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Solvomercuration–Demercuration. 7. Regio- and Stereochemistry of the Oxymercuration–Demercuration of Alkyl-Substituted Cyclohexenes and Cyclopentenes[1]

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The oxymercuration–demercuration (OM–DM) of several methyl- and *tert*-butylcyclohexenes and -cyclopentenes has been investigated. The conformationally flexible 4-methylcyclohexene undergoes hydration in a nonregioselective but remarkably stereoselective fashion, giving a 50:50 ratio of the *trans*-3- and *cis*-4-methylcyclohexanols with only ~1% each of the other two isomers. In the case of 3-methylcyclohexene, hydration occurs both regio- and stereoselectively to give 79% *trans*-3-, 12% *cis*-2-, 5% *cis*-3-, and 4% *trans*-2-methylcyclohexanols. A similar, but higher, selectivity is observed for the conformationally locked 3-*tert*-butyl analogue. In contrast, both 4-methyl- and 4-*tert*-butylcyclopentene exhibit a strong preference, 4:1 and 7:1, respectively, for cis hydration. Furthermore, the 3-alkylcyclopentenes give still different results. The 3-methyl derivative undergoes hydration preferentially at the 3 position with a 6:1 preference for the *trans*-alcohol. On the other hand, the 3-*tert*-butyl olefin shows no significant regioselectivity, but a strong, 93:7, preference for trans hydration. 3,4-Dimethylcyclopentene results in a 9:1 predominance of the 3 isomer with only a slight preference for the *cis*-cyclopentanol. The presence of a methyl group in the 1 position of this system results in the formation of only the two tertiary alcohols, however, with a 3:1 favoring of the *trans*-alcohol. Virtually identical regio- and stereochemical results are observed for 2,3-dimethylcyclopentene.

The oxymercuration–demercuration (OM–DM) procedure provides a convenient synthetic method for effecting the Markownikoff hydration of a carbon–carbon double bond.[5-7] The oxymercuration reaction usually proceeds with no rearrangements and unhindered acyclic olefins react with amazingly high regioselectivity. Pasto and Gontarz[8] have examined the OM of several conformationally rigid cyclohexenes. In view of this, as well as the remarkable results obtained with the acyclic and simple cyclic olefins, it appeared desirable to examine several other alkyl-substituted cyclohexenes as well as cyclopentenes.

Results and Discussion

Monoalkylcyclohexenes. 4-Methylcyclohexene (**1**) undergoes the oxymercuration reaction rapidly (T_1 = 16 s). After 30 min, T_2, in situ demercuration with aqueous alkaline sodium borohydride results in a mixture of four alcohols in 90% yield. (For definitions[5] of T_1 and T_2, see General Procedure, Experimental Section.) The major products are *trans*-3-methylcyclohexanol in 47% yield and the *cis*-4 derivative in 51% yield. The other two possible isomers were observed in ~1% yield each (Scheme I).

This high stereoselectivity, coupled with the absence of regioselectivity which is exhibited by this conformationally flexible olefin, is virtually identical with that realized by Pasto[8] and Whitham[9] for the conformationally locked 4-*tert*-butylcyclohexene (**2**). In this case, both the mercury and the hydroxyl groups were introduced in an axial fashion[10] (Scheme II).

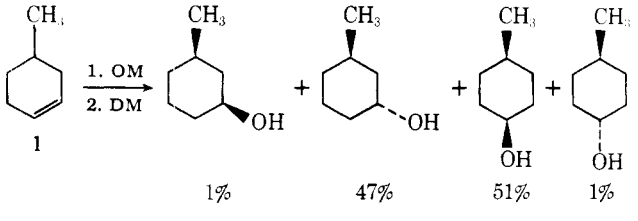
In contrast, both 3-methyl- (**3**) and 3-*tert*-butylcyclohexenes (**4**) undergo reaction with high regio- and stereoselectivity for the *trans*-3-alkylcyclohexanol (Schemes III and IV). In the case of **4**, however, the OM stage is unusually slow (T_1 = 42 min). Thus, after 5 h only a 78% yield of the four alcohols is obtained.

While a 4-alkyl group exerts no significant steric effect on the oxymercuration of **1** and **2**,[8] a 3-alkyl group clearly does in the case of **3** and **4**.

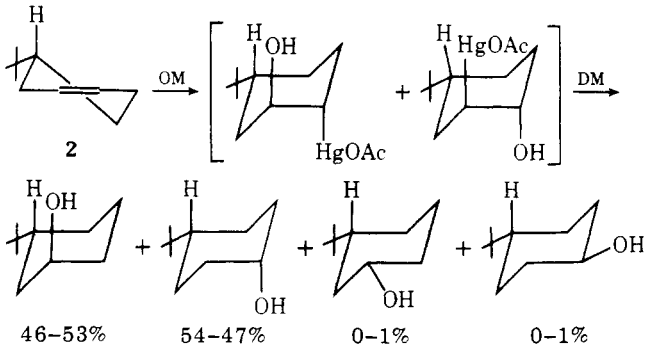
If one assumes trans diaxial addition, then the more stable equatorial conformer of **3** undergoes hydration in a highly regioselective fashion. On the other hand, hydration of the less stable axial conformer is nonregioselective (Scheme V).

