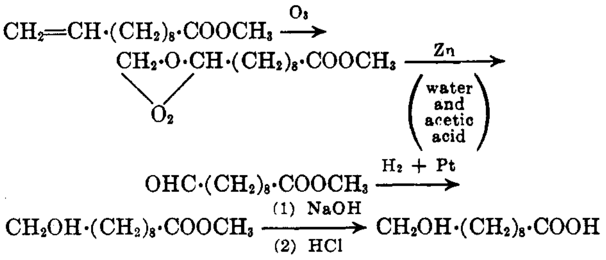
reported by Lycan and Adams is the most direct but requires four steps:



$$CH_2{=}CH\cdot(CH_2)_8\cdot COOCH_3 \xrightarrow{O_3} CH_2\cdot O\cdot CH\cdot(CH_2)_8\cdot COOCH_3 \xrightarrow[\left(\text{water and acetic acid}\right)]{Zn} OHC\cdot(CH_2)_8\cdot COOCH_3 \xrightarrow{H_2 + Pt} CH_2OH\cdot(CH_2)_8\cdot COOCH_3 \xrightarrow[(2)\ HCl]{(1)\ NaOH} CH_2OH\cdot(CH_2)_8\cdot COOH$$

The method reported herein eliminates two of these steps, conversion of methyl undecenoate ozonide to the aldehydo ester, and catalytic hydrogenation of the hydroxy ester. Instead, the ozonide is reduced directly to methyl 10-hydroxydecanoate with sodium borohydride. 10-Hydroxydecanoic acid is then obtained in an overall yield of nearly sixty per cent by saponification of the ester. Although reduction of ozonides has been accomplished with lithium aluminum hydride,[5] sodium borohydride was employed to avoid concomitant reduction of the ester moiety.[6]

EXPERIMENTAL

10-Hydroxydecanoic acid. A solution of 20.0 g. of methyl 10-undecenoate in 60 ml. of ethyl acetate, maintained at a temperature of −50 to −60°, was treated approximately for 1¹/₄ hr. with a slow stream of ozone in oxygen until ozone was detected in the exit gases. The solution of ozonide[7] was then added rapidly (within 2 min.) to a vigorously stirred ice cold mixture of 6.0 g. of sodium borohydride and 120 g. of tetraethylene glycol dimethyl ether. The mixture was stirred for 2 hr. at ice-bath temperature and an additional hour at room temperature after which it was poured into 1 l. of water containing 30 ml. of concentrated hydrochloric acid. The hydrolysis mixture was saturated with salt; the oil which formed was separated and the aqueous fraction extracted with three 100-ml. portions of diethyl ether. The combined oil and ether extracts was washed successively with water, aqueous sodium carbonate, and water and dried over anhydrous magnesium sulfate. After removal of ether by evaporation under reduced pressure, the residual oil was heated at reflux temperature for 30 min. with 50 ml. of 20% aqueous sodium hydroxide. The saponification mixture was then steam distilled until turbidity and odor were no longer detected in the distillate, after which it was cooled in an ice bath and acidified with 1:1 aqueous hydrochloric acid. The resulting precipitate was filtered, washed with water until free from mineral acid, and dried. It was dissolved in hot ethylene dichloride, filtered to remove a small amount of insoluble material, and allowed to recrystallize. In this manner, 12.0 g. (59%) of a colorless crystalline product, m.p. 75–76°, was obtained.

Anal.[8] Neut. equiv. Calcd.: 188.2. Found: 189.2. Hydroxyl value. Calcd.: 9.02. Found: 9.15.

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(7) The ozonide solutions were kept cold at all times and no difficulty was experienced in handling them under these conditions. As an added safety precaution, however, operations may be carried out behind an explosion-proof shield.

(8) The authors are indebted to Mr. L. D. Metcalfe for these analyses.

Conformational Analysis of the Prins Reaction

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It has been shown that the Prins reaction gives stereospecifically *trans*-2-hydroxymethylcyclohexanol when cyclohexene is employed as the olefin.[2,3] In an effort to elucidate the initial conformation of the products of this reaction we have employed the rigid *trans*-Δ^2-octalin[4] system (I).

It is generally agreed[3,5,6] that the first step in a Prins reaction involves the addition of a proton to a neutral formaldehyde molecule. The stereospecific *trans* addition of the hydroxy and the hydroxymethylene groups to the double bond of a cyclic olefin argues against a free carbonium ion but can be rationalized on the basis of a solvated cyclic intermediate. By comparison with other addition reactions involving cyclic intermediates, *i.e.* bromination, the product would be predicted to exhibit a diaxial conformation[7] of the hydroxy and hydroxymethylene groups. Our results confirm the above postulation.

Under the conditions of the Prins reaction, *trans*-Δ^2-octalin, I, gave *trans*-2-hydroxymethyl-3-hydroxy-*trans*-decalin, II. The conformation of this compound was proved in the following manner: The *mono*-tosylate, III, was prepared and subsequently displaced by cyanide ion. The latter re-

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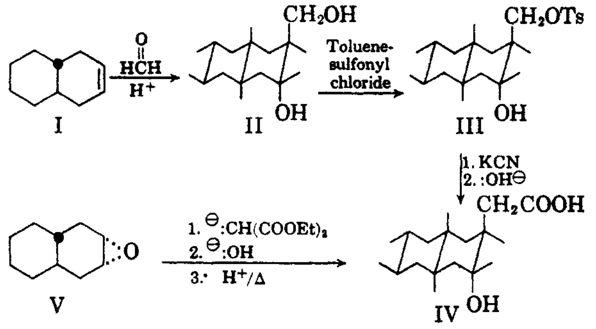
action was performed in dimethyl sulfoxide solution[8] and gave an uncrystallizable nitrile (4.43 μ). The nitrile was subjected to alkaline hydrolysis and yielded a hydroxy acid, IV.

