end of this period 60 ml. of water and 15 ml. of dilute hydrochloric acid were added. A cloudy solution resulted but no crystalline precipitate formed. After standing overnight, the now clear solution was extracted first with chloroform and then ether. Evaporation of the ether layer gave about 0.01 g. of long needles, which melted with decomposition at 173–182° with sublimation above 120°. The chloroform layer was evaporated to a red oil. Extraction of this red oil with ether gave, upon evaporation, a mixture of oil and crystals. This mixture was filtered and washed with a small amount of chloroform to give 0.25 g. of 1,1-cyclopentanedicarboxylic acid, m.p. 185–192° dec. (lit., m.p. 184–185° dec.,[18] m.p. 190° dec.[17]). The total yield of the diacid was 0.26 g. (15%).

Benzylidene 1,1-cyclopentanedicarboxylate. To a solution of 1.4 g. (7.3 mmoles) of benzylidene malonate and 1.57 g. (7.3 mmoles) of 1,4-dibromobutane in 50 ml. of dimethylformamide was added 0.39 g. (7.3 mmoles) of powdered sodium methoxide. After 53 hr. at room temperature, the clear yellow solution was poured into cold water. Precipitation resulted. Filtration gave 0.1 g. (6%) of benzylidene 1,1-cyclopentanedicarboxylate, m.p. 176–178° with sublimation above 120°. The product was insoluble in 5% sodium bicarbonate solution. Recrystallization from acetone-water and then from ethyl acetate gave the pure product, m.p. 177–178° in a capillary tube.

(18) E. Haworth and W. H. Perkin, Jr., *J. Chem. Soc.*, 86 (1894).

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.96; H, 5.71.

Unsuccessful attempts to prepare isopropylidene 1,1-cyclobutanedicarboxylate. A. *With sodium methoxide in dimethylformamide.* To a mixture of 7.2 g. (0.05 mole) of isopropylidene malonate and 5.4 g. (0.10 mole) of sodium methoxide in 60 ml. of dimethylformamide at room temperature was added 10.1 g. (0.05 mole) of 1,3-dibromopropane. Heat was evolved and the mixture was cooled. After stirring for 11 hr., the mixture was allowed to stand for 48 hr. The addition of water caused no precipitation. Evaporation of ether and chloroform extracts gave no solid products. Concentration of the remaining water layer gave only the monosodium salt of isopropylidene malonate.

B. *With sodium ethoxide and ethanol.* A sodium ethoxide solution was prepared from 0.9 g. (40 mg.-atoms) of sodium and 80 ml. of absolute ethanol. To this sodium ethoxide solution at room temperature were added 2.9 g. (20 mmoles) of isopropylidene malonate and 4.0 g. (20 mmoles) of 1,3-dibromopropane in 80 ml. of absolute ethanol. No reaction was observed. Concentration of the ethanol gave only monosodium salt.

C. *With sodium ethoxide and refluxing ethanol.* The amounts of the reactants were the same as in part B. The 1,3-dibromopropane was added to the refluxing mixture and heating was continued for 5 hr. Work-up of the reaction mixture gave only malonic acid.

URBANA, ILL.

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Epoxy Ketones. V.[1] Stereochemistry of 2-Benzal-4,4-dimethyl-1-tetralone Oxide. Diol Synthesis

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The boron trifluoride rearrangement of 2-benzal-4,4-dimethyl-1-tetralone oxide (I) gives 6-phenyl-9,9-dimethylbenzocycloheptane-5,7-dione which was isolated in a diketo and mixed enol form. The structures of the products resulting from the reaction of hydrogen chloride and methanol-sulfuric acid solutions with I have been shown to be 2-hydroxy-2-(α-chlorobenzyl)-4,4-dimethyl-1-tetralone (VII) and 2-hydroxy-2-(α-methoxybenzyl)-4,4-dimethyl-1-tetralone (XI), respectively, by diagnostic chemical methods. The spiro-epoxy ketone I has been converted to various hydroxy ketones, epoxy alcohols and 1,2-diols through various hydrogenations or reaction with a Grignard reagent. A study of the infrared spectra, hydrogen bonding and the stereostructure of these hydroxy tetralin derivatives was investigated and tentative assignments of conformations and configurations have been made.

In a previously reported study[3] proton-donor, acid catalyzed reactions of 2-benzal-1-tetralone oxides were found to lead to cleavage of the epoxide ring and 2-hydroxy-1-tetralones were postulated as products, mainly on the basis of absorption spectra studies. As is discussed in detail later this has definitely now been shown to be the case.

When the spiroepoxy ketone, 2-benzal-4, 4-dimethyl-1-tetralone oxide[4] (I), was treated with the Lewis acid, boron trifluoride (see Chart 1), under the conditions described by House and Wasson for rearranging 2-benzalcyclohexanone-1 oxide,[5] an 85% yield of a product was obtained which has the analytical and spectral characteristics of the expected seven membered ring 1,3-diketone, 6-phenyl-9,9-dimethylbenzocycloheptane-5,7-dione (II). This product had none of the characteristics to be expected for the isomeric 1,2-diketone, 7-phenyl-9,9-dimethylbenzoheptane-5,6-dione. The diketo form II is readily converted to an enolic isomer IIA-C on recrystallization from acidified methanol. The enol structures IIA and IIB would be favored over IIC which does not allow for conjugation between the carbonyl oxygen and the hydroxyl

(1) *a.* For paper IV in this series see, N. H. Cromwell, F. H. Schumacher, and J. L. Adelfang, *J. Am. Chem. Soc.* **83**, 974 (1961); *b.* Presented in part at the American Chemical Society Meeting, September 1960, New York, N. Y.

