of acid-washed C-22 firebrick (40–60 mesh) coated with Ucon Polar substrate were connected in parallel. These columns were heated at 210° under 10 p.s.i. of helium. The detector was maintained at 255° at 250 ma.

A typical chromatogram showed a large leading peak (22 min.) and a trailing minor peak (28 min.). The leading peak showed a trailing shoulder.[18] The first material was collected up to the approximate time that the shoulder appeared. The combined first peak material (26.5 g.) was a mushy solid which showed no evidence of any of the trailing peak material upon rechromatography on a microcolumn. It was dissolved in 26 ml. of absolute ethanol and the solution was chilled to −15° to give 23.1 g. of sticky solid. This solid was recrystallized from 23 ml. of absolute ethanol to give 20.2 g. of solid, m.p. 43–47°, and this product was recrystallized from 25 ml. of ethanol to give 18.9 g. Recrystallization a fourth and fifth time from 30 ml. and 25 ml. of alcohol, respectively, with cooling to 5° afforded 14.4 g. of *trans-anti-trans*-perhydroanthracene (V), m.p. 48.0–49.3°. The material collected from the macro vapor phase column which corresponded to the trailing peak amounted to 6.5 g. It was combined with the corresponding fraction described below.

The process of separation described above was the more satisfactory of the two macro separations and was done after the techniques of collection had been perfected on the first half of the sample. The first portion of the hydrocarbon mixture was put through the Megachrom apparatus equipped with tubes containing Apiezon J. In this run the total first peak material was combined (24.1 g.) and recrystallized from 24 ml. of absolute ethanol, again from 28 ml. of this solvent and a third time from 32 ml. of the same solvent to give 10.9 g. of needles, m.p. 46.0–48.5°. Three further recrystallizations from absolute ethanol afforded 7.4 g. of needles, m.p. 48.2–49.2°. Two final recrystallizations gave 5.2 g. of *trans-anti-trans*-perhydroanthracene (V) m.p. 48.5–49.7°, after being dried for 7 hr. at 25° (15 mm.) and 8 hr. at 25° (1.6 mm.). The solid recovered by concentration of the filtrate from the last recrystallization and the 5.2-g. sample melted over an identical range. A mixture of this material and the *cis-trans* isomer II,[13] m.p. 39–40.5°, liquefied at 25°.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.5; H, 12.4.

The filtrates from the first three recrystallizations of the first peak material from the Apiezon J column were combined, diluted with 300 ml. of water, and this mixture was extracted twice with pentane. The pentane extracts were washed with water, dried over sodium sulfate, and the pentane was removed by warming the solution to a final temperature of 135°. The residual oil, 10.1 g., showed an infrared spectrum in which all bands could be accounted for by the *cis-trans* and the *trans-anti-trans* hydrocarbons with the latter strongly predominating. The 10.1 g. of oil was chilled to 0°, seeded with the *trans-anti-trans* isomer, and left standing at 0° for 6 days. The oil remaining, 2.8 g., was separated by centrifugation and its infrared spectrum examined for evidence of the presence of the *trans-syn-trans* (III) or the *cis-syn-cis* (I) isomers. None was found.

The material corresponding to the second peak from the Apiezon J column amounted to only 0.9 g. due to technical difficulties. This 0.9 g. was combined with the 6.5 g. of corresponding second peak material from the Ucon Polar column described above and this 7.4 g. of solid was recrystallized twice from absolute ethanol to give 5.2 g. of white needles, m.p. 122–123.5°, of *cis-anti-cis*-perhydroanthracene (IV). The infrared spectrum of this material was identical with that of IV prepared earlier in this Laboratory by another method.[4] A mixture melting point of these two samples showed no depression.

The best estimates, of yields should be based on the results from use of the Ucon Polar column for separation. Since the amount of material put on this column is known to be only *approximately* half of the original 90 g. of hydrocarbon, the calculated 21% yield of pure *trans-anti-trans* isomer V and 7% yield of pure *cis-anti-cis* isomer IV are not exact values.

Relative retention times for the five perhydroanthracenes were determined using the Perkin–Elmer Vapor Fractometer under the conditions described earlier. Isomers II, III and V, having relatively short retention times, were each mixed with IV for comparison. Isomer I was then mixed with V. These comparisons showed the relative retention times to be II ≅ III < V < I < IV.

(18) The retention time of this shoulder was too low to correspond to isomer I; its identity was never established.

[CONTRIBUTION NUMBER 1629 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY, NEW HAVEN, CONN.]

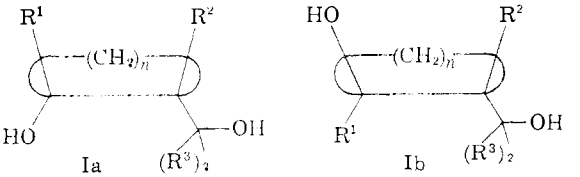
The Cleavage Reaction of 1,3-Diols. IV[1]

BY THOMAS E. MAGGIO[2] AND JAMES ENGLISH, JR.

RECEIVED AUGUST 2, 1960

The syntheses of *cis*- and *trans*-1-phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentanol and *cis*- and *trans*-1-phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol have been accomplished. The influence of the geometry of the 1,3-diol system on the cleavage reactions of these diols has been studied and a mechanism proposed to account for the results.

In a continuation of our studies on the cleavage reactions of 1,3-diols[3] the preparation of di-tertiary-1,3-diols in which the hydroxyl groups are *cis* or *trans* to one another respect to a ring system was undertaken. Although diols of the type desired had previously been prepared,[4–6] in only one case[7]—the isopulegol hydrates—were both *cis* and *trans* isomers known. The isopulegol hydrates, however, do not undergo cleavage as the major reaction on treatment with acid. Because of the known[3] effect of configuration on the nature of the cleavage reaction, it seemed worthwhile to study a pair such as Ia and Ib in which R^1 is aromatic. Aromatic groups are known[8] to increase the amount of the cleavage reaction compared to other acid-catalyzed processes.



Acting on the hypothesis that earlier efforts[3] to obtain both of the isomeric 1,3-diols from the reac-

(1) This work was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 49(638)37.

(2) Du Pont Teaching Fellow 1958–1959; Eastman Kodak Research Fellow 1959–1960.

(3) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2294 (1954).

(4) T. Geissman and V. Tulagin, *ibid.*, **66**, 719 (1944).

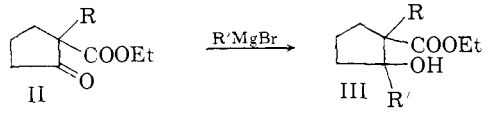
(5) F. V. Brutcher and H. I. Cenci, *J. Org. Chem.*, **21**, 1543 (1956).

