ADDITIONS TO BICYCLIC OLEFINS—X

STEREOCHEMISTRY OF THE OXYMERCURATION-DEMERCURATION OF cis-BICYCLO[3.3.0]OCT-2-ENE, endo-TRIMETHYLENE-NORBORN-8-ENE AND RELATED OLEFINS^{1,2}

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(Received in USA 23 March 1978; Received in UK for publication 6 July 1978)

Abstract—The stereochemistry of the oxymercuration-demercuration (OM-DM) of olefins related to the cisbicyclo[3.3.0]octane and endo-2,3-trimethylenenorbornane structures was determined. In the case of cis-bicyclo[3.3.0]oct-2-ene, hydration occurs preferentially at the less hindered 3-position, with little preference shown for exo vs endo. The more hindered 2-product shows a 11:1 preference for the exo-product. The presence of Me groups at positions 2- or 3-, results in the formation of the tertiary alcohols with approximately a 4:1 favoring of the exo-isomer. (The oxymercuration intermediate exhibits a rapid equilibration with time. Consequently, the 4:1 ratios may not represent the true limit for the isomer distribution in the initial kinetic product.) Similarly, 2-methylenebicyclo[3.3.0]octane reveals an 8:1 preferential formation of the exo-alcohol. In the case of endotrimethylene-norborn-8-ene, the oxymercuration stage is extraordinarily slow and the results do not fit this pattern. Possibly the very slow oxymercuration stage permits equilibration of the initial reaction product. On the other hand, the reaction is fast with 8-methylene-endo-trimethylenenorbornane and the product is 100% of the tertiary exo-alcohol. The same behavior is observed for 2-methylenenorbornane. Surprisingly, 2-methylene-endo-trimethylenenorbornane fails to undergo oxymercuration. Consequently, both endo-trimethylenenorborn-8-ene and 2methylene-endo-trimethyleneorbornane exhibit an exceptional inertness toward oxymercuration, presumably related to the highly rigid U-shaped structure of the parent system.

The oxymercuration-demercuration sequence (OM-DM) in aqueous tetrahydrofuran with mercuric acetate is a mild, convenient method for affecting the Markovnikov hydration of olefins in very high yields.⁴ Rearrangements which normally occur in the reactions of olefins with other electrophiles are generally not observed.

The stereochemistry of the oxymercuration of olefins has received much attention in attempts to define the factors which control the mode of addition.⁵⁻¹¹ The *cis*-bicyclo[3.3.0]octyl (1), norbornyl (2) and *endo*-trimethylene norbornyl (3) skeletons are U-shaped and contain various degrees of steric hindrance. These systems have been proven very effective in revealing the effects of increasing steric hindrance on several reactions which proceed by different mechanisms.¹²

Consequently, it was of interest to undertake a systematic study of the oxymercuration-demercuration of several olefinic structures related to 1, 2 and 3 to determine the effects of increasing steric hindrance in these systems on the stereochemistry of hydration.



RESULTS

cis-Bicyclo[3.3.0]oct-2-ene (4) undergoes rapid oxymercuration under the standard conditions (T_1 , 5.5 min). After a total reaction time of 1 hr, in situ reduction by sodium borohydride gave a 90% overall yield of four alcohols. Hydration occurred preferentially at the more remote, less hindered 3-position, giving equal amounts of the exo and endo alcohols. Hydration at the more hindered 2-position proceeds stereoselectively to the *exo*-alcohol (Scheme 1).



The introduction of Me groups at the 3-(5) or 2positions (6) reduces the number of isomeric alcohols produced in the reaction to two, the tertiary derivatives. In each case the initial product contains *exo*-alcohol predominating over the *endo*-epimer by a factor of approximately 4:1 (Schemes 2 and 3).

The yields of alcohols in these cases were low, in the range of 40-50%. Moreover, the isomeric distribution of the alcohols changed rapidly to produce more of the *endo*-epimer (Table 1). Evidently, the initial oxymercuration stage is both incomplete and rapidly reversible, resulting in a change from the *exo*-OH derivative to the *endo*-OH.



