mother liquor. Recrystallization from 1:8 ether–pentane afforded large colorless crystals of **5** in 34% yield. The compound was stored at −15°; nmr (CDCl$_3$–TMS) τ 2.61–2.84 (multiplet).

Ether Adducts. Compounds **2**–**4** were dissolved in a minimum amount of the appropriate ether. Several volumes of heptane were added and the solution was filtered. The filtrate was cooled to −20°. Large colorless crystals (which tend to take on an orange surface coloration) were obtained. The adducts were stored at −20°.

Analyses of the ether adducts were performed by pumping on weighed air-dried samples until they reached constant weight. The analytical results for **3f** are high due to loss of the mercurial by sublimation during pumping.

Compound **2d** was pumped for 2 days before reaching constant weight. Ir of the residue revealed it to be **2a**. Grinding of this opaque white residue in cyclohexane caused it to turn yellow; the ir spectrum of this mull showed the predominant presence of **2b**. Apparently **2d** must have a structure closely related to that of unstable **2a**, which is unable to convert rapidly to the more stable **2b** in the solid state. Solution ir spectra reveal that **2** in solution consists of a mixture of **2a** and **2b** in an approximate 1:1 ratio.

Photolysis of 3a. A solution of 1.0 g of **3a** in 40 ml of dry cyclohexene was irradiated with a medium-pressure mercury lamp for 60 hr through Pyrex. The solution was filtered and the solvent removed under reduced pressure: the oily residue was chromatographed on silica gel. Compounds **6** and **8** were eluted by hexane. Traces of an unidentified carbonyl compound was eluted with benzene. No product with an ir absorption at 1012 cm^{-1}, characteristic of a spiroadduct,[34] could be isolated.

Acknowledgment. The authors thank the National Science Foundation for a grant in support of this work.

Additions to Bicyclic Olefins. VI. Stereochemistry of the Oxymercuration–Demercuration of Norbornene, 7,7-Dimethylnorbornene, and Related Olefins[1,2]

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Abstract: The oxymercuration–demercuration of norbornene, 7,7-dimethylnorbornene, and related olefins reveals the stereochemical and regioselective effects of methyl substituents in this bicyclic system. The reaction of these norbornene derivatives with mercuric acetate in aqueous tetrahydrofuran is essentially quantitative, addition of both moieties proceeding predominantly exo. Reduction of the oxymercurial with sodium borohydride produces the corresponding norbornanol derivative essentially exclusively exo (>99.8%). Consequently, in this reaction the presence of the bulky 7,7-dimethyl substituents fails to prevent exo addition. 2-Methylnorbornene undergoes rapid transformation into 2-methyl-*exo*-norbornanol. Oxymercuration–demercuration of 1-methylnorbornene and bornylene provides roughly equal amounts of the 2- and 3-exo alcohols, indicating no significant directive influence of the 1-methyl substituent. The additional observation that the intermediate kinetic mercurial adduct has the cis-exo structure by pmr in both the norbornyl and 7,7-dimethylnorbornyl derivatives lends doubt to the existence of a cyclic symmetrical mercurinium ion as a significant intermediate in the oxymercuration reaction.

Based on the results realized in the reduction of ketones by complex metal hydrides, it has been argued that the 7,7-dimethyl substituents in the norbornyl system will make exo addition so difficult that all electrophilic additions, in the absence of the intervention of a "special effect," σ-bridging, would go preferentially endo.[4,5] However, very little is known about the relative steric requirements for the reaction of complex metal hydrides with ketones and the steric requirements of other reactions with the norbornyl moiety. Consequently, such an argument rests largely upon untested assumptions and should not be accepted without more definitive data.[6] Indeed, there are presently known several instances in which there is a strong preference for exo substitution in both the norbornyl and 7,7-dimethylnorbornyl systems for reactions which do not involve cationic intermediates.[7]

It is now well recognized that all reactions of the norbornane system reveal a strong preference for exo attack and exo substitution, attributed to the greater steric influence of the endo-5,6-hydrogen atoms as compared to that of the syn-7-hydrogen atom.[7] The steric requirements of a *syn*-7-methyl group must be considerably larger than those of the syn-7-hydrogen atom. Consequently, a systematic study of additions to norbornene, 7,7-dimethylnorbornene, and related olefins was undertaken in order to evaluate the relative importance of the endo-5,6-hydrogen atoms *vs.* the *syn*-7-methyl group in controlling the stereochemistry of additions to the norbornyl system. In previous papers it was established that exo additions to the norbornyl system which go through cyclic transition states or intermediates, such as hydroboration,[7,8] epoxidation,[9] silver nitrate complexation,[7] addition of ni-

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(1) Solvomercuration–Demercuration. V.