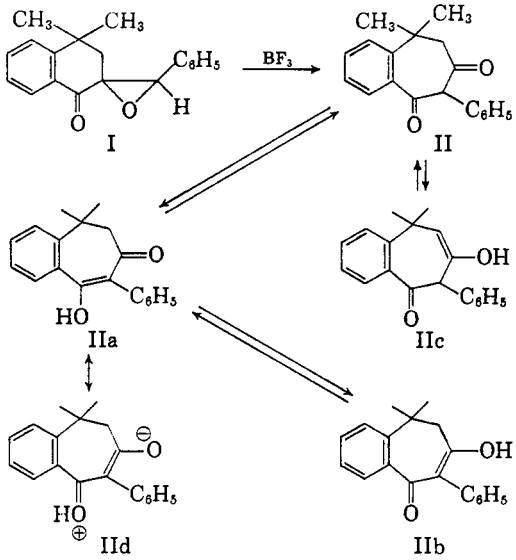
(2) Abstracted from the Ph.D. thesis of R. E. Bambury, University of Nebraska, January 1960.

(3) N. H. Cromwell, R. E. Bambury, and R. P. Barkley, *J. Am. Chem. Soc.*, **81**, 4294 (1959).

(4) A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).

(5) H. O. House and R. L. Wasson, *J. Am. Chem. Soc.* **78**, 4394 (1956).

CHART 1



group. This is an important factor in the stabilization of enolized cyclic 1,3-diketones.[6] The presence of an infrared band (3500 cm.$^{-1}$) in the free or weakly hydrogen bonded O—H stretching region of the spectrum of the enol form, IIA and/or IIB, is expected since "conjugated chelation," as experienced[7] with open chain 1,3-diketones, is not possible. The enol IIA and/or IIB shows a broad double peak (1625 and 1635 cm.$^{-1}$) which indicates that in carbon tetrachloride solution the enol form of II exists as a mixture of two structures (*e.g.* IIA and IIB). House and Wasson[5] reported only a single peak in this region at 1615 cm.$^{-1}$ for the enol form of the symmetrical 2-phenyl-1,3-cyclohexanedione. Resonance of the type implied in IIA $\longleftrightarrow$ IID is mainly responsible for the great lowering of the carbonyl band in the β-hydroxy-α,β-unsaturated carbonyl structures.

The pure diketo form II showed no infrared absorption in the O—H stretching region of the spectrum and two carbonyl bands (γ C=O, aliphatic, 1731 cm.$^{-1}$ and γ C=O, aromatic, 1691 cm.$^{-1}$) in the expected regions. Dioxane solutions of the enol forms IIA,B and of the diketo form II show identical ultraviolet and infrared spectra indicating that they exist as tautomeric mixtures in this media.

The structures tentatively assigned in a previous report [3] to the hydrogen chloride and acid-catalyzed, methanol epoxide ring cleavage products of I have now been definitely established. Catalytic hydrogenation of the chlorohydrin VII in the presence of sodium bicarbonate gave an excellent yield of 2 - hydroxy - 2 - benzyl - 4,4 - dimethyl - 1 - tetralone (VIII). The structure of VIII was verified in several ways. Treatment of VIII with a sulfuric acid–acetic anhydride mixture at room temperature produced 2-benzyl-3,4-dimethyl-1-naphthol acetate (IX). Undoubtedly VIII undergoes a dehydration to 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene which has previously[4] been shown to give a dienone-phenol rearrangement to produce IX under these conditions. The α-hydroxy ketone VIII was shown to be stable to sodium methoxide or activated alumina.

The catalytic hydrogenation of the α-hydroxy ketone VIII gave 1,2-dihydroxy-2-benzyl-4,4-dimethyltetralin (IV), identical with the product obtained by the lithium aluminum hydride reduction of I. The 1,2-diol IV consumed 90% of the theoretical amount of periodate.

The structure of 2-hydroxy-2-(α-methoxybenzyl)-4,4-dimethyl-1-tetralone[4] (XI) has now been verified by catalytically reducing it to 1,2-dihydroxy-2-(α - methoxybenzyl) - 4,4 - dimethyltetralin (XII), which was shown to consume 91% of the theoretical amount of periodate expected for the 1,2-diol structural arrangement.

The conversion of the spiroepoxy ketone I to various epoxy alcohols and diols was carried out to study the stereochemistry of the reactions involved. An assignment of conformations and configurations for the various 1,2-diols involved in these synthetic studies is given in a special section.

The "reverse addition" of the methyl Grignard reagent to I gave a good yield of what at first appeared to be one isomer of 1-hydroxy-2-benzal-1,4,-4-trimethyltetralin oxide (III). However, the lithium aluminum hydride reduction of III gave a product, X, with a wide melting range but which was found to take up 99% of the theoretical amount of periodate. Chromatographing this mixed product on alumina resulted in the isolation of one pure diastereoisomer, m.p. 112–113°. It seems probable that the epoxy alcohol III is also a mixture of diastereoisomers since it has been shown repeatedly that lithium aluminum hydride reduction of epoxides is a stereospecific reaction.[8]

A widely melting product X from which the same diastereoisomer, m.p. 112–113°, was also obtained, resulted from the reaction of methylmagnesium bromide with 2-hydroxy-2-benzyl-4,4-dimethyl-1-tetralone (VIII). This reaction of VIII to produce X would not necessarily be expected to be stereospecific but possibly stereoselective. Again the gross product X took up 96% of the expected amount of periodate in the cleavage experiment indicating that it probably is a mixture of the diastereoisomers.