(6) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2285 (1954).

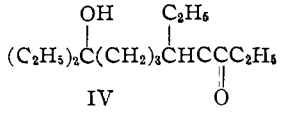
(7) H. E. Zimmerman and J. English, Jr., *ibid.*, **75**, 2367 (1953).

(8) F. V. Brutcher and J. English, Jr., *ibid.*, **74**, 4279 (1952).

tion of organometallics on 2-keto-cyclohexanecarboxylic esters and 2-keto-cyclopentanecarboxylic ester had failed for steric reasons the introduction of larger *R* groups on the α-carbon atom (II) was tried. It was hoped that a mixture of isomers would then result as hindrance to both sides of the



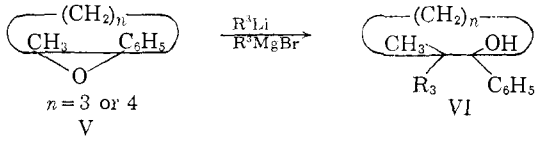
ring carbonyl became more nearly equal. It was found that when R = C_2H_5 (II) reaction with ethylmagnesium bromide gave attack exclusively at the ketonic carbonyl-forming III. At higher temperatures cleavage occurred with production of IV.



The reaction of 2-methyl-2-benzoylcyclopentanone with Grignard reagents also led predominantly to cleavage, although 2-methyl-2-benzoylcyclohexanone with phenylmagnesium bromide yielded a diol Ia (R^1, R^3 = C_6H_5, R^2 = CH_3, n = 4). As in previous work[8] only a single isomer, believed to be *cis* (see below), could be isolated.

By reaction of 1-methyl-2-ketocyclohexanecarboxylic ester and 1-methyl-2-ketocyclopentanecarboxylic ester first with phenylmagnesium bromide (inverse addition) and then, after hydrolysis and isolation of the β-hydroxy ester, with methylmagnesium iodide, pure diols of structure in Ia (R^1 = C_6H_5, R^2, R^3 = CH_3, n = 3 and 4) were readily obtained. Vapor phase chromatography of the hydroxy esters III (R = CH_3, R^1 = C_6H_5) failed to disclose the presence of more than one component and only a single diol Ia (R^1 = C_6H_5, R^2, R^3 = CH_3, n = 3 or 4) could be detected. The reaction of the ring carbonyl with phenyl Grignard reagent appears to be completely stereospecific.

On the assumption that the diols obtained were *cis* (Ia), attempts were made to obtain the *trans* forms by opening the epoxides V with organometallic reagents suitable for eventual conversion, through esters, to carbinol groups.



Epoxides V (n = 3 and n = 4) were prepared by the action of peracids on the corresponding pure olefins (see Exptl.) and treated with lithium phenylacetylide, lithium methylacetylide and *n*-propyllithium under various conditions. The only products isolated in appreciable quantities were derived from rearrangement of the epoxides to ketones prior to reaction with the organometallic reagents. Under most conditions the epoxides remained unchanged.

The route finally developed (Fig. 1) involves epoxidation of the known[9] unsaturated esters VII

(9) M. S. Newman, *J. Am. Chem. Soc.*, **75**, 349 (1953).

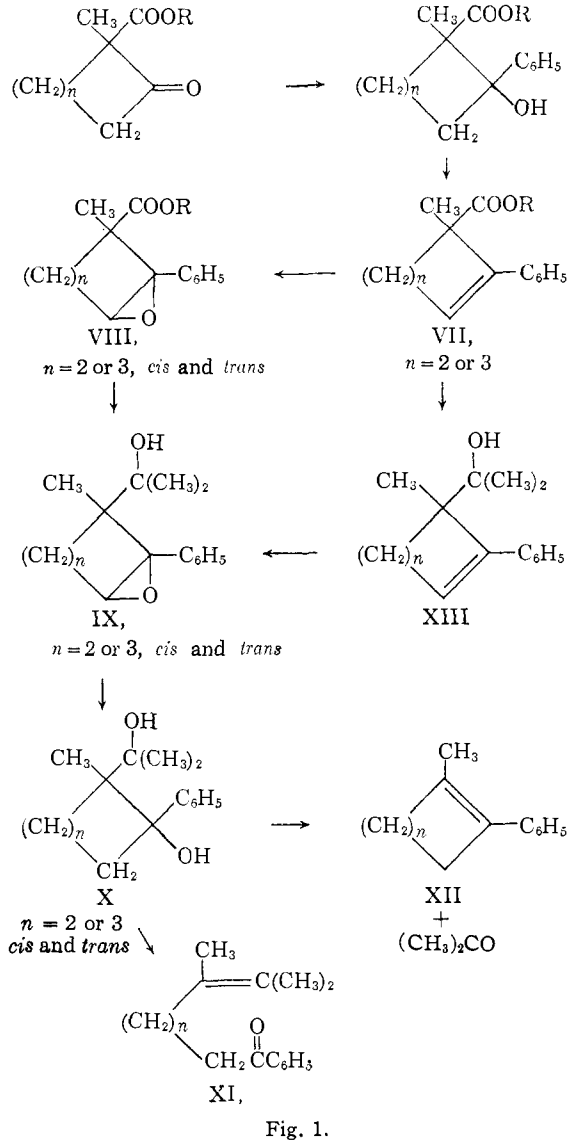


Fig. 1.

(n = 2 and n = 3) to *cis–trans* mixtures of epoxy esters VIII. Little stereoselectivity was observed in these epoxidations: the *trans*-forms predominated, 3:2 (n = 2) and 5:4 (n = 3). In the epoxidation of the corresponding tertiary carbinols XIII at room temperature no stereospecificity was observed: at 0° the *cis* isomer predominated 3:2 (XIII, n = 2).

The epoxy esters were separated by vapor phase chromatography and treated separately with methyllithium to form the *cis*- and *trans*-epoxy alcohols IX (n = 2 and 3).

Lithium aluminum hydride reduction of the separated isomers IX gave crystalline diols X (n = 2 and 3). The alternate route *via* the isomers XIII was less successful due to partial thermal rearrangement of the epoxy alchols IX during separation by vapor phase chromatography. The separation of the diols X by chromatography on alumina was unsuccessful, largely due to cleavage occurring on the absorbent. These diols X, surprisingly, withstood purification by vapor phase chromatography (on a 5 ft. × ¼″ column of de-

tergent, Span, at 160°) although long retention times (several hours) were involved. The greatest difficulty was encountered in the purification of the highly hindered *trans*-diols Ib (n = 3); a major impurity, isolated by vapor chromatography, was the unsaturated alcohol 1-phenyl-2-methyl-2-(2-hydroxyisopropyl)-cyclopentene. This substance appeared during the reduction of the pure epoxide by $LiAlH_4$. Once seed crystals of *trans*-X (n = 2) were obtained, the *cis–trans* mixture could be separated by fractional crystallization, the *trans* form being the more soluble in benzene.