(2) A preliminary account of a portion of this study has appeared earlier: H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, **89**, 1525 (1967).

(3) Graduate research assistant on Grants G 19878 and GP 6492X supported by the National Science Foundation.

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

(5) S. Winstein, *et al.*, *J. Amer. Chem. Soc.*, **87**, 376, 378, 379, 381 (1965).

(6) H. C. Brown, *Chem. Brit.*, 2, 199 (1966).

(7) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *J. Amer. Chem. Soc.*, **95**, 2209 (1973), and references cited therein.

(8) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 1991 (1970).

(9) H. C. Brown, S. Ikegami, and J. H. Kawakami, *ibid.*, **92**, 6914 (1970).

trosyl chloride,[7] addition of benzenesulfenyl chloride,[7] and addition of dichlorocarbene,[7] are hindered strongly by the presence of the 7,7-dimethyl substituents. Such reactions either fail to proceed in the presence of such substituents, or the stereochemistry is altered to preferentially endo. It was therefore of interest to study the stereochemistry of the oxymercuration of such bicyclic olefins because it has long been believed that such oxymercuration reactions proceed through a cyclic mercurinium intermediate.[10]

Results

Surprisingly, the oxymercurations of norbornene (**1**), 1-methylnorbornene (**2**), 2-methylnorbornene (**3**), 7,7-dimethylnorbornene (**4**), and bornylene (1,7,7-trimethylnorbornene) (**5**) all yielded cis-exo mercurials essentially ($\geq 98\%$) exclusively, as established by ir and pmr. Reduction of the mercurials *in situ* with sodium borohydride and analysis of the products by gas chromatography indicated that solvent addition occurs exclusively exo, as shown in Table I for norbornenes, both with and without 7,7-dimethyl substituents.

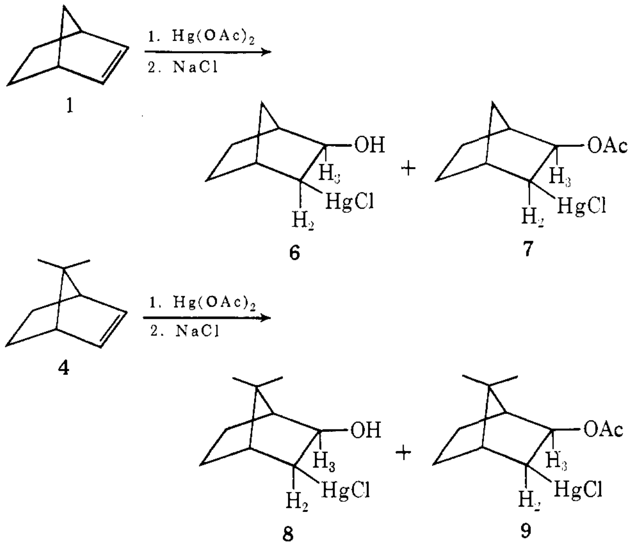
Table I. Oxymercuration–Demercuration of Norbornenes

Olefin	Time[a]	Yield,[b] %	Product, % 2-exo	Product, % 2-*endo*-Methyl	Product, % 3-exo
Norbornene (**1**)	10 sec	92	99.6		
	30 min	100	99.8		
	2 hr	97	99.8		
1-Methylnorbornene (**2**)	5 min	100	48	4	48
	60 min[c]	93	46	0.5	53.5
2-Methylnorbornene (**3**)	10 min	86		99.8[f]	
7,7-Dimethylnorbornene	20 min		99.8		
(**4**)	73 min	84	99.8		
Bornylene (**5**)	15 min[d]	40	49	7	44
	90 min	83	51	8	41
	6.5 hr	100	53	6	41

[a] Time for oxymercuration stage. [b] Analyzed by glpc. [c] One equivalent of sodium acetate was added. [d] At 5°.

Although there appeared to be a significant difference in rate between norbornene (**1**) and 7,7-dimethylnorbornene (**4**), as indicated in Table I, both the mercurials and the corresponding alcohols, derived from the mercurials by *in situ* treatment with sodium borohydride, were essentially exo derivatives which did not change observably with reaction time. The addition of sodium acetate to the reaction mixture decreased the reaction rate considerably and decreased the amount of rearranged adduct from 1-methylnorbornene (**2**), but no change in exo stereochemistry was noted. The results make it clear that for the oxymercuration addition to the norbornene structure, exo stereochemistry is strongly favored even in the presence of the bulky 7,7-dimethyl groups. As will be discussed later, we believe these results support the conclusion that oxymercuration must proceed through a two-stage addition process not involving cyclic intermediates.

