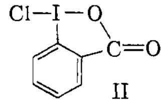
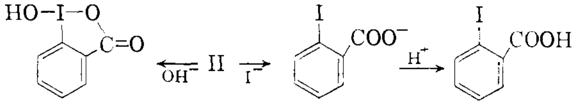
(presumed to be the dichloride) rapidly evolved a gas in the dry state and changed in crystalline character to form a product which, although it oxidized iodide ion, had a lower iodometric equivalent weight than the theoretical value for iodobenzoic acid dichloride. Because of the instability of the dichloride, plans to study its equilibration with its components were abandoned.



II

The behavior which has been described was noted many years ago and explained without confirming evidence, on the assumption that the dichloride evolved hydrogen chloride to produce II.[9a] Confirmation of this lactone structure has been obtained through study of the reactions, described below, of II in dilute solutions of potassium iodide and sodium hydroxide. Complete details are given in the Experimental section.



Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

DAVIS, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

The Stereoisomers of 10-Methyl-2-decalol[1,2]

BY ROBERT H. BAKER, L. S. MINCKLER AND ALLEN S. HUSSEY

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An improved synthesis of *cis*-10-methyl-2-*trans*-decalol (I) and the synthesis of the *trans-trans* isomer (II) of the *cis-cis* isomer (III) and of the *trans-cis* isomer (IV) by procedures which permit assignment of configuration are reported. Absorption bands in the infrared spectra of these and related compounds appear to be diagnostic of the nature of the ring fusion geometry.

Two of the four isomers of 10-methyl-2-decalol have been described previously.[3-7] Both of these isomers melt in the region of 65–70° at very nearly the same temperature. The *p*-nitrobenzoate of one has been reported to melt at 65–67°,[5,7] the 3,5-dinitrobenzoates to melt at 110.6–111.2° and at 97.5–98.5°.[4] The isomer which forms the higher melting 3,5-dinitrobenzoate has been synthesized from a 10-carboxy-2-decalol which forms a lactone.[4] Also, when oxidized with chromic anhydride, this isomer has furnished 10-methyl-2-*trans*-decalone.[6] It is therefore *cis*-10-methyl-2-*trans*-decalol (I). We have found the *p*-nitrobenzoate derivative to melt at 71–73°; hence it would appear to be identical with that described by Yanagita and coworkers.[5,7]

While compound I can be prepared in three steps from 2-methylcyclohexanone by way of 10-methyl-$\Delta^{1,9}$-octal-2-one,[3,4,7,8] we have come to prefer the synthetic sequence to 10-methyl-2-*trans*-decalone, as developed by Dreiding,[9] followed by reduction with lithium aluminum hydride. In spite of the nine steps involved, the over-all yield of I is 35–40% and the product is much less subject to contamination by isomeric impurities.

When compound I, prepared in this way, was converted to its *p*-toluenesulfonate and the latter was refluxed with potassium acetate in acetic acid–acetic anhydride solvent, the epimeric acetate was formed in 25–30% yield. Considerable (*ca.* 30%) elimination accompanied the displacement reaction. Saponification and a chromatographic procedure on alumina led to the isolation of *trans*-10-methyl-2-*trans*-decalol (II) m.p. 89.5–90.5°. The *p*-nitrobenzoate and the 3,5-dinitrobenzoate of II melted at 153–154° and 122–123°, respectively. Therefore the second isomer previously reported[4] is not the *trans-trans* isomer II.

The synthesis of *cis*-10-methyl-2-*cis*-decalol (III) and of *trans*-10-methyl-2-*cis*-decalol (IV) involved the common starting material, 10-hydroxymethyl-2 *cis*-decalone (V)[10] as follows: V was converted to its *p*-toluenesulfonate VI and the latter was reduced with sodium borohydride to a mixture of the epimeric 10-[*p*-toluenesulfonoxymethyl]-2-*cis*-decalol isomers. By way of a fractional crystallization procedure, the epimeric *p*-nitrobenzoates were separated to furnish 17% of the *cis-cis* isomer VII and 71% of the *trans-cis* isomer VIII. The former melted at 114–116° and showed no depression of melting point when mixed with an authentic sample of VII, m.p. 115–116°, from *cis*-10-hydroxymethyl-2-*cis*-decalol.[10] Similarly VIII, m.p. 161–162°, did not depress the melting point of an authentic sample, m.p. 161–163°, prepared from *trans*-10- hydroxymethyl-2-*cis*-decalol.[10]

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[1] Presented, in part, before the Division of Organic Chemistry, 129th Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1956.

[2] A grant from the Research Corporation assisted the carrying out of this research.

[3] E. C. du Feu, F. J. McQuillen and R. Robinson, *J. Chem. Soc.*, 53 (1937).