In the case of olefin **4**, only the *trans*-3- and the *cis*-2-alcohols can arise from diaxial addition to the equatorial con-

Scheme I



Scheme II



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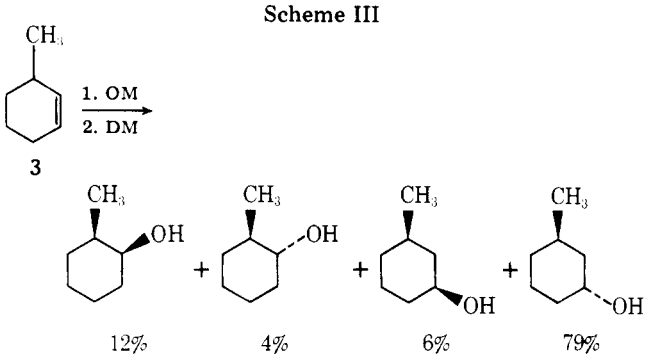
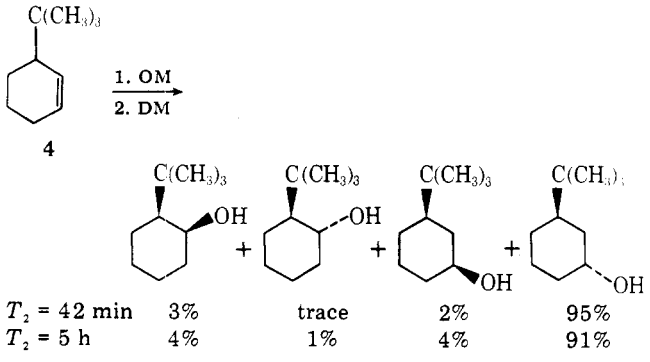
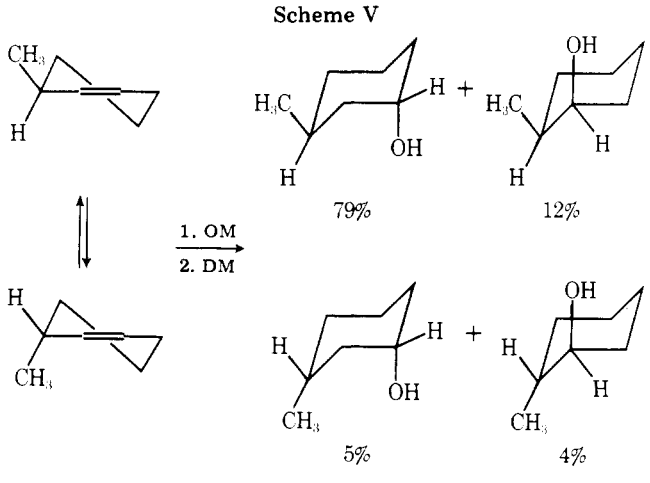
Scheme III



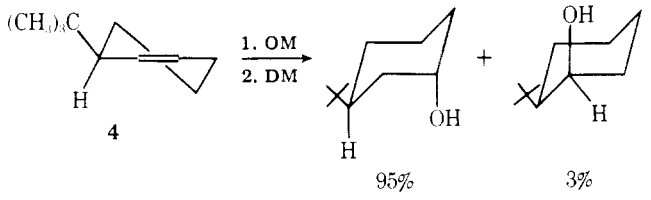
Scheme IV



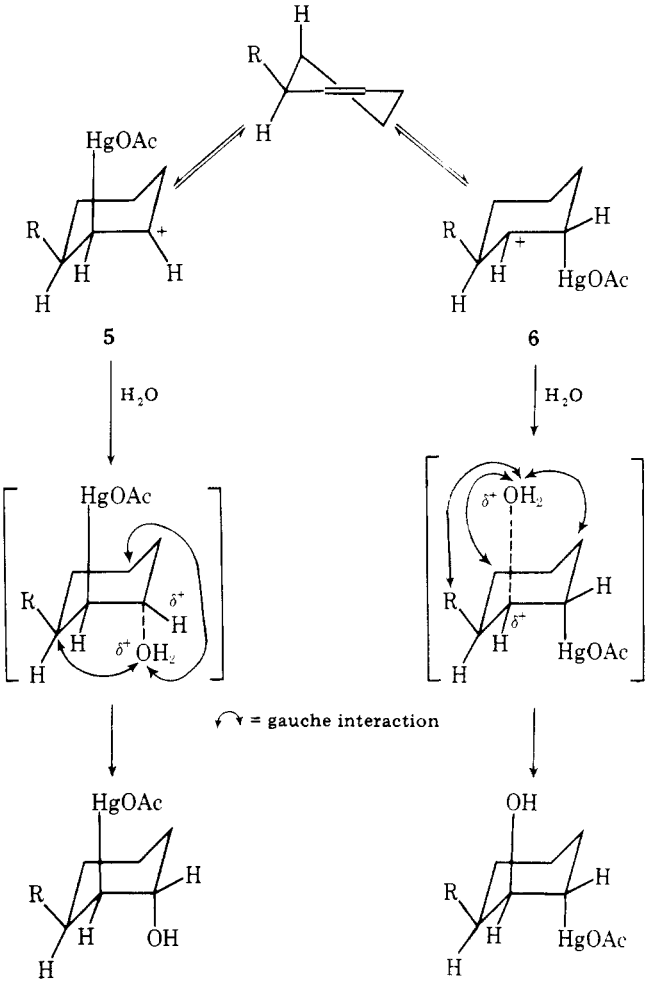
Scheme V



Scheme VI



Scheme VII



former (Scheme VI). The other two isomers which are produced must arise from a diequatorial addition of the elements of HgOAc–OH. However, it should be pointed out that due to the sluggishness of the OM of **4**, it is quite possible that these isomers are arising as the result of an equilibration of the parent oxymercurials.

Pasto and Gontarz[8] have examined the effect of a 3-alkyl group in several rigid cyclohexenes and have interpreted the results in terms of torsional effects. Indeed, the results for **3** and **4** are readily attributable to such torsional effects (Scheme VII).[11]

Attack by the mercury electrophile on the equatorial conformer of the olefin in an axial manner should generate both ions **5** and **6** with equal facility. Nucleophilic attack on these ions by water will then give the intermediate oxymercurials.

An examination of the transition states of the two product-determining steps clearly reveals why one is more favorable energetically over the other. Attack by water on ion **5** results in two gauche ring C–O interactions as indicated. On the other hand, a similar attack on ion **6** will result in not only the two gauche C–O interactions but an additional R–O interaction as well. Consequently, the product-determining transition state leading to the mercurated *trans*-3-methylcyclohexanol involves less torsional strain than the other pathway. Moreover, this should lead to the expectation of higher regio- and stereoselectivity in the case where R = *tert*-butyl than when R = methyl. This is observed.