The structures of the crude mercurials from **1** and **4** were established by pmr examination in DMSO-d_6–D_2O. Norbornene **1** gave a 95% isolated yield of adduct which consisted of 81% of the hydroxymercurial **6** (H_3, δ 3.64, d, $J = 6$ Hz) and 19% of the acetoxymercurial **7** (H_3, δ 4.77, d, $J = 6$ Hz), whereas **4** yielded 80% of adduct containing 75% of the hydroxymercurial **8** (H_3, δ 3.8, d, $J = 7$ Hz) and 25% of the acetoxymercurial **9** (H_3, δ 4.7, d, $J = 7$ Hz). These pmr spectra are only consistent with the cis-exo oxymercurials **6**, **7**, **8**, and **9**.[11–15]



Infrared analysis and the stereospecific reduction of the mercurials with sodium amalgam in D_2O also confirmed the assigned structures as cis-exo.[16] Previous workers had obtained similar results for substituted norbornenes, but their results were frequently based upon the examination of a minor amount of the oxymercurial isolated from the reaction mixture.[10,17–19]

The development of an essentially quantitative *in situ* mercuration–demercuration procedure[2,20] made it possible to circumvent the difficulties inherent in the nonquantitative isolation of the organomercurial intermediate (80–95% in the present study). Application of this procedure to norbornene, 7,7-dimethylnorbornene, and related olefins of interest in the present study permitted us to establish quantitatively the stereochemistry of the step involving addition of the solvent in the oxymercuration reaction. The olefin was added to an equimolar amount of mercuric acetate in 50% aqueous tetrahydrofuran. This was followed by the *in situ* reduction of the mercurial at various reaction times with sodium borohydride under alkaline conditions.[20,21] These results, summarized in Table I, reveal a remarkable stereospecificity favoring essentially exclusive exo addition of solvent.

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(10) For reviews and detailed references, see (a) N. S. Zefirov, *Russ. Chem. Rev.*, 34, 527 (1965); (b) W. Kitching, *Organometal. Chem. Rev.*, 3, 61 (1968).

(11) F. A. L. Anet, *Can. J. Chem.*, **38**, 789 (1961).

(12) T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963).

(13) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(14) J. J. Miller, Ph.D. Thesis, University of California, Berkeley, 1966.

(15) H. C. Brown, M.-H. Rei, and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 1760 (1970).

(16) See the Experimental Section and ref 10, 17, and 18.

(17) A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968).

(18) T. T. Tidwell and T. G. Traylor, *ibid.*, **33**, 2614 (1968).

(19) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

(20) H. C. Brown and P. J. Geoghegan, Jr. *ibid.*, **89**, 1522 (1967); *J. Org. Chem.*, **35**, 1844 (1970).

(21) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966).

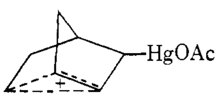
More recently, it has proven possible to examine the adducts formed quantitatively from mercuric trifluoroacetate with norbornene and 7,7-dimethylnorbornene in perdeuteriobenzene solution without isolation of the product.[15] The results establish that the reactions proceed cleanly exo-cis ($\geq$98%) with both olefins.

Discussion

The present results have important implications for the proposal that exo reaction in the 7,7-dimethylnorbornyl system is inexplicable in the absence of σ-bridging,[4,5] as well as for the proposal that oxymercuration must proceed through a mercurinium ion intermediate which controls the stereochemistry.[10] Let us consider each of these proposals in turn.

The oxymercuration–demercuration of norbornene and its derivatives examined in the present study reveals the almost exclusive formation of the exo alcohols (Table I). Unfortunately, while the difficulties involved in achieving a quantitative isolation of the oxymercurial adducts make it necessary to be more equivocal about the results, the data reveal the predominant formation of the cis-exo mercurial derivatives from both norbornene[19] (**6** and **7**) and from 7,7-dimethylnorbornene[18] (**8** and **9**).

It is tempting to account for the remarkably high exo selectivity by the formation of σ-bridged intermediates[4,5] (**10** and **11**), which direct the entering nucleophile to the exo position. However, such σ-bridged species would be expected to yield some Wagner–Meerwein rearranged products, mercurials containing the entering groups in the 2,7 position. Such derivatives have not been observed.[17–19]



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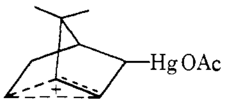

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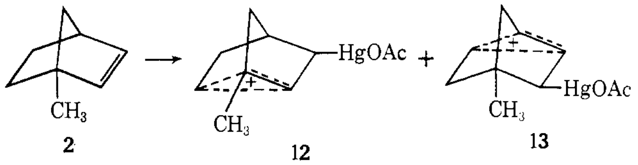
The results realized in the oxymercuration–demercuration of 1-methylnorbornene (**2**) and bornylene (**5**), as well as earlier results with 1,4,7,7-tetramethylnorbornene, appear to rule out such σ-bridged ions as significant intermediates. Both **2** and **5** yield equal amounts of the 2- and 3-exo alcohols, with 4 and 7% of rearranged tertiary alcohols, respectively.