[4] A. S. Hussey, H. P. Liao and R. H. Baker, THIS JOURNAL, **75**, 4727 (1953). See footnote 3 for the naming convention used to designate the geometry of these isomers.

[5] M. Yanagita and A. Tahara, *J. Org. Chem.*, **18**, 792 (1953).

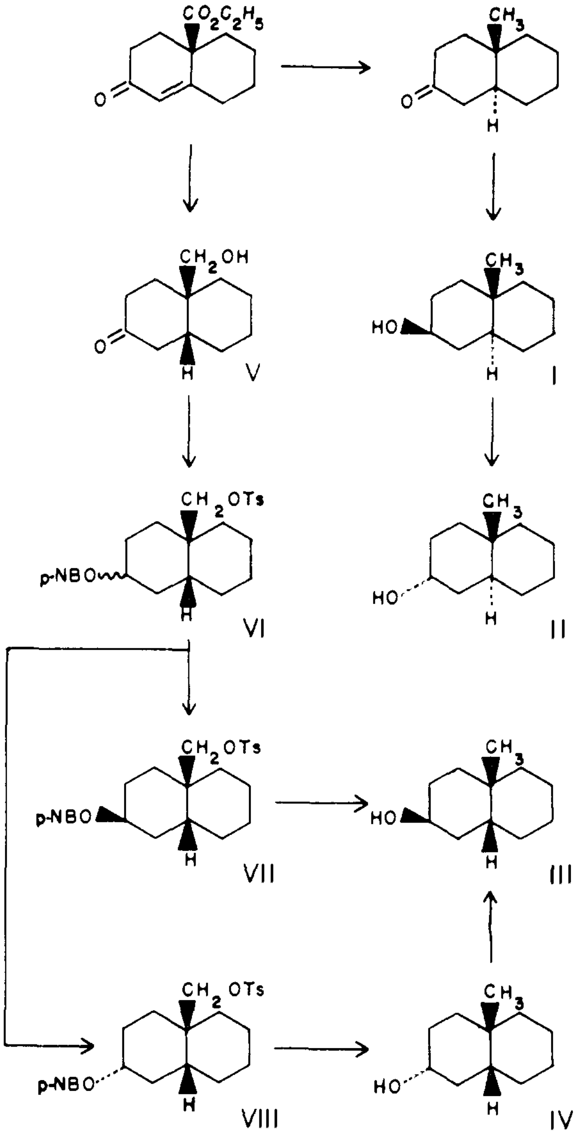
[6] A. S. Dreiding and A. J. Tomasewski, THIS JOURNAL, **77**, 168 (1955).

[7] M. Yanagita, K. Kamakawa and A. Tahara, *J. Org. Chem.*, **20**, 1767 (1955).

[8] See F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952); A. L. Wilds, C. H. Hoffman and T. H. Pearson, THIS JOURNAL, **77**, 647 (1955); and F. Sondheimer and D. Russell, *ibid.*, **80**, 3995 (1958), for variations in the preparation of this intermediate.

[9] A. S. Dreiding and A. J. Tomasewski, *ibid.*, **77**, 411 (1955).

[10] L. S. Minckler, A. S. Hussey and Robert H. Baker, *ibid.*, **78**, 1009 (1956).



When VII was saponified, crystalline *cis*-10-[*p*-toluenesulfonoxymethyl]-2-*cis*-decalol (IX), m.p. 78–79°, was obtained. Conversion of IX to *cis*-10-methyl-2-*cis*-decalol (III) involved displacement of the *p*-toluenesulfonate group with hydrosulfide[9] and then desulfurization with Raney nickel catalyst.[11] Prepared in this way, III proved to be an uncrystallizable oil which distilled at 109–110° at 4 mm. The *p*-nitrobenzoate of III melted at 74–75°. The 3,5-dinitrobenzoate derivative of III melted at 95–97° but mixture melting points with the 3,5-dinitrobenzoate of I and of the second methyldecalol isomer previously reported[4] were both depressed to below 75°.

By an identical sequence of steps (saponification, conversion to the mercapto derivative and desulfurization), VIII was converted to the *trans-cis* isomer IV. When recrystallized from petroleum pentane, IV melted at 67.5–68.5°. It depressed the melting points of I, II and III, but did not depress the melting point of the second isomer previously reported.[4] Its *p*-nitrobenozate and 3,5-dinitrobenzoate melted at 104–105° and 101–102°, respectively. Mixture melting points demonstrated the identity of these derivatives and the corresponding derivatives (m.p. 102–103° and 97.5–98.5°, respectively), of the second methyldecalol isomer previously reported.[4] The assignment of a *trans-cis* configuration proposed earlier[4] for the isomer produced by catalytic hydrogenation of 10-methyl-$\Delta^{1,9}$-octal-2-one therefore has been confirmed.

