system may be related to the oxidation potential of the ferro–ferriperoxidase couple, which may be too positive to be reduced by ascorbic acid. Whether or not a higher oxidation state of the peroxidase iron atom may participate is apparently open to question. Mason suggested that compound III of peroxidase, which predominates in systems containing peroxidase and dihydroxyfumaric acid, is a ferrous form of the enzyme. Chance, however, was able to reduce compound III with $Na_2S_2O_4$ to a form which reacted with CO,[30] suggesting that this species contains iron in a higher oxidation state than +2. Spectral evidence also indicated the presence of compound II, the +4 iron form of the enzyme. On the basis of the available information, the behavior of the model system, at least, appears to be satisfactorily explained by a free radical mechanism. Stated in another way, there appears to be no good reason for accepting a mechanism involving +4 iron species as long as the data are compatible with the radical mechanism involving conventional intermediate species. This is not to exclude any participation by a ferryl species which may actually be involved to some extent. In the case of the enzyme itself, some evidence of the +4 iron species exists, although the reaction products are again compatible with the free radical mechanism as the principal one.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Terpenoids. XLII.[1] The Absolute Configuration of (−)-Methylisopulegone[2]

BY E. J. EISENBRAUN, F. BURIAN,[3] JEANNE OSIECKI AND CARL DJERASSI

RECEIVED DECEMBER 15, 1959

The stereochemistry of the direct alkylation product of (+)-pulegone (I)—(−)-methylisopulegone (II)—has been established by determining the absolute configuration of the quaternary carbon atom and this was found to be contrary to earlier expectation (III). The stereochemical assignment was based on a multi-stage degradation of (−)-methylisopulegone (II) to (+)-α-methyl-α-isopropylglutaric acid (XII), which was related by Fredga's quasi-racemate method to the known (+)-α-isopropylglutaric acid (XVI). Alternatively, (−)-methylisopulegone (II) was transformed to (−)-2-methyl-2-isopropylbutane-1,4-diol (IX), also derivable from the known (−)-α-methyl-α-isopropylsuccinic acid.

Direct methylation of (+)-pulegone (I)[4] is known[5] to lead in good yield to (−)-methylisopulegone (2,5-dimethyl-2-isopropenylcyclohexanone). While there exists no question about the structure of this product, its stereochemistry can be represented by either II or III and a tentative preference for the latter has been expressed recently.[6] In connection with extensive studies in this Laboratory[7] on the relationship of rotatory dispersion and conformation of monocyclic cyclohexanones, (−)-methylisopulegone (II or III), constituted a key intermediate and it was felt necessary to establish its stereochemistry by unambiguous means. The solution of this stereochemical problem also has a bearing on the mechanism of alkylation[7] of conformationally flexible cyclohexanones and no secure *a priori* predictions can be made in view of recent information[8] on the preferred conformations of (−)-menthone and (+)-isomenthone, which suggests that in the latter an axial isopropyl substituent adjacent to the ketone function may be preferred over an axial methyl group in the 3-position of a cyclohexanone.

The extensive quasi-racemate studies of Fredga[9] and his collaborators have led to the elucidation of the absolute configurations of a variety of alkylated succinic and glutaric acids. We felt, therefore, that the most straightforward solution to the stereochemistry of (−)-methylisopulegone (subsequently shown to be II) would be a systematic degradation of its reduction product, methyldihydroisopulegone (2,5-dimethyl-2-isopropylcyclohexanone) (IV), to a substituted succinic or glutaric acid which would then be amenable to interrelation with one of Fredga's reference acids.[4]

(−)-Methylisopulegone (II),[5] carefully purified by regeneration of its crystalline semicarbazone, was hydrogenated to (+)-methyldihydroisopulegone (IV)[4] and then brominated in aqueous solution. A homogeneous, crystalline monobromide, (−)-2-bromo-3,6-dimethyl-6-isopropylcyclohexanone (V), was obtained in high yield and careful, high-resolution infrared spectroscopic measurements in solvents of different polarities[10] indicated that the substance existed as a mixture of two conformational isomers, the conformer with the equatorial bromine atom[11] predominating (71%

(1) Paper XLI, D. Arigoni, D. H. R. Barton, R. Bernasconi, C. Djerassi, J. S. Mills and R. E. Wolff, *J. Chem. Soc.*, 1900 (1960).