The rearranged products must be due to the acid-catalyzed reaction of the cis-exo mercurials, because the presence of an equivalent quantity of sodium acetate in the reaction mixture involving 1-methylnorbornene markedly reduces the amount of the tertiary alcohol to approximately 0.5%.

The presence of a methyl group on an electron-deficient center greatly stabilizes that center. Consequently, the σ-bridged species **12** should be considerably more stable than **13**. However, oxymercuration–demercuration yields essentially equal amounts of the two isomeric alcohols, 1-methyl-*exo*-norbornanol and 4-methyl-*exo*-norbornanol.[22]

These results appear to rule out conclusively the possibility that σ-bridging plays any significant role in the oxymercuration of norbornene and related bicyclic olefins.



2 12 13

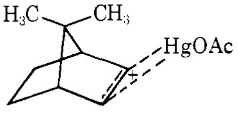
The observation that the oxymercuration of cyclohexene takes place stereospecifically trans has been considered to require the intervention of a mercurinium ion intermediate which controls the stereochemistry of the solvent addition stage.[10] The failure to realize trans oxymercuration of norbornene has led to proposals which retain the mercurinium ion, but add a cis opening of this cyclic intermediate by the solvent.[10,17–19] The present results challenge the role of a mercurinium ion intermediate in the oxymercuration reaction.

The mercurinium ion was originally proposed as an intermediate in the oxymercuration of olefins in 1939[23] and has continued to dominate interpretation of the oxymercuration reaction.[10,24] This proposal has received support in recent years from certain chemical evidence,[25,26] molecular orbital calculations,[27] and spectroscopic studies in very strong acid media.[28]

However, kinetic,[29] nuclear magnetic resonance,[30] oxymercuration of optically active olefins,[31] and trapping studies[32] have failed to provide evidence for a mercurinium ion intermediate.

Our earlier studies have revealed that all known addition reactions involving cyclic transition states or intermediates of three or four ring members proceed exo with norbornene, but preferentially endo or not at all with 7,7-dimethylnorbornene.[10] If the mercurinium ion is an essential intermediate in the oxymercuration reaction, what might we expect for 7,7-dimethylnorbornene (**4**)?

The *exo*-mercurinium ion **14** would place the mercurinium ion in a sterically difficult position relative to the *syn*-7-methyl group. Presumably, the endo isomer (**15**) would be more favorable for such a cyclic species. This is indicated by the fact that epoxidation proceeds preferentially endo in **4**.[9] Moreover, the addition of benzenesulfenium chloride to **4** proceeds preferentially through the endo episulfonium ion.[7]



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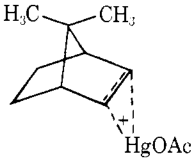

15

The usual postulated trans opening of **15** by solvent would give a trans oxymercurial, with the mercury endo. Alternatively, a cis opening of the intermediate **15**

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(22) A similar lack of directive effect by the 1-methyl substituent has been previously observed for the addition of acids to 1-methylnorbornene and bornylene: H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **89**, 3898 (1967); P. v. R. Schleyer, *ibid.*, **89**, 3901 (1967).

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would give a cis oxymercurial, with both groups endo. Both conclusions are contrary to the experimental results, exo-cis addition to both **1** and **4**.

As the mercurinium ion intermediate is analogous to the relatively stable silver ion complexes of olefins,[33] let us consider the behavior of silver ion with **1** and **4**. Silver ion forms a stable complex with **1**, but does not react with the double bond of **4**.[7] In contrast, the oxymercuration of **4** proceeds with reasonable speed (Table I), the rate being 1/15 of that for **1**, a much lower ratio than for cyclic processes.[7–9]

It has been suggested that the cis addition of mercuric acetate to **4** and similar molecules might be accounted for on the basis of a six-center molecular addition of mercuric acetate.[34] However, this interpretation appears to be incompatible with the formation of Markovnikov product in the oxymercuration–demercuration of 2-methylnorbornene (Table I) and the acceleration of the oxymercuration rate in the presence of acid.