When the *p*-toluenesulfonate of IV (two interconvertible crystalline forms: m.p. 96.0–96.5° from hexane, 86.5–87.5° from ethanol) was refluxed with potassium acetate in acetic acid–acetic anhydride, 70% of a mixture of octahydronaphthalene elimination products was obtained but only 7.6% of III, isolated as its acetate.

The infrared spectra of the four isomers, of their derivatives and of many of the intermediates involved in their synthesis show absorption bands in the 1450–1475 cm.$^{-1}$ region which appear to be diagnostic of a methylene group in the angular position of the *cis*- or of the *trans*-decalin system. The doublet characteristic of the *cis* ring fusion and the single strong band characteristic of the *trans* ring fusion are illustrated in Fig. 1. This feature can be discerned in the spectra of Idelson and Becker,[12] although not so strikingly because the intense absorption of the relatively thick liquid films they employed tends to obscure these details of their spectra in this region. The absorption spectra of *cis*- and *trans*-decalin[13] do not show this striking difference; rather, both of these isomers have a single symmetrical band in this region. Unfortunately, this region of the spectra of steroids is rather complex, so this criterion of the ring fusion geometry cannot be extended to these more complicated ring systems.[14]

Experimental[15,16]

cis-**10-Methyl-2-***trans***-decalol (I).**—An ether solution containing 4.20 g. (25 millimoles) of 10-methyl-2-*trans*-decalone[9] was added slowly to an ether solution containing 0.5 g. (13 millimoles) of lithium aluminum hydride. After two hours at room temperature the mixture was hydrolyzed by slow addition of 1 cc. of water. The ether filtrate and washings were evaporated to yield 3.6 g. (85%) of liquid alcohol. Crystallization from pentane at −70° gave 2.12 g. (50%), m.p. 64–68°, and a second crop, 0.48 g., m.p. 45–55°. The uncrystallizable residue gave 12% of a **3,5-dinitrobenzoate**, m.p. 108–109°, undepressed by admixture with authentic material.[4] A second preparation gave 3.17 g. (75%) of crystalline **I** after purification by chromatography on alumina with pentane–ether.

The *p***-nitrobenzoate** was prepared using *p*-nitrobenzoyl chloride in pyridine by heating at 100° for three hours. It melted at 71–73° after recrystallization from pentane.

Anal. Calcd. for $C_{18}H_{23}NO_4$: C, 68.1; H, 7.3. Found: C, 67.7; H, 7.0.

cis-**10-Methyl-2-***trans***-decalyl** *p***-Toluenesulfonate.**—In 10 cc. of cold pyridine there was dissolved 2.00 g. (12 millimoles) of the alcohol, m.p. 64–68°, and 3 g. (16 millimoles) of *p*-toluenesulfonyl chloride. After four days at 10°, the solution was treated with 1 cc. of water and after an addi-

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(11) D. Papa, E. Schwenk and H. F. Ginsberg, *J. Org. Chem.*, **14**, 723 (1949).

(12) M. Idelson and E. I. Becker, THIS JOURNAL, **80**, 908 (1958).

(13) A. P. I. Research Project 44, Infrared Spectral Data, Book III, Serial No. 1086, 1087, Feb. 28, 1950.

(14) See for example R. N. Jones and A. R. H. Cole, THIS JOURNAL, **74**, 5648 (1952).

(15) Analyses by Miss Hildegarde Beck, Microanalytical Laboratory, Chemistry Department, Northwestern University.

(16) All melting points observed on micro melting stage, 6× and 12×, with polarizing eyepiece.

tional hour the mixture was poured into water and extracted with ether. The ether extract was washed with dilute hydrochloric acid, then with sodium bicarbonate solution, and finally dried and evaporated. The oil, 3.84 g., was crystallized from absolute alcohol at 0° to give two fractions, 3.03 g. (79%), m.p. 44–47°, and 0.40 g. (10%), m.p. 42–47°. They were combined and recrystallized from 95% alcohol at 0° to give two crops 2.41 g. (63%), m.p. 55–56.5°, and 0.54 g. (14%), m.p. 53–55°. The head fraction was analyzed.

Anal. Calcd. for $C_{18}H_{26}O_3S$: C, 67.0; H, 8.1. Found: C, 66.8; H, 8.0.