No evidence could be obtained for any 1,2-diols in the reduction mixtures and the attack of hydride on these epoxides apparently proceeded as usual at the least hindered point.[10]

The assignment of configurations to the cyclopentane diol pair X (n = 2) is based on infrared spectra and on the identity of the more readily isolated, *cis*, isomer, m.p. 158°, with the product obtained by reaction of ethyl α-methylcyclopentanonecarboxylate with methylmagnesium iodide. This isomer showed strong hydrogen-bonded hydroxyl absorption at 2.89 μ which did not decrease in relative intensity with dilution in carbon tetrachloride to 2.5×10^{-4} M.[11] An inspection of models shows clearly that only the *cis* isomer can be expected to show internal hydrogen bonding. The more soluble, less easily isolated *trans* isomer, m.p. 98°, on the other hand, shows very little internal hydrogen bonding; the chief OH absorption occurring at 2.79 μ and showing no infrared evidence of intramolecular H-bonding.

In the cyclohexane series the distinction is less clear; again, the more abundant isomer (m.p. 145°) is identical to the product from reaction of methylmagnesium iodide with cyclohexanonecarboxylic ester and is believed to be the *cis* form. Here, however, the *trans* form (m.p. 118°) actually shows a more intense bond at 2.93 μ attributable to intramolecular hydrogen bonding than the *cis* isomer (m.p. 145°). These spectra were also obtained in carbon tetrachloride at concentrations as low as 2.5×10^{-3} M. This can be interpreted by a consideration of the conformational arrangement of the groups; only the *trans* model can have both the ring hydroxyl and the carbinol side chain in equatorial positions which allow sufficient proximity of these two groups for hydrogen bridging interaction to be important. Several attempts to confirm these assignments by formation of cyclic carbonates etc. were unsuccessful due to the unreactivity of the tertiary hydroxyl groups. The solubilities, retention times on vapor phase analysis and melting points in the cyclohexane series parallel those in the cyclopentane series where the infrared evidence seems clear; a similar parallelism in cleavage behavior (see below) lends further support to the assignments.

The acid-catalyzed cleavages of the diols X were carried out in 10% sulfuric acid in boiling ethanol; some of the ethanol was distilled off until no more volatile products (acetone) could be detected in the distillate and the residue examined for other carbonyl products with 2,4-dinitrophenylhydrazine.

(10) R. E. Parker, *Chem. Revs.*, **59**, 737 (1959).
(11) L. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

Table I shows the results: the yields given are based on the amount of pure 2,4-dinitrophenyl hydrazones isolated. Each cleavage was run at least twice and the results in the table were found reproducible within less than 5%; a very careful examination of the reaction products confirmed the low yields of acetone shown for the *cis* isomers.

TABLE I

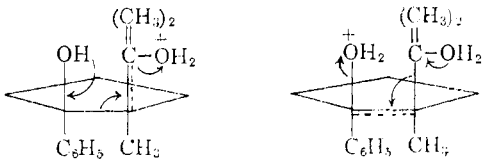
CLEAVAGE OF 1,3 DIOLS

1,3-Diol (n)	Cleavage products, % XI	XII[a]
cis-X (2)	81	7
trans-X (2)	43	33
cis-X (3)	42	5
trans-X (3)	54	43
cis-I (4, R = C_6H_5, R^2 = H, R^3 = CH_3)	55	0

[a] As % acetone.

No evidence for the isomerization of *trans*-I (n = 2) to *cis*-I (n = 2) under cleavage conditions could be obtained. A sample of *trans*-I (n = 2) was heated for a short time (incomplete cleavage) and the spectra of the mixture examined for the characteristic strong 2.89 μ absorption of the *cis* isomer; only the expected peaks of the *trans* form and of cleavage products were observed. The possibility that the acetone isolated from the stable *cis*-I (n = 2, n = 3) arose *via* equilibration to the *trans* form remains, but seems unlikely and of little importance in view of the small yield of acetone from this isomer.

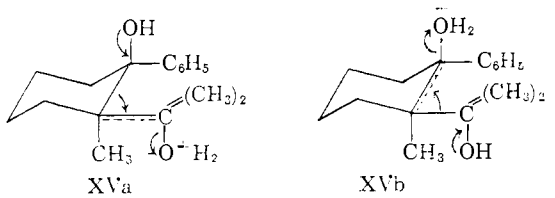
These results can most readily be accommodated on the assumption that the requirements for a planar arrangement involving elimination which is *trans* with the respect to the incipient double bond controls the course of the cleavage. In the case of *cis*-I (n = 2) the two possible cleavage reactions may be diagrammed



XIVa XIVb

Here the incipient double bond (dotted line) resulting from *trans* elimination XIVa (leading to XI) predominates. A consideration of the corresponding *trans* isomer shows that both possible reactions can occur through a *trans* elimination mechanism, and indeed both are observed in nearly equal amounts (Table I).

Again in the cyclohexane series, assuming the most favored conformation for *cis*-X (n = 3), the two possible cleavage reactions may be diagrammed



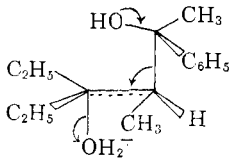
XVa XVb

In the elimination XVa, the double bond results from a more ideal *trans* elimination to form XI

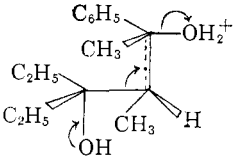
than in XVb; this is in agreement with the observed predominance of cleavage to XI. In the *trans* case (*trans*-X, $n = 3$) both bulky groups cannot be equational at once and either conformation allows a true *trans* elimination—one to give XI the other XII; this again is in agreement with experiment.

Brutcher and English[12] had reported the cleavage of 2-methyl-4-phenyl-2,4-pentanediol (XVI) with $KHSO_4$ to yield acetone and no acetophenone. Since this is an exact open chain analog of our cyclic diols it seemed surprising that, in view of the above results, no other cleavage products were found. The nearly exclusive formation of acetone is presumably due to the ease of formation of a carbonium ion at carbon 4 in the heterogeneous media: in homogeneous solution the relative energies of the two possible carbonium ions may be equalized through solvation. It was in fact found that cleavage in dilute alcoholic sulfuric acid led to about equal amounts of acetone and acetophenone as would be anticipated from the results of cleavage of the *trans* cyclic analogs (*trans*-I).