(2) The major portion of the experimental work was performed in the Department of Chemistry of Wayne State University. Grateful acknowledgment is made to the Division of Research Grants (grant No. RG-3863 and RG-6840) of the National Institutes of Health, U. S. Public Health Service, for financial assistance.

(3) Undergraduate (sophomore) research fellow, 1958–1959.

(4) All structural formulas in the present paper imply absolute configurational representations using the steroid convention: dotted bonds denote a substituent below the plane of the paper, while a solid bond refers to one above it.

(5) G. A. R. Kon and J. H. Nutland, *J. Chem. Soc.*, 3101 (1926); J. M. Conia, *Bull. soc. chim. France*, 943 (1954).

(6) A. Melera, D. Arigoni, A. Eschenmoser, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **39**, 441 (1956).

(7) J. Osiecki, E. J. Eisenbraun and C. Djerassi, to be published. See also paper presented by C. Djerassi, L. E. Geller, J. Osiecki and E. J. Eisenbraun at Symposium on Conformational Analysis, A.C.S. Meeting, San Francisco, Calif., April, 1958, Abstracts, p. 30-N.

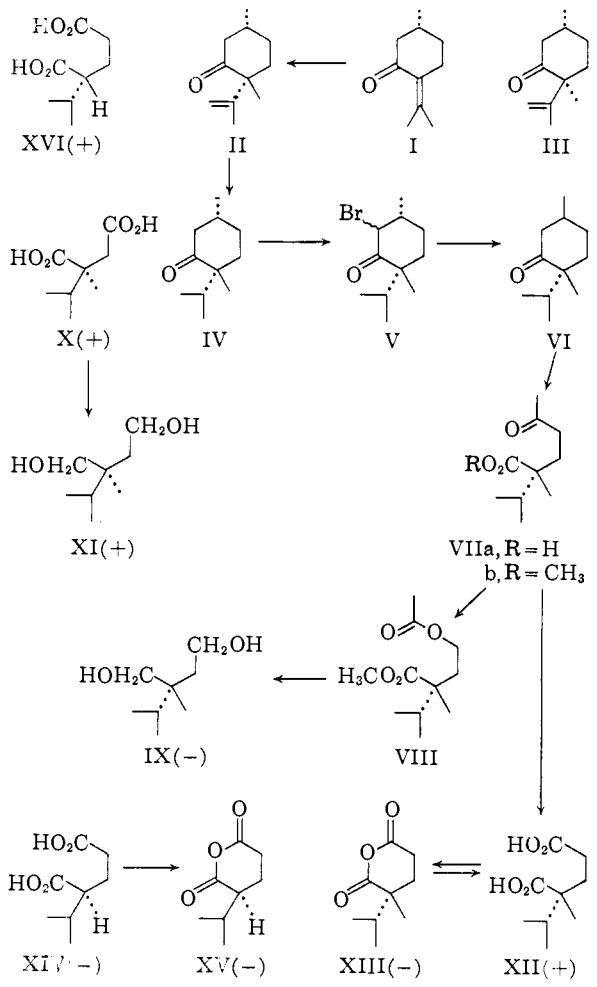
(8) C. Djerassi, "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1960, Chapter 7, Section 3.

(9) See A. Fredga, *Tetrahedron*, **8**, 126 (1960), and *Svensk. Kem. Tid.*, **67**, 343 (1955) for review and leading references.

(10) J. Allinger and N. L. Allinger, *ibid.*, **2**, 64 (1958); N. L. Allinger and J. Allinger, THIS JOURNAL, **80**, 5476 (1958).