***trans*-10-Methyl-2-*trans*-decalol (II).**—The *p*-toluenesulfonate of I (2.2 g., 6.8 millimoles) and anhydrous potassium acetate (4 g., 40 millimoles) were dissolved in 20 cc. of glacial acetic acid and 2 cc. of acetic anhydride. The solution was refluxed 19 hours after which it was cooled and poured into water containing 20 g. of potassium hydroxide. This was warmed and then after cooling was extracted with 1:1 ether-pentane. Evaporation left 0.961 g. of oil. The oil was adsorbed on 25 cc. of 80 mesh alumina in a 1-cm. tube and was eluted with 30-cc. portions of pentane. The first fraction, 0.325 g., proved to be mostly olefin but contained 16 mg. of acetate of II. The next six fractions gave 0.406 g. of non-crystalline acetate. Subsequent elutions with ether furnished 69 mg. (6%) of II, m.p. 72–75°.

The acetate was saponified by refluxing three hours in ethanol containing 1 g. of potassium hydroxide. Extraction with pentane gave 0.326 g. (29%) of crude alcohol, m.p. 70–75°.[17] Crystallization twice from pentane, in which it is quite soluble, gave long needles which melt with sublimation at 89.5–90.5°. The analytical sample was sublimed at 1 mm.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.5; H, 12.0. Found: C, 78.5; H, 11.9.

The 3,5-dinitrobenzoate was prepared using 3,5-dinitrobenzoyl chloride in pyridine by heating for three hours at 100°. It was crystallized from pentane with considerable loss due to solubility and gave plates, m.p. 122–123°.

Anal. Calcd. for $C_{18}H_{22}N_2O_6$: N, 7.7. Found: N, 8.1.

The *p*-nitrobenzoate, prepared as with I above, melted at 153–154° after recrystallization from hexane.

Anal. Calcd. for $C_{18}H_{23}NO_4$: N, 4.4. Found: N, 4.7.

Oxidation of the *trans-trans*-Decalol.—The alcohol (116 mg., 0.70 millimole) in 5 cc. of acetic acid was treated dropwise with 50 mg. (0.50 millimole) of chromic anhydride dissolved in 4 cc. of acetic acid during 25 minutes at 50°. The liquid ketone was recovered by extraction with pentane. It and 150 mg. (15% excess) of 2,4-dinitrophenylhydrazine were taken into solution in 25 cc. of boiling ethanol then 2 cc. of concd. hydrochloric acid was added. After refluxing for an additional 15 minutes the solution was cooled to produce 210 mg. (87%) of 10-methyl-2-*trans*-decalone 2,4-dinitrophenylhydrazone. Recrystallization from 20 cc. of alcohol and then from 20 cc. of dry ether raised the m.p. to 174.5–176°, microscopic hot-stage.[18]

10-[*p*-Toluenesulfonoxymethyl]-2-*cis*-decalone (VI).—A reaction mixture composed of 4.60 g. (25.3 millimoles) of 10-hydroxymethyl-2-*cis*-decalone,[10] (V) and 6.20 g. (32.7 millimoles) of recrystallized *p*-toluenesulfonyl chloride in 20 cc. of pyridine was heated at 70° for 1 hour and allowed to stand overnight. The mixture was poured onto 70 g. of ice and 30 cc. of concentrated hydrochloric acid. Ether extracts were combined, washed free of chloride ion and concentrated to about 20 cc., at which point crystals appeared. The addition of an equal volume of pentane, cooling and filtering permitted the recovery of 8.33 g. (98%) of V, m.p. 78–84°. An analytical sample recrystallized from ethanol melted at 84.5–85.5°.

Anal. Calcd. for $C_{18}H_{24}O_4S$: C, 64.3; H, 7.2. Found: C, 64.3; H, 6.7.

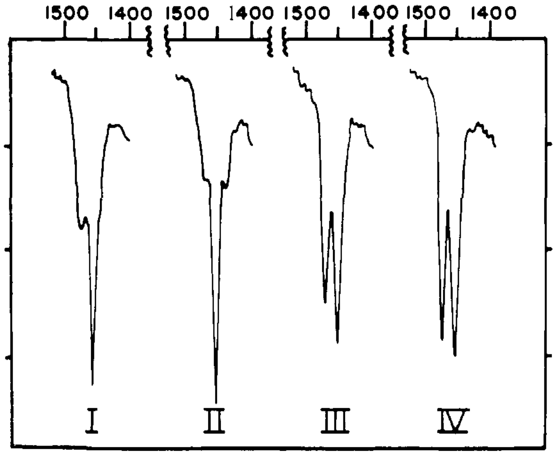

Fig. 1.