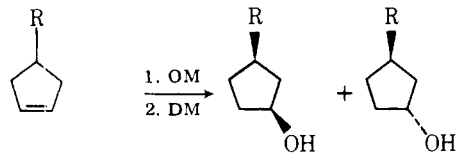
Furthermore, a similar analysis of the OM of the axial conformer of **3** reveals that both products are formed from transition states of comparable torsional strain, i.e., the same number and type of gauche interactions. This nicely explains the lack of regioselectivity which is observed in this case.

Monoalkylcyclopentenes. Both 4-methyl- (**7**) and 4-*tert*-butylcyclopentenes (**8**) undergo reaction in a stereoselective fashion with a 4:1 and 7:1 preference, respectively, for the *cis*-3-alkylcyclopentanol (Scheme VIII).

The OM of 3-methylcyclopentene (**9**) is both regio- and stereoselective. Hydration occurs primarily at the 3 position with a 6:1 preference for the *trans*-alcohol. Similarly, hydration at the 2 position occurs with a 9:1 preference for the trans product (Scheme IX).

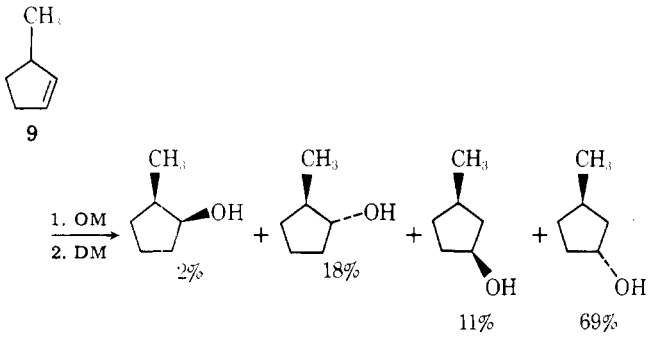
The 3-*tert*-butyl analogue **10** exhibits markedly different characteristics, however. The oxymercuration is nonregiose-

Scheme VIII

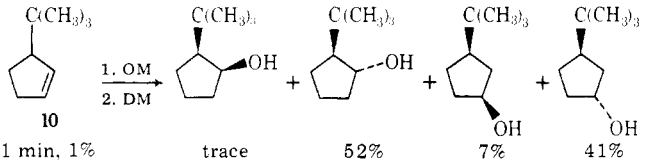


7, R = CH_3	77%	23%
8, R = $C(CH_3)_3$	88%	12%

Scheme IX



Scheme X



1 min, 1%	trace	52%	7%	41%
2 min, 5%	1%	55%	6%	38%
6 h, 69%	trace	71%	12%	17%
24 h, 66%	trace	65%	24%	11%

lective, but highly stereoselective, for the *trans*-alcohols. Moreover, this olefin undergoes an extraordinarily sluggish reaction (T_1 = 33 min), which is incomplete and evidently also reversible as indicated by the observed equilibration of the alcohols with time (Scheme X).

In contrast to the results of the cyclohexene series, the results of the cyclopentenes are not attributable to any reasonable explanation. This is due to the fact that flexible cyclopentanes are pseudorotational with very small energy barriers, which has precluded a clear determination of their conformational characteristics.

Polyalkylcyclopentenes. The OM–DM of *cis*-3,4-dimethylcyclohexene (11) results in predominant hydration at the more remote 4 position with a slight favoring for the formation of the *cis*-cyclopentanol (Scheme XI).

A methyl group at the 1 position (12) of this system results in only the tertiary alcohols. In this case, however, there is a 3:1 preference for the trans product (Scheme XII).

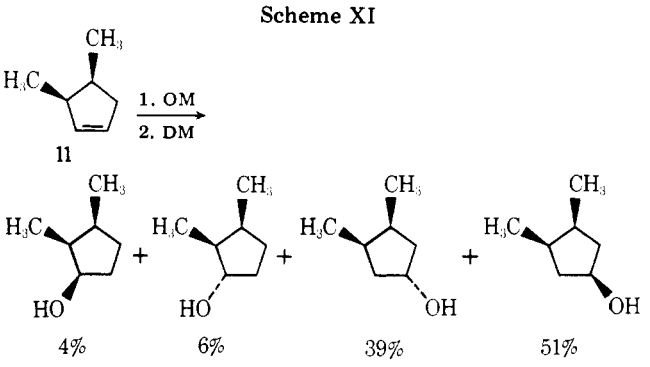
2,3-Dimethylcyclopentene (13) exhibits a similar selectivity (Scheme XIII). However, a small amount of equilibration occurs with time.

Conclusion

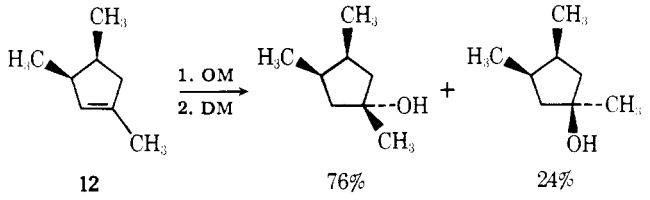
4-Alkyl substituted cyclohexenes undergo oxymercuration–demercuration in a remarkably stereoselective, but nonregioselective, fashion. On the other hand, 3-alkyl substituted cyclohexenes undergo hydration in a regio- and stereoselective manner, favoring the *trans*-3-alkylcyclohexanol because of torsional effects.

However, flexible alkyl-substituted cyclopentenes undergo oxymercuration in an unpredictable fashion. The presence or absence of regio- and stereoselectivity is intricately dependent on the size and position of the alkyl group.

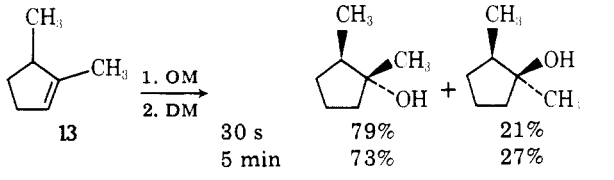
Scheme XI



Scheme XII



Scheme XIII



30 s	79%	21%
5 min	73%	27%

Experimental Section

Materials. 3-Methylcyclopentene, 99.7% pure, and 4-methylcyclopentene, 99.4% pure, were A.P.I. standard samples obtained from the Carnegie Institute of Technology. 2,3-Dimethylcyclopentene, 99% pure, 3-methylcyclohexene, 99% pure, and 4-methylcyclohexene, 99% pure, were obtained from Chemical Samples Co. The other olefins were prepared, and details are given below. Mercuric acetate and tetrahydrofuran (THF) were commercially available and used as obtained.