Scheme 3.

At first sight, it appears puzzling that equilibration should increase the formation of the more hindered, more strained *endo*-alcohol. However, it should be recalled that the equilibration involves the oxymercurial and we are not in a position to speculate as to the relative thermodynamic stabilities of the four possible diastereomers involved in the oxymercuration intermediate. It is regretable that the objectives of the present study did not permit establishing the stereochemistry of the mercurial moiety.

In the case of 2-methylenebicyclo[3.3.0]octane (7), the oxymercuration reaction proceeds rapidly to completion $(T_1, 15 \text{ sec})$. The product, in essentially quantitative yield, is predominantly the *exo*-tertiary alcohol (Scheme 4).



Scheme 4.

HO TCH3

11%

In this case, there is no evidence for equilibration of the oxymercurial derivative under the reaction conditions.

For comparison, we examined the behavior of 2methylenenorbornane (8). This also reacted rapidly $(T_1, 20 \text{ sec})$ and completely (yield essentially quantitative). The product consisted of 99.5% of 2-methyl-*exo*norbornanol and 0.5% of 2-methyl-*endo*-norbornanol.

Although we did not test *endo*-trimethylenenorbornene (9), it would evidently react normally, yielding the *exo*-alcohol.



Surprisingly, *endo*-dicyclopentadiene (10) undergoes oxymercuration cleanly at the norbornene double bond to give the alcohol in a yield of 89%.¹¹



Olefin		T ₂ . min ^b	Yield of alcohols, %	— Isomers, X —	
	T ₁ . min ^a			exO	endo
	5	5	42	84	16
$\left(\right) $		15	48	65	34
$\vee \gamma$		45	54	42	58
6 сн ₃		180	56	26	74
	5	5		78	22
人人人		15		65	35
V V 1H3		180		15	85
5					

Table 1. Oxymercuration-demercuration of 5 and 6

^{α}Time required for the yellow color to disappear. ^bTime before the addition of 3 N sodium hydroxide.

There was no evidence for any attack on the double bond in the 5-membered ring. Traylor has obtained similar results with a mercuric chloride-mercuric oxide mixture in aqueous acetone.^{6d}

In accordance with this remarkable selectivity, the corresponding monoene (11), containing the double bond at the 8-position, proved to be extraordinarily inert.



Even after 7.5 days under standard conditions, reduction produced only a 36% overall yield of the four alcohols. Since intermediate organomercurials are known to undergo facile isomerization in less time than required for the oxymercuration stage in this exceptionally sluggish reaction, one can have no confidence that the products correspond to the kinetic species desired.



Scheme 5.

Consequently, the observation that the reaction exhibits none of the stereoselectivity observed for 4, 5, 6 and 7 suggests that the products (Scheme 5) indeed arise from a concurrent oxymercuration-equilibration.

In an attempt to improve the yield of alcohols obtained from 11, and if possible, to achieve the identification of the kinetic products, the effects of several strong acids were investigated. The addition of one equivalent of either of the following acids, p-toluenesulfonic, methanesulfonic, perchloric, nitric and trifluoroacetic, to the mixture resulted in faster reactions with overall yields of *ca.* 50-70% of the four alcohols in 20 hr. Longer reaction times of up to 40 hr proved detrimental in some cases (Table 2). The utilization of mercuric trifluoroacetate in place of mercuric acetate resulted in a 62% overall yield of the alcohols in just 3 hr (Scheme 6).



Scheme 6.

However, the products still failed to reveal the high regio- and stereoselectivity anticipated for a U-shaped structure of high rigidity. It is probable that these modifications in the oxymercuration procedure facilitates both the oxymercuration and the equilibration (demercuration) steps to an equivalent extent, thereby causing the product to reflect only the thermodynamic properties of the oxymercuration intermediate.

Table 2. Effect of strong acids on the oxymercuration-demercuration of 11

Acid	Time, hr ^a	Yield of alcohols, $b x$
p-TsOH	20	66
•	40	61
CH2SO2H	. 20	66
	40	56
HC104	20	68
	40	61
HNO ₃	20	63
	40	52
CF3C02H	20	59
	40	. 61

^aBefore addition of 3 N sodium hydroxide. ^bVPC analysis.