***cis*-(VII) and *trans*-10-[*p*-Toluenesulfonoxymethyl]-2-*cis*-decalyl *p*-Nitrobenzoate (VIII).**—A solution of 0.52 g. (14 millimoles) of sodium borohydride in 10 cc. of ethyl alcohol was added over 5 minutes to a solution of 7.60 g. (22.6 millimoles) of VI in 40 cc. of ethyl alcohol with shaking to mix and cooling below 40°. This mixture stood at room temperature for 20 hours then was treated with 2 cc. of water and 1 cc. of glacial acetic acid. After the evolution of hydrogen was complete, the mixture was heated on the steam-bath for 2 hours. The solvent was removed on the water-pump and 40 cc. of water was added. Ether extracts were combined, washed with water and dried over magnesium sulfate. The solvent was removed, finally at 50° at 1 mm., leaving 7.69 g. (100%) of pale yellow, viscous product which would not crystallize.

(A) A sample of this hydroxytosylate (3.88 g., 11.5 millimoles) was dissolved in 30 cc. of anhydrous pyridine and 2.34 g. (12.6 millimoles) of *p*-nitrobenzoyl chloride was added all at once. The reaction mixture was heated on the steam-bath for 15 minutes and then let stand at room temperature for 45 minutes. When poured onto 100 g. of ice and scratched, the product crystallized and was filtered, washed with dilute hydrochloric acid, dilute potassium carbonate and finally with water. Recrystallization from acetone–alcohol gave 3.87 g. (69%) of the *p*-nitrobenzoyl derivative of VIII, m.p. 161–162°, no depression when mixed with the sample prepared from pure *trans*-10-hydroxymethyl-2-*cis*-decalol as described below. From the recrystallization filtrate, an additional 0.12 g. of *p*-nitrobenzoyl derivative of m.p. 160–162° was obtained; total yield 3.99 g. (71%).

Further concentration of this filtrate deposited crystals of the *p*-nitrobenzoyl derivative of the epimeric *cis*-10-[*p*-toluenesulfonoxymethyl]-2-*cis*-decalol (VII), m.p. 112–115°. A fractional crystallization procedure involving alcohol, ether and ether–acetone solvents finally furnished 0.96 g. (17%) of this material, m.p. 114–116°.

Anal. Calcd. for $C_{25}H_{29}NO_7S$: C, 61.6; H, 6.0; N, 2.9. Found: C, 61.2; H, 5.9; N, 3.0.

(B) A sample of *cis*-10-hydroxymethyl-2-*cis*-decalol,[10] m.p. 122–123° (18.5 g., 0.100 mole), was added to 19.5 g. (0.102 mole) of recrystallized *p*-toluenesulfonyl chloride in 50 cc. of pyridine. Heat was liberated. After 24 hours at room temperature, the mixture was poured into 60 cc. of concentrated hydrochloric acid cooled and diluted by 100 g. of ice. Ether extracts were dried thoroughly, then concentrated, and the total residue was added to 23 g. (0.124 mole) of recrystallized *p*-nitrobenzoyl chloride in 100 cc. of pyridine. Heat was evolved. The product was isolated by pouring onto ice and extracting with ether. The crude VII weighed 47.0 g. (96%) and melted at 100–110°. A sample recrystallized several times from ethanol and ethanol–ether melted at 115–116°, no depression when mixed with VII from (A), above.

(C) A sample of pure *trans*-10-hydroxymethyl-2-*cis*-decalol,[10] m.p. 139–140° (500 mg., 2.70 millimoles) and 1.14 g. (6.0 millimoles) of *p*-toluenesulfonyl chloride were dissolved in 25 cc. of chloroform containing 0.95 g. (12 millimoles) of pyridine. This mixture was heated on the steam-

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(17) Calculating the first chromatographic fraction as olefin, 0.325 g. (32% yield), the ratio of displacement to elimination products is approximately the same as in the cholestane series; L. C. King, and M. J. Bigelow, THIS JOURNAL, **74**, 3338 (1952).

(18) For a discussion of literature values see R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *ibid.*, **74**, 4223 (1952), and earlier work in this Laboratory cited by Dreiding and Tomasewski.[6] The method of preparation described in the text avoids the lower melting forms and the tedious purification.

bath for 30 minutes, then poured into water and extracted with chloroform. Evaporation of the solvent left an amorphous residue which would not crystallize. This material showed strong absorption at 2.70–3.00 μ and at 7.35 and 8.50 μ indicating both hydroxyl and sulfonate ester structure.

All of this material (900 mg., 2.70 millimoles) was dissolved in 15 cc. of pyridine and 555 mg. (3.00 millimoles) of *p*-nitrobenzoyl chloride was added. After one hour on the steam-bath, water was added to a point of incipient cloudiness and heating was continued for 15 minutes. The product was washed with water by decantation, then with aqueous potassium carbonate. Recrystallization from ethanol gave 520 mg. (40%) of VIII, m.p. 154–156°. A sample for analysis melted at 161–163°, from ethanol.