(11) In spite of the fact that the infrared measurements demonstrate the predominance of an equatorially oriented bromine atom, we are presently refraining from an absolute configurational assignment of the bromine atom in V, since this is partly dependent upon the conforma-

(carbon tetrachloride)–82% (dimethyl sulfoxide)). Dehydrobromination[12] of the bromo ketone V with lithium bromide and lithium carbonate in dimethylformamide solution produced (−)-3,6-dimethyl-6-isopropyl-Δ^2-cyclohexenone (VI), which was ozonized to (+)-2-methyl-2-isopropyl-5-oxocaproic acid (VIIa). Its methyl ester VIIb, further characterized as the crystalline 2,4-dinitrophenylhydrazone, was subjected to peroxytrifluoroacetic acid oxidation[13] and the resulting acetate VIII was reduced with lithium aluminum hydride to (−)-2-methyl-2-isopropylbutane-1,4-diol (IX). The antipode XI of this alcohol was formed in the lithium aluminum hydride reduction of (+)-α-methyl-α-isopropylsuccinic acid (X) of established absolute configuration,[14] thus leading to the absolute configurational representations[4] II–IX in the above-mentioned degradation sequence. The antipodal nature of the alcohols IX and XI was demonstrated by coincidence of their respective infrared spectra and their specific rotations ($[\alpha]_D$ − 2.06° *vs.* $[\alpha]_D$ + 2.07°), but since we were unable to prepare a crystalline derivative and the magnitude of the rotations was very low, a second independent configurational tie-up was sought.



For this purpose, the keto-acid VIIa was oxidized with sodium hypobromite to the crude glutaric acid XII. For purification, the latter was transformed into the crystalline (−)-α-methyl-α-isopropylglutaric anhydride (XIII) and then reconverted into (+)-α-methyl-α-isopropylglutaric acid (XII). These two substances could now be used for quasi-racemate studies, since Fredga and Miettinen[15] had related (−)-α-isopropylglutaric acid (XIV) to (+)-α-methylsuccinic acid (and hence[14] to (+)-α-methyl-α-isopropylsuccinic acid (X)); in contrast to the α-methyl-α-isopropyl series (XII, XIII), there is no change in the sign of rotation[16] in going from α-isopropylglutaric acid (XIV) to its anhydride XV. As shown in Fig. 1, the melting point diagrams of mixtures of (+)-α-methyl-α-isopropylglutaric acid (XII) and (−)-α-isopropylglutaric acid (XIV)[16] (Fig. 1a) as well as of (−)-α-methyl-α-isopropylglutaric anhydride (XIII) and (−)-α-isopropylglutaric anhydride (XV) (Fig. 1b) definitely show the formation of quasi-racemates. The melting point diagram (Fig. 1c) of mixtures of (+)-α-methyl-α-isopropylglutaric acid (XII) and (+)-α-isopropylglutaric acid (XVI),[16] however, is of the common eutectic type in accordance with expectation.

In summary, the stereochemical conclusions reached by the quasi-racemate procedure involving the substituted glutaric acids (XII, XIV) and their anhydrides (XIII, XV) are in complete agreement with those derived from the degradative sequence to (−)-2-methyl-2-isopropylbutane-1,4-diol (IX). It follows, therefore, that (−)-methylisopulegone possesses the absolute configuration implicit in stereoformula II.

Acknowledgment.—We are indebted to Prof. A. Fredga of the University of Uppsala for gifts of several optically active dicarboxylic acids and to Dr. Berndt Sjöberg for help in the quasi-racemate studies.

Experimental[17]

(−)-2-Bromo-3,6-dimethyl-6-isopropylcyclohexanone (V).—To a stirred suspension of 2.29 g. of (+)-dihydromethylisopulegone (IV)[7] (semicarbazone, m.p. 187–188°) in

tional representation of IV which will be discussed in another paper (see ref. 7).

(12) R. Joly, J. Warnant, G. Nominé and D. Bertin, *Bull. soc. chim. France*, 366 (1958).

(13) W. D. Emmons and G. B. Lucas, THIS JOURNAL, **77**, 2287 (1955).

