Anal. Calcd. for $C_{13}H_{20}O_8$: C, 51.31; H, 6.63. Found: C, 51.17; H, 6.60.

Dimethyl α,α'-Dicarboxypimelate.—This compound was prepared by the procedure given above for diethyl α,α'-dicarboxypimelate except that methanol was used as the solvent. From 60.9 g. (0.20 mole) of tetramethyl ester was obtained 56.0 g. (theor. 55.2 g.) of dimethyl α,α'-dicarboxypimelate, m.p. 107–111° dec. Attempts to purify this compound have not been successful. The infrared spectrum of this compound was essentially the same as found for the diethyl analog.

In a manner similar to that used for the diethyl analog, 2.8 g. (0.011 mole) was decarboxylated by heating and hydrolyzed with 10% aqueous sodium hydroxide to yield, on acidification, 1.2 g. (68.5%) of pimelic acid, m.p. 103–104°.

Dimethyl α,α'-Dimethylenepimelate.—The Mannich reaction was carried out on dimethyl α,α'-dicarboxypimelate as described for the diethyl analog above with a slight modification in the workup procedure. The product was extracted from the reaction mixture with low petroleum ether, concentrated and cooled to crystallize the product. From 56.0 g. (0.20 mole) of diester-diacid was obtained 17.3 g. (27%) of dimethyl α,α'-dimethylenepimelate, m.p. 34.0–35.5°. Recrystallization did not change the melting point. The infrared spectrum was essentially the same as that found for the diethyl analog. The yield can probably be significantly increased.

This compound has also been prepared by treating α,α'-dimethylenepimelic acid with diazomethane by standard procedures.[12] The products obtained by both procedures were identical.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.33; H, 7.59.

Polydimethyl α,α'-Dimethylenepimelate.—A six-ounce screw-cap polymerization bottle was charged with 4.740 g. of monomer, 8.0 g. of Office of Rubber Reserve soap and 0.5 ml. of a 3% aqueous potassium persulfate solution. The bottle was swept for three minutes with nitrogen, capped, placed in a 50° bath and tumbled for 24 hr. The polymer was precipitated with H_2SO_4–NaCl coagulant and purified by reprecipitation six times in a benzene–methanol system. The yield of polymer was 2.4 g. (64.5% based on unrecovered monomer). The intrinsic viscosity determined in chloroform (0.241 g./100 ml. chloroform) at 25.0° was 0.73 which corresponds to a molecular weight of about 200,000 to 300,000 in a linear polymer system.[13] This polymer was completely soluble in chloroform, benzene and similar organic solvents. No carbon–carbon double bond absorption was observed in the infrared spectrum. This material gives a clear, glassy melt at a temperature of about 300°.

Anal. Calcd. for $(C_{11}H_{16}O_4)_n$: C, 62.25; H, 7.60. Found: C, 62.37; H, 7.46.

Partial Dehydrogenations.—According to the procedure of Patai and Rajbenback,[14] 0.75 g. of polydimethyl α,α'-dimethylenepimelate was heated with 2.25 g. of potassium perchlorate in a sealed, thick-walled Pyrex tube at 380–395° for 16 hr. After the tube had cooled, it was wrapped in a towel and opened. The dark brown solids were transferred to a Soxhlet extractor and extracted with methylene dichloride for 2.5 days. The extracts fluoresced strongly under the influence of ultraviolet light. The infrared spectrum (CH_2Cl_2) of the concentrated extracts showed acid (3610, 3500, 1695–1715 cm.$^{-1}$), ester (1715–1735 cm.$^{-1}$) and unsaturation in the aromatic region (1620, 1595, 1500 cm.$^{-1}$). The ultraviolet spectrum (CH_2Cl_2) was consistent with aromaticity in this product having a λ_{max} at 255 mμ.

A sample of poly-α,α'-dimethylenepimelic acid was treated in a similar manner with comparable results.

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[12] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 378.

[13] J. H. Baxendale, S. Bywater and M. G. Evans, *J. Poly. Sci.*, **1**, 237 (1946).