Anal. Found: C, 61.9; H, 5.8.

***cis*-10-Methyl-2-*cis*-decalol (III).**—A sample of 15.01 g. (30.8 millimoles) of VII, m.p. 112–116°, was saponified by shaking it with a hot solution of 2.2 g. of potassium hydroxide in 100 cc. of ethanol until all dissolved. The solvent was removed at the water-pump and an ether extract of the residue was washed and dried. Acidification of the ether-insoluble residue furnished 5.09 g. (99%) of *p*-nitrobenzoic acid. Evaporation of the ether solution gave 9.55 g. (92%) of crude *cis*-10-[*p*-toluenesulfonoxymethyl]-2-*cis*-decalol, m.p. 55–70°. Recrystallization from benzene–hexane gave 9.43 g. (90%) of product melting at 75–78°. A sample for analysis, from ether, melted at 78–79°.

Anal. Calcd. for $C_{18}H_{26}O_4S$: C, 63.9; H, 7.7. Found: C, 63.4; H, 7.8.

All of the latter material (27.7 millimoles) was dissolved in 20 cc. of re-distilled dimethylformamide and a solution of 35 g. of 25% aqueous sodium hydrosulfide in 50 cc. of dimethylformamide was added.[9] This mixture was refluxed under nitrogen in a flask equipped with an air condenser, 40 mm. in diameter, topped with a water-jacketed condenser. The large diameter condenser was necessary to prevent clogging by dimethylammonium hydrosulfide which accumulates and sublimes. After 20 hours, the mixture was cooled and poured into 200 cc. of saturated sodium chloride solution. Slightly odoriferous *cis*-10-mercaptomethyl-2-*cis*-decalol was recovered by extraction with ether, 5.60 g. (100%).

The whole of this was dissolved in 60 cc. of absolute alcohol without further purification and this solution was added all at once to an active nickel catalyst, W-5,[19] prepared from 75 g. of Raney alloy dispersed in 50 cc. of absolute alcohol. The mixture was maintained at reflux for 2.5 hours, then cooled and filtered. The slightly pyrophoric nickel residue was washed with several portions of solvent and the combined filtrates were concentrated by removal of the solvent through a 3-plate column. The addition of water to the residue, extraction with pentane and removal of this solvent furnished 5.5 g. of pentane-soluble residue. This was vacuum distilled at 110–112° at 4 mm. to give 4.00 g. (85%) of III which would not crystallize.

The 3,5-dinitrobenzoate prepared as above melted at 95–97°, from hexane.

Anal. Calcd. for $C_{18}H_{22}N_2O_6$: C, 59.7; H, 6.1. Found: C, 59.4; H, 5.9.

The *p*-nitrobenzoate melted at 74–75°, from pentane.

Anal. Calcd. for $C_{18}H_{23}NO_4$: C, 68.1; H. 7.3. Found: C, 67.9; H, 7.3.

Mixture melting points of these derivatives of III with the corresponding derivatives of I, II and of the earlier described 10-methyl-2-decalol[4] all showed depression

***trans*-10-Methyl-2-*cis*-decalol (IV).**—A sample of 24.38 g. (50.1 millimoles) of VIII was saponified by heating for 0.5 hour on the steam-bath with 3.42 g. (55.0 millimoles) of 90% potassium hydroxide in 150 cc. of ethyl alcohol. Removal of the solvent at reduced pressure, addition of water and extraction with ether furnished 16.92 g. (100%) of uncrystallizable product and 8.20 g. (98%) of *p*-nitrobenzoic acid.

A small sample of the product from above (0.714 g., 2.11 millimoles) with 0.43 g. (2.3 millimoles) of *p*-nitrobenzoyl chloride in 10 cc. of pyridine gave 0.876 g. (85%) of VIII after recrystallization from ethyl alcohol, m.p. 161–162°.

The remainder of the saponification product (16.19 g., 47.9 millimoles) was converted to IV exactly as described above for the preparation of III except that proportionately larger amounts of reagents and solvents were used. The 10.34 g. of *trans*-10-mercaptomethyl-2-*cis*-decalol furnished 8.34 g. of pentane-soluble desulfurization product. This crystallized on standing. The product was filtered, washed with pentane cooled below −50°, and dried under vacuum. The white platelets obtained weighed 4.99 g. and melted at 49–61°. A second crop of crystals of the same melting range amounted to 0.29 g.; total crude yield 65%. Several recrystallizations from pentane furnished needles, m.p. 67.5–68.5°; 3.31 g. (41%). A chromatographic procedure on alumina permitted the recovery of an additional 1.45 g. (18%) of pure IV from the recrystallization filtrates. A second preparation employing 0.111 mole of VIII furnished 17.1 g. (92%) of IV when the crude product after desulfurization was vacuum distilled (98–99° at 2 mm.). This crystallized on standing, m.p. 60–65°. It did not depress the melting point of the alcohol earlier assigned this structure.[4]

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.5; H, 12.0. Found: C, 78.9; H, 11.8.