General Oxymercuration–Demercuration Procedure. Into a 100-mL round-bottom flask equipped with a magnetic stirring bar was placed 3.19 g (10.0 mmol) of mercuric acetate. To this was added 10.0 mL of water, and the mixture was stirred until the salt dissolved to produce a clear solution. Then was added 10.0 mL of THF to produce a yellow precipitate. To this vigorously stirred suspension was added 10.0 mmol of the olefin, and the flask was stoppered. The time needed for the yellow color to disappear was recorded as T_1. The reaction mixture was stirred for an appropriate time, T_2. Then 10.0 mL of 3.0 M NaOH solution was added, followed by 10.0 mL of a solution of 0.50 M $NaBH_4$ in 3 M NaOH with vigorous stirring. The mixture was stirred until amost all of the mercury had coagulated (usually 0.5 h), a suitable GLC standard was added, and the aqueous phase was saturated with K_2CO_3 (or NaCl). The upper layer was separated, dried over K_2CO_3 (or $MgSO_4$), and analyzed by GLC using an appropriate column.

GLC Analyses. The following columns were employed for special analyses: column A, 150 ft × 0.01 in. Quadrol; column B, 150 ft × 0.01 in. 1,2,3-tris(2-cyanoethoxy)propane; column C, 150 ft × 0.01 in. Ucon-50-HB-2000; column D, 150 ft × 0.01 in. diethylene glycol succinate; column E, 12 ft × 0.25 in. 20% β,β'-oxydipropionitrile on 60/80 Chromosorb P; column F, 12 ft × 0.25 in. 30% $AgNO_3$-saturated ethylene glycol on 60/80 Chromosorb W, AW/DMCS; column G, 12 ft × 0.25 in. 19.5% Carbowax 20M, 0.5% Armac 18-D on 60/80 Chromosorb W, AW/DMCS; column H, 7 ft × 0.75 in. 20% tetracyanothylated pentaerythritol on 40/60 Chromosorb W. Analyses for product yields were done on standard Carbowax, SE-30, and DC-710 columns.

A Perkin-Elmer Model 226 equipped with a FID was used for capillary column analyses. Peak areas were measured by a disc chart integrator or a Keuffel and Esser Co. planimeter. Unless otherwise noted, it was assumed that isomeric alcohols have the same FID response. Unless otherwise noted, isomer peaks were identified by mixed

injection of the reaction mixture with approximately an equal amount of the compound in question.

Olefin Preparations. 3-*tert*-Butylcyclohexene. 3-*tert*-Butylcyclohexene was prepared by the addition of *tert*-butyllithium to 3-bromocyclohexene (Chemical Samples Co.) using a slight modification of a literature procedure (only pentane instead of pentane/ether as solvent). The crude olefin isolated in 30% yield, bp 63–64 °C (18 mm) [lit.[13] bp 76–78 °C (23 mm)], contained a number of impurities by GLC analysis. The material was purified first by preparative GLC on column H. Examination of the purity of the material thus obtained on column F indicated 3% of a shorter retention time impurity and 8% of a longer retention time impurity. Consequently, the material was purified by preparative GLC on column F to give the pure olefin used in the OM–DM reactions: NMR (CCl_4) δ 0.88 (s, 9), 1.3–2.1 (m, 7), 5.67 (s, 2).

3-*tert*-Butylcyclopentene. *trans*-2-*tert*-Butylcyclopentanol (8.51 g, 60 mmol), whose preparation is described below, was converted to a white solid tosylate (17.76 g, 98% yield) by the method of Schleyer.[14] The tosylate (8.70 g, 29.4 mmol) was then heated at 56–58 °C for 8 h in a solution of $KOC(CH_3)_3$ prepared from potassium metal (2.9 g, 74 mmol) and 55 mL of *tert*-butyl alcohol. The solution was cooled, poured into ice (10 g) and water (50 mL), and extracted with two 50-mL portions of pentane. The combined pentane extracts were washed with two 50-mL portions of water and then dried over K_2CO_3. Distillation afforded 2.00 g (54%) of olefin, bp 135 °C [lit.[15] bp 139 °C], which was contaminated by small amounts of *tert*-butyl alcohol and pentane. The *tert*-butyl alcohol was removed by distillation of the olefin over $LiAlH_4$ to give 1.92 g of olefin, bp 52 °C (40 mm), contaminated by small amounts of pentane. The pentane was removed on a rotary evaporator to afford 1.06 g of olefin: IR (neat) 3.24, 7.14, 7.30 μm; NMR (CCl_4) δ 0.87 (s, 9), 1.4–2.6 (m, 5), 5.70 (s, 2).[16] GLC analysis on column E indicated that the olefin was 91% pure, containing 5% of 1-*tert*-butylcyclopentene and 4% of the rearranged olefin 2,3,3-trimethylcyclohexene. By GLC analysis the latter impurity arose not during the elimination but rather during the first atmospheric distillation. Analyses of the oxymercuration–demercuration products from this 91% pure olefin were independently shown to be unaffected by the oxymercuration–demercuration products from either 1-*tert*-butylcyclopentene or 2,3,3-trimethylcyclohexene. Furthermore, results of the oxymercuration–demercuration of the >99.8% pure 3-*tert*-butylcyclopentene, collected by preparative GLC on column F as a byproduct during the isolation of 4-*tert*-butylcyclopentene given below, were identical with those using this 91% pure material.

4-*tert*-Butylcyclopentene. β-*tert*-Butyladipic acid was prepared by the ammonium vanadate catalyzed nitric acid oxidation of 4-*tert*-butylcyclohexanol (99%, Chemical Samples) in 78% yield of recrystallized product, mp 115.5–116.5 °C [lit.[17] 87% yield, mp 117 °C]. Cyclization with $Ba(OH)_2$ according to the literature procedure[17] gave 3-*tert*-butylcyclopentanone in 73% yield: bp 92–94 °C (18 mm); $n^{21}{}_D$ 1.4484 [lit.[17] 64–70%, bp 200–201 °C (759 mm), $n^{20}{}_D$ 1.4505].