The steric effects observed by Zimmerman and English in the cleavage of open-chain diastereomeric diols may also be rationalized by the requirement for a *trans* elimination mechanism. Thus a consideration of the two possible conformations of α-2-phenyl-3-methyl-4-ethyl-2,4-hexanediol allowing cleaving by a *trans* elimination may be shown, XVIIa and b



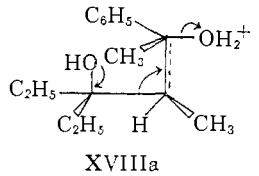
XVIIa



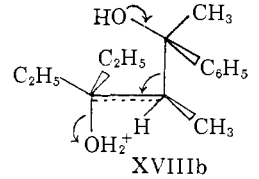
XVIIb

Here it can be seen that XVIIb requires an eclipsing of the phenyl and methyl groups (and also the ethyl groups on C_4 and the groups on C_2), while the hindrance in XVIIa appears less; hence the observed cleavage of this isomer *via* XVIIa to give predominantly acetophenone can be understood.

Likewise the conformation XVIIIa and b of the β-isomer required for *trans* elimination reactions involve more steric interaction in one case (XVIIIb) than the other (XVIIIa) and this is



XVIIIa



XVIIIb

again in accord with the observed formation of diethyl ketone as the chief ketone cleavage product in this case.

Acknowledgment.—The authors are indebted to Professor Harold Conroy for helpful suggestions and discussions as to the proposed reaction mechanism.

(12) F. V. Brutcher and J. English, Jr., *J. Am. Chem. Soc.*, **74**, 4279 (1952).

Experimental[13]

Reactions of 2-Ethyl-2-carbethoxycyclopentanone with Organometallic Reagents. A. Ethylmagnesium Bromide.—A solution of 2-ethyl-2-carbethoxycyclopentanone, (18.4 g., 0.1 mole) in 20 ml. of ether was added to 0.5 mole of ethylmagnesium bromide in 200 ml. of ether. The reaction mixture was poured on ice and dilute hydrochloric acid, the organic layer separated, and the aqueous layer extracted with ether. The combined extracts were washed with dilute sodium bicarbonate and then with water until neutral. Distillation yielded 14 g. of a clear, mobile oil, b.p. 84° (0.8 mm.) which appears to be 1,2-diethyl-2-carbethoxycyclopentanol. The structural assignment is based on the presence of hydroxyl (2.78 μ) and ester (5.83 μ) absorption and the absence of cyclopentanonecarbonyl (5.75 μ) in the infrared. *Anal.* Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.70; H, 10.75.

Essentially the same reaction was run using di-*n*-butyl ether as the solvent. Infrared analysis of the product showed it to be a carbonyl compound identical to that produced with ethyllithium.

B. Ethyllithium.—The reaction of 2-ethyl-2-carbethoxycyclopentanone (0.05 mole) with excess ethyllithium in ether (reflux, 24 hours) yielded 5 g. of a clear oil which was found to be a non-saponifiable compound, b.p. 90–93° (0.5 mm.). The compound presumably is 3,7-diethyl-8-ketodecanol-3, based on hydroxyl (2.79 μ) and ketonic (5.85 mμ) absorption in the infrared. *Anal.* Calcd. for $C_{14}H_{28}O_2$: C, 73.68; H, 12.36. Found: C, 73.58; H, 11.98.

C. Phenylmagnesium Bromide.—The reaction of 2-ethyl-2-carbethoxycyclopentanone with excess phenylmagnesium bromide in ether (24 hours at room temperature) yielded principally a viscous oil, b.p. 140–142° (1 mm.), a hydroxy ester, which was assigned the structure 1-phenyl-2-ethyl-2-carbethoxycyclopentanol based on the close resemblance of its infrared spectrum to that of 1-phenyl-2-methyl-2-carbethoxycyclopentanol. *Anal.* Calcd. for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.54; H, 8.49.

Reaction of 2-Methyl-2-carbethoxycyclopentanone with Phenyllithium.—To 100 ml. of a stirred solution of 2 *N* phenyllithium in ether, was added, dropwise, 2-methyl-2-carbethoxycyclopentanone (8.5 g., 0.05 mole) in 20 ml. of ether. The stirred reaction was heated under reflux for 5 hours and then poured onto a mixture of ice–ammonium chloride solution. The ether layer was separated, the aqueous layer extracted twice with ether and the combined extracts were washed with water until neutral and then dried over sodium sulfate. The infrared spectrum of the concentrated reaction products showed the presence of hydroxyl and of strong carbonyl absorption at 5.93 μ, indicative of a benzoyl group.

The crude oil was treated with another 0.2 mole of phenyllithium and on workup 13.1 g. of a white solid was isolated, m.p. 153–154°. This was shown to be 1,1,6,6-tetraphenyl-2-methylhexanediol-1,6 by comparison with an authentic sample; m.p. authentic sample 153.5–155°, mixed m.p. 153°.

2-Methyl-2-benzoylcyclopentanone.—To a solution of 2-benzoylcyclopentanone (7 g., 0.034 mole) in 10 ml. of ethanol was added 1.3 g. of sodium hydroxide in 10 ml. of water while the mixture was stirred vigorously on an ice-bath. To the homogeneous mixture was added methyl iodide (5.7 g., 0.04 mole, 20% excess). The mixture was stirred for 6 hours at 60°, whereupon ethyl alcohol was distilled from the mixture and the residue separated into two layers. Extraction of the aqueous layer with benzene and subsequent washing of the combined organic layers with 5% potassium carbonate to remove any non-methylated diketone was followed by distillation of the product.

2-Methyl-2-benzoyl cyclopentanone, 3.8 g., was collected, b.p. 142° (1.2 mm.), m.p. 53.5–54.5°. The product gave a negative ferric chloride test. *Anal.* Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.54; H, 7.17.

Reaction of 2-Methyl-2-benzoylcyclopentanone with Phenylmagnesium Bromide.—2-Methyl-2-benzoylcyclopentanone (5 g., 0.025 mole) in 10 ml. of benzene was added to a stirred solution of phenylmagnesium bromide (0.1 mole)

(13) All vapor phase chromatography was carried out on an Aerograph, with columns purchased from the manufacturer (Wilkens Instrument and Research Co., Walnut Creek, Calif.).

in 30 ml. of benzene. The reaction mixture was heated under reflux overnight and then poured onto ice–ammonium chloride solution. After working up in the usual way the product showed benzoylcarbonyl absorption (5.93 μ) in the infrared. The crude product was dissolved in 20 ml. of benzene and again added to 0.1 mole of phenylmagnesium bromide. After refluxing overnight and working up a white crystalline solid was isolated weighing 4.5 g., m.p. 157°. The product was shown to be 1,1,6,6-tetraphenyl-2-methylhexanediol-1,6 (no depression of melting point when mixed with an authentic sample).