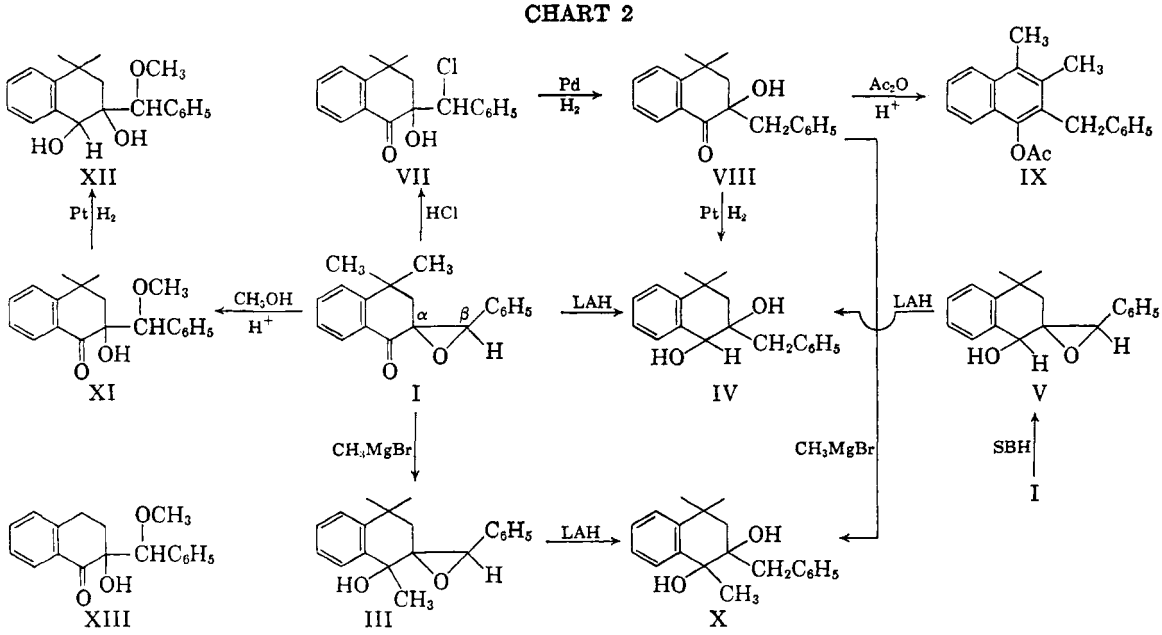
The reduction of the spiroepoxy ketone I with various reagents gave varying results. With sodium borohydride the only solid product isolated was 1-hydroxy-2-benzal-4,4-dimethyltetralin oxide (V) which was readily reduced by lithium aluminum

(6) *a.* N. H. Cromwell and R. D. Campbell, *J. Org. Chem.*, 22, 520 (1957); *b.* R. D. Campbell and N. H. Cromwell, *J. Am. Chem. Soc.*, 79, 3456 (1957).

(7) R. Rasmussen, D. Tunnicliff, and R. Brattain, *J. Am. Chem. Soc.*, 71, 1068 (1949).

(8) E. L. Eliel, *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1956, M. S. Newman, ed., p. 106.

CHART 2



hydride to 1,2-dihydroxy-2-benzyl-4,4-dimethyltetralin (IV), identical with that obtained by the lithium aluminum hydride reduction of I, or the platinum oxide catalyzed hydrogenation of VIII.

The platinum catalyzed hydrogenation of I produced at least a 50% yield of V and a 29% yield of the unstable 2-(β-hydroxybenzyl)-4,4-dimethyl-1-tetralone (VI) which was readily dehydrated by alumina in the chromatographic separation to 2-benzal-4,4-dimethyl-1-tetralone.[4]

When the spiroepoxy ketone I was hydrogenated in benzene with a palladium-on-charcoal catalyst a mixed product resulted which calculations indicate was made up of 25% of the 1,2-diol IV (isolated) and 70% of VI which again was readily dehydrated on the chromatographic column of alumina to 2-benzal-4,4-dimethyl-1-tetralone (isolated). The unstable oil, which was mainly VI, was shown to have infrared bands in the expected locations (γOH, 3550 cm.$^{-1}$ and γC=O, 1695 cm.$^{-1}$) and no absorption at 1673 cm.$^{-1}$ as expected for 2-benzal-4,4-dimethyl-1-tetralone.[4] The aldol VI was shown to undergo readily a reverse aldol condensation to produce some benzaldehyde in the presence of potassium hydroxide.

These results from the catalytic hydrogenation of spiroepoxy ketone I are interesting in comparison with findings from comparable reductions of the less sterically restricted *trans*-chalcone oxide[9] which produces mainly the α-hydroxy ketone. Apparently the β-position in I is even less available than the α-position for hydrogen transfer by these catalysts. On the other hand lithium aluminum hydride attacks the spiroepoxy ketone I and/or 1-hydroxy-2-benzal-4,4-dimethyltetralin oxide (V) exclusively at the *beta* position. This is analogous to the behavior of *trans*-chalcone oxide with this reagent.[9]

VanderWerf has given[10] an excellent discussion of the factors effecting direction of ring opening for unsymmetrical epoxides. For the spiroepoxy ketone I the β-position would appear to be the center of lower electron density in contrast with the α-position but the position actually attacked obviously varies with the hydrogenation reagent employed.

In the prior study[3] the spiroepoxy ketone I was shown to be inert to reaction with amines. *Trans*-chalcone oxide has been found to undergo an SN2 attack by piperidine at the β-position, a reaction which undoubtedly involves a Walden inversion.[1a,11] As was pointed out in the previous report[3] the epoxide ring in I is readily cleaved with hydrogen chloride in a reaction which involves attack by a chloride ion at the β-carbon in a transition state involving inversion at this center.