8-Methylene-*endo*-trimethylenenorbornane (12) does exhibit the anticipated effect of the rigid U-shaped structure. Oxymercuration-demercuration of this olefin proceeded rapidly to give within 5 min a virtually quantitative yield of tertiary alcohols (Scheme 7).

In this case, the product must be the kinetic species no evidence for equilibration was observed under the reaction conditions.

On the other hand, 2-methylene-*endo*trimethylenenorbornane (13) failed to undergo oxymercuration under the standard reaction conditions.





It should be recalled that 2-methylenenorborane undergoes oxymercuration-demercuration without difficulty. In this case, the steric requirements of the rigid bicyclic structure evidently prevents completion of the reaction.

DISCUSSION

In simple cyclic systems (14), oxymercuration involves a *trans* addition to the double bond.



In norbornene (15), the reaction proceeds with a *cis* addition to the double bond.



In a less rigid bicyclic, bicyclo[2.2.2]oct-2-ene (16), the addition proceeds to give both isomers.^{6c,8b}



Bach and Richter have studied the oxymercurations of several bicyclic olefins. In the case of bicyclo[4.2.0]oct-7ene (17), they established that the oxymercuration can



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occur either *cis* or *trans*. The results varied with solvent.⁸ Their results indicate the effects of steric hindrance result in predominantly *exo* attack by solvent and an even greater predominance for *exo* attack by mercury.

The oxymercuration-demercuration of bicyclo[3.2.1]oct-2-ene (18) with mercuric acetate in aqueous tetrahydrofuran gives a mixture of three alcohols: 73% exo-2-ol; 20% endo-3-ol; 7% exo-3-ol.⁸e



Their studies on the oxymercuration of bicyclo[2.2.2]oct-2-ene clearly reveal the effects of different mercuric salts, solvents, added nucleophiles, and even concentrations on the nature of the products and the stereospecificity.^{85.*} An explanation of the stereochemistry of addition to this and other olefins has been offered in terms of twist strain^{6c} and perturbation of the double bond by the mercury electrophile.^{8*}

Regretably, there has been no work done on defining the stereochemistry of the addition of the mercurial moiety to the olefins derived from the bicyclooctane structure (1) or the *endo*-trimethylenenorbornane structure (3). Consequently, we must restrict ourselves to considering the effect of structure on the stereochemistry for the addition of water to the initial intermediate, whatever that may be.¹³

It is evident from the results with 4-6 that there is a modest preference for addition of solvent from the *exo* direction.

It would be anticipated that the effect would be even larger with 11. However, the results indicate little stereoselectivity. This olefin reveals exceptional inertness. As discussed earlier, the reaction is so slow that equilibration of the oxymercuration product may well be competitive. Consequently, it is not possible to say whether the observed products are the true kinetic species. Inamoto *et al.*¹⁰ reported that tricyclo[$5.2.2.0.^{2.6}$]undec-3-ene (19), which differs from 11 by only one C atom in the bridge, underwent oxymercuration with mercuric acetate in aqueous tetrahydrofuran at a rate



comparable to 11 and exhibited a similar regioselectivity. Regretably, the stereochemistry of only two of the four alcohols was determined. Consequently, because of this and the possibility of equilibration of the mercurials, a comparison of their results with our is not possible.

The methylene derivatives provide a far better test of the proposal that the addition of solvent to the oxymercuration intermediate is sterically controlled to give preferential addition from the *exo* direction.

Such steric control would be expected to increase from 7 to 8 to 12. Indeed, the results conform to the expected pattern. The extremely rapid reaction of 7, 8 and 12 compared to 5 and 6 is consistent with a previous study on the relative reactivities of olefins in the oxymercuration reaction¹⁷ and also with the thermodynamic stabilities of endocyclic and exocyclic double bonds.¹⁸ As mentioned previously, the unreactivity of 13 must be attributable solely to steric hindrance manifested by the rigid U-shaped skeleton. Similar conclusions about the effects of steric hindrance were obtained in previous studies on the rates and stereochemistry of the oxymercuration of norbornenes.^{94,19}

The unusually low yield of products obtained from 5and 6 is puzzling and we have no experimentally tested explanation for this unusual behavior at the present time.