3-*tert*-Butylcyclopentanone (28.2 g, 201 mmol) in 100 mL of ether was added dropwise to $LiAlH_4$ (2.85 g, 75 mmol) in 100 mL of ether over a 1-h period. After the mixture was stirred for an additional 2 h, 40 mL of 3 M NaOH was added and the ether was decanted. The solid was washed with ether, and the combined ether layers were dried over K_2CO_3. Distillation gave a mixture of 3-*tert*-butylcyclopentanols[18] (24.0 g, 84% yield): bp 99–101 °C (17 mm); IR (neat) 2.98 μm; NMR (CCl_4) δ 0.87 (s, 9), 1.2–2.0 (m, 7), 3.25 (m, 1, OH), 4.23 (m, 1).

The mixture of alcohols (22.7 g, 160 mmol) was converted to the tosylates by the method of Schleyer[14] to give 44.2 g (94%) of an oil which was not purified. The entire tosylate mixture was then heated at 50 °C for 14 h in a solution of 27.2 g of potassium *tert*-butyl alcoholate in 160 mL of dry *tert*-butyl alcohol. The solution was cooled, poured into 200 g of ice and water, and extracted with two 125-mL portions of pentane. The combined pentane extracts were washed with three 100-mL portions of H_2O and then dried over K_2CO_3. The solution was flash distilled at 17 mm, and the distillate was redistilled at atmospheric pressure to give fractions containing 7.9 g (40% yield) of olefins: bp 126–128 °C; GLC analysis on column F at 50 °C showed only two peaks at 14.0 and 28.4 min in a ratio of 19:81, respectively. Isolation of the shorter retention time peak by preparative GLC on column F showed (NMR) that it was identical with the 3-*tert*-butylcyclopentene prepared above. The longer retention time peak was also isolated and identified as 4-*tert*-butylcyclopentene by its NMR spectrum: NMR (CCl_4) δ 0.87 (s, 9), 2.17 (s, 5), 5.60 (s, 2) [lit.[18] NMR δ 0.85, 2.18, 5.67].

4-*tert*-Butylcyclopentene used for the OM–DM reactions was isolated in the same manner as above (100-μL injections, column F), and its purity (>99%) was checked by reinjection. The 3-*tert*-butylcyclopentene byproduct was collected at the same time and its purity (>99.8%) determined.

***cis*-3,4-Dimethylcyclopentene.** To 65.6 mmol of $LiAlH_4$ in 40 mL of THF was added dropwise a solution of 8.0 g (71.4 mmol) of *cis*-3,4-dimethylcyclopentanone (99% purity, Chemical Samples Co.) in 30 mL of THF. The reaction mixture was stirred for 2 h at room temperature, and the excess hydride was then destroyed by the careful addition of water. Then 40 mL of a saturated solution of sodium potassium tartrate was added, the layers were separated, and the aqueous phase was extracted with 30 mL of ether. The combined extracts were dried over $MgSO_4$ and filtered, and the solvent was removed on a rotary evaporator. The resulting residual oil was converted directly to a mixture of tosylates by the method of Tipson.[19] The tosylate mixture thus obtained was not purified but was added to 11.2 g (100 mmol) of sublimed potassium *tert*-butoxide in 50 mL of *tert*-butyl alcohol. The mixture was stirred at 50 °C for 6 h and then at room temperature overnight. Ice water (500 mL) was added, and the solution was extracted with three 100-mL portions of pentane. The combined extracts were washed with 200 mL of water and twice with 100 mL of 25% $CaCl_2$ solution. The pentane layer was dried ($CaCl_2$), concentrated, and distilled to give 1.9 g (28% based on ketone) of olefin: bp 89–91 °C; $n^{21}{}_D$ 1.4297; NMR (neat) δ 0.85 (d, 3), 0.95 (d, 3), 1.7–2.9 (m, 4), 5.5 (s, 2).

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.70; H, 12.85.

***cis*-1,3,4-Trimethylcyclopentene.** In a typical Grignard reaction, 22.4 g (200 mmol) of *cis*-3,4-dimethylcyclopentanone was added to excess CH_3MgI in ether. The reaction mixture was hydrolyzed with NH_4Cl solution and extracted with ether. The combined extracts were washed with cold 5% H_2SO_4, saturated $NaHCO_3$ solution, and saturated NaCl solution and then dried over $MgSO_4$. Distillation gave 16.4 g (64%) of product: bp 90 °C (41 mm); $n^{20}{}_D$ 1.4483. GLC analysis on column A showed an 89:11 mixture of two alcohols.

The mixture of alcohols (11.1 g, 86.5 mmol) was heated with 0.5 mL of 85% H_3PO_4 to 140 °C in a distilling flask. Water was separated from the olefin distillate, and the distillate was dried over $CaCl_2$ and then distilled to give 7.8 g (82%) of olefin: bp 114 °C; $n^{21}{}_D$ 1.4346; IR (neat) 6.0 μm; NMR (neat) δ 0.87 (t, 6), 1.65 (s, 3), 1.7–2.9 (m, 4), 5.2 (m, 1).

Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 86.97; H, 12.89.

