1 lead to optically active products and are highly stereospecific.

(14) (a) R. L. Burwell, B. K. Shim, and H. C. Rowlinson, *ibid.*, **79**, 5142 (1957); (b) W. A. Bonner and T. W. Greenlee, *ibid.*, **81**, 3336 (1959).

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The Oxymercuration-Demercuration of Representative Olefins. A Convenient, Mild Procedure for the Markovnikov Hydration of the Carbon-Carbon Double Bond

Sir:

The hydroboration-oxidation of olefins provides a highly convenient procedure for the anti-Markovnikov hydration of carbon-carbon double bonds.¹ The oxymercuration reaction,² combined with reduction of the oxymercureal intermediate by sodium borohydride³ *in situ*, provides an equally convenient mild method to achieve the Markovnikov hydration of carbon-carbon double bonds without observable rearrangement.

The procedure is remarkable in its simplicity and speed. In a small flask, fitted with a magnetic stirrer, is placed 3.19 g (10.0 mmoles) of mercuric acetate. To this flask is added 10.0 cc of water, followed by 10.0 cc of tetrahydrofuran. Then 10.0 mmoles of 1-hexene is added. The reaction mixture is stirred for 10 min (at room temperature, approximately 25°) to complete the oxymercuration stage. Then 10.0 cc of 3 M sodium hydroxide is added, followed by 10.0 cc of a solution of 0.5 M sodium borohydride in 3.0 M sodium hydroxide. Reduction of the oxymercureal is almost instantaneous. The mercury is allowed to settle. Sodium chloride is added to saturate the water layer. The upper layer of tetrahydrofuran is separated—it contains an essentially quantitative yield of 2-hexanol (96%).

This simple procedure appears to be broadly appli-

(1) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(2) There is an enormous literature on the oxymercuration reaction, most of it concerned with the mechanism of the reaction, the stereochemistry of the products, and similar questions of primarily theoretical interest. For reviews with pertinent literature references, see J. Chatt, *Chem. Rev.*, **48**, 7 (1951), and N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965).

(3) (a) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959); (b) J. H. Robson and G. F. Wright, *Can. J. Chem.*, **38**, 21 (1960); (c) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); (d) F. G. Bordwell and M. L. Douglass, *ibid.*, **88**, 993 (1966).

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

Olefin	Reaction time		Product	Yield, ^c %
	t ₁ ^a	t ₂ ^b		
1-Hexene	45 sec	10 min	2-Hexanol	96
1-Dodecene ^d	7 min	70 min	2-Dodecanol	91
<i>cis</i> -2-Pentene	45 sec	10 min	65% 2-, 35% 3-pentanol	98
<i>trans</i> -2-Pentene	65 sec	15 min	54% 2-, 46% 3-pentanol	95
2-Methyl-1-butene	10 sec	5 min	2-Methyl-2-butanol	90
2-Methyl-2-butene	20 sec	10 min	2-Methyl-2-butanol	95
3,3-Dimethyl-1-butene	2 min	20 min	3,3-Dimethyl-2-butanol	94
2,3-Dimethyl-2-butene	3.5 min	35 min	2,3-Dimethyl-2-butanol	86
2,4,4-Trimethyl-1-pentene	10 min	30 min	2,4,4-Trimethyl-2-pentanol	96
Cyclopentene	20 sec	1 hr	Cyclopentanol	91
Cyclohexene	55 sec	11 min	Cyclohexanol	99
Cyclooctene ^d	2 hr	3 hr	Cyclooctanol	88
1-Methylcyclopentene	20 sec	6 min	1-Methylcyclopentanol	93
1-Methylcyclohexene	20 sec	5 min	1-Methylcyclohexanol	100
Methylenecyclohexane	10 sec	5 min	1-Methylcyclohexanol	99
Styrene	25 sec	5 min	1-Phenylethanol	96
α -Methylstyrene	45 sec	10 min	2-Phenyl-2-propanol	95

^a Time for yellow color to disappear. ^b Complete reaction time for the oxymercuration stage, before addition of the 3.0 M sodium hydroxide. ^c Analysis by glpc with an internal standard. ^d Reaction heterogeneous, with olefin possessing only limited solubility in the reaction mixture. The longer reaction time may be, in part, due to this factor.

cable, as indicated by the results in Table I and those reported in the accompanying communications.^{4,5}

We have encountered no serious difficulty in scaling the procedure up to runs on a preparative scale. However, it should be recognized that both the oxymercuration and reduction stages are vigorously exothermic, so that the rate of addition of olefin and the rate of addition of borohydride should be controlled (and cooling baths used) to maintain the temperature at approximately 25°.