EXPERIMENTAL

B.pts are corrected. NMR spectra were taken on a Varian A-60 spectrometer using TMS as the reference.

Materials. All of the olefins were prepared by procedures described below. THF (Mallinckrodt Chemical Co. and J. T. Baker Chemical Co.) and mercuric acetate (Mallinckrodt and J. T. Baker) were used as obtained. Mercuric trifluoroacetate was generously supplied by Dr. M.-H. Rei.

General oxymercuration-demercuration procedure. 10 mmol (3.19 g) of mercuric acetate was dissolved in 10 ml water. 5 ml of THF was added which produced a yellow suspension. 10 mmol of the olefin dissolved in 5 ml THF was rapidly added and the time for the yellow suspension to disappear was recorded as T₁. After stirring for the appropriate time, 10 ml of 3 N NaOH was added, followed by 10 ml of 0.5 M NaBH₄ in 3 N NaOH. An appropriate internal standard was added and the mixture was saturated with N₃Cl. The organic layer was dried over MgSO₄ and was then analyzed by gas chromatography. The same procedure was followed when mercuric trifluoroacetate was used.

Acid catalyzed oxymercuration-demercuration procedure. The reaction was carried out as described above, except that 10 mmol of the acid was added prior to the addition of the olefin. In all cases, with the exception of p-toluenesulfonic acid, the addition of the acid produced a clear colorless soln. Addition of p-TsOH resulted in a white suspension.

Gas chromatographic analyses. Analyses for isomer distribution were carried out on a Perkin Elmer Model 226 instrument fitted with a 150 ft \times 0.01 in Golay column containing 20% Quadrol and a Perkin Elmer Model 154 Vapor Fractometer using 20% Quadrol or 20% Carbowax 20M column. Peak areas were determined by a planimeter (Keuffel and Esser Co.). Isomeric alcohols were identified on the basis of comparison with authentic compounds whose preparation and characterization are described below.

cis-Bicyclo[3.3.0]oct-2-ene. A modification of Stapp and Kleinschmidt's procedure²¹ was used. 2 mol (216 g) of 1,3-cyclooctadiene²² was refluxed with 0.2 mol (7.8 g) of K under N₂ for 7 hr. The mixture was cooled to 0° and the K was destroyed by the cautious addition of abs MeOH. After stirring overnight to insure destruction of all of the catalyst, water and diethyl ether were added and the layers separated. The organic layer was washed with NaCl aq and then dried over MgSO₄. The solvent was removed by distillation and the product was distilled through an 18 in Vigreux column. The distillate was then fractionated through a Todd column resulting in a yield of 114 g (53%), b.p. 130.5-131° (746 mm); n_{D}^{20} 1.4746 [lit.:²¹ b.p. 132-133°, n_{D}^{20} 1.4750; lit.:²³ b.p. 131-133°; n_{D}^{20} 1.4760].²⁵

2-Methyl-cis-bicyclo[3.3.0]oct-2-ene. 1 ml of 85% phosphoric acid was added to 0.3 mol (42 g) of 2-methyl-cis-bicyclo[3.3.0]octan-endo-2-ol in a 50 ml round bottom flask fitted with a distillation head. The mixture was heated to 160° and the olefin codistilled with water. Pentane was added to the distillate and the layers were separated. The organic layer was dried over MgSO₄. Distillation gave 29.4 g (80% yield); b.p. 153° (748 mm); n_D^{12} 1.4742; NMR (neat) δ 5.15 (broad s, 1H), 0.8-3.2 (m, 13H) [lit.:²⁴ n_D^{20} 1.4802]. 3-Methyl-cis-bicyclo[3.3.0]oct-2-ene. A procedure similar to the one used for the preparation of the 2-Me derivative was followed. From 231 mmol (28.1g) of 3-methyl-cis-bicy-clo[3.3.0]octan-endo-3-ol was obtained 21.1g (75% yield) of the olefin, b.p. 150° (752 mm); n_D^{22} 1.4723 [lit..²⁴ b.p. 153°, n_D^{20} 1.4712].