1-Methyl-2-phenylcyclopentene.—2-Methylcyclopentanone (40 g., 0.42 mole) was added to 0.5 mole of phenylmagnesium bromide in 100 ml. of ether and the reaction mixture was heated under reflux overnight. The reaction mixture was poured onto a mixture of ice–HCl and extracted with ether. The concentrated ether extracts were stirred with an equal volume of 90% formic acid and heated under reflux for 4 hours. The reaction mixture was poured onto ice and extracted with ether. The ether extracts were washed with 5% sodium bicarbonate solution and then with water till neutral and finally dried over magnesium sulfate. Distillation yielded 1-methyl-2-phenylcyclopentene, 35.1 g., b.p. 128° (30 mm.).

Examination of the distilled product using v.p.c. showed it to be at least 90% one isomer. The structure of the main product was determined by its n.m.r. spectrum which showed it to be the tetrasubstituted isomer and which confirmed the isomer distribution ratio obtained by v.p.c.

1-Methyl-2-phenylcyclopentene Oxide.—1-Methyl-2-phenylcyclopentene (15.8 g., 0.1 mole) was mixed with 200 ml. of 0.72 *N* perphthalic acid in ether and allowed to stand at 5° overnight. Precipitated phthalic acid was removed by filtration and the filtrate was extracted with 5% sodium bicarbonate solution and then washed with water until it was neutral. On distillation 1-methyl-2-phenylcyclopentene oxide, 13.7 g., b.p. 85° (1.5 mm.), was collected, $n^{23}D$ 1.5309. *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.39; H, 8.02.

Reaction of Methyl-2-phenylcyclopentene Oxide with Vinylmagnesium Bromide.—To 100 ml. of 1.13 *M* vinylmagnesium bromide in tetrahydrofuran was added 1-methyl-2-phenylcyclopentene oxide (8 g., 0.045 mole) and the stirred mixture was heated under reflux for 24 hours. The reaction mixture was poured onto a mixture of ice–ammonium chloride solution and extracted with ether. The ether extracts were combined, dried, and concentrated *in vacuo*. Distillation yielded two fractions. The first fraction (2.2 g., b.p. 90–100° (1.5 mm.)) consisted principally of starting epoxide with a small amount of a carbonyl compound absorbing at 5.75 μ. The second fraction (2.4 g., b.p. 105–110° (1.5 mm.)) was a hydroxy compound which was shown to be 1-vinyl-2-methyl-2-methyl-2-phenylcyclopentanol. *Anal.* Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.41; H, 9.29.

The product isolated above (2.4 g.) was stirred with $KMnO_4$ in acetone–water for 24 hours at room temperature. Precipitated manganese dioxide was removed by filtration and the aqueous solution was treated with potassium bisulfite to destroy the remaining permanganate. On acidification and extraction with ether 1.2 g. of a clear oil was obtained and shown to be 2-methyl-2-phenylcyclopentanone by conversion to a solid semicarbazone, m.p. 190–191°, reported[14] 191–191.4°. *Anal.* Calcd. for $C_{13}H_{17}O$: C, 67.50; H, 7.41. Found: C, 67.53; H, 7.22.

1-Methyl-2-phenylcyclohexene.—2-Phenylcyclohexanone (0.45 mole) was treated with methylmagnesium iodide prepared from 0.7 mole of magnesium and 0.7 mole of methyl iodide in 150 ml. of ether. The product was refluxed with an equal volume of 90 % formic acid for 3 hours and worked up exactly as the cyclopentene analog. Distillation yielded 1-methyl-2-phenylcyclohexene, 30 g., b.p. 82° (1.5 mm.), n^{23} 1.5469. Vapor phase chromatography (silicon packing, 1/4'' dia., 5' stainless steel column at 180°) indicates that a mixture of isomers is produced; n.m.r. spectrum of the chromatographed products demonstrated that the isomer mixture consists of 2.5 parts, 1-methyl-2-phenylcyclohexene to 1 part 5-methyl-1-phenylcyclohexene.

1-Methyl-2-phenylcyclohexene Oxide.—The olefin mixture produced in the preceding experiment (5.4 g., 0.033 mole) was added to 75 ml. of 0.75 *N* monoperphthalic acid in ether. The mixture was stirred on in ice-bath for 4 hours, then at room temperature for 24 hours. After this, phthalic acid was removed by filtration and the ether solution extracted with 5% sodium bicarbonate solution and washed with water until the washings were no longer basic. Concentration of the dried ether solution and subsequent distillation yielded 1-methyl-2-phenylcyclohexene oxide, 3.4 g., b.p. 93° (1.5 mm.), n^{23} 1.5270. *Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.88; H, 8.45.

N.m.r. analysis of the epoxide showed no evidence of a split methyl peak indicating that the epoxide is pure 1-methyl-2-phenylcyclohexene oxide. The corresponding 4-methyl-1-phenylcyclohexene oxide presumably was not isolated. This could be due either to its slower rate of information or its destruction during distillation. Both of these possibilities are suggested in view of the difficulties observed in attempting to produce analogous tertiary-secondary epoxy compounds.

1-Phenyl-5-methyl-5(α-hydroxyisopropyl)-cyclopentene.—1-Phenyl-5-carbethoxy-5-methylcyclopentene[15] 12 g., (56 mmoles) in 10 ml. of dry ether was added dropwise and with stirring to methylmagnesium iodide, 0.14 mole, in 20 ml. of ether. The stirred reaction mixture was heated under reflux for 5 hours and poured onto a mixture of ice-saturated ammonium chloride solution. The ether layer was separated and the aqueous layer was extracted three times with 20-ml. portions of ether. The combined ether extracts were washed with water (neutral to *p*H paper) and dried over sodium sulfate. Ether was removed at reduced pressure and subsequent distillation yielded 9 g. of 1-phenyl-5-methyl-5-(α-hydroxyisopropyl)-cyclopentene, b.p. 105–107° (0.5 mm.). An analytical sample was prepared by v.p.c. on a 1/2'' dia. 5-ft. detergent column at 180°. *Anal.* Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.48; H, 9.55.