(14) The absolute configurations in this series are all based on the quasi-racemate method of Fredga (ref. 9). Thus, (+)-α-methylsuccinic acid has been related (A. Fredga, *Arkiv Kemi Mineral. Geol.*, **15B**, No. 23 (1942)) with (+)-α-mercaptosuccinic acid and this in turn (A. Fredga, *ibid.*, **14B**, No. 27 (1941)) with D-(+)-malic acid. Alternatively, (+)-α-methylsuccinic acid has been obtained (J. v. Braun and F. Jostes, *Ber.*, **59**, 1091 (1926); E. J. Eisenbraun and S. M. McElvain, THIS JOURNAL, **77**, 3383 (1955)) from (+)-pulegone (I), whose absolute configuration is known (see K. Freudenberg, *et al.*, *Ann.*, **587**, 213 (1954)). Furthermore, the α-methyl-, α-ethyl- and α-isopropylsuccinic acids of the same sign (in terms of $[\alpha]_D$) have all been shown (A. Fredga and E. Leskinen, *Arkiv Kemi Mineral. Geol.*, **19B**, No. 1 (1944)) to belong to the same stereochemical series and (+)-α-isopropylsuccinic acid, which has thus been related to D-(+)-malic acid, has been demonstrated (J. Porath, *Arkiv Kemi*, **1**, 385 (1949)) to exhibit the same configuration (with respect to the isopropyl group) as (+)-α-methyl-α-isopropylsuccinic acid (X). The methyl group of the latter (X), can therefore be equated stereochemically to hydrogen.

(15) A. Fredga and J. K. Miettinen, *Acta Chem. Scand.*, **1**, 371 (1947).

(16) A. Fredga, *Arkiv Kemi Mineral. Geol.*, **23B**, No. 2 (1946).

(17) Melting points and boiling points are uncorrected. The infrared measurements were performed by Miss B. Bach with a Beckman model IR-4 double beam spectrophotometer. Unless noted

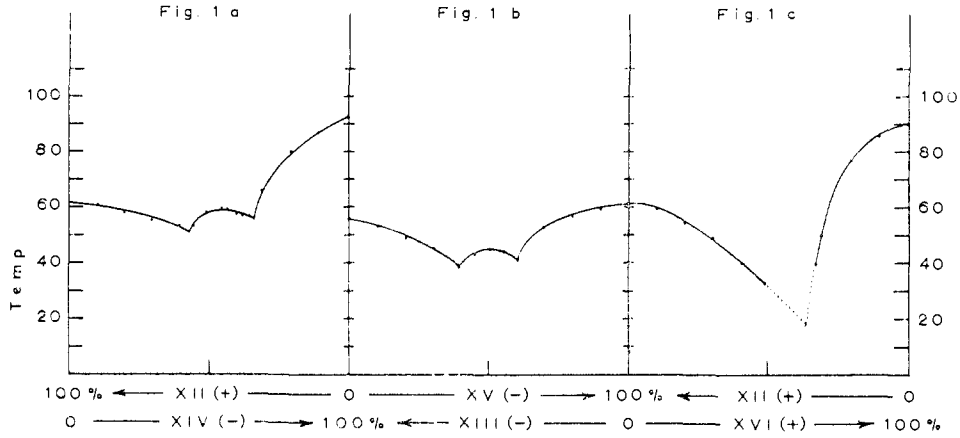


Fig. 1.—Melting point diagrams for various compositions of (a) (+)-XII *vs.* (−)-XIV; (b) (−)-XIII *vs.* (−)-XV; (c) (+)-XII *vs.* (+)-XVI, the points on the curves actually representing experimental melting points. In Fig. 1c, the dotted line refers to the region where liquefaction occurred without any resolidification.

8 cc. of water was added dropwise over a period of 3 hr. 2.38 g. of bromine. After complete decolorization (*ca.* 8 hr.), the product was extracted with ether, the extract was washed with water, dried over anhydrous magnesium sulfate and the ether was removed. The residue was distilled from a trace of magnesium oxide and the colorless distillate (b.p. 110–115° (0.8 mm.)) solidified; yield 3.26 g., m.p. 74–79°. The analytical specimen was recrystallized three times from pentane whereupon it exhibited m.p. 80–81°, $[\alpha]_D$ −156.4° (*c* 1.23), λ_{max}^{MeOH} 290 mμ (log ε 1.53), λ_{max}^{octane} 317 mμ (log ε 1.50). The parent ketone IV exhibited single infrared peaks at 5.88 (dimethyl sulfoxide) and 5.86 μ (carbon tetrachloride); under the same conditions, the bromoketone V showed two peaks (relative intensities given in parentheses): $\lambda_{max}^{dimethyl\ sulfoxide}$ 5.82 (0.470) and 5.88 μ (0.140); $\lambda_{max}^{CCl_4}$ 5.80 (0.509) and 5.87 μ (0.238), leading to the conclusion[10] that in dimethyl sulfoxide and in carbon tetrachloride, the substance exists to the extent of 82%, respectively, 71% in that conformation in which the bromine atom is equatorially oriented.