2-Methylene-cis-bicyclo[3.3.0]octane. A 300-ml, 3-necked, round bottom flask fitted with a mechanical stirrer, reflux condenser with a drying tube and a pressure equalizing dropping funnel was flame dried under a slow stream of N2. Methyltriphenyl phosphonium bromide (23 g, 64.5 mmol, Aldrich Chemical Co., Inc.) and 80 ml of dry THF was added. n-BuLi (42 ml of 15% by weight in hexane, 64.5 mmol) was added dropwise (exothermic). The dropping funnel was charged with 50 mmol (6.2 g) of cis-bicyclo[3.3.0]octan-2-one in 25 ml of dry THF while the Wittig reagent was heated to 70°. The ketone soln was added dropwise and the reaction was refluxed for 17 hr. After cooling, water was added to destroy the excess ylide. Anhyd-MgSO4 was added. The mixture was cooled to 0° and filtered. The solvent was removed by distillation through a short Vigreux column. 20 ml pentane was added; the mixture was cooled to -70° and filtered immediately. Distillation gave 2.4 g of olefin, b.p. 161°. The olefin was prepped out on a 10 in Carbowax 20M column at 100° to remove trace impurities, n_D^{19} 1.4798; IR (neat) μ 3.2, 3.4, 6.03, and 11.4; NMR (CCl₄) δ 4.7 (m, 2H), 0.9-3.0 (m, 12H). (C₉H₁₄)C, H.

8-Methylene-endo-trimethylenenorbornane. A procedure similar to the one above was employed. The olefin was isolated by preparative gas chromatography (5 ft 10% Neopentyl Glycol Adipate on Firebrick at 187°C), n_{20}^{20} 1.5098; IR (neat) μ 3.2, 3.35, 6.03, 6.75, 6.9, 6.95, 8.5, 11.4; NMR (CCl₄) δ 4.83 (t, 1H), 4.64 (t, 1H), 1.0-3.0 (m, 14H). (C₁₁H₁₆) C, H.

endo-Trimethylene-8-norbornene. The procedure of Brown et al. was used.^{11a} Thus from 1.24 mmol (164 g) of endo-dicyclopentadiene was obtained 136 g of olefin (82%), b.p. 182-187° (735 mm). Recrystallization from MeOH gave a solid, m.p. 49-50° [lit.:²⁶ m.p. 50-51°].

OM-DM Products from cis-bicyclo[3.3.0]oct-2-ene 4. A hydroboration-chromic acid oxidation sequence²⁷ was carried out on 4 to give a mixture of 2- and 3-cis-bicyclo[3.3.0]octanones which were separated by the preferential formation of the bisulfite addition compound of the 3-ketone. The endo-2- and -3-ols and the exo-3-ol were prepared by Cope's procedure²⁸ from these ketones. The exo-2-ol was prepared by Rosenblum's procedure.²⁹

cis-Bicyclo[3.3.0]octan-2-one and cis-bicyclo[3.3.0]octan-3one. Following Brown and Garg's procedure,²⁷ 1.05 mol (113.8 g) of 4 gave the 3-one in 31% yield, b.p. 90° (13.5 mm); n_{20}^{20} 1.4801 [lit.:³⁰ b.p. 78° (10 mm); n_{20}^{18} 1.4811] and the 2-one in 33% yield, b.p. 84° (14 mm); n_{20}^{20} 1.4762 [lit.:³¹ b.p. 50° (2.3 mm); n_{20}^{23} 1.4766].