The 3,5-dinitrobenzoate melted at 101–102° after recrystallization from pentane. When mixed with the 3,5-dinitrobenzoate, described earlier[4] to melt at 97.5–98.5°, the melting point was observed to be 98–102°.

The *p*-nitrobenzoate melted at 104–105°, from hexane; no depression when mixed with a sample prepared from the IV isolated earlier.[4]

Anal. Calcd. for $C_{18}H_{23}NO_4$: C, 68.1; H, 7.3. Found: C, 67.9; H, 7.2.

The *p*-toluenesulfonate was prepared, as described above for this derivative of I, from 6.30 g. (37.7 millimoles) of IV. Crystallization from ethanol gave 8.91 g. (73%) of product which melted over a range from 85–94°. A sample recrystallized from hexane formed massive crystals, m.p. 96–96.5°. The melt resolidified in a feathery form, m.p. 86–87°. These forms could be interconverted by seeding hexane and ethanol solutions with a crystal of the high-melting or low-melting form, respectively.

Anal. Calcd. for $C_{18}H_{26}O_3S$: C, 67.0; H, 8.1. Found: C, 67.5; H, 7.8.

After 8.05 g. (25.0 millimoles) of this *p*-toluenesulfonate, m.p. 92–94°, was subjected to a displacement reaction as described above for the *p*-toluenesulfonate of I, vacuum distillation gave 2.29 g. (61%) of 9-methyloctalins, b.p. 82° at 16 mm., and 0.897 g. of higher-boiling material. The latter was treated with 0.25 g. of lithium aluminum hydride in anhydrous ether and the reaction mixture was hydrolyzed and worked up in the usual way. The crude product weighed 0.687 g. and was purified by a chromatographic procedure on alumina using pentane, pentane–ether, ether and water-saturated ether in sequence. An additional 0.356 g. (9%) of methyloctalins was recovered from the early pentane fractions and 0.317 g. of III was recovered from the final wet ether eluates. The *p*-nitrobenzoate of this material melted at 72–74°, no depression with this derivative of III prepared as described above.

Infrared Spectra.—The infrared spectra of chloroform solutions of I and II and of the related compounds 9-hydroxymethyl-2-*trans*-decalin,[4] *cis*-10-hydroxymethyl-2-*trans*-decalol,[4,10] *trans*-10-hydroxymethyl-2-*trans*-decalol,[10] 10-hydroxymethyl-2-*trans*-decalone,[10] the dioxolan derivative of the latter[10] and 10-methyl-2-*trans*-decalone[18] all exhibited a single strong absorption band at 1448–1452 cm.$^{-1}$. Much weaker bands, 10–20 wave numbers above and below this strong band, were present in most of these spectra.

The infrared spectra of chloroform solutions of III and IV and of the related compounds VII, VIII, the saponification products of the latter two, 10-hydroxymethyl-2-*cis*-decalone[10] and the dioxolan derivative of the last[10] all exhibited a strong absorption band at 1450–1455 cm.$^{-1}$ and a second strong band of just slightly lower intensity at 1470–1475 cm.$^{-1}$.

Other differences in the otherwise very similar spectra of I, II, III and IV were observed in the 990–1060 cm.$^{-1}$

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(19) H. R. Billica and Homer Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 176.

region, where each isomer exhibited a unique ratio of intensities, and slight displacements, of three prominent absorption bands: I, 1030 > 1058 > 1007; II, 997 > 1030 > 990 (shoulder); III, 1023 > 1055 > 1008; IV, 1060 > 1035 > 1010.

EVANSTON, ILL.

[JOINT CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SYNTEX, S.A., AND THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Optical Rotatory Dispersion Studies. XXIII.[1] α-Haloketones (Part 3)[2]

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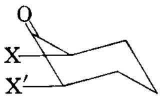
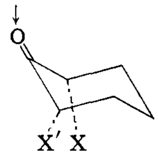
The earlier work on the optical rotatory dispersion of steroidal α-haloketones has been extended to include equatorial iodo- and fluoroketones. An examination of the rotatory dispersion curves of 21-fluoro-, chloro-, bromo- and iodo-20-keto steroids as well as of 17α-chloro- and 17α-bromo-20-ketones suggests that under certain circumstances, the "axial haloketone rule" may be employed to differentiate between free rotational isomers.