Anal. Calcd. for $C_{11}H_{19}BrO$: C, 53.53; H, 7.75; Br, 32.35; O, 6.49. Found: C, 53.63; H, 7.59; Br, 32.51; O, 6.55.

(−)-3,6-Dimethyl-6-isopropyl-Δ²-cyclohexenone (VI).—A mixture of 0.82 g. of the once-recrystallized bromo ketone V (m.p. 79–81°), 0.6 g. of anhydrous lithium carbonate, 0.5 g. of anhydrous lithium bromide and 14 cc. of freshly distilled dimethylformamide[12] was heated at 90–95° for 18 hr. while passing a current of nitrogen through the system. Water was added and the mixture was steam distilled until about 60 cc. of distillate was collected. This was saturated with sodium chloride, extracted with ether, washed once with water, dried and the ether was evaporated. Distillation yielded a colorless liquid (0.509 g.) with b.p. 60° (1.6 mm.) which was suitable for the next step. The analytical specimen of the unsaturated ketone VI was redistilled: b.p. 60° (1.6 mm.), $[\alpha]_D$ −65.6° (*c* 1.07 in hexane), −86° (*c* 1.45 in $CHCl_3$), $\lambda_{max}^{CHCl_3}$ 6.02 μ, λ_{max}^{EtOH} 235 and 322 mμ (log ε 4.15 and 1.87).

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.08; H, 10.61.

(+)-2-Methyl-2-isopropyl-5-oxocaproic Acid (VIIa).—Ozone was passed through a solution of 0.624 g. of the unsaturated ketone VI in 20 cc. of methylene chloride at −80° until a blue color persisted whereupon the solution was permitted to warm to room temperature with continued passage of ozone for another 30 min. Water was added, the mixture was stirred at room temperature for 6 hr. and at 80° for 30 min., followed by the addition of 2 cc. of 90% hydrogen peroxide and 100 cc. of 1% aqueous potassium hydroxide. The solution was heated at 80° until all the methylene chloride had been removed, the excess hydrogen peroxide was decomposed by the addition of a small amount of platinum oxide, concd. hydrochloric acid was added and the acid was extracted with ether. After washing and drying the ether extract, the solvent was removed and the acid was distilled at a bath temperature of 130° and 0.3 mm.; yield 0.59 g., $[\alpha]_D$ +3.3° (*c* 1.52).

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74; mol. wt., 186.3. Found: C, 64.05; H, 9.57; neut. equiv., 187.

The methyl ester VIIb was prepared by treating the acid VIIa with an ethereal solution of diazomethane for 5 min. and was distilled at a bath temperature of 100° and 1.5 mm., $[\alpha]_D$ +14.1° (*c* 1.07). The homogeneity of the ester was confirmed by gas phase chromatography at 130° using 1:10 silicone oil on crushed firebrick as support.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.40; H, 9.97.

The yellow **2,4-dinitrophenylhydrazone** of the methyl ester VIIb was purified by filtration in benzene solution through a short alumina column and recrystallization from methanol; m.p. 66–67°, $[\alpha]_D$ +32° (*c* 0.93).

Anal. Calcd. for $C_{17}H_{24}N_4O_6$: C, 53.67; H, 6.36; O, 14.73. Found: C, 53.76; H, 6.30; O, 14.53.

(−)-2-Methyl-2-isopropylbutane-1,4-diol (IX).—To a solution of 1.86 g. of methyl 2-methyl-2-isopropyl-5-oxocaproate (VIIb) in 40 cc. of methylene chloride containing 20 g. of dry disodium hydrogen phosphate was added dropwise with stirring a methylene chloride solution of peroxytrifluoroacetic acid (prepared from 6 cc. of trifluoroacetic anhydride, 1 cc. of 90% hydrogen peroxide and 10 cc. of methylene chloride). After heating under reflux for 1 hr., the mixture was cooled, a saturated sodium sulfite solution was added followed by the gradual addition of water over a period of 30 min. The solution was then made basic with 10% potassium hydroxide and extracted thoroughly with ether. The resulting product (1.57 g.,) after distillation still contained some unreacted starting material by gas phase chromatographic analysis and the oxidation was, therefore, repeated with a tenfold excess of peracid. Distillation yielded 1.30 g. of **methyl 2-methyl-2-isopropyl-4-acetoxybutyrate (VIII)**, b.p. 85° (0.5 mm.), $\lambda_{max}^{CHCl_3}$ 5.79 and 7.98 μ, which was homogeneous by gas phase chromatography.

