Dinitrobenzenesulfenyl chloride (0.24 g. in 20 ml. dry benzene) failed to react with antimony(III) fluoride (0.18 g.) on refluxing 100 min. Only unchanged sulfenyl chloride was found. Repetition of the experiment with the addition of bromine in amount equivalent to SbF_3 (to activate the fluorinating agent[14]) caused vigorous interaction, with decomposition of the organic materials, and isolation only of dark tarry residues.

Reaction of *p*-Toluenesulfenyl Chloride with Antimony(III) Fluoride and Antimony(III) Chloride. (a).—To a solution of 10.0 g. of the sulfenyl chloride in 25 ml. of dry carbon tetrachloride, 11.4 g. of antimony(III) fluoride was added. The reaction proceeded rapidly, and when the mixture turned deep green, it was filtered through a sintered-glass funnel. The filtrate was let stand for 0.5 hr. and the intensely blue crystals which deposited were collected, washed with dry chloroform and dried at 80° and 15 mm. pressure; m.p. 144–146°. The yield of product was quite low (*ca.* 5%), for it was necessary to filter the reaction solution before reaction was complete, to avoid precipitation of the product in the presence of the insoluble antimony(III) fluoride.

Anal. Calcd. for $C_7H_7ClF_3SSb$: S, 9.50. Found: S, 9.26.

The blue adduct dissolved readily in organic solvents—such as ketones, nitroalkanes, amines, dioxane, benzene, nitrobenzene, and chloro- or bromobenzene—to give deep blue solutions. In all but the last four solvents, the color faded completely in one to three minutes, but a distinct product could not be obtained from the resulting colorless solutions. A dilute nitrobenzene solution of the adduct required several minutes to become colorless. The blue color was, however, regained when the solution was heated, and this process of color change seemed indefinitely reversible, suggesting a preferential complexing of the antimony fluoride by nitrobenzene at the lower temperature. The adduct was practically insoluble in carbon tetrachloride or chloroform. On long storage, it decomposed—as evidenced by change in color, low analysis for fluorine and etching of the glass vial. In bromo- and in chlorobenzene, at room temperature, the blue color of the solutions required several hours to fade. The aged solutions had a dark brown or reddish color. Removal of solvent left a brown-red oil which could not be identified.

(b).—The reaction of antimony(III) chloride with *p*-toluenesulfenyl chloride gave a 1:1 adduct whose color and solubility characteristics were entirely similar to those of the one with antimony trifluoride, but which was obtained in better yield (50–60%), since the problem of contamination (*cf.* above) with the chloroform-soluble antimony(III) chloride did not arise.

Anal. Calcd. for $C_7H_7Cl_4SSb$: Cl, 37.07. Found: Cl, 37.07.

(14) R. N. Haszeldine and A. G. Sharpe, "Fluorine and Its Compounds," Methuen and Co., Ltd., London, 1951, p. 67.

LOS ANGELES 7, CALIFORNIA

Cyclic Dienes. XII. Substituted Cyclohexadienes[1]

BY WILLIAM J. BAILEY[2] AND MILTON MADOFF[3]

RECEIVED JULY 21, 1954

Since the cyclic diene, 1,2-dimethylenecyclohexane, was used successfully to produce a high molecular weight all-*cis* diene polymer,[4] it seemed possible that some derivative of 1,3-cyclohexadiene also would produce an all-*cis* polymer. Cyclohexadiene itself would not be expected to produce a high molecular weight product with free radical initiators since the active hydrogens on the end of the diene system allow the monomer to react as its own chain transfer agent. For this reason, derivatives of cyclohexadiene I, II and III which do not contain any allylic hydrogens were prepared. The cyclic diene, 1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (I), which was prepared according to the method of Ziegler,[5] Woodward and Loftfield[6] was reduced with lithium aluminum hydride to produce a 71% yield of 1,2-dimethyl-1,2-dimethylol-3,5-cyclohexadiene (II). II was converted to the dibenzoate III by treatment with benzoyl chloride and pyridine.

Peroxide-catalyzed polymerization of the cyclic diene I produced only a low molecular weight polymer IV. Under similar conditions neither II nor III gave high polymers. Since it is unlikely that an impurity that could act as a polymerization inhibitor would persist through the two reactions and subsequent recrystallizations, it must be concluded that steric hindrance prevents the formation of a high polymer.

Experimental[7]

Polymerization of 1,2-Dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic Acid (I).—The 1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (I), m.p. 147–148° dec., was prepared by a modification of the method of Ziegler[5] and Woodward and Loftfield.[6] In a 100-ml., round-bottom flask was placed a solution of 0.40 g. of 1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (I) and 0.002 g. of benzoyl peroxide in 45-ml. of dry benzene. After this solution was heated under reflux for 24 hours, the benzene was evaporated and the residue was reprecipitated several times from benzene with petroleum ether to obtain 0.34 g. of poly-1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (IV), softening point 76–78°, intrinsic viscosity (benzene) 0.08. Because of the very low molecular weight of IV no attempt was made to determine its structure.