We discard the symmetrical mercurinium ion in interpreting our results. We prefer the concept of electrophilic attack by the mercury species, ^+HgX, at the least substituted carbon atom of the double bond. This produces a mercury-substituted carbonium ion which reacts rapidly with solvent from the trans direction, if that is unhindered, but from the cis direction in molecules such as norbornyl in which the endo direction is strongly hindered. As has been pointed out by Traylor and his coworkers,[35] such mercury-substituted carbonium ions would retain much of the charge on the mercury moiety. Consequently, only a portion of the charge would be on carbon, sufficient to achieve the observed Markovnikov addition, but too small to bring about many of the usual rapid carbonium ion rearrangements.

Experimental Section

Materials. Deuterium oxide (Columbia), mercuric acetate (Mallinckrodt), and sodium chloride (Baker Analyzed) were used without purification. Sodium amalgam was prepared by a literature method.[36] Norbornene (Aldrich) was distilled, mp 46° (lit.[37] mp 46.0–46.5°). Other olefins were prepared as described previously.[8]

Gas Chromatography (Glpc). The analyses were carried out on the Perkin-Elmer Model 226 instrument fitted with 150 ft × 0.01 in. Golay column of appropriate liquid stationary phases.

Spectra. The pmr spectra were taken on a Varian A-60A spectrometer with a solution of about 10–20% by weight, with tetramethylsilane as an internal standard. The hydroxy stretching frequencies of the mercurials and parent alcohols (0.5% by weight) in carbon tetrachloride were measured on the Perkin-Elmer 421 using the slowest gear scan with a slit width of 51. All other infrared spectra were on the Perkin-Elmer 221. Mass spectral analysis confirmed that all deuterated samples contained greater than 95% of one deuterium based on calibration runs with undeuterated samples.

Oxymercuration–Demercuration of Norbornene. To a 50-ml flask fitted with a magnetic stirring bar was added 3.19 g (10 mmol) of mercuric acetate, 10 ml of water, and 8 ml of tetrahydrofuran. To this red-orange reaction mixture was added 0 94 g (10 mmol) of norbornene dissolved in 2 ml of tetrahydrofuran with vigorous stirring at room temperature. In 10 sec the colorless reaction mixture was frozen with a Dry Ice–acetone bath and 10 ml of ice-cold 3 *M* sodium hydroxide was added in 2 min as soon as the frozen mixture started to melt. Then 10 ml of a 0.5 *M* sodium borohydride solution in 3 *M* sodium hydroxide (20 mmol of "hydride") was added at room temperature in 2 min. The temperature rose approximately 5°. After several minutes, 10 g of sodium chloride was added and the grey-black reaction mixture was warmed with a 50° water bath. The addition of sodium chloride and heating the mixture helps to coagulate and settle mercury rapidly. The organic layer was separated, washed with a saturated solution of sodium chloride, and dried over magnesium sulfate. A 1-ml aliquot was taken from the reaction mixture, cyclohexanol was added as an internal standard, and the yield (92%) was determined by vpc. The solvent of the remaining reaction mixture was removed by rotatory evaporation, acetic anhydride and a few drops of dry pyridine were added, and the mixture was heated at 100° for several hours to convert the alcohol quantitatively into the corresponding acetate. Hydrolysis of the excess acetic anhydride with water, extraction with pentane, and glpc analysis (TCEP, 70° [10 psi], retention time 2 hr) indicated 99.6% *exo*- and 0.4% *endo*-norbornyl acetate. The analysis of the 30-min reaction time run indicated 99.8% exo and 0.2% endo acetate. The analysis of the alcohols from the reaction mixture (Carbowax 20M, 100° [20 psi]), however, indicated greater than 99.8% *exo*-norbornanol.

Oxymercuration in the Presence of Sodium Acetate–Demercuration. To a round-bottomed flask fitted with a magnetic stirring bar was added 3.19 g (10 mmol) of mercuric acetate, 0.82 g (10 mmol) of sodium acetate, and 50 ml of 50% aqueous tetrahydrofuran. With vigorous stirring, 0.94 g (10 mmol) of norbornene in 1 ml of tetrahydrofuran was added at 21°. In 13 min the color disappeared. In 2 hr the mixture was cooled to *ca.* 5° and 10 mmol of a saturated sodium chloride solution was added in 1 min. A white precipitate formed. Then 10% sodium hydroxide was added in 4 min at 2–3° until the pH went up to *ca.* 10 (10 ml). The white precipitate dissolved completely. This was followed by 2 ml (10 mmol of 2.5 *M* sodium borohydride in 10% sodium hydroxide) of a sodium borohydride solution (addition 1 min) at *ca.* 2°. The temperature went up to 4°. The reaction mixture was worked up as before and analyzed by glpc, following addition of cyclohexanol as an internal standard. Even after the reaction mixture was heated, there was still present 35% acetate along with 65% alcohol in a total yield of 97%. The mixture was converted to the alcohol with lithium aluminum hydride. Analysis indicated greater than 99.8% *exo*-norbornanol.