A systematic study[2] of the rotatory dispersion curves of a variety of α-bromo- and α-chloroketones of the steroid series has led to certain generalizations[2,4] which can be summarized briefly as follows: In a cyclohexanone (Ia) existing in the chair form,[5] introduction of *equatorial* chlorine or bromine in the α-(Ib) or α'-(Ic) positions does not affect the sign of the single Cotton effect curve[6] of the parent ketone Ia although there may be noted differences in amplitude.[6] On the other hand *axial* chlorine or bromine may alter the situation profoundly and the sign of the Cotton effect curve can be predicted by employing the following, empirical device.[2,4] By looking down the $O{=}C$ axis as indicated by the arrow (II), a cyclohexanone derivative with chlorine or bromine to the left (IIa) of the observer will show a negative Cotton effect while if the halogen atom is located to the right (IIb), a positive Cotton effect will be predicted.



Ia, X = X′ = H
b, X = Cl or Br; X′ = H
c, X = H; X′ = Cl or Br



IIa, X = Cl or Br; X′ = H
b, X = H; X′ = Cl or Br

This "axial haloketone rule"—for which no exception has as yet been noted—affords a simple means to establish absolute configurations and it has been used[7] recently to demonstrate conformational mobility in *trans*-2-chloro-5-methylcyclohexanone. In order to define more precisely the scope of these generalizations, we have determined the optical rotatory dispersion curves of a number of additional steroidal α-haloketones and the present paper is concerned with these results.

In our earlier communication,[2] attention was directed to the observation that the few steroidal α-fluoroketones which had been measured—9α-fluoro-11-ketones or 12α-fluoro-11-ketones—did not follow this rule since in these cases the axial fluorine had exactly the opposite effect from that observed for chlorine or bromine; no data were available for α-iodoketones.

We have now repeated the preparation of 2α-iodocholestan-3-one (IIIa)[8] and measured its rotatory dispersion curve. This substance was of particular interest since its ultraviolet absorption maximum occurs at 258 mμ[8] as compared to 279–282 mμ recorded[9] for 2α-chloro- (IIIc) and 2α-bromocholestan-3-one (IIIb). In view of the excellent correlation between ultraviolet absorption and rotatory dispersion data,[2] it might have been anticipated that the peak (or trough) of 2α-iodocholestanone (IIIa) would be encountered at a lower wave length than reported[2] for the chloro and bromo analogs, but this did not prove to be the case. As can be seen from the data listed in the Experimental section, 2α-iodocholestan-3-one exhibited a positive Cotton effect curve with a peak in the 310 mμ region, identical with that observed[2] for 2α-chloro- or 2α-bromocholestan-3-one. The simplest explanation is that in addition to the reported[8] ultraviolet absorption maximum at 258 mμ, there exists a carbonyl band in the 280 mμ region (apparently masked by the stronger 258 mμ maximum and hence not detected) which is optically active and which is responsible for the observed rotatory dispersion curve.

Quite recently, 2α-fluorocholestan-3-one (IIId)—the first known steroidal equatorial α-fluoroketone—has been synthesized[10] and its rotatory dispersion curve also has been found to be characterized by a single, positive Cotton effect. From the data collected in Table I, one can enlarge the scope of our earlier generalization[2] by stating that *equatorial* halogen does not appear to alter the sign of the Cotton effect of the parent ketone, irrespective of

[1] Paper XXII, C. Djerassi, L. A. Mitscher and B. J. Mitscher, THIS JOURNAL, **81**, 947 (1959).

[2] Part 2, C. Djerassi, J. Osiecki, R. Riniker and B. Riniker, *ibid.*, **80**, 1216 (1958).

[3] This material represents part of the professional thesis submitted by Srta. Irma Fornaguera to the Escuela Nacional de Ciencias Químicas de la Universidad Nacional Autónoma de México for the degree "Químico Farmacéutico Biólogo."

[4] C. Djerassi and W. Klyne, THIS JOURNAL, **79**, 1506 (1957).

[5] The applicability of these generalizations to boat forms will be discussed in a forthcoming article from this Laboratory.

[6] For nomenclature see C. Djerassi and W. Klyne, *Proc. Chem. Soc.*, 55 (1957).

[7] C. Djerassi and L. E. Geller, *Tetrahedron*, **3**, 319 (1958).

[8] G. Rosenkranz, O. Mancera, J. Gatica and C. Djerassi, THIS JOURNAL, **72**, 4077 (1950).

[9] R. C. Cookson, *J. Chem. Soc.*, 282 (1954).

[10] R. B. Gabbard and E. V. Jensen, *J. Org. Chem.*, **23**, 1406 (1958). We are greatly indebted to these investigators for a gift of 2α-fluorocholestan-3-one (IIId).