Infrared absorption spectra, hydrogen bonding and stereostructure of hydroxy tetralin derivatives. In these studies a lithium fluoride prism was used in the spectrophotometer to increase its sensitivity in the O–H stretching region.

The infrared spectra of the α-hydroxy ketones studied in this investigation showed splitting. The band splitting effects in α-hydroxy ketones have been ascribed by Jones[12] and others[3] to intramolecular hydrogen bonding. This type of

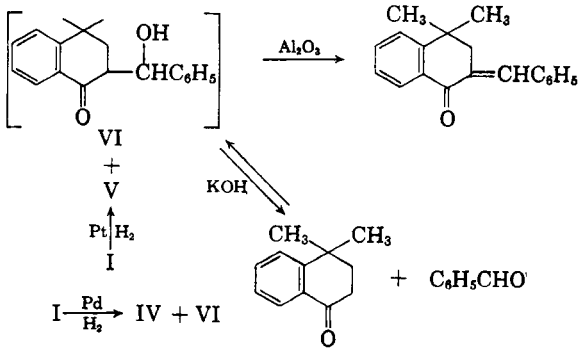
(9) W. Herz, *J. Am. Chem. Soc.*, 74, 2928 (1952).

(10) A. Feldstein and C. A. VanderWerf, *J. Am. Chem. Soc.*, 76, 1626 (1954).

(11) N. G. Barker and N. H. Cromwell, *J. Am. Chem. Soc.*, 73, 1051 (1951).

(12) R. N. Jones *et al. J. Am. Chem. Soc.*, 74, 2820 (1952).

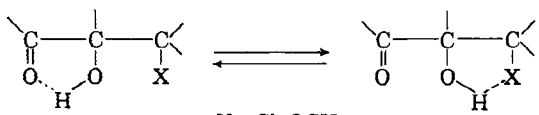
CHART 3



equilibrium would give rise to a free and a H-bonded O—H band and a free and H-bonded carbonyl band.

With 2-hydroxy-2-benzyl-4,4-dimethyl-1-tetralone (VIII) the carbonyl region of the spectrum shows a non-bonded band at 1695 cm.$^{-1}$ and a shoulder at 1680 cm.$^{-1}$ ascribed to the presence of the H-bonded carbonyl form (H-bonding is expected to increase the ρ-character of the carbonyl bond resulting in a lowering of frequency). The hydroxyl region of the spectrum of VIII gave evidence of H-bonded (3512 cm.$^{-1}$) and free (3562 cm.$^{-1}$) O—H bands. It seems probable that the hydroxyl group is axial and the benzyl group equatorial.[4]

The introduction of α-electronegative groups in the benzyl group introduces an additional effect and it is indicated that the chlorohydrin (VII) and the two hydroxymethoxy ketones (XI) and 2-hydroxy-2-(α-methoxybenzyl)-1-tetralone (XIII)



X = Cl, OCH_3

show the following equilibrium in carbon tetrachloride. These compounds show a bifurcated carbonyl band indicating the presence of free and hydrogen bonded carbonyl groups. These compounds also show two hydroxyl peaks both in the hydrogen bonded region of the spectrum. A dilution study with VII, VIII, XI and XIII showed nearly the same relative intensities of the carbonyl and hydroxyl bands at high and low dilution, indicating the hydrogen bonding effects here are probably not intermolecular.

The infrared spectra of the two epoxy alcohols III and V prepared in this work showed a free O—H peak and an H-bonded OH peak at high concentrations. On dilution the lower H-bonded band disappeared, indicating that H-bonding in these cases is intermolecular in nature.[13] Another factor which must be taken into account in assigning the O—H bands for III and V is the knowledge that tertiary hydroxyl bonds absorb 10–15 cm.$^{-1}$ lower than the secondary O—H group. This type of lowering seems to be consistent for several types of secondary and tertiary alcohols.[14]

Kuhn[14] and Cole and Jefferies[15] have used infrared spectroscopy as a tool for assigning conformations to many cyclohexane-1,2-diols. The following generalizations have been found to be true: (1) secondary alcohols have a hydroxyl group stretching frequency 10–15 cm.$^{-1}$ higher than tertiary alcohols with the free hydroxyl group frequencies occurring between 3600–3640 cm.$^{-1}$ and the intramolecular H-bonded bands between 3580–3600 cm.$^{-1}$; (2) in cyclohexane *cis*-1,2-diols, where one group is equatorial and the other axial, the latter is involved in intramolecular H-bonding in preference to the former.

An examination of models of the 1,2-dihydroxytetralins prepared in this work (IV, X, XII) indicates that the cyclohexene ring of the tetralin nucleus is probably in a chair conformation. Therefore substituent groups on the cyclohexene ring will have near axial and equatorial conformations. In order that we may use the infrared spectral data to assign probable conformations and configurations to the 1,2-dihydroxytetralins, IV, X and XII, one basic and reasonable assumption must be made about the conformations of these compounds. This is that the bulky benzyl group in the 2-position of the three compounds takes an equatorial position in preference to the smaller 2-hydroxyl group. An examination of models of these compounds shows that if the benzyl group is forced into an axial position there is considerable interaction between it and one of the methyl groups at the 4-position. The benzyl group in 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone[4] was found to have an equatorial conformation. Also the isopropyl group takes an equatorial position in favor of a hydroxyl group in the cyclohexane diols.[15]

To make sure that the H-bonding observed with the tetralin-1,2-diols IV, X and XII was essentially intramolecular in nature, dilution studies were done. No significant change in the relative intensities of the hydroxyl bands were observed on changing from high to low concentrations.