Crude *exo-cis*-3-Hydroxynorbornylmercuric Chloride (6). Norbornene (0.94 g, 10 mmol) was treated with 3.19 g (10 mmol) of mercuric acetate in 20 ml of 50% aqueous tetrahydrofuran and the product was converted to the chloride with 30 mmol of sodium chloride. The solvent was removed at room temperature on the rotary evaporator. The solid was dissolved in ethyl acetate, dried over magnesium sulfate, and isolated to give 3.3 g of mercurial (95%) after evacuating at 1 mm for 1 hr at room temperature. The pmr spectrum taken in dimethyl-d_6 sulfoxide–deuterium oxide indicated the presence of 81% hydroxy (δ 3.64, d, $J = 6$ Hz) and 19% acetoxy (δ 4.77, d, $J = 6$ Hz) mercurials.

***exo-cis*-3-Hydroxynorbornylmercuric Chloride (6).** Norbornene (1.88 g, 20 mmol) was oxymercurated in 100 ml of 50% aqueous tetrahydrofuran and converted to the chloride with 20 mmol of sodium chloride. Then 20 ml of 10% sodium hydroxide was added at 4° in 10 min. By the time 15 ml of base was added, the reaction mixture was clear and colorless. The reaction mixture was stirred at room temperature for 1 hr. Then 14 ml of 2.5 *M* aqueous hydrochloric acid was added at 4° to pH 5. The white solid was filtered and dried at 1 mm for 12 hr. There was obtained a 96% yield (6.76 g) of *cis-exo*-3-hydroxynorbornylmercuric chloride, mp 129–130°. Recrystallization from ethyl acetate–heptane gave the product, mp 129.5–130.0° (lit.[2] mp 131–131.5°). The hydroxy stretching frequency was 3603 cm^{-1} while *exo*-norbornanol was 3623 cm^{-1}.[38] The pmr (DMSO-d_6-D_2O) indicated a doublet at δ 3.64 ppm ($J = 7$ Hz). *Anal.* Calcd for $C_7H_{11}OHgCl$: C, 24.20; H, 3.19. Found: C, 24.48; H, 3.44.

***exo-cis*-3-Acetoxynorbornylmercuric Chloride (7).** Norbornene

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[34] R. C. Fahey, *Top. Stereochem.*, 3, 237 (1968).

[35] (a) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971); (b) T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, 30, 599 (1972).

[36] W. R. Brasen and C. R. Hauser, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 508.

[37] P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958).

[38] A hydroxyl stretching frequency difference of 18–22 cm^{-1} between the parent alcohol and the corresponding hydroxy mercurial indicates a cis structure, whereas a difference of 6–10 cm^{-1} indicates a trans one. See ref 19.

(0.94 g, 10 mmol) was oxymercurated with 3.19 g (10 mmol) of mercuric acetate in 30 ml of glacial acetic acid. After 30 min the mixture was poured into 5% aqueous sodium chloride with stirring. The solid was filtered to give a 3.6-g (93%) yield of *exo-cis*-3-acetoxynorbornylmercuric chloride, mp 125–126° (lit.[16] mp 130°). The pmr in pyridine indicated a doublet at δ 4.98 (J = 6 Hz) and a methyl singlet at δ 1.9.

Reduction of 6 with Sodium Borodeuteride. To a 100-ml flask equipped with a magnetic stirring bar was added 1.73 g (5 mmol) of the mercurial and 50 ml of 50% aqueous tetrahydrofuran. To the cooled (~2°) reaction mixture was added 5 ml of 10% sodium hydroxide in 5 min. When 0.064 g (6 mmol of hydride) of sodium borodeuteride was dissolved in 5 ml of 10% sodium hydroxide, some bubbling occurred. This solution was added to the reaction flask at 20° in 3 min The grey-black mixture was worked up as usual to give a 70% yield by glpc. Another reduction on a 10-mmol sample gave a 63% yield by glpc. Sublimation gave an alcohol, mp 125.5–127.5°. The pmr in benzene did not exhibit a clean doublet at δ 3.6 indicating that the reaction was not stereospecific.[14,21]

3-*exo*-*d*-2-*exo*-Norborneol. The *exo-cis*-3-hydroxynorbornylmercuric chloride was reduced with 2% sodium amalgam in deuterium oxide.[19,39] Sublimation gave an alcohol with mp 126–128°. The infrared in CCl_4 exhibits a strong band at 10 μm for *exo*-norbornanol but no band at 10 μm for 3-*exo*-*d*-2-*exo*-norbornanol. Presumably the 10-μm band comes from the 3-exo hydrogen. The pmr for 3-*exo*-*d*-2-*exo*-norbornanol in benzene exhibited a clean doublet at δ 3.6 (J = 7 Hz). The pmr of an alcohol obtained from the deuterioboration of norbornene was identical with that obtained from the sodium amalgam reduction in deuterium oxide.