[14] S. Patai and L. Rajbenbach, THIS JOURNAL, **73**, 862 (1951).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of α-Santalene and of *trans*-$\Delta^{11,12}$-Iso-α-santalene

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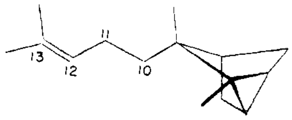
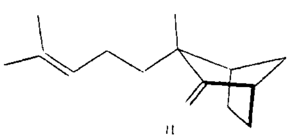
Synthesis of natural α-santalene (I) in six steps and of *trans*-$\Delta^{11,12}$-iso-α-santalene (XV) in nine steps have been carried out starting with (+)-α-bromocamphor.

Among the most noteworthy sesquiterpene hydrocarbons with regard to structure and chemical interest are the two main hydrocarbon components of East Indian sandalwood oil, α-santalene (I) and β-santalene (II). Little is known about the chemistry of these substances beyond the limited number of degradation reactions from which the structures were derived,[3] including the key degradations of α-santalene to teresantalic acid (III) and tricycloekasantalic acid (IV), both of which have been synthesized subsequently.[4,5] An interest in the chemistry of α-santalene, together with the difficulty of obtaining pure material from natural sources and the availability to us of suitable synthetic intermediates from other work in the sesquiterpene field, prompted the investigation of the synthesis of α-santalene which is described herein.



I



II

α-*trans*-π-Dibromo-(+)-camphor (VI), which was prepared directly from α-bromo-(+)-camphor (V) by a modified procedure based on the method of the Takeda workers,[6] was converted to *trans*-π-bromocamphor (VII) by treatment with zinc–hydrogen bromide in methylene chloride[7] and thence to (−)-π-bromotricyclene (VIII) *via* the hydrazone derivative by oxidation. The bromide VIII was

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[1] Alfred P. Sloan Foundation Postdoctoral Fellow, 1956–1957.

[2] Allied Chemical and Dye Corp. Fellow, 1955–1957; Alfred P. Sloan Foundation Summer Fellow, 1956.

[3] Reviewed in (Sir) J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, 2nd Ed., University Press, Cambridge, 1952, p. 98

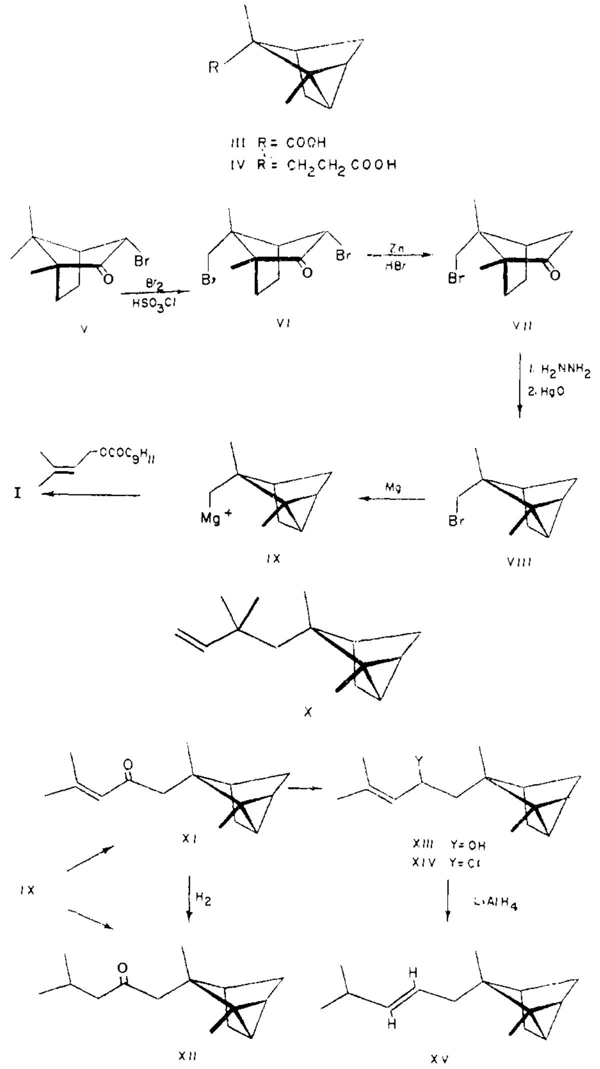
[4] Y. Asahina, M. Ishidate and T. Momose, *Ber.*, **68**, 83 (1935).

[5] P. C. Guha and S. C. Battacharyya, *J. Indian Chem. Soc.*, **21**, 271 (1944).