The infrared spectrum of IV showed two hydroxyl peaks, a non-bonded one at 3620 cm.$^{-1}$ and a bonded one at 3579 cm^{-1}. Since both bonded and non-bonded bands occur, the "true *trans*" or diaxial conformation for the diol is eliminated. A molecule with a "true *trans*" conformation shows only a non-bonded hydroxyl band since intramolecular H-bonding is sterically impossible.[14,15] Therefore the hydroxyl groups in IV have either an equatorial, equatorial (e, e) conformation or an axial, equatorial (a, e) arrangement since the spectrum indi-

(13) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1958, p. 96.

(14) L. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); *J. Am. Chem. Soc.*, **76**, 4323 (1954).

(15) A. Cole and P. Jefferies, *J. Chem. Soc.*, 4391 (1956).

cates intramolecular H-bonding does occur. The assignment of the benzyl group at the 2-position in IV to an equatorial conformation automatically assigns the hydroxyl group at the 2-position to an axial conformation. Thus the conformation of the hydroxyl group at the 1-position is apparently equatorial and the conformation of IV is a, e. This tentative assignment of the a, e conformation to the hydroxyl groups in IV suggests that they probably have a *cis* configuration since adjacent *trans* groups in cyclic compounds can have only e, e or a, a conformations.

The same considerations used in the assignment of the configuration of IV can also be used to assign the configuration of X. The spectrum of X also shows a bonded and non-bond hydroxyl peak and so 1,2-dihydroxy-2-benzyl-1,4,4-trimethyltetralin (X) has its hydroxyl groups in an a, e conformation in a *cis* configuration. The free hydroxyl stretching frequency is about 10 cm.$^{-1}$ lower than the free hydroxyl stretching frequency of IV as expected from the generalization (1) given above, since the free hydroxyl group of X is tertiary whereas the free hydroxyl group of IV is probably the secondary hydroxyl group in accord with generalization (2). It will be interesting to see the spectrum of the unknown diastereoisomer of X. The one studied here apparently has the *cis* configuration so the other isomer should have a *trans* arrangement of the hydroxyl groups and, therefore, show only one tertiary non-bonded hydroxyl peak.

The spectrum of 1,2-dihydroxy-2-(α-methoxybenzyl)-4,4-dimethyltetralin (XII) shows three hydroxyl peaks, two bonded and one non-bonded. The appearance of the third band in XII is undoubtedly due to H-bonding of one of the hydroxyls with the methoxy group. The low frequency of the band and its broad shape indicates that it is a very strong H-bond.[14] A methoxy group has been shown to be a better proton acceptor than a hydroxyl group.[16] Although the presence of the third band complicates the spectrum of XII it is still possible tentatively to assign an a, e conformation to the hydroxyls on the 2-position and 1-position, respectively, using the same reasoning as employed with IV and X. Thus 1,2-dihydroxy-2-(α-methoxybenzyl)-4,4-dimethyltetralin (XII) is assumed to be a *cis* diol.

EXPERIMENTAL[17]

Rearrangement of 2-benzal-4,4-dimethyl-1-tetralone oxide (I) *to 6-phenyl-9,9-dimethylbenzocycloheptane-5,7-dione* (II). House's[6] conditions for rearranging epoxy ketones were employed. A 2.2-g. sample of the epoxy ketone I produced 1.9 g. (86% yield) of a colorless product II, m.p. 100–105°. Several recrystallizations of II from acidified methanol and water produced IIA,B, m.p. 116–128°; λ_{max} 235 and 297 mμ (broad bands) (ε 10,000, 5800). The infrared spectrum with 10 mg./ml. in a 1.0-mm. cell using sodium chloride optics: γ_{OH}, 3500/25; $\gamma_{C=O}$, 1635/45 and 1625/50. The compound gave no isolable product with phenylhydrazine or *o*-phenylenediamine.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.98; H, 6.53.

When IIA,B was dissolved in benzene, washed with 20% potassium carbonate, the solution dried over anhydrous magnesium sulfate and recrystallized from the hot solution to which petroleum ether (b.p. 60–70°) was added, II, m.p. 100–105°, resulted. The infrared spectrum with 10 mg./ml. in a 1.0-mm. cell using sodium chloride optics showed: $\gamma_{C=O}$, aliphatic, 1731/85; $\gamma_{C=O}$, aromatic, 1691 broad/85; γphenyl, 1600/25.

In dioxane both IIA,B and II showed λ_{max} 285 mμ (broad) ε 4000; γ_{OH}, 3650/60, $\gamma_{C=O}$, 1730/40, 1690/70, 1625/50 (Perkin-Elmer Infracord).

Reaction of I *with methylmagnesium bromide.* From 4.4 g. (0.016 mole) of epoxy ketone I and 0.021 mole of commercial methylmagnesium bromide (Grignard reagent solution added slowly to ketone solution), 3.1 g. (66% yield) of 1-hydroxy-2-benzal-1,4,4-trimethyltetralin oxide (III) was obtained, m.p. 165–167°, recrystallized from petroleum ether (b.p. 60–70°) and benzene; γOH, 3595/35 (5.0 mm. cell, 2.5 mg./ml.), 3595/20 (1.0 mm. cell, 7.5 mg./ml.), 3595/35 and 3474 (broad)/5 (1.0 mm. cell, 15 mg./ml.).

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.31; H, 7.55.