In this reaction the mercuric acetate originally dissolves in the water to give a clear solution. However, the addition of the tetrahydrofuran forms a yellow suspension. As the reaction proceeds, this suspension first becomes lighter, and then the reaction mixture becomes colorless and clear, frequently in a matter of seconds, although in some cases, such as cyclooctene, longer periods were required. The oxymercuration reaction is not complete at this point. Nevertheless, the disappearance of the yellow color provides an approximate indication of the time required. Usually we allowed the reaction to proceed for five to ten times the length of time required for the yellow color to vanish before initiating the reduction stage.

In some cases we observed that long reaction times for the oxymercuration stage were deleterious. For example, the yield of 2,3-dimethyl-2-butanol from 2,3-dimethyl-2-butene was only 44% in 2.25 hr, as compared to 86% in 35 min. Similarly, 2,4,4-trimethyl-1-pentene provided a 96% yield of the tertiary alcohol in 0.5 hr, 71% in 1.75 hr, and 20% in 15 hr. In the literature very long reaction times have frequently been utilized for the oxymercuration reaction. For example, Henbest and Nicholls utilized 2 to 7 days in their study of the oxymercuration of 4-substituted cyclohexenes.^{3a} This may be the explanation why certain olefins, such as 2,3-dimethyl-2-butene, which we have found to undergo oxymercuration readily, have been reported in the literature to be unreactive.^{6,7}

(4) H. C. Brown and W. J. Hammar, *J. Am. Chem. Soc.*, **89**, 1524 (1967).

(5) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

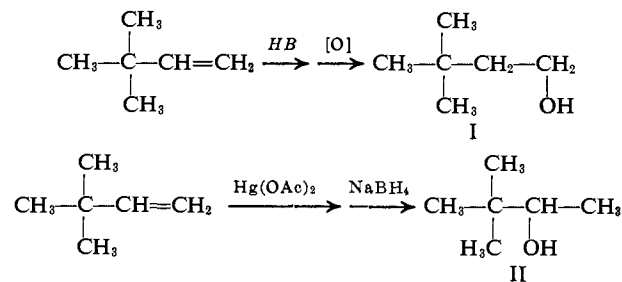
In the past, numerous reagents have been utilized for removal of the mercury from the oxymercuration, among them hydrazine, sodium amalgam, and various borohydrides.⁸ In practically all cases, the oxymercuration was first isolated from the reaction mixture, usually by precipitation as the chloride, before being subjected to the demercuration stage. The excellent yields realized in the present procedure make it clear that there is no disadvantage in carrying out the demercuration stage with sodium borohydride, *in situ*, without isolation of the intermediate.

The simplicity and the speed of the present procedure suggest that it should provide a highly convenient synthetic route for the Markovnikov hydration of carbon-carbon double bonds. Moreover, the observation (Table I) that 3,3-dimethyl-1-butene is readily converted to 3,3-dimethyl-2-butanol without observable rearrangement suggests that this hydration procedure may be as free from skeletal rearrangements as the hydroboration-oxidation technique and provide a useful companion to that hydration procedure (I, II). Consequently, we are undertaking a detailed exploration of the full

(6) See Chatt² for representative examples.

(7) We have not yet investigated the nature of the product produced from the initially formed oxymercuration intermediate in the case of these highly branched olefins. It is probable that the "Denigés product" is formed: K. Ichikawa, K. Fujita, and O. Itoh, *Bull. Inst. Chem. Res. Kyoto Univ.*, **42**, 221 (1964).