The above ester (0.73 g.) was reduced in ether solution with 2 g. of lithium aluminum hydride by heating under reflux for 2 hr. After the addition of saturated sodium sulfate solution, followed by anhydrous sodium sulfate, the product was extracted thoroughly with ether, dried and the solvent evaporated. Distillation at a bath temperature of 100° and 0.8 mm. afforded 0.412 g. of **(−)-2-methyl-2-isopropylbutane-1,4-diol (IX)** as a colorless, viscous liquid, which was homogeneous by gas phase chromatography, $[\alpha]_D$ −2.06° (*c* 1.01).

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.71; H, 12.41. Found: C, 65.67; H, 12.62.

The infrared spectrum was identical with that of a sample of the (+)-antipode XI, $[\alpha]_D$ +2.07° (*c* 1.01) obtained by

otherwise, all rotations were measured in chloroform solution with 1-dcm. tubes. The microanalyses are due to Dr. A. Bernhardt, Mülheim, Germany.

lithium aluminum hydride reduction of (+)-α-methyl-α-isopropylsuccinic acid (X)[18] (our measurements: $[\alpha]_D$ +14.8° (*c* 0.85 in methanol)).

Anal. Found: C, 65.34; H, 11.98.

Attempts to prepare a crystalline 3,5-dinitrobenzoate, α-naphthylurethan or diphenylurethan failed.

(+)-α-Methyl-α-isopropylglutaric Acid (XII).—To a stirred and ice-cold solution of 0.4 g. of sodium hydroxide in 50 cc. of water was added dropwise 0.3 cc. of bromine, the temperature being maintained below 10°. After stirring for 30 min., a slightly basic aqueous solution of 200 mg. of (+)-2-methyl-2-isopropyl-5-oxocaproic acid (VIIa) was added dropwise and the mixture was stirred until it had decolorized (4 hr.). The basic solution was steam distilled, the distillate was discarded, the residue was acidified and again steam distilled. The aqueous residual solution from the second steam distillation was saturated with sodium chloride and extracted continuously with ether. Drying and evaporation of the ether left a viscous liquid (63 mg.) of the crude glutaric acid, which resisted initial attempts at crystallization. For purposes of purification, the entire material was heated under reflux for 1 hr. with 15 cc. of acetic anhydride and the excess acetic anhydride and acetic acid were removed by distillation at atmospheric pressure. The brownish residue solidified upon cooling and was sublimed twice at 60° (0.05 mm.) to yield 41 mg. of colorless (−)-**α-methyl-α-isopropylglutaric anhydride (XII)**, m.p. 55–56°, $[\alpha]_D$ −6.1° (*c* 0.99), $\lambda_{max}^{CHCl_3}$ 5.56 and 5.67 μ (typical[19] bands of a glutaric anhydride).

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.05; H, 8.51.

The solid anhydride was mixed in an evaporating dish with water and placed in an oven heated to 100°. After the water had evaporated, the container was cooled and the residue was recrystallized from ether–pentane to afford colorless crystals of (+)-α-methyl-α-isopropylglutaric acid (XII), m.p. 60–62°, $[\alpha]_D$ +8.7° (*c* 0.8).

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 56.90; H, 8.42.

α-Isopropylglutaric Anhydride.—For the quasi-racemate studies (see Fig. 1), the following anhydride was prepared by the above procedure:

(−)-α-Isopropylglutaric acid (XIV)[16] (m.p. 90–92°, $[\alpha]_D$ −13.1° (*c* 1.13)) was transformed into (−)-α-isopropylglutaric anhydride (XV), which was purified by sublimation, m.p. 60–62°, $[\alpha]_D$ −11.2° (*c* 1.17).

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found; C, 61.24; H, 7.59.