The acid, IV, was identical in all properties with one prepared by Johnson and Bauer[9] through the opening of 2,3-epoxy-*trans*-decalin, V, with the anion of malonic ester, followed by hydrolysis and monodecarboxylation. This method could only give rise to a diaxial product, IV, hence the Prins product, II, must have the diaxial conformation.



EXPERIMENTAL

trans-2(a)-Hydroxymethyl-3(a)-hydroxy-trans-decalin, II. A mixture of 12 g. (0.4 mole) paraformaldehyde, 90 ml. glacial acetic acid, and 2 ml. sulfuric acid was heated to 85° while stirring. After solution was effected the temperature was lowered to 65° and 19 g. (0.14 mole) *trans*-Δ^2-octalin was allowed to drop into the stirred reaction mixture over a period of 0.5 hr. The mixture was then stirred at room temperature for 10 hr. and subsequently diluted with 150 ml. of water and extracted with three 150-ml. portions of ether. The combined ether extracts were then washed with 200 ml. water and with saturated sodium carbonate solution until the ethereal solution was neutral. The ethereal solution was then washed with 200 ml. of water and dried over anhydrous magnesium sulfate. The ether was removed and the residual oil was dissolved in a solution of 12 g. sodium hydroxide in 150 ml. ethanol and refluxed for 2 hr. The reaction mixture was diluted with 300 ml. water and extracted with three 200-ml. portions of ether. The solution was dried, the ether removed, and the residual oil crystallized on standing. Recrystallization from benzene yielded 8 g. (25%) of the product, m.p. 159–160°.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.93; H, 10.35.

trans-2(a)-Tosyloxymethyl-3(a)-hydroxy-trans-decalin, III. A solution of 20 ml. pyridine, 1 g. (0.006 mole) *p*-toluene sulfonyl chloride, and 1 g. (0.005 mole) *trans*-2(*a*)-hydroxymethyl-3(*a*)-hydroxy-*trans*-decalin was allowed to react at room temperature for 1 hr. The solution was then poured into an ice slurry of dilute hydrochloric acid. The resulting precipitate was filtered and recrystallized from Skellysolve B. White needles, m.p. 103.5–104° were obtained in a yield of 1.10 g. (55%).

Anal. Calcd. for $C_{18}H_{26}O_4S$: C, 62.93; H, 7.46; S, 9.88. Found: C, 63.40; H, 7.43; S, 9.47.

trans-2(a)-Cyanomethyl-3(a)-hydroxy-trans-decalin. A stirred mixture of 1.0 g. (0.003 mole) of the monotosylate, III, 1.2 g. (0.18 mole) potassium cyanide, and 20 ml. dimethylsulfoxide was heated at 210° for 5.5 hr. The reaction mixture was diluted with 150 ml. of water and extracted with three 100-ml. portions of ether. The ethereal extracts were then washed with two 75-ml. portions of water and dried over anhydrous magnesium sulfate. The ether was removed and the residual oil would not crystallize. Attempts to purify the oil by distillation failed. The infrared spectrum was in good agreement with the expected product and a sharp nitrile band at 4.43 μ was observed.

trans-2(a)-Carboxymethyl-3(a)-hydroxy-trans-decalin, IV. The crude nitrile was dissolved in 20 ml. of a solution of 10% sodium hydroxide in diethylene glycol and heated at 170° for 3 hr. The reaction mixture was diluted with 100 ml. water and extracted with two 150-ml. portions of ether. The aqueous layer was made acidic with 5*N* HCl and extracted with three 100-ml. portions of ether. The ether solution was then washed with water and dried. The ether was removed and the residual oil was chromatographed on a silicic acid–chloroform column using chloroform as the eluant. The acid was removed from the column as a distinct yellow band with 50% ethanol in chloroform. The solvent was removed and the residue crystallized on standing. Recrystallization from ethyl acetate gave 0.3 g. (50% based on the tosyl compound) of white crystalline material, m.p. 115–116°. There was no depression of melting point on admixture of this acid with that prepared by Johnson and Bauer. The infrared spectra were superimposable.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.26; H, 9.40.

Acknowledgment. We are grateful to Dr. W. S. Johnson and Dr. V. Bauer for a sample of *trans*-2-(*a*)-carboxymethyl-3(*a*)-hydroxy-*trans*-decalin.

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Some Reactions of 1,1,1-Trichloro-2-propanol[1]

O. R. Pierce, E. E. Frisch, and D. D. Smith[2]

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The dehydration of 1,1,1-trichloro-2-propanol has been studied by various researchers who have assigned to the product either the structure 3,3,3-trichloro-1-propene[3–5] or 1,1,2-trichloro-1-propene.[6] In this laboratory it was found that dehydration of the alcohol with phosphorus pentoxide did produce 1,1,2-trichloro-1-propene in confirmation of the work of Kirrmann.[6] Reaction of 1,1,1-trichloro-2-propanol with alumina at elevated temperatures or with zinc chloride in hydrochloric acid solution

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[1] Presented before the Organic Division, 132nd Meeting of the American Chemical Society, New York, September, 1957.

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