Ethyl 1-Methyl-2-phenylcyclohexene-2-carboxylate.—Ethyl 2-hydroxy-2-phenyl-1-methylcyclohexanecarboxylate 6 g., prepared according to Newman,[4] and fused potassium bisulfate (3 g.) was heated at 150° in an oil-bath for 1 hour. Direct distillation of the reaction mixture yielded ethyl 1-methyl-2-phenylcyclohexene-2-carboxylate, 5.3 g., b.p. 110° (0.05 mm.), n^{24} 1.5288. *Anal.* Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.77; H, 8.09.

Ethyl *cis*- and *trans*-1-Methyl-2-phenyl-2-epoxycyclopentanecarboxylate.—A mixture of 12.3 g. (0.05 mole) of ethyl 1-methyl-2-phenylcyclopent-2-enecarboxylate and 45 ml. of 1.6 *N* monoperphthalic acid in ether was stirred at room temperature for 24 hours during which time an equivalent of peracid was consumed. The precipitated phthalic acid was removed by filtration and the ether solution was washed with saturated aqueous sodium bicarbonate solution until the washings remained basic and then with water until the washings were neutral to *p*H paper. The ether extracts were dried over sodium sulfate and then concentrated at reduced pressure to yield 10 g. of epoxycyclopentanecarboxylate.

The isomeric mixture was resolved using vapor phase chromatography on a 1/2" dia. 5 ft., detergent-packed column at 160°. The isomer ratio was found to be 3 parts *trans* to 2 parts *cis*. Configurational assignments are based on subsequent conversion of the *cis*-epoxide to the *cis*-diol (*cf.* below). The separated isomers were analyzed directly.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: (1) ethyl 1-methyl-*trans*-2-phenyl-2-epoxycyclopentanecarboxylate: C, 73.32; H, 7.49. (2) Ethyl 1-methyl-*cis*-2-phenyl-2-epoxycyclopentane-carboxylate: C, 73.22; H, 7.42.

Ethyl *cis*- and *trans*-1-Methyl-2-phenyl-2-epoxycyclohexanecarboxylate.—The isomeric mixture of epoxides (8 g.) was separated using v.p.c. on a 1/2" dia. 5-ft. detergent-packed column at 160°. The isomer ratio was found to be approximately 4 parts *cis* to 5 parts *trans*. Configurational assignments are based on subsequent conversion of the *cis*-epoxide to the *cis*-diol, etc. (*cf.* below).

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.32; H, 7.74. Found ethyl 1-methyl-2-phenyl-2-epoxycyclohexanecarboxylate: *trans* isomer: C, 73.50; H, 7.94. *cis* isomer: C, 73.43; H, 7.90.

***cis* and *trans*-1-Phenyl-5-methyl-5-(α-hydroxyisopropyl)-cyclopentene Oxide. A. *cis* Isomer.**—To a solution of 1.5

(14) M. S. Newman and M. D. Farbman, *J. Am. Chem. Soc.*, **66**, 1550 (1944).

(15) M. S. Newman, *ibid.*, **75**, 349 (1953).

g. (6.1 mmoles) of ethyl 1-methyl-*cis*-2-phenyl-2-epoxycyclopentanecarboxylate in 3 ml. of dry ether was added, dropwise with stirring, 30 ml. of 0.7 *M* methyllithium in ether. The reaction mixture was stirred at room temperature for 18 hours and then poured onto a mixture of ice–ammonium chloride. The ether layer was separated and the aqueous layer extracted several times with ether. The combined etheral extracts were washed with water till neutral (*p*H paper). The ether solution was dried over sodium sulfate and then concentrated at reduced pressure to yield 1.1 g. of *cis*-1-phenyl-5-methyl-5-(α-hydroxyisopropyl)-cyclopentene oxide. Infrared showed the absence of any absorption in the carbonyl region and presence of hydroxyl absorption in the 2.7–2.9 μ region. Attempts to purify a sample for analysis by v.p.c. were unsuccessful (probably because of dehydration and rearrangement on the column). The compound was not further purified but reduced directly with $LiAlH_4$.

B. *trans* Isomer.—Essentially the same procedure as that employed for the *cis* isomer was used to convert the *trans*-epoxy ester to the *trans*-epoxy alcohol. Again attempts to prepare an analytical sample by v.p.c. proved fruitless and the compound was reduced with $LiAlH_4$ without further purification.

cis- and *trans*-1-Phenyl-6-methyl-6-(α-hydroxyisopropyl)-cyclohexene Oxide. A. *cis* Isomer.—A solution of 1.5 g. (6 mmoles) of ethyl 1-methyl-*cis*-2-phenyl-2-epoxycyclohexanecarboxylate in 3 ml. of dry ether was treated with methyllithium in the same way. The reaction product weighed 1 g. after concentration *in vacuo*. Infrared analysis showed presence of hydroxyl and absence of carbonyl absorption. Attempts to purify an analytical sample by v.p.c. at 160° were unsuccessful due to rearrangement on the column to carbonyl compounds (bands at 5.85 and 5.95 μ). *cis*-1-Phenyl-6-methyl-6-(α-hydroxyisopropyl)-cyclohexene oxide was reduced directly without further purification.

B. *trans* Isomer.—Essentially the same procedure was used to convert the *trans*-epoxy ester to the *trans*-epoxy alcohol. The reaction product, as above, was reduced directly without further purification.

cis-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentanol. Method A. *Via* Grignard Reaction.—1-Phenyl-2-methyl-2-carbethoxycyclopentanol (12.4 g. 0.05 mole) in 10 ml. of dry ether was added dropwise and with stirring to the Grignard reagent prepared from the reaction of magnesium (4.8 g., 0.2 mole) with methyl iodide (28 g., 0.2 mole) in 40 ml. of ether. The stirred reaction mixture was heated under reflux for 5 hours and then poured on a mixture of ice–ammonium chloride. The ether layer was separated and the aqueous layer extracted with several portions of ether. The combined ether extracts were washed with water till neutral and dried over sodium sulfate. A white crystalline solid separated on concentrating the ether solution. Filtration of the solid and recrystallization from benzene yielded 3.3 g. of *cis*-1-phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentanol, m.p. 157.5–158°. *Anal.* Calcd. for $C_{15}H_{22}O_2$: C, 77.05; H, 9.41. Found: C, 77.14; H, 9.61.