cis-Bicyclo[3.3.0]octan-endo-2-ol. Cope's procedure²⁸ was followed with the exception that LAH was used in place of NaBH₄. Thus to 10 mmol LAH in dry THF was added 2.5 mmol of cis-bicyclo[3.3.0]octan-2-one in 5 ml dry THF. After 1 hr stirring at room temp., 1 ml of water was cautiously added and the soln was saturated with sodium potassium tartrate. The layers were separated and the organic layer was dried over MgSO₄. The product was isolated by preparative VPC (4ft 20% Carbowax 20M on Chromosorb W at 125°). The phenyl urethane derivative had a m.p. 87.5-88° [lit.:²⁸ m.p. 87°].

cis-Bicyclo[3.3.0] octan-endo-3-ol. The above procedure was followed except that t-BuOH was added to LAH. Preparative VPC isolation (same conditions) gave the product. Phenyl urethane derivative, m.p. 115.5-116° after recrystallization from aqueous MeOH. [lit.: 32 m.p. 116°].

cis-Bicyclo[3.3.0]octan-exo-3-ol. Cope's procedure was followed.²⁶ Thus, cis-bicyclo[3.3.0]octan-endo-3-ol was converted to its p-toluenesulfonate derivative in 37% yield, m.p. 29.5-30.5°. ($C_{15}H_{20}SO_3$) C, H.

The tosylate was then converted to the desired alcohol in 42% yield. Phenylurethane derivative, m.p. $74-75^{\circ}$. (C₁₅H₁₇NO₂) C, H.

cis-Bicyclo[3.3.0]octan-exo-2-ol. 25 ml of EtOH and 1 ml of 0.2 M ethanolic platinum chloride soln (Englehard Industries, Inc.) and 1 g of Darco KB decolorizing carbon was added to a 125-ml hydrogenation flask. The flask was connected to a Brown[□]

hydrogenator.^{33,34} The apparatus was purged with H_2 by adding 10 ml of a 1 M ethanolic NaBH₄ soln to the H_2 generator flask. 5 ml of 1 M ethanolic NaBH₄ soln was rapidly added to the hydrogenation flask. After 1 min, 4 ml of glacial AcOH was added. The flask was then charged with 40 mmol (4.96 g) of *cis*-bicyclo[3.3.0]oct-2-en-*exo*-3-ol dissolved in abs. EtOH. The buret was then filled with 1 M ethanolic NaBH₄ soln. The reaction required 9 ml of this soln. The platinum and carbon were removed by filtration. Distillation gave 3.70 g (74%), b.p. 84-86° (16 mm); n_D^{-0} 1.4792 [lit.:²⁸ b.p. 79° (5 mm); n_D^{-5} 1.4883]; IR indicated the presence of a CO containing impurity. VPC analysis showed 7% *cis*-bicyclo[3.3.0]octan-2-one. Phenylurethane derivative, m.p. 74.8-75.2° [lit:²⁸ m.p. 75.0-75.2°].

cis-Bicyclo [3.3.0]oct-2-en-exo-3-ol. Rosenblum's procedure was followed.²⁹ Thus, 50 mmol of 4 (16.2 g) yielded 6.67 g (36%) of the desired alcohol, b.p. 98–99° (17.5 mm); n_D^{20} 1.5008; NMR (CCl₄) δ 5.65 (s, 2H), 4.3 (broad s, 1H), 3.6 (broad s, 1H), 3.25 (m, 1H), 2.7 (m, 1H), 1.5 (m, 6H). (C₈H₁₂O) C, H.

p-Nitrobenzoate derivative, m.p. 83.5–84.5°. ($C_{15}H_4NO_4$) C, H, N.

OM-DM Products of 2-methyl-cis-bicyclo[3.3.0]oct-2-ene and 2-methylene-cis-bicyclo[3.3.0]octane. The endo alcohols were prepared by the addition of MeMgI to the corresponding ketone. The exo alcohols were prepared from olefin 6 by an epoxidation reduction sequence.