1,2-Dimethyl-1,2-dimethylol-3,5-cyclohexadiene (II).—In a 1-liter, three-necked flask, equipped with a stirrer, a dropping funnel and an exhaustive ether extractor, was placed 5.67 g. (0.16 mole) of lithium aluminum hydride in 400 ml. of ether. The ether in the reaction flask was refluxed as rapidly as possible to extract from the reservoir of the extractor 12.4 g. (0.063 mole) of 1,2-dimethyl-3,5-cyclohexadiene-1,2-dicarboxylic acid (I) in 3.5 hours. After the addition of the diacid I was complete, the reaction mixture was heated for an additional 2 hours. The excess hydride was decomposed with water and just enough 10% hydrochloric acid was added to dissolve the aluminum precipitate. The aqueous layer was extracted for 3 days in an exhaustive ether extractor and the ether extracts were added to the original ether layer. The resultant solution was dried over potassium carbonate, the ether was removed by distillation and the solid residue was recrystallized from a mixture of petroleum ether and chloroform to yield 3.4 g. (71%) of very light tan 1,2-dimethyl-1,2-dimethylol-3,5-cyclohexadiene (II), m.p. 172–173°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52; mol. wt., 168. Found: C, 71.41; H, 9.70; mol. wt. (Rast), 164.

Attempts to polymerize II by the procedure described above led only to recovery of starting material.

1,2-Dimethyl-1,2-di-(benzoxymethyl)-3,5-cyclohexadiene (III).—In accordance with the procedure of Hickinbottom,[8] a mixture of 0.2 g. (0.0012 mole) of 1,2-dimethyl-1,2-dimethylol-3,5-cyclohexadiene (II), 0.8 g. (0.0057 mole) of benzoyl chloride and 2 ml. of pyridine in 30 ml. of benzene was heated under reflux for 36 hours in a 50-ml. flask. The reaction mixture was diluted with 100 ml. of ether and extracted in succession with 30 ml. of 2 *N* hydrochloric acid,

(1) Previous paper in this series, THIS JOURNAL, **77**, 992 (1955).

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(3) Office of Naval Research Fellow, 1949–1950.

(4) W. J. Bailey and H. R. Golden, THIS JOURNAL, **76**, 5418 (1954).

(5) K. Ziegler, G. Schenck, E. W. Krockow, A. Siebert, A. Wenz and H. Weber, *Ann.*, **551**, 1 (1952).

(6) R. B. Woodward and R. G. Loftfield, THIS JOURNAL, **63**, 3167 (1941).

(7) All melting points are corrected. The authors are grateful to Arthur Tomasewski for the analyses.

(8) W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1938, p. 99.

30 ml. of 2 *N* sodium hydroxide and finally with water. After the organic layer was dried overnight with magnesium sulfate, the solvent was removed by distillation. The residue was recrystallized three times from a mixture of chloroform and petroleum ether to yield 0.18 g. (40%) of 1,2-dimethyl-1,2-di-(benzoxymethyl)-3,5-cyclohexadiene (III), m.p. 102.5–103.5°.

Anal. Calcd. for $C_{24}H_{24}O_4$: C, 76.59; H, 6.39. Found: C, 76.70; H, 6.28.

Treatment of III with benzoyl peroxide in benzene produced only a very low molecular weight substance.

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The Stereochemistry of Santonin, β-Santonin and Artemisin

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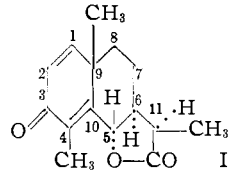
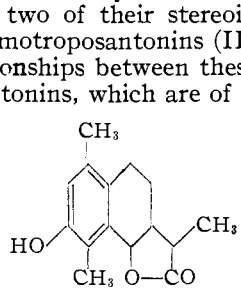
RECEIVED OCTOBER 25, 1954

Although the Clemo–Haworth–Walton structure for santonin[1] has been confirmed beyond doubt by numerous chemical studies and, more recently, by total synthesis,[2] the stereochemistry of santonin has remained an unsolved problem.[3] The purpose of the present note is to adduce evidence in favor of stereoformula I for (−)-santonin[4] and IX and X for the related β-santonin and artemisin.