Method B: *Via* Reduction of Epoxy Alcohol.—*cis*-1-Phenyl-5-methyl-5-(α-hydroxyisopropyl)-cyclopentene oxide (1.1 g., 6 mmoles) in 5 ml. of ether was added dropwise and with stirring to suspension of $LiAlH_4$ (1 g., 25 m moles) in 30 ml. of ether. The stirred mixture was heated under reflux for 7 hours and then excess ethyl acetate was added to decompose any unreacted $LiAlH_4$. The mixture was poured on ice–ammonium chloride solution and the ether layer separated. The aqueous layer was extracted with ether, the combined, washed ether extracts dried over sodium sulfate and then concentrated at reduced pressure. A white crystalline solid separated which after filtration and recrystallization weighed 700 mg. and melted at 157°. The infrared spectrum was identical to that of the diol prepared by method A and a mixed melting point determination with the latter showed no depression (156–157°).

Determination of Infrared Spectra at High Dilution.—The method of Kuhn was employed to study the effect of dilution on hydroxyl absorption.[11]

Dilute solutions of the diol in carbon tetrachloride were examined in the infrared over the range of 2.5–3.5 μ. A 2-cm. cell was used for 3 concentrations of diol, $2.5 \times 10^{-3}M$, and $1.25 \times 10^{-3}M$, and $2.5 \times 10^{-4}M$.

trans-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentanol.—*trans*-1-Phenyl-5-methyl-5-(α-hydroxyisopropyl)-cyclopentene oxide (1 g., 5.5 mmoles) in 5 ml. of ether was added dropwise and with stirring to a suspension of $LiAlH_4$ (1 g., 25 mmoles) in 30 ml. of ether. The stirred mixture was heated under reflux for 7 hours and then excess ethyl acetate was added to decompose unreacted $LiAlH_4$. The mixture was treated just as the corresponding *cis* isomer; however, on concentration of the dried ether extracts no solid separated. The reaction product was then chromatographed using v.p.c. ($1/2''$ dia. 5' detergent column at 160°) and found to consist of two components. The first, apparently the major product of the hydride reduction, was an unsaturated alcohol whose infrared spectrum is identical with that of 1-phenyl-4-methyl-4-(α-hydroxyisopropyl)-cyclopentanol. The second, a white solid, was *trans*-1-phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentanol which when recrystallized from heptane melted at 97.5–98° and weighed 100 mg. *Anal.* Calcd. for $C_{15}H_{22}O_2$: C, 77.05; H, 9.41. Found: C, 77.45; H, 9.55.

The infrared spectrum of this isomer is very similar to that of the *cis* (m.p. 158°) isomer showing differences in the "fingerprint" region and showing absence of the very strong intramolecular hydrogen bonded peak present at 2.89 μ in the *cis* isomer.

Once "seed" crystals were obtained it was possible to reduce a mixture of the isomeric *cis*- and *trans*-1-phenyl-4-methyl-4-(α-hydroxyisopropyl)-cyclopentene oxides (prepared by monoperphthalic acid epoxidation of the olefinic alcohol) without first separating the *cis*- and *trans*-epoxides. The 158° *cis*-diol separated from the mixture, usually without seeding, and on filtering off the 158° melting solid and seeding the concentrated filtrates with a little of the 98° diol the *trans* isomer crystallized leaving the unsaturated alcohol in solution.

1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentene (15 g.) was treated with 20% excess monoperphthalic acid in ether to yield 10 g. of mixed *cis*- and *trans*-epoxides. The epoxide ratio was shown to be approximately a 50–50 mixture of the two isomers by v.p.c. Reduction with a fourfold excess of $LiAlH_4$ and usual workup yielded 8 g. of a viscous oil. On standing, 3.5 g. of a crystalline solid separated and was found to be essentially pure 158° isomer (mixed m.p.). The mother liquors were then "seeded" with a little 98° isomer and on standing overnight 400 mg. of the *trans* isomer crystallized. Infrared investigation of the residual oil showed it to be chiefly 1-phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentene, demonstrating that its presence is not attributable to dehydration on the hot v.p.c. column; v.p.c. analysis of the starting epoxide mixture showed it contained no 1-phenyl-4-methyl-4-(α-hydroxyisopropyl)-cyclopentene.

cis-1-Phenyl-2-methyl-2(α-hydroxyisopropyl)-cyclohexanol. Method A. *Via* Grignard Reaction.—1-Phenyl-2-methyl-2-carbethoxycyclohexanol (2 g., 8.5 mmoles) in 2 ml. of ether was added dropwise to a solution of 0.1 mole of methylmagnesium iodide in 30 ml. of ether and the stirred reaction mixture was heated under reflux for 24 hours and then poured onto a mixture of ice–ammonium chloride solution. The ether layer was separated and the aqueous layer extracted with several portions of ether. The combined ether extracts were washed with water until neutral and dried over sodium sulfate. A dark oil remained after concentration of the ether layer *in vacuo;* this crystallized after seeding with a crystal obtained from the synthesis of the same compound by method B (see below). *cis*-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol (0.2] g.) recrystallized from benzene–heptane melted at 145–147°

Method B. *Via* Reduction of the Epoxy Alcohol.—*cis*-1-Phenyl-6-methyl-6-(α-hydroxyisopropyl)-cyclohexene oxide (1. g., 5 mmoles) in 3 ml. of ether was added dropwise to a stirred suspension of $LiAlH_4$ (1 g., 25 mmoles) in 30 ml. of ether. The stirred mixture was heated under reflux for 7 hours and then excess ethyl acetate was added to decompose any unreacted $LiAlH_4$. The mixture was poured on ice–ammonium chloride solution and extracted with ether. The washed ether extracts were dried over sodium sulfate and concentrated *in vacuo*. No solid separated from the concentrated extracts even after standing for several days. Seed crystals were obtained by vapor phase chromatography of a small portion of the reaction product and used to seed the oil. A white crystalline solid separated and after

recrystallization from benzene–heptane weighed 150 mg., m.p. 146–147.5°. (The reaction product obtained in A, above, was treated with a seed obtained by this procedure and the solid diol precipitated as described.) The infrared spectra of the products obtained by both method A and method B are superimposable and a mixed melting point determination of the two solids showed no depression (145–147°). *Anal.* Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.27; H, 9.70.

trans-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol.—*trans*-1-Phenyl-6-methyl-6-(α-hydroxyisopropyl)-cyclohexene oxide (1 g., 5 mmoles) was reduced with $LiAlH_4$ (1 g., 25 mmoles) using exactly the same procedure as that used for the *cis* isomer described in the previous experiment (method B). Again it was necessary to obtain seed crystals by vapor phase chromatography. Seeding the oily product yielded *trans*-1-phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol, 150 mg. on recrystallization from heptane, m.p. 118–119.5°. *Anal.* Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.30; H, 9.75.