Hydrogenation of I. A. *With lithium aluminum hydride.* A 4.4-g. sample of I in 250 ml. of dry ether was added to a well stirred slurry of 2.0 g. of lithium aluminum hydride in 100 ml. of dry ether over a period of 30 min. After stirring for an additional hour, working up the reaction mixture produced 3.8 g. (87% yield) of 1,2-dihydroxyl-2-benzyl-4,4-dimethyltetralin (IV), m.p. 140.5–142.5°, recrystallized from benzene and petroleum ether; γ_{OH}, 3620/45 and 3579/35; consumption of periodate, 90%.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.91; H, 7.85. Found: C, 80.88; H, 7.84.

B. *With sodium borohydride.* Reduction of 1.1 g. of I by boiling with 0.08 g. (1 molar equiv.) of sodium borohydride for a few minutes and then stirring for 1 hr. produced 0.45 g. of a solid product which after recrystallization from benzene and petroleum ether gave 1-hydroxy-2-benzal-4,4-dimethyltetralin oxide (V), m.p. 136–139°. A mixed melting point experiment with V obtained in the following experiment showed no depression and the infrared spectra were identical. Some unidentified oily material also resulted from the sodium borohydride reduction.

C. *With platinum oxide and hydrogen.* A 2.0-g. sample of I in 200 ml. of dry ether was shaken with 0.2 g. of platinum oxide under 35 lb./in.^{2} of hydrogen for 45 min. at room temperature. Recrystallization of the product from petroleum ether (b.p. 60–70°) produced 0.7 g. of 1-hydroxy-2-benzal-4,4-dimethyltetralin oxide (V), m.p. 139.5–141°; γOH, 3609/65 and 3475 (broad)/10 (20 mg./ml.), 3609/50 and 3475 (broad)/2 (10 mg./ml.), 3609/45 (2.5 mg./ml.).

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.55; H, 7.15.

The filtrate from the isolation of V was poured onto a 24 cm. × 2 cm. activated alumina (Merck) column which had previously been saturated with petroleum ether (b.p. 60–70°). The column was developed with petroleum ether-benzene mixtures and finally eluted with methanol-benzene

(16) G. W. Wheland, *Resonance in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1955, p. 47.

(17) All melting points corrected. Ultraviolet absorption spectra were determined with a Cary Model 11-MS recording spectrophotometer employing matched 1 cm. fused silica cells and $10^{-4}M$ reagent grade methanol solutions over the range of 200–400 mμ. Infrared spectra were measured with a Perkin-Elmer Model 21 double-beam recording instrument over the frequency range of 4000–600 cm.$^{-1}$ using a sodium chloride or lithium fluoride prism and matched sodium chloride cells. Unless otherwise indicated lithium fluoride optics and 2.5 mg./ml. carbon tetrachloride solutions with 5 mm. cells were used.

mixtures. A yellow band which developed at the top of the column and moved down to be in the first eluates, produced 0.55 g. of 2-benzal-4,4-dimethyl-1-tetralone[4], m.p. 108–109°. The second eluate was found to contain 0.3 g. of V. Thus the total yield of isolated products from this reduction were 1.0 g. (50% yield) of V and 0.55 g. (29% yield) of 2-benzal-4,4-dimethyl-1-tetralone.

Attempted platinum oxide catalyzed hydrogenations of I in alcohol, dioxane or tetrahydrofuran were not successful and the starting material was recovered.

D. *With palladium-on-charcoal and hydrogen.* Hydrogenation of 2.0 g. of I in 100 ml. of benzene in the presence of 1.0 g. of 10% palladium-on-charcoal catalyst under 45 lb./in.[2] after 2 hr. shaking produced an oily product. Crystallization from petroleum ether (b.p. 60–70°) gave 0.08 g. of IV, m.p. 140–143°. A mixed melting point experiment and its infrared spectrum showed this product to be identical with IV obtained from the lithium aluminum hydride reduction of I.

The filtrate from the isolation of IV contained 1.9 g. of a clear viscous oil; γ_{C-O}, 1695, γ_{OH}, 3550 cm.$^{-1}$. A chromatographic separation of a 0.3-g. sample of this oil on an alumina column, as described previously, produced 0.2 g. of 2-benzal-4,4-dimethyl-1-tetralone,[4] m.p. 106–108°, and 0.06 g. of IV, m.p. 140–142°.

A 0.1-g. sample of the viscous oil residue (1.9 g.) from the original isolation of IV was dissolved in 4% methanolic potassium hydroxide and allowed to stand 1 hr. The solution turned yellow and gave off a strong odor of benzaldehyde; 0.02 g. of IV was isolated from this mixture. These experiments indicate that this hydrogenation produces at least a 70% yield of *2-(α-hydroxybenzyl)-4,4-dimethyl-1-tetralone*, (VI) which is dehydrated by the basic alumina to 2-benzal-4,4-dimethyl-1-tetralone.

Reduction of 2-hydroxy-2-(α-chlorobenzyl)-4,4-dimethyl-1-tetralone (VII) *to 2-hydroxy-2-benzyl-4,4-dimethyl-1-tetralone* (VIII). The chlorohydrin[4] VII (5.9 g., 0.019 mole) dissolved in 250 ml. of benzene was shaken with 2.1 g. of 10% palladium on charcoal and 2.0 g. of sodium bicarbonate for 1.5 hr. at 45 lb./in.[2] of hydrogen. The oily product was recrystallized from petroleum ether to give 5.0 g. (95% yield), m.p. 93.5–94.5°, of VIII; λ_{max}, 250 and 290 mμ (ε 11,800, 1600); with 1.0 mm. cell and 15 mg./ml.: γ_{OH}, 3560 (Sho.)/20 and 3510/30; γ_{C-O}, 1695/70 and 1680 (Sho.)/60; with 5.0 mm. cell and 2.5 mg./ml.: γ_{OH}, 3562/15 and 3512/25; γ_{C-O}, 1695/75 and 1680 (Sho.)/65.