[6] H. Nishimitsu, M. Nishikawa and M. Hagiwara, *Proc. Japan Acad.*, **27**, 285 (1951).

[7] E. J. Corey and R. A. Sneen, THIS JOURNAL, **78**, 6269 (1956).

transformed into the magnesium derivative IX which reacted smoothly with γ,γ-dimethylallyl mesitoate to produce α-santalene as the only detectable sesquiterpene. The infrared spectrum and vapor phase chromatographic analysis of this product indicated the absence of the isomer X which would have been formed if allylic rearrangement had occurred during the alkylation process (no vinyl $\overset{\mathrm{H}}{\diagdown}\!\underset{\diagup}{C}{=}CH_2$, absorption).[8] Reaction of the synthetic α-santalene with nitrosyl chloride afforded a crystalline adduct agreeing in properties and composition with the derivative reported for natural α-santalene (see Experimental).



Reaction of γ,γ-dimethylallyl bromide with the Grignard reagent IX was not a satisfactory route to α-santalene since it yielded a difficultly separable mixture which consisted of two major C_{15}-components as determined by vapor phase chromatography. Infrared and chromatographic data indicated that the mixture contained 50–70% α-santalene and 50–30% of a companion, tricyclene-type unsaturated hydrocarbon which is probably the "abnormal," allylic rearrangement product X since strong absorption characteristic of vinyl occurred at 910 cm.$^{-1}$ in the infrared. The crystalline nitrosyl chloride adduct of α-santalene could be isolated from the mixture. Catalytic reduction of the mixture of I and X gave a mixture of two dihydro compounds as determined by gas chromatography—the relative amounts of the dihydro compounds being the same as those of I and X in the original mixture. The formation of *different* dihydro compounds excludes the possibility that the two sesquiterpenes from IX and γ,γ-dimethylallyl bromide differ only in the location of the double bond (*e.g.*, $\Delta^{12,13}$- and $\Delta^{13,14}$-isomers) and shows that they must have different carbon skeletons.

γ,γ-Dimethylallyl 2,4,6-triethylbenzoate, on the other hand, was much less reactive toward IX than the mesitoate and failed to give appreciable yields of α-santalene or *other* C_{15} product.

During investigation of another possible route to α-santalene, the synthesis of the hitherto unknown *trans*-$\Delta^{11,12}$-iso-α-santalene (XV) was also accomplished starting with π-tricyclylmagnesium bromide. The sesquiterpene skeleton was formed by acylation of the Grignard reagent with β,β-dimethylacrylyl chloride which provided α-santalene-11-one (XI) as indicated by infrared absorption at 1680 and 1620 cm.$^{-1}$ (chloroform) and ultraviolet absorption at 238 mμ (log ϵ 4.05) characteristic of the α,β-unsaturated ketone system. Further confirmation of the structure XI was obtained by catalytic hydrogenation to a saturated dihydro derivative (infrared absorption 1715 cm.$^{-1}$) identical with dihydro-α-santalene-11-one (XII) prepared from π-tricyclylmagnesium bromide and isovaleryl chloride. Reduction of the unsaturated ketone XI with sodium borohydride or lithium aluminum hydride–aluminum chloride (1:1) led to a mixture of epimeric secondary alcohols (XIII) in varying proportion depending on the reagent, the latter being considerably more stereoselective than the former.[9] The crude alcohol mixture was converted to the corresponding chloride(s) (XIV) by reaction with thionyl chloride in ether-pyridine under conditions which allow the transformation of crotyl alcohol to crotyl chloride without formation of α-methylallyl chloride.[10] Reduction of the chloride XIV with lithium aluminum hydride in ether afforded *trans*-$\Delta^{11,12}$-iso-α-santalene (XV) as the only detectable product, free of α-santalene as determined by infrared absorption. Whereas the infrared spectrum of α-santalene exhibits absorption characteristic of RCH=C(CH$_3$)$_2$ at 840 cm.$^{-1}$, *trans*-$\Delta^{11,12}$-iso-α-santalene does not but shows instead a strong, sharp band at 975 cm.$^{-1}$ characteristic of a *trans*-R—CH=CH—R′ group. Both α-santalene and *trans*-$\Delta^{11,12}$-iso-α-santalene show