(18) J. Porath, *Arkiv Kemi*, **1**, 385 (1949).

(19) G. Stork and R. Breslow, THIS JOURNAL, **75**, 3291 (1953).

STANFORD, CALIF.

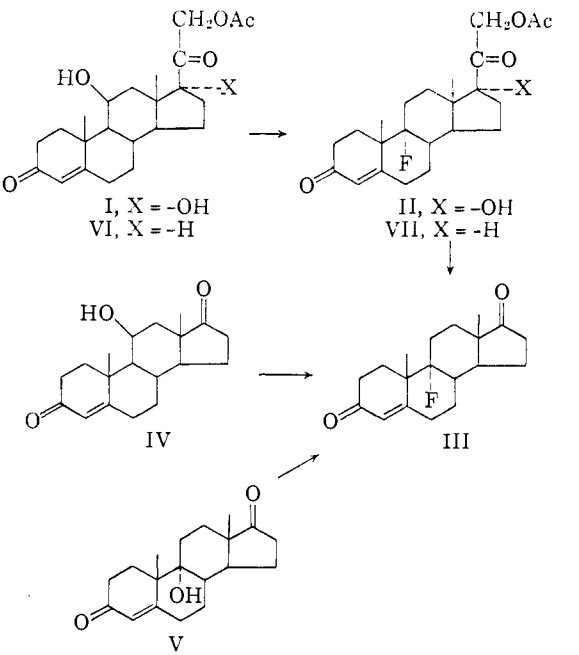
COMMUNICATIONS TO THE EDITOR

THE PREPARATION OF 9-FLUOROSTEROIDS

Sir:

In recent years a large number of 9α-fluoro-11-oxygenated steroids have been prepared,[1] and the enhancement of the biological activity of the 11-oxygenated cortical hormones by a 9α-fluoro group has been demonstrated clearly. However, no 9α-fluoro-steroid devoid of further substitution in ring C has yet been reported. Here, we wish to report the preparation and properties of such steroids.

Treatment of 17α-hydroxycorticosterone acetate (I) with a solution of hydrogen fluoride in pyridine (*ca.* 70% hydrogen fluoride by weight), and conversion of the $\Delta^{9,11}$-olefin in the mixture to the 9,11β-epoxide in the usual way,[2] gave, after chromatographic separation on silica gel, 9,11β-epoxy-17-hydroxydeoxycorticosterone 21-acetate[2] and 9α-fluoro-17-hydroxydeoxycorticosterone 21-acetate (II), m.p. 264–267°; $\lambda_{max}^{methanol}$ 238 mμ (ε 18,200); $[\alpha]_D$ +123° ($CHCl_3$); (found: C, 67.73; H, 7.59; F, 4.5, 4.3). The fact that the fluorine was attached to the steroid nucleus and not to the side chain was demonstrated by the hydrolysis of I to 9α-fluoro-17-hydroxydeoxycorticosterone, m.p. 235–238°; $\lambda_{max}^{methanol}$ 238 mμ (ε 17,100); $[\alpha]_D$ +105.5° ($CHCl_3$); (found: C, 69.37; H, 7.78); which in turn was oxidized to 9α-fluoro-4-androstene-3,17-dione (III), m.p. 227–228°; $\lambda_{max}^{methanol}$ 237 mμ (ε 17,800); $[\alpha]_D$ +158° ($CHCl_3$); (found: C, 74.98; H, 8.26). 9α-Fluoroandrostenedione (III) also could be obtained by treating either 11β-



hydroxyandrostenedione (IV) or 9α-hydroxyandrostenedione[3] (V) with the hydrogen fluoride–pyridine reagent. Compound III was not obtained from 11α-hydroxyandrostenedione when treated under the same conditions as IV or V. It was formed slowly and only in very small quantities (paper chromatographic study) from 9(11)-dehydroandrostenedione. In fact, semi-quantitative paper chromatographic studies showed that

(1) J. Fried and A. Borman, "Vitamins and Hormones," Vol. XVI. Academic Press, Inc., New York, N. Y., 1958, p. 303.

(2) J. Fried and E. F. Sabo, THIS JOURNAL, **79**, 1130 (1957).

(3) R. M. Dodson and R. D. Muir, *ibid.*, **80**, 6148 (1958).