Stereochemical Assignments. OM–DM Products from 3- and 4-Methylcyclohexenes. Authentic samples of the four epimeric 2- and 3-methylcyclohexanols were obtained from Chemical Samples Co., whereas the two epimeric 4-methylcyclohexanols were obtained from Aldrich. Analysis of isomers from 3-methylcyclohexene was done directly on column A with essentially base line resolution between all four isomers. Analysis of the four isomers from 4-methylcyclohexene was more involved since we were unable to find a column which gave base line resolution of all four peaks. Analysis on column B of the reaction mixture showed a mixture of 98.5% of partially overlapping *trans*-3- plus *cis*-4-methylcyclohexanol peaks with 1.5% of a mixture of partially overlapping *cis*-3- and *trans*-4-methylcyclohexanol peaks. The latter two compounds were present in roughly 1:2 proportions, respectively. In order to get the proportion of 3- and 4-substituted isomers, the upper THF layer containing an internal GLC hydrocarbon standard from the OM–DM reaction was separated and dried and the THF was removed on a rotary evaporator. The residue was oxidized using procedure B of Brown, Garg, and Liu.[20] The resulting ketones were analyzed for yield (91% from the alcohols resulting from OM–DM or 83% overall from the olefin) and then for isomer distribution on column C (52.6% of 4-methylcyclohexanone and 47.4% of 3-methylcyclohexanone). The validity of this oxidation technique for determining the amount of 3- and 4-substituted products was established by control experiments using synthetic mixtures of *trans*-3-methylcyclohexanol and *cis*-4-methylcyclohexanol. (Found for a mixture of 50.3% *trans*-3-methylcyclohexanol and 49.7% *cis*-4-methylcyclohexanol was 49.5% of 3-methylcyclohexanone and 50.5% of 4-methylcyclohexanone with an overall ketone yield of 91%).

OM–DM Products from 3-*tert*-Butylcyclohexene. Reduction of 2-*tert*-butylcyclohexanone with BH_3 in THF gave a mixture of *trans*- and *cis*-alcohols. The trans isomer was identified by mixed injection with an authentic sample available from the group's chemicals, mp 82–85 °C (lit.[21] *trans*-3-*tert*-butylcyclohexanol mp 84–85 °C and *cis*-2-*tert*-butylcyclohexanol mp 57–58 °C). The remaining peak was shown not to be residual ketone and therefore was assumed to be the cis isomer.

Reduction of 3-*tert*-butylcyclohexanone with BH_3 in THF according to Varma's procedure[22] gave a mixture of 72% *cis*- and 28% *trans*-alcohols by GLC analysis. Assignment of peaks followed from the reported percentage values (70% cis, 30% trans).[22]

Analyses for isomer composition on the OM–DM reactions as well as for the reductions above were done on column A with base line resolution between all four isomers.

OM–DM Products from 3- and 4-Methylcyclopentenes. GLC analysis of the isomeric secondary alcohols proved to be difficult so product mixtures were converted to their acetates (Ac_2O/pyridine) prior to analysis on column D. Baseline resolution of the *cis*- and *trans*-3-methylcyclopentyl acetates was not achieved. Consequently, the product ratios were determined by both peak height and peak areas (triangular method with planimeter) with a maximum assessed error of 5%.

The configurational assignments of *cis*- and *trans*-3-methylcyclopentyl acetates were determined by the chemical shift of the 3-methyl protons. An NMR spectrum of the acetates from the oxymercuration–demercuration of 4-methylcyclopentene showed two methyl doublets at δ 1.07 and 0.98 with the former doublet being of larger area than the latter. Fuchs and Haber, who have synthesized the *cis*- and *trans*-acetates,[23] noted that the methyl doublet in the cis isomer lies further downfield than in the *trans*-acetate.[24] On this basis then, the major isomer (77% by GLC) from the OM–DM of 4-methylcyclopentene is the *cis*-3-methylcyclopentanol.

trans-2-Methylcyclopentyl acetate in the acetate mixture from the OM–DM of 3-methylcyclopentene was identified by preparation of the pure acetate from the hydroboration–oxidation of 1-methylcyclopentene followed by acetylation (Ac_2O/pyridine).

The remaining unidentified acetate from the OM–DM of 3-methylcyclopentene was then assigned the *cis*-2-methylcyclopentyl structure.

OM–DM Products from 3- and 4-*tert*-Butylcyclopentenes. Assignment of configuration for the *cis*- and *trans*-3-*tert*-butylcyclopentanols followed from the preparation of an authentic sample of a mixture of both isomers of known composition. Reduction of 3-*tert*-butylcyclopentanone with $LiAlH_4$ in ether according to the procedure given above for the preparation of 4-*tert*-butylcyclopentene gave a mixture of 58% *cis*- and 42% *trans*-3-*tert*-butylcyclopentanols by VPC analysis on column A. Assignment of configuration followed from the reported percentage values (60% cis, 40% trans) for this reaction.[18]

The *trans*-2-*tert*-butylcyclopentanol present in the OM–DM of 3-*tert*-butylcyclopentene was identified by the synthesis of the pure compound by a route involving the addition of *tert*-butyllithium to cyclopentanone to produce 1-*tert*-butylcyclopentanol followed by dehydration of this alcohol to 1-*tert*-butylcyclopentene, which was in turn subjected to hydroboration–oxidation to produce the desired *trans*-2-*tert*-butylcyclopentanol. The *trans*-2-*tert*-butylcyclopentanol was also used above in the synthesis of 3-*tert*-butylcyclopentene. The entire synthetic scheme is described below.

1-*tert*-Butylcyclopentanol. Cyclopentanone (0.80 mol) was added dropwise to 0.79 mol of *tert*-butyllithium in pentane at −78 °C according to the procedure of Buhler.[25] Hydrolysis followed by extraction with ether, drying (K_2CO_3), and then distillation afforded 30.5 g (27%) of 1-*tert*-butylcyclopentanol: bp 76–80 °C (17 mm); $n^{20}D$ 1.4606; IR (neat) 2.77, 7.32, 8.50 μm; NMR (CCl_4) δ 0.95 (s, 9), 1.33 (s, 1), 1.4–2.0 (m, 8).

A portion of the 1-*tert*-butylcyclopentanol was converted to its *p*-nitrobenzoate ester (*n*-BuLi/*p*-$NO_2C_6H_4COCl$) according to the literature procedure,[26] mp 106–107 °C.