Reduction of VIII *to* IV. A solution of 0.1 g. of VIII in 60 ml. of dry ether was shaken with 0.1 g. of platinum oxide catalyst for 2 hr. under 45 lb./in.[2] of hydrogen. The oily product was crystallized from methanol and water, then benzene and petroleum ether to give 0.08 g. of 1,2-dihydroxy-2-benzyl-4,4-dimethyl-tetralin (IV), m.p. 141–142.5°, identical with the product obtained from the lithium aluminum hydride reduction of I.

Acid-catalyzed dehydration-rearrangement of VIII *to 2-benzyl-3,4-dimethyl-1-naphthol acetate* (IX). A 0.28-g. sample of VIII was allowed to stand at room temperature for 2 days in 20 ml. of acetic anhydride containing 1 ml. of concd. sulfuric acid. Dilution with water and neutralization with sodium hydroxide produced 0.2 g. of IX, m.p. 115–116°, recrystallized from methanol. The compound was identical with that previously prepared.[4]

2-Hydroxy-2-benzyl-4,4-dimethyl-1-tetralone (VIII) was stable to standing for 3 days in 4% methanolic sodium methoxide; it also was unchanged by activated alumina at 25–30°.

Reaction of VIII with methylmagnesium bromide. A 0.5-g. sample of VIII in 100 ml. of ether was treated with 7 ml. of commercial methylmagnesium bromide (excess) and stirred for 4 hr. The crude product, 0.55 g., m.p. 108–131° consumed 96% of the theoretical amount of periodate, indicating that it may be a mixture of the *erythro* and *threo* forms of 1,2-dihydroxy-2-benzyl-1,4,4-trimethyltetralin (X). This mixed product was chromatographed on alumina to produce only a low melting isomer of X in pure form, m.p. 112–113°; γOH, 3610/30 and 3587/50.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.21; H, 8.41.

Reduction of 2-hydroxy-2-(α-methoxybenzyl)-4,4-dimethyl-1-tetralone (XI). A solution of 0.5 g. of XI in 100 ml. of ether was shaken for 1 hr. with 0.1 g. of platinum oxide catalyst under 45 lb./in.[2] of hydrogen. The resulting 1,2-dihydroxy-4,4-dimethyl-2-(α-methoxybenzyl)tetralin (XII), 0.46 g. (92% yield), m.p. 139–139.5°, was recrystallized from benzene and petroleum ether. This product, XII, used up 91% of the calculated amount of periodate in a cleavage experiment. The infrared spectrum showed: with 15 mg./ml. in a 0.1 mm. cell, γ_{OH}, 3618/5, 3582/5, 3480/2; with 7.5 mg./ml. in a 1.0 mm. cell, γ_{OH}, 3618/30, 3581/26, 3478/5; with 2.5 mg./ml. in a 5 mm. cell, γ_{OH}, 3618/47, 3582/40, 3480/9.

Anal. $C_{20}H_{24}O_2$: C, 76.89; H, 7.74. Found: C, 76.98; H, 7.41.

Reduction of 1-hydroxy-2-benzal-4,4-dimethyltetralin oxide (V). A 0.84-g. sample of V in 100 ml. of dry ether was added slowly (2 hr.) with stirring to an ether slurry of 0.5 g. of lithium aluminum hydride. A 0.6-g. amount of 1,2-dihydroxy-2-benzyl-4,4-dimethyltetralin (IV), m.p. 140–143°, was isolated which was identical with that produced by the lithium aluminum hydride reduction of I.

Reduction of 1-hydroxy-2-benzal-1,4,4-trimethyltetralin oxide (III). An attempted reduction of III with lithium aluminum hydride in dry ether returned only the starting material. A 0.5-g. sample of III dissolved in 50 ml. of dry tetrahydrofuran was added slowly to a stirred slurry of 0.6 g. of lithium aluminum hydride in 100 ml. of the same solvent. The mixture was refluxed for 8 hr. and allowed to stand at room temperature for 12 hr. Isolation gave 0.46 g. of a mixed product, m.p. 95–128°, which consumed 99% of the calculated amount of periodate for a mixture of the *erythro* and *threo* forms of the expected diol, 1,2-dihydroxy-2-benzyl-1,4,4-trimethyltetralin (X). Chromatographing on alumina produced 0.1 g. of the low melting isomer of X, m.p. 112–113°, identical with that prepared by the reaction of methylmagnesium bromide with 2-hydroxy-2-benzyl-4,4-dimethyl-1-tetralone (VIII). Attempts to isolate a higher melting isomer of X in pure form were not successful.

Periodate cleavage of 1,2-diols. The procedure employed for cleaving the 1,2-diols prepared in this investigation was essentially the method outlined in *Organic Analysis*[18] for analyzing monoglycerides. Using this procedure, ethylene glycol consumed 97% of the calculated amount of periodate, benzoin 101%, 1-hydroxy-2-benzal-1,4,4-trimethyltetralin oxide (III) 0%, 1-hydroxy-2-benzal-4,4-dimethyltetralin oxide (IV) 0%, 2-hydroxy-2-(α-methoxybenzyl)-4,4-dimethyl-1-tetralone (XI) 0%, 2-hydroxy-2-(α-methoxybenzyl)-1-tetralone[3] (XIII) 0%, 2-benzal-4,4-dimethyl-1-tetralone oxide[4] (I) 0%, and 2-hydroxy-2-benzal-4,4-dimethyl-1-tetralone (XIII) 0%. The results for the 1,2-diols prepared in this investigation are given with the description of the syntheses.