Oxymercuration–Demercuration of 7,7-Dimethylnorbornene (4). To a 50-ml flask equipped with a magnetic stirring bar was added 5 ml of water, 5 ml of tetrahydrofuran, and 1.59 g (5 mmol) of mercuric acetate. To this stirred mixture was added 0.61 g (5 mmol) of 7,7-dimethylnorbornene at 20°. Almost all the color disappears in 15 min. In 20 min the mixture was frozen with a Dry Ice–acetone bath. Ice-cold 3 *M* sodium hydroxide (5 ml) was added in 2 min at *ca.* 2°. Then 5 ml of 0.5 *M* sodium borohydride in 3 *M* sodium hydroxide was added in 2 min. The greyish-black mixture was worked up as usual and treated with lithium aluminum hydride. Analysis by glpc (UCON LB 550X [5%], 100° [10 psi], retention time 1.5 hr) indicated 99.84% *exo*- and 0.16% *endo*-7,7-dimethyl-2-norbornanol. (About 2% of alcohols from the oxymercuration of 5,5-dimethylnorbornene, an impurity in 7,7-dimethylnorbornene, had shorter retention times.) A reaction time of 73 min gave an 84% yield of greater than 99.8% exo alcohol and 10% 7,7-dimethylnorbornene. The crude mercurial was also isolated as the chloride and reduced under the same conditions to give 95% alcohol and 5% 7,7-dimethylnorbornene. The small amount of olefin probably comes from the crude mercurial (oil) rather than from elimination during reduction. The pmr of the crude alcohol in 5% deuterium oxide–95% pyridine exhibited a quartet at δ 4.02 and methyl resonances at 1.45 and 0.95 ppm. Identification of the alcohol was also confirmed by introducing a mixture of alcohols obtained from the solvolysis of *endo*-camphenilyl brosylate in 60% aqueous diglyme. The major product in the solvolysis, 7,7-dimethyl-*exo*-norbornanol,[5] corresponded to the major oxymercuration–demercuration product. Moreover, the major product obtained in the hydroboration of 7,7-dimethylnorbornene, 7,7-dimethyl-*endo*-norbornanol, corresponded to the minor alcohol in the oxymercuration–demercuration reaction.

Crude Mercurial from the Oxymercuration of 7,7-Dimethylnorbornene. Oxymercuration of 7,7-dimethylnorbornene (0.65 g, 5.33 mmol) and conversion to the chloride gives 1.6 g (80%) of crude mercurial. The pmr in DMSO-d_6–D_2O indicated 25% acetoxy (δ 4.7, d, J = 7 Hz) and 75% hydroxy (δ 3.8, d, J = 7 Hz) mercurials. The methyl resonances corresponding to the hydroxy mercurial were at 0.93 and 1.47 ppm.

***exo-cis*-3-Hydroxy-2-apobornylmercuric Chloride (8).** To a 100-ml flask equipped with a magnetic stirring bar was added 2.99 g (7.4 mmol) of *exo-cis*-3-acetoxy-2-apobornylmercuric chloride and 30 ml of 50% aqueous tetrahydrofuran. The reaction mixture was cooled to 5°, pH 5, and 7.4 ml of 10% sodium hydroxide was added in 2 min, pH 10. After stirring at room temperature for 1.5 hr, the reaction mixture was acidified to pH 5 with 2.0 *M* hydrochloric acid. The oil crystallized overnight to give a 2.45-g (88%) yield of mercurial, mp 115–117°. Recrystallization twice from ethyl acetate–heptane gave mp 133–133.5°. The hydroxy stretching frequency was 3609 cm^{-1} for the mercurial and 3627 cm^{-1} for the parent alcohol.[38] *Anal.* Calcd for $C_9H_{15}OHgCl$: C, 28.78; H, 4.03. Found: C, 28.68; H, 3.98.