Cleavage Study: *cis*-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentanol.—The *cis* isomer (100 mg., 0.427 mmole) placed in a 5-ml. semi-micro distilling apparatus; 3 ml. of 10% sulfuric acid in ethanol was added to the flask, the flask was then warmed in an oil-bath and 2 ml. of ethanol was distilled through a water condenser into a receiver which was surrounded by a brine–ice mixture. Heating was discontinued and the still-pot was allowed to cool to room temperature. The contents of the receiver were transferred to a test-tube and 0.4 mmole of dinitrophenylhydrazine was added. The mixture was acidified with several drops of concd. H_2SO_4 and allowed to stand for several hours during which time a precipitate of acetone 2,4-dinitrophenylhydrazone formed. After drying *in vacuo* the hydrazone melted at 125–126° (rept. 126°) and weighed 7.5 mg. (.0293 mmole) corresponding to 6.9% cleavage to give acetone.

The still-pot residue was diluted with 2 ml. of ethanol, and transferred to a test-tube containing 0.4 mmole of 2,4-dinitrophenylhydrazine. After warming on a steam-bath to effect solution, a fluffy yellow precipitate formed in the test-tube and the hot mixture was allowed to cool to room temperature. After drying *in vacuo*, the precipitate weighed 143.5 mg. (0.347 mmole) and melted over a wide range, 138–148°. On recrystallization, the hydrazone weighed 129 mg. (90% recovered) and melted sharply at 147–148°. This corresponds to 81.4% cleavage to 2,3-dimethyl-6-benzoylhexene-2.

A sample of the 2,3-dimethyl-6-benzoylhexene-2 obtained in a larger run was purified by v.p.c. on a 1/2" detergent column sent for analysis. *Anal.* Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.61; H, 9.34.

The 2,4-dinitrophenylhydrazone melted at 149–150° and its m.p. was not depressed when mixed with the 147–148° melting compound obtained above. *Anal.* Calcd. for $C_{21}H_{24}N_4O_4$: C, 63.63; H, 6.06. Found: C, 63.51; H, 5.81.

Cleavage Study: *trans*-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclopentanol.—The *trans* isomer (100 mg., 0.427 mmole) was treated exactly as the corresponding *cis* isomer; 36.5 mg. (0.143 mmole) of acetone 2,4-dinitrophenylhydrazone was isolated, m.p. 126°. This corresponds to 33.5% cleavage to yield acetone. 2,3-Dimethyl-6-benzoylhexene-2 2,4-dinitrophenylhydrazone (76.8 mg., 0.186 mmole) was isolated, m.p. 146–148°. This corresponds to 43.5% cleavage to yield the benzoyl compound.

Cleavage Study: *cis*-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol.—Using the same procedure as with the cyclopentane analog there was obtained from 100 mg. of diol 5.2 mg. of acetone 2,4-dinitrophenylhydrazone, m.p. 118–123°. The yield of once-recrystallized material, m.p. 126°, corresponds to less than 5% of theory. From the non-volatile portion there was isolated 90 mg. of the 2,4-dinitrophenylhydrazone of 2,3-dimethyl-7-benzoyl-2-heptene, m.p. 158° dec. *Anal.* Calcd. for $C_{22}H_{26}O_4N_4$: C, 64.37; H, 6.39. Found: C, 64.08; H, 6.07.

Cleavage Study: *trans*-1-Phenyl-2-methyl-2-(α-hydroxyisopropyl)-cyclohexanol.—The *trans* isomer (100 mg., 0.404 mmole) was treated exactly as the corresponding *cis* isomer; 41.5 mg. (0.173 mmole) of acetone 2,4-dinitrophenylhydrazone was isolated m.p. 125–126°. This corresponds to 42.8% cleavage to yield acetone. 2,3-Dimethyl-7-benzoylheptene-2,2,4-dinitrophenylhydrazone (71.0 mg., 0.174 mmole) was isolated, m.p. 155°. This corresponds to 43% cleavage to yield the benzoyl compound.

Cleavage Study: 2-Phenyl-4-methyl-2,4-pentanediol.—A sample (100 mg.) of this diol prepared by Brutcher[5] was cleaved exactly as described above for the cyclic analog. There was isolated 65.9 mg. (49%) of acetone-2,4-dinitrophenylhydrazone, m.p. 125°, and 76.1 mg. (46%) of acetophenone 2,4-dinitrophenylhydrazone, m.p. 242°. No depression was observed on mixed m.p. with authentic acetophenone 2,4-dinitrophenylhydrazone.

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Epoxyketones. IV.[1] Stereostructure, Absorption Spectra and Three-ring Carbonyl Hyperconjugation

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RECEIVED FEBRUARY 16, 1960

trans-4'-Phenylchalcone oxide and 4-phenylacrylophenone oxide were each made by two different methods. The epoxide ring in several arylaroylethylene oxides was found to be resistant to cleavage by an amine and a stereochemical interpretation of the results from this type of reaction with *trans*-chalcone oxide is given to help in assigning configurations to amine addition products of α-bromochalcone. A detailed examination of spectroscopic data previously gathered and of new measurements indicates: (1) in the solid ground state aroylethylene oxides and *cis*- and *trans*-aryl aroyl ethylene oxides have a non-conjugated *gauche* conformation; (2) in CCl_4 solution the aroyl and *trans*-aryl aroyl ethylene oxides exist as mixtures of *gauche* and *cisoid* (conjugated) conformers; (3) the ethylene oxide ring transmits an electrical effect of a β-phenyl group, but *p*-substituents in the β-phenyl group do not extend the conjugation; (4) α-methoxy-4-phenylacetophenone shows conformational isomerism in CCl_4 solution which is similar to that which has been demonstrated for α-halo- and α-aminoketones.

Ultraviolet absorption spectra studies with *cis* and *trans* pairs of aryl aroyl ethylene oxides[1-3] have given results which have been discussed[1,4] in terms of three-ring carbonyl hyperconjugation. Because it was thought that the ethylene oxide ring would not be able to support a partial positive charge as effectively as the ethylenimine ring, it was suggested[1,5] that the infrared spectra of epoxy ketones might fail to show significant electrical interaction between the three-ring and the carbonyl group in the ground state as had been found to be the case for the ethylenimine ring.[6]

(1) For paper III see, N. H. Cromwell and R. A. Setterquist, THIS JOURNAL, **76**, 5752 (1954).

(2) H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955).

(3) C. L. Stevens, *et al.*, *J. Org. Chem.*, **19**, 522, 533 (1954).

(4) N. H. Cromwell, *Rec. Chem. Prog.*, **19**, 214 (1958).

(5) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952).

(6) See N. H. Cromwell, R. E. Bambury and J. L. Adelfang, THIS JOURNAL, **82**, 4241 (1960), and previous papers in the series.