I

The first important evidence on the stereochemistry of santonin was obtained by a study of the well-known (−)-α- and (+)-β-desmotroposantonins (II) (obtained by the action of acids on santonin) and two of their stereoisomers, (−)-β- and (+)-α-desmotroposantonins (II). The stereochemical relationships between these four isomeric desmotroposantonins, which are of key importance



II

to the stereochemistry of santonin, have been elucidated elegantly by Huang-Minlon[5] and are summarized in Table I. As has been pointed out by Huang-Minlon the six-membered-alicyclic and lactone rings are *cis* locked in all four known desmotroposantonins. The *cis* fusion, which is the more stable one in the desmotroposantonins and the hyposantonins and which is the only one encountered in the desmotropo series, is not present in santonin itself which possesses a *trans* juncture of the lactone and six-membered alicyclic rings.[5,6]

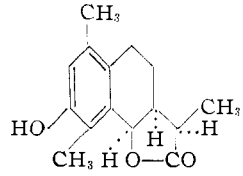
TABLE I

RELATIVE CONFIGURATIONS OF THE DESMOTROPOSANTONINS[a]

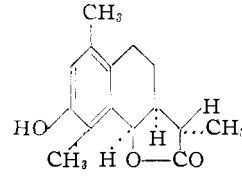
Compound	$[\alpha]_D$	Configuration at $C_{(5)}$	$C_{(6)}$	$C_{(11)}$
(−)-α-Desmotropo	−140	(−)	(+)	(+)
(+)-α-Desmotropo	+130	(+)	(−)	(−)
(−)-β-Desmotropo	−106	(−)	(+)	(+)
(+)-β-Desmotropo	+106	(+)	(−)	(−)

[a] The symbol (+) refers to the more dextrorotatory configuration and the symbol (−) to the opposite configuration.

(−)-α-Desmotroposantonin is unstable relative to (+)-β-desmotroposantonin and can be converted to it by isomerization in 50% sulfuric acid.[7] During this transformation the configuration at $C_{(11)}$ remains unchanged, but the configurations at $C_{(5)}$ and $C_{(6)}$ are both inverted. As a consequence, in one isomer the methyl substituent at $C_{(11)}$ is *cis* to the carbons attached to $C_{(5)}$ and $C_{(6)}$, whereas in the other isomer the methyl group at $C_{(11)}$ is *trans* to the carbons attached to $C_{(5)}$ and $C_{(6)}$. Clearly, the former is the unstable and the latter is the stable arrangement. Thus, the methyl group at $C_{(11)}$ in (−)-α-desmotroposantonin (III) is *cis* to the carbons attached to $C_{(5)}$ and $C_{(6)}$ and the methyl group at C_{11} in (+)-β-desmotroposantonin (IV) is *trans* to the carbons attached to $C_{(5)}$ and $C_{(6)}$. As is to



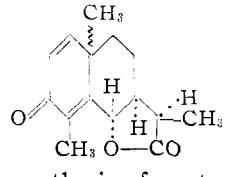
+ mirror image
III, α-series



+ mirror image
IV, β-series

be expected from the Huang-Minlon assignments (Table I) (+)-α-desmotroposantonin can be isomerized to (−)-β-desmotroposantonin.[8]

The configurations at $C_{(6)}$ and $C_{(11)}$ in santonin are known to be the same as in (−)-α-desmotroposantonin whereas the configuration at C_5 is opposite in two compounds.[5,9] Thus, santonin must be represented by expression V or its mirror image.



V

The recent synthesis of santonin[2] permits correlation of the configurations at $C_{(6)}$ and $C_{(9)}$ as follows. The intermediate from which santonin was synthesized is the bicyclic malonic ester VII which was prepared by the Michael addition of methylmalonic ester to the dienone VI. Since the

(1) G. R. Clemo, R. D. Haworth and E. Walton, *J. Chem. Soc.*, 2368 (1929).

(2) Y. Abe, T. Harukawa, H. Ishikawa, T. Miki, M. Sumi and T. Toga, *Proc. Japan Acad.*, **30**, 116, 119 (1954).

(3) For a recent discussion see W. Cocker and T. B. H. McMurray, *Chem. and Ind.*, 1199 (1954).

(4) *I.e.*, naturally occurring, (−)-α-santonin.

(5) Huang-Minlon, THIS JOURNAL, **70**, 611 (1948).

(6) The *trans* structure for the desmotropo- and hyposantonins involves strong steric interaction between the lactonic oxygen and the nearby methyl substituent at $C_{(4)}$ whereas the *cis* locked structure which has the a′ orientation of oxygen is free of this interaction.

(7) G. Bargellini and A. Mannino, *Gazz. chim. ital.*, **39**, II, 101 (1909).

(8) Huang-Minlon, C. Lo and L. Chu, THIS JOURNAL, **65**, 1780 (1943); *J. Chinese Chem. Soc.*, **10**, 126 (1943).

(9) D. H. R. Barton, *J. Org. Chem.*, **15**, 466 (1950).