Infrared absorption spectra studies: A. *With 2-hydroxy-2-(α-methoxybenzyl)-1-tetralones* (XI) *and* (XIII). For 2.5 mg. of XI/ml. in a 5 mm. cell, γ_{OH}, 3555/30 and 3510/15, γ_{C-O}, 1692/65 and 1680/75; for 12 mg. of XI/ml. in a 1.0 mm. cell with sodium chloride optics, γ_{OH}, 3530/30 and 3480/20, γ_{C-O}, 1685 (shoulder)/80 and 1675/90; for 2.5 mg. of XIII/ml. in a 5 mm. cell, γ_{OH}, 3575/10 and 3510/27, γ_{O-C}, 1695/68 and 1682/70; for 15 mg. of XIII/ml. in a 1.0 mm. cell, γ_{OH}, 3573/15 and 3510/37, γ_{C-O}, 1694/78 and 1682/78.

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(18) J. Mitchell, Jr., ed., *Organic Analysis*, Vol. I., Interscience Publishers, New York, 1953, pp. 44–46.

B. *With 2-hydroxy-2-(α-chlorobenzyl)-4,4-dimethyl-1-tetralone* (VII). With 2.5 mg. of VII/ml. in a 5 mm. cell, γ_{OH}, 3545/20 and 3490/20; $\gamma_{C=O}$, 1696/70 and 1682/65; with 10 mg./ml. in a 1.0 mm. cell with sodium chloride optics, γ_{OH}, 3550/20 and 3500/23, $\gamma_{C=O}$, 1695–1683/80.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

An Indone to Naphthol Ring Expansion

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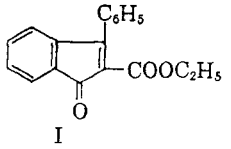
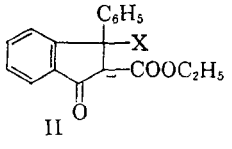
2-Carbethoxy-3-phenylindone (I) adds phenacyl chloride in a Michael reaction, and the resulting anion at once eliminates chloride forming a cyclopropane (III). This product is attacked further by bases, which cause it to rearrange into a naphthol (IV).

After 2-carbethoxy-3-phenylindone (I) was found to add certain anions forming II,[1] it became of interest to alkylate the products, but all attempts to do this failed. In explanation it may be noted first that anions II are weakly basic, the corresponding acids dissolving in carbonate, and second that C_2 in II is flanked by bulky groups on C_3, and it is well known that analogous mono-*tert*-alkylated malonic or acetoacetic esters are resistant to alkylation.

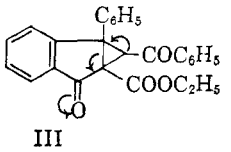


I

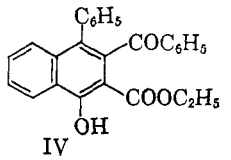


II

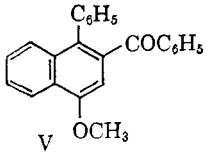
These inhibiting effects would be less important in an intramolecular reaction, and accordingly conditions were arranged so that a Michael reaction leading to II could be followed by an intramolecular alkylation. This was done by treating I with phenacyl chloride. In accordance with expectation, the cyclopropane III was formed smoothly.



III



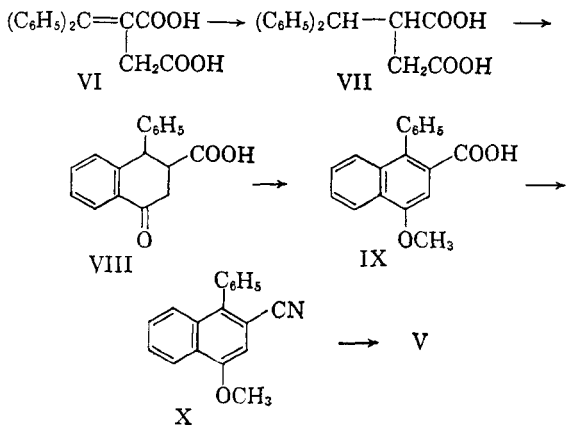
IV



V

Compound III was found to be quite sensitive to alkali. Although it could be isolated in good yield when proper conditions prevailed, use of excess base in the Michael reaction or treatment of isolated III with base led to formation of IV. The mechanism for the isomerization is indicated by arrows in formula III, and it is seen that the process is analogous to one studied recently by Wawzonek and Morreal.[2]

Structure IV for the rearrangement product was confirmed; hydrolysis, decarboxylation and methylation yielded V, and this substance was synthesized by the route indicated in formulas VI–X.



Diphenylitaconic acid (VI) was reduced by use of Raney alloy and sodium hydroxide[3] as recommended by Drake and Tuemmler[4] but the product was found to be not VII, but an aluminum complex of this acid, a fact which accounts for the low yield obtained by Drake and Tuemmler in their further use of the substance. The complex was remarkably stable; its clear solution in dilute bicarbonate deposited it unchanged on acidification; it was boiled with concentrated hydrochloric acid without change and it crystallized as described from ethyl acetate-benzene. Isolation of VII from the complex was accomplished by esterification (methanol-sulfuric acid) followed by saponification, or better by precipitation of the barium salt of VII directly from

(1) C. F. Koelsch, *J. Org. Chem.*, 25, 2088 (1960).

(2) S. Wawzonek and C. E. Morreal, *J. Am. Chem. Soc.*, 82, 439 (1960).

(3) D. Papa, E. Schwenk, and B. Whitman, *J. Org. Chem.*, 7, 587 (1942).

(4) N. L. Drake and W. B. Tuemmler, *J. Am. Chem. Soc.*, 77, 1209 (1955).