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[8] The alkylation of Grignard reagents by allylic mesitoate esters (see R. T. Arnold, *et al.*, THIS JOURNAL, **63**, 344 (1941), **64**, 2875 (1942)) proceeds *without* allylic rearrangement in the case of the γ-methylallyl (crotyl) ester (R. T. Arnold and R. W. Liggett, *ibid.*, **67**, 337 (1945)) but mainly *with* allylic rearrangement with the α-methylallyl ester (K. W. Wilson, J. D. Roberts and W. G. Young, *ibid.*, **71**, 2019 (1949); R. T. Arnold and S. Searles, Jr., *ibid.*, **71**, 2021 (1949)).

[9] *Cf.* O. H. Wheeler and J. L. Mateos, *Chemistry & Industry*, 395 (1957), for similar observations.

[10] R. H. Dewolfe and W. G. Young, *Chem. Revs.*, **56**, 815 (1956).

sharp absorption at 858 cm.$^{-1}$ which typifies all tricyclene derivatives encountered in our work including VIII and XI. Catalytic reduction of α-santalene and *trans*-$\Delta^{11,12}$-iso-α-santalene with platinum catalyst in alcohol resulted in uptake of one equivalent of molecular hydrogen and yielded the same saturated dihydro compound as judged from the infrared spectra which were superimposable and from identity of other physical properties. The spectra manifested tricyclene absorption at 858 cm.$^{-1}$ but no bands at 840 or 975 cm.$^{-1}$ as appear in the spectra of the precursors I and XV.

In connection with the above reactions two incidental points are worthy of mention. The first is that the reduction of the allylic chloride XIV by lithium aluminum hydride does not yield significant amounts of the normal replacement product α-santalene but only the isomeric $\Delta^{11,12}$-iso compound XV. Since several examples of replacement of chlorine by hydrogen involving allylic chlorides and lithium aluminum hydride are known in which the *normal* product is formed predominantly, *e.g.*, from *cis*- and *trans*-γ-methylallyl chlorides.[11] the exclusive formation of *abnormal* product from XIV is striking. The extreme result in the present case would seem to indicate that the large π-tricyclyl group obstructs normal displacement at C_{11} and thereby allows the competing abnormal process to predominate.

A second point of interest is the consistent formation of a saturated, crystalline hydrocarbon, $C_{20}H_{30}$, as a by-product during preparation of π-tricyclylmagnesium bromide. This substance manifests infrared absorption very similar to that of tricyclene itself and is presumably bi-π-tricyclyl. Use of a large excess of magnesium powder and rapid stirring were not sufficient to prevent formation of the by-product.

The above synthesis of α-santalene makes the substance readily available in very pure form and at present is the most practical way of obtaining the pure sesquiterpene. The separation of α- and β-santalenes from sandalwood oil requires repeated and lengthy fractional distillations and, in fact, probably still has not been effected completely.

trans-$\Delta^{11,12}$-Iso-α-santalene is not a naturally occurring substance, as far as we are aware, and is available only by synthesis.

ADDED IN PROOF (9-13-57).—After submission of this paper, there came to our attention the announcement by S. C. Bhattacharyya, *Sci. and Culture*, **13**, 208 (1947), of the synthesis of α-santalene. We have not been able to find published details of these syntheses nor information on the purity of the α-santalene, which, from the method of synthesis, is suspect.

Experimental[12]

α,π-Dibromo-(+)-camphor.—In a 2-l. three-necked flask provided with condenser, stirrer and thermometer and cooled in an ice-bath to below 10° was placed 350 ml. of chlorosulfonic acid. Bromine (105 ml., 310 g., 1.93 moles) was dissolved in the chlorosulfonic acid and α-bromo-(+)-camphor (444.5 g., 1.9 moles) was then added with stirring at a rate to maintain the reaction temperature between 25–30°. The reaction mixture was stirred for 5 hr. at 25–30°, poured into ice and stirred until the product became granular. The excess bromine was decomposed with solid sodium bisulfite and the precipitated dibromocamphor was collected by filtration and washed with water, 5% sodium hydroxide and again with water. The crude α,π-dibromo-(+)-camphor was pressed as dry as possible, dissolved in methylene chloride and the solution dried. Addition of hot methanol containing a little sodium methoxide and concentration gave α,π-dibromo-(+)-camphor (310 g.) as fine colorless needles, m.p. 152–156°. Concentration of the mother liquor yielded an additional 40 g. (total yield, 59.4% of the theoretical). The ultraviolet spectrum had λ_{max} 306 mμ, ε 120 (in ethanol); the infrared spectrum showed carbonyl absorption at 1762 cm.$^{-1}$ (in carbon tetrachloride).