***exo-cis*-3-Acetoxy-2-apobornylmercuric Chloride (9).** Oxymercuration of 7,7-dimethylnorbornene (0.186 mol) with 57.4 g (0.180 mol) of mercuric acetate in 180 ml of glacial acetic acid gives, after 30 min at room temperature, 69.9 g (88%) of crude mercurial precipitating from 1 l. of 5% aqueous sodium chloride, mp 109–112°. The mercurial was recrystallized twice from 95% ethanol to give a mercurial, mp 121–121.5°. The pmr in pyridine exhibited doublets at δ 2.78 (J = 8 Hz) and 5.18 (J = 8 Hz) for the proton α to mercury and acetoxy, respectively. Methyl resonances came at δ 1.5 and 0.9 and the acetoxy methyl at δ 1.9. *Anal.* Calcd for $C_{11}H_{17}O_2HgCl$: C, 31.64; H, 4.11. Found: C, 31.41; H, 3.94.

Reduction of Exo-Cis Mercurial with Sodium Amalgam in Deuterium Oxide. To a 100-ml flame-dried flask equipped with a magnetic stirring bar was added 22 ml of deuterium oxide and 0.25 g (10 mmol) of sodium pieces under a slow flow of nitrogen in about 5 min. After cooling to room temperature, 4.16 g (10 mmol) of *exo-cis*-3-acetoxy-2-apobornylmercuric chloride was added with stirring. To this stirred mixture was added 34 g of 2% sodium amalgam in about 10 portions over a 2-min period. It appears that most of the mercurial reacts rapidly. The reaction mixture was stirred overnight at room temperature. The mixture was extracted with 50 ml of ether, washed twice with a saturated sodium chloride solution, and dried, and the solvent removed on the rotary evaporator. Recrystallization from 10 ml of petroleum ether gave a 0.90-g (64%) yield, mp 132–136°, of 3-*exo*-*d*-7,7-dimethyl-*exo*-norbornanol. Sublimation gave mp 139–141°. Analysis by pmr gave a sharp doublet at δ 4.02 (J = 8 Hz) for the α-methine proton and methyl resonances at δ 0.95 and 1.45 in 95% pyridine–5% deuterium oxide. The pmr in benzene gave a doublet at δ 3.6 (J = 7.5 Hz) and methyl resonances at δ 0.88 and 1.28. The infrared indicated the absence of the strong 10-μm band found in the undeuterated compound.

Reduction of 9 with Sodium Borodeuteride. To a 20-ml flame-dried flask equipped with a magnetic stirring bar was added 5 ml of deuterium oxide, 5 ml of tetrahydrofuran (distilled from lithium aluminum hydride), and 2.08 g (5 mmol) of *exo-cis*-3-acetoxy-2-apobornylmercuric chloride. The mixture was cooled to 2° and 2 ml of 3 *M* sodim deuteroxide was added to the slurry in 2 min. Then 0.106 g (10 mmol of hydride) of sodium borodeuteride in 2 ml of 3 *M* sodium deuteroxide was added dropwise in 30 sec. The reaction mixture was worked up as usual and the solvent evaporated. The acetate was saponified in alkaline methanol, extracted with ether, recrystallized from pentane, and sublimed, mp 141–143.5°. A relatively strong band in the infrared at 10 μm indicated that most of the deuterium is 3-endo. The pmr in 95% pyridine–5% deuterium oxide indicated a mixture of doublets with J = 8 and 3.5 Hz at δ 4.02. The methyl resonances came at δ 0.95 and 1.45. Because the 3-exo proton at δ 2.02 is almost completely resolved in the solvent, it was possible to determine that 65.5 ± 10% of the 3-deuterium was endo by integration.

Oxymercuration–Demercuration of 1-Methylnorbornene. The oxymercuration–demercuration in 10 sec gives a 65% yield of 47% 2-exo, 50% 3-exo, and 3% of the tertiary alcohol. In 5 min a 100% yield of 48% 2-exo, 48% 3-exo, and 4% tertiary alcohols was obtained. With 1 equiv of sodium acetate in 1 hr, a 93% yield of 46% 2-exo, 54% 3-exo, and 0.5% tertiary alcohols was obtained.

Oxymercuration–Demercuration of Bornylene. Oxymercuration–demercuration at 5° in 16 min gave a 40% yield of 49% 2-exo, 44% 3-exo, and 7% of the rearranged tertiary alcohol. In 90 min at 20° there was obtained an 83% yield of 51% 2-exo, 41% 3-exo, and 8% tertiary alcohol. In 6.5 hr at 20° a 100% yield of 53% 2-exo, 41% 3-exo, and 6% tertiary alcohol was obtained.

Oxymercuration–Demercuration of 2-Methylnorbornene. An 86% yield of greater than 99.8% 2-*endo*-methyl-2-*exo*-norborneol was obtained.

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(39) J. K. Stille and S. C. Stinson, *Tetrahedron*, 20, 1387 (1964).