1-*tert*-Butylcyclopentene. 1-*tert*-Butylcyclopentanol (27.8 g, 0.196 mol) was heated with 0.5 g of I_2 so that the olefin produced distilled at a moderate rate. The iodine-colored distillate was taken up in pentane, washed twice with aqueous sodium thiosulfate solution, and dried over K_2CO_3. Filtration followed by atmospheric distillation gave 22.4 g of material, bp 132–140 °C. However, the distillate came over as a red liquid. Consequently, the distillate was stirred over $LiAlH_4$ for 1 h and then flash distilled from the $LiAlH_4$ under reduced pressure (~50 mm) into a dry ice/acetone cooled trap to give 21.4 g (88%) of colorless liquid olefins. VPC analysis on column G indicated a mixture of 82% of the desired 1-*tert*-butylcyclopentene, 16% of 2,3,3-trimethylcyclohexene, and 2% of an unidentified component. (The latter two components were absent when the dehydration was run on a 5-mmol scale experiment, which preceded this larger scale reaction.) The entire mixture was separated by atmospheric distillation through a Nester-Faust Auto-Annular Teflon Spinning Band Distillation System under a static N_2 atmosphere to give a combined mass of 16.9 g (70% yield) of 1-*tert*-butylcyclopentene fractions, which taken together would analyze for ~98% purity: bp 138–140 °C; IR (neat), 3.24, 6.09, 7.18, 7.33 μm; NMR (CCl_4) δ 1.03 (s, 9), 1.87 (m, 2), 2.26 (m, 4), 5.27 (m, 1) [lit.[27] bp 137–139 °C (740 mm); IR 6.13 μm; NMR (CCl_4) δ 1.03 (*tert*-butyl), 5.27 (vinyl H)]. A portion of the higher boiling 2,3,3-trimethylcyclohexene was isolated: bp 146 °C [lit.[28] bp 144–146 °C (746 mm)]; IR (neat) 3.28, 6.01, 7.24, 7.33 μm; NMR (CCl_4) δ 0.98 (s, 6), 1.63 (d, J = 2 Hz) in a 1.4–2.1 (m) of total area for 9 H, 5.27 (m, 1).

***trans*-2-*tert*-Butylcyclopentanol.** Hydroboration–oxidation of 1-*tert*-butylcyclopentene was patterned after that described for (−)-thujopsene by Acharya and Brown.[29] Thus, 1-*tert*-butylcyclopentene (15.5 g, 125 mmol) in 40 mL of THF was hydroborated with 50 mL of 2.54 M BH_3 in THF (125 mmol of BH_3)[30] for 2 h at 0 °C and then at room temperature for 3 h. Oxidation with 45 mL of 3 M NaOH followed by 45 mL of 30% H_2O_2, saturation of the aqueous phase with K_2CO_3, extraction with ether, drying (K_2CO_3), and then distilling gave 15.5 g (88%) of *trans*-2-*tert*-butylcyclopentanol: bp 92–94 °C (18 mm); IR (neat) 2.96, 7.18, 7.32 μm; NMR (CCl_4) δ 0.93 (s, 9), 1.60 (m, 7), 2.48 (m, 1, OH), 4.00 (m, 1); MS *m/e* 142.

Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 76.19; H, 12.98.

OM–DM Products from *cis*-3,4-Dimethylcyclopentene. GLC analysis for isomer distribution of the four alcohols arising from OM–DM was accomplished by acetylating (Ac_2O/pyridine) the reaction product. The resulting acetates were analyzed on column D to give four resolvable peaks.

Configurational assignments for the *cis*-3,4-dimethylcyclopentyl acetates were made as follows. Reduction of *cis*-3,4-dimethylcyclopentanone with $LiAlH_4$ gave a reaction product which showed two methyl doublets centered at δ 1.12 and 0.98 of a relative intensity of 4:1, respectively. By analogy to Fuchs' data,[24] the low field doublet must arise from the all-cis isomer. Thus, as is consistent with steric effects, the all-cis isomer predominates in the hydride reduction. This all-cis osmer from the reduction was identical with the 51% component in the OM–DM of *cis*-3,4-dimethylcyclopentene. Similarly, the minor isomer from the reduction was identical with the 39% component in the OM–DM reaction mixture and was thus assigned the *trans*-3,*trans*-4-dimethylcyclopentanol structure.

Configurational assignments for the *cis*-2,3-dimethylcyclopentyl acetates were made as follows. 2,3-Dimethylcyclopentene was hydroborated, oxidized, and acetylated to give a mixture (57.7:42.3) of acetates. A mixture of these acetates and the products from the OM–DM of *cis*-3,4-dimethylcyclopentene showed five peaks on GLC analysis. Only one of the acetates from 2,3-dimethylcyclopentene is possible in the OM–DM of *cis*-3,4-dimethylcyclopentene, namely, the acetate of *trans*-2,*trans*-3-dimethylcyclopentanol. A mixed GLC injection thus established the structure of the 6% component in the OM–DM of *cis*-3,4-dimethylcyclopentene. The fourth peak, 4%, present in the OM–DM mixture was then assigned to the remaining possible acetate structure, namely, *cis*-2,*cis*-3-dimethylcyclopentyl acetate.

OM–DM Products from 2,3-Dimethylcyclopentene. Assignment of configuration for *cis*-1,2-dimethylcyclopentanol followed from its synthesis by hydroboration–oxidation of 1,2-dimethylcyclopentene according to the literature procedure.[31] The other isomer, *trans*-1,2-dimethylcyclopentanol, was also available from another study.[32]

OM–DM Products from *cis*-1,3,4-Trimethylcyclopentene. OM–DM of this olefin gave a 76:24 alcohol mixture by GLC on column A. Structures were determined by NMR in a manner analogous to that used for the assignment of the 3-methylcyclopentanols. A hydroxyl cis to a 3-methyl group deshields those protons, and thus they appear downfield with respect to the methyl protons in the other isomer. The mixture of the trimethylcyclopentanols from the OM–DM shows a smaller methyl doublet (J = 6 Hz) centered at δ 0.83. The minor isomer with the downfield methyl doublet was then assigned the *trans*-1,*trans*-3,*trans*-4-trimethylcyclopentanol[33] structure. The major component with the high field methyl doublet was then assigned to *cis*-1,*cis*-3,*cis*-4-trimethylcyclopentanol.[33]