(8) For a more complete discussion, with pertinent literature references, see Bordwell and Douglass.^{3d} The use of borohydrides for demercuration appears to have been introduced by Henbest and Nicholls,^{3a} whereas Robson and Wright^{3b} and Traylor and Baker^{3c} appear to have first used borohydride in aqueous solution for demercuration. However, we are indebted to Bordwell and Douglass^{3d} for the first detailed study of such reductions in aqueous media and the recording of the great speed of that reaction. In practically all of these early cases the initial oxymercuration product was precipitated as the chloride and this intermediate reduced in a separate operation. In only one case does it appear that the initial oxymercuration product was reduced *in situ* with sodium borohydride to yield the alcohol. However even here, the details, as reported by T. G. Traylor, *J. Am. Chem. Soc.*, **86**, 244 (1964), were not encouraging—only a 25% yield was realized in converting bicyclo[2.2.2]octene to the corresponding alcohol. We have not yet explored just what feature or features of the present process, such as the use of tetrahydrofuran as a cosolvent or the use of much shorter times for the oxymercuration stage or the use of strong alkali in the reduction stage, are responsible for the remarkably high yields realized in the present combined procedure.



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

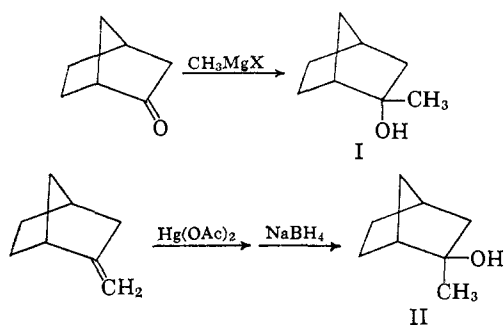
(9) National Defense Education Act Fellow (Title IV) at Purdue University.

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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 side¹ (I). We wish to report that the hydration of related bicyclic olefins by the oxymercuration-demercuration procedure² 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.

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.

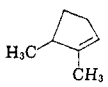
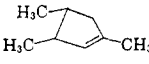
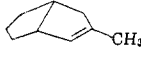
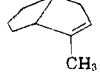
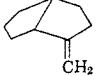
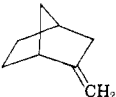
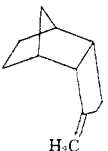
The data clearly reveal that the hydration of the initial mercury intermediate, whatever its structure may be,³ occurs predominantly from the less hindered side of the molecule. This results in the preferential

(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).

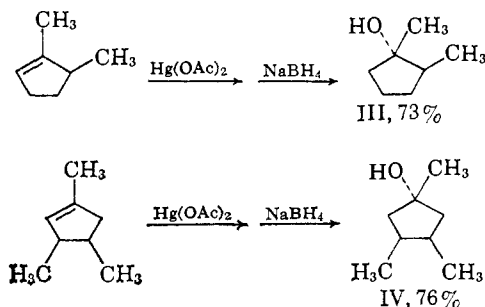
(3) For a review of the stereochemistry of the oxymercuration reaction and the various conflicting proposals that have been advanced to account for the experimental results, see N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965).

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

Olefin ^a	Reaction time		Products ^d
	<i>t</i> ₁ ^b	<i>t</i> ₂ ^c	
	30 sec	5 min	73% 1, <i>cis</i> -2-dimethyl- 27% 1, <i>trans</i> -2-dimethyl- cyclopentanol
	1 min	15 min	76% 1, <i>cis</i> -3, <i>cis</i> -4-trimethyl- 24% 1, <i>trans</i> -3, <i>trans</i> -4-tri- methylcyclopentanol
	5 min	5 min	78% <i>exo</i> (<i>t</i> -OH) 22% <i>endo</i>
	5 min	5 min	84% <i>exo</i> 16% <i>endo</i>
	15 sec	5 min	89% <i>exo</i> 11% <i>endo</i>
	20 sec	5 min	99.5% <i>exo</i> 0.5% <i>endo</i>
	20 sec	1 min	100% <i>exo</i> 0% <i>endo</i>

^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.

formation of the *cis*-dimethyl- and *cis*-trimethylcyclopentanol, in the case of the two cyclopentenes examined (III, IV)



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