2-Methyl-cis-bicyclo[3.3.0]octan-endo-2-ol. 1.6 mol of MeMgI was prepared and to it was added 0.8 mol of cis-bicyclo[3.3.0]octan-2-one dissolved in 200 ml of diethyl ether at 0°. After 15 min of refluxing, the mixture was poured into a soln of 84 g NH₄Cl in 200 ml water. The aqueous phase was extracted with ether and the combined extracts were washed with cold 5% H_2SO_4 (2×150 ml), satd NaHCO₃ (2×100 ml) and with water. The ether extracts were dried over MgSO₄. Distillation gave 93.1 g (84%) of the product, b.p. 90° (14 mm); n_D^2 1.4848; IR (neat) μ 2.95, 3.4, 3.5, 6.9, 7.3, 7.7, 8.7 and 10.8; NMR (CDCl₃) δ 1.26 (s), 1.1-2.7 (m). (C₉H₁₆O) C, H.

2-Methyl-cis-bicyclo[3.3.0]octan-exo-2-ol. To a soln of 238 mmol (29.0 g) of 6 in 350 ml CHCl₃ was added dropwise at 0° a soln of 238 mmol (53 g) of 80% m-chloroperbenzoic acid in 500 ml CHCl₁. After stirring for 30 min, 10% NaHCO₁ ag was added until the mixture gave a negative starch iodide paper test. The mixture was filtered at 0°, and the filtrate was washed with cold satd NaHCO3 aq, sat NaCl aq, and dried over MgSO4. VPC analysis (3 ft 20% Quadrol on Chromosorb W) showed a mixture of two epoxides (18:83). The solvent was removed on a rotary evaporator and the residue was dissolved in 100 ml of dry THF. This soln was added dropwise to a mixture of 9.03 g LAH in 250 ml dry THF at 0°. After stirring for 1 hr, water was cautiously added to destroy the excess hydride. The mixture was washed with sat sodium potassium tartrate (2×100 ml). The organic layer was dried over MgSO4. VPC analysis showed a 83:17 mixture of alcohols. After removal of the solvent, a solid was obtained and after two recrystallizations (pentane), 12.6 g of VPC pure alcohol was obtained, m.p. 79.0-79.5°; IR (CCl₄) µ 2.9, 3.4, 6.85, 7.25, 9.0, 9.6 and 10.9; NMR (CDCl₃) δ 1.26 (s), 0.8-2.9 (m).

OM-DM Products from 3-methyl-cis-bicyclo[3.3.0]oct-2-ene. The endo-tertiary alcohol was prepared by a methyl Grignard addition to the ketone and the exo-tertiary alcohol was prepared by an epoxidation of 7 followed by hydride reduction.

3-Methyl-cis-bicyclo[3.3.0]endo-3-ol. The previously described procedure for the Grignard addition was followed. Thus, from 37.2 g of ketone, 30.9 g (73%) of product was obtained, b.p. 88° (9 mm); m.p. 37.5-38.0°; IR (melt) μ 3.0, 3.4, 3.5, 6.8, 6.9, 7.27, 7.7, 8.0, 8.7 and 10.55; NMR (CDCl₃) δ 1.25 (s), 1.1-2.7 (m). (C₉H₁₆O) C, H.

3-Methyl-cis-bicyclo[3.3.0]exo-3-ol. The previously described procedure for the epoxidation-reduction sequence was followed. Thus from 21.1 g of 7 was obtained 7.24 g (30%) of recrystallized product, m.p. 78-78.5°; IR (Nujol) μ 3.0, 3.4, 6.9, 7.3, 8.1, 9.6 and 11.1; NMR (CDCl₃) δ 2.70 (m, 2H), 1.3 (s) and 0.8-2.2 (m, 14H). (C₉H₁₆O) C, H.

OM-DM Products from endo-trimethylene-8-norbornene. The alcohols were kindly provided by Dr. I. Rothberg.

OM-DM Products from 8-methylene-endo-trimethylenenor-

bornane. The alcohols were kindly provided by Dr. D. L. Vander Jagt.

OM-DM Products from 2-methylenenorbornane. The alcohols were obtained by a previously reported preparation.³⁵ Data obtained for the OM-DM of 2-methylenenorbornane was obtained by Dr. S. Ikegami.

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