Registry No.—**1**, 591-47-9; **3**, 591-48-0; **4**, 14072-87-8; **7**, 1759-81-5; **8**, 5581-97-5; **9**, 1120-62-3; **10**, 6189-88-4; **11**, 56039-55-5; **12**, 16491-16-0; **13**, 16491-15-9; *cis*-3-methylcyclohexanol, 5454-79-5; *trans*-3-methylcyclohexanol, 7443-55-2; *cis*-4-methylcyclohexanol, 7731-28-4; *trans*-4-methylcyclohexanol, 7731-29-5; *cis*-2-methylcyclohexanol, 7443-70-1; *trans*-2-methylcyclohexanol, 7443-52-9; *cis*-2-*tert*-butylcyclohexanol, 7214-18-8; *trans*-2-*tert*-butylcyclohexanol, 5448-22-6; *cis*-3-*tert*-butylcyclohexanol, 10488-10-5; *trans*-3-*tert*-butylcyclohexanol, 16201-66-4; *trans*-3-methylcyclopentanol, 5631-24-3; *trans*-3-methylcyclopentanol 5590-95-4; *cis*-3-*tert*-butylcyclopentanol, 5581-95-3; *trans*-3-*tert*-butylcyclopentanol, 5590-97-6; *cis*-2-methylcyclopentanol, 25144-05-2; *trans*-2-methylcyclopentanol, 25144-04-1; *cis*-2-*tert*-butylcyclopentanol, 40557-25-3; *trans*-2-*tert*-butylcyclopentanol, 40557-26-4; *cis*-2,*cis*-3-dimethylcyclopentanol, 69779-88-0; *trans*-2,*trans*-3-dimethylcyclopentanol,

56846-14-1; *trans*-3,*trans*-4-dimethylcyclopentanol, 26704-31-4; *cis*-3,*cis*-4-dimethylcyclopentanol, 26704-30-3; *cis*-1,*cis*-3,*cis*-4-trimethylcyclopentanol, 69745-45-5; *trans*-1,*trans*-3,*trans*-4-trimethylcyclopentanol, 69745-46-6; *cis*-1,2-dimethylcyclopentanol, 16467-04-2; *trans*-1,2-dimethylcyclopentanol, 16467-13-3; *trans*-2-*tert*-butylcyclopentanol tosylate, 69745-47-7; β-*tert*-butyladipic acid, 10347-88-3; 3-*tert*-butylcyclopentanone, 5581-94-2; *cis*-3,4-dimethylcyclopentanone, 19550-72-2; 3-methylcyclohexanone, 591-24-2; 4-methylcyclohexanone, 589-92-4; 2-*tert*-butylcyclohexanone, 1728-46-7; 3-*tert*-butylcyclohexanone, 936-99-2; cyclopentanone, 120-92-3; 1-*tert*-butylcyclopentanol, 69745-48-8; 1-*tert*-butylcyclopentanol *p*-nitrobenzoate ester, 52118-37-3; 1-*tert*-butylcyclopentene, 3419-67-8; 2,3,3-trimethylcyclohexene, 69745-49-9.

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Electrophilic Substitution of 4*H*-Cyclopenta[*def*]phenanthrene. Nitration

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4*H*-Cyclopenta[*def*]phenanthrene gave 1-, 2-, 3-, and 8-nitro isomers by nitration. Also, 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene and cyclopenta[*def*]phenanthren-4-one afforded exclusively 2- and 8-nitro derivatives. The corresponding amines and acetylamines were synthesized.

4*H*-Cyclopenta[*def*]phenanthrene (**1**)[1] (Chart I) is one of the interesting arenes. The active methylene of **1** was observed to possess reactivities similar to those of fluorene in ring expansion reactions.[2] In our previous communication,[3] ozonolysis of the C_8–C_9 bond of **1** has been shown to differ significantly from that of phenanthrene and also that of pyrene.

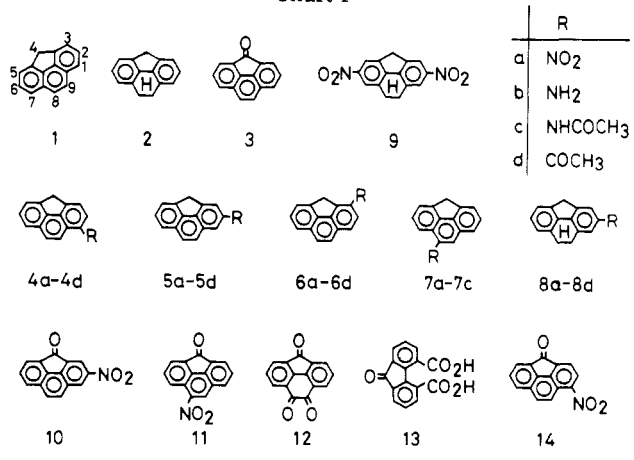
The only examples of electrophilic substitution of **1–3** found were the acetylation of **1**[4] and the succinylation of **2**.[5] The present paper deals with the nitration of **1–3** and shows properties of the related compounds. Some of these may be of interest in view of carcinogenic testing.

The nitration of **1** afforded the 1- (**4a**), 2- (**5a**), 3- (**6a**), and 8-nitro (**7a**) derivatives, as shown in Table I. Nitration of **2** gave 2-nitro compound **8a** in high yield under mild conditions, but under vigorous conditions **2** yielded **5a**, dinitro derivative **9**, and ketone **10**. Nitration of **3** afforded 8-nitro ketone **11**, accompanied by an oxidation product **12**.

The UV spectrum of **8a** exhibits many resemblances to those of 4-nitrobiphenyl[6] and 2-nitrofluorene.[7] The spectra of **4a, 5a, 6a,** and **7a** are similar to those of mononitrophenanthrene.[8]

The structures of **4a, 5a, 6a,** and **8a** were substantiated in connection with the authentic ketones **4d,**[4] **5d,**[9] **6d,**[10] and **8d**[9] via the corresponding acetylamines **4c, 5c, 6c,**[10] and **8c** and amines **4b, 5b, 6b,**[10] and **8b,** according to the method described by Sieglitz and Schidlo.[10] Oxidation of **7a** with manganese dioxide gave ketone **11,** which on treatment with potassium

Chart I



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