π-Bromo-(+)-camphor.—To α,π-dibromocamphor (155 g., 0.5 mole) dissolved in 600 ml. of methylene chloride was added 104 g. (1.6 moles) of zinc powder. A gentle stream of hydrogen bromide was passed into the mixture with stirring for 2.5–4 hr. Occasionally, it was necessary to moderate the reaction by cooling with a water-bath. The mixture was filtered and the methylene chloride solution was washed with water and dried over magnesium sulfate. Removal of methylene chloride by distillation on a steam-bath yielded 109 g. (95%) of the crude product which was recrystallized from hexane. There was obtained 74 g. of π-bromo-(+)-camphor, m.p. 93–95°, $[\alpha]^{26}\text{D}$ +115° (chloroform). Concentration of the mother liquor yielded an additional 12.7 g., m.p. 80–90°, $[\alpha]^{26}\text{D}$ +115°. The compound had infrared absorption at 1750 cm.$^{-1}$ (carbon tetrachloride) and ultraviolet absorption at λ_{max} 289 mμ, ε 58.7 (ethanol).

(−)-π-Bromotricyclene.—*trans*-π-Bromocamphor hydrazone was prepared by refluxing the ketone with four moles of 95% hydrazine and one mole of acetic acid for 4 hr. in three times its weight of absolute ethanol. The reaction was shown to be complete at this time by measurement of optical rotation. After removing the ethanol at aspirator pressure, the reaction mixture was brought to near its original volume with ether, the lower hydrazine layer was removed and the reaction mixture was washed with 10% sodium hydroxide saturated with sodium chloride and three times with saturated sodium chloride solution. Removal of ether at aspirator pressure gave crude π-bromocamphor hydrazone which was used without further purification.

A solution of 23 g. of π-bromocamphor hydrazone obtained from 21.5 g. (0.0930 mole) of the ketone in 40 ml. of dry methanol was treated with 32 g. (0.148 mole) of yellow mercuric oxide, and the mixture was stirred and heated overnight on a steam-bath. The solution was decanted from the pasty residue, filtered by gravity, combined with seven pentane rinses of the paste, and the total volume was brought to about 250 ml. with pentane. The lower layer was saturated with salt, separated, washed with pentane, and the combined pentane solution washed with saturated salt solution and dried. Slow removal of pentane at atmospheric pressure and distillation of the residue at aspirator pressure gave 13.6 g. (68%) of (−)-π-bromotricyclene, b.p. 116–119° (23–24 mm.), $n^{26.5}\text{D}$ 1.5079. An analytical sample had $n^{24}\text{D}$ 1.5092, b.p. 111° (17 mm.), $[\alpha]^{27}\text{D}$ −10.5° (*c* 1.5 in chloroform).

Anal. Calcd. for $C_{10}H_{15}Br$: C, 55.82; H, 7.03; Br, 37.15. Found: C, 56.04; H, 7.22; Br, 37.28.

The infrared spectrum determined in carbon tetrachloride has bands assignable to cyclopropane ring hydrogen (3050 cm.$^{-1}$), C–Br (1255 cm.$^{-1}$) and the tricyclene system (850, 857 and 865 cm.$^{-1}$). There is no absorption within 15 cm.$^{-1}$ of the 1000–1020 region where cyclopropane derivatives are reported to absorb. The infrared spectrum of tricyclene in carbon tetrachloride has bands at 3050, 850, 860 and 875 cm.$^{-1}$; there is no absorption from 985–1040 cm.$^{-1}$.

α-Santalene-11-one.—The Grignard reaction vessel was a three-necked flask equipped with a stopcock at the bottom for drainage of the Grignard reagent into a second flask below. All connections were standard taper and the apparatus was dried at 125–150°, assembled while hot, heated again with a free flame and cooled under a nitrogen atmosphere.

Magnesium powder (90 g., 3.75 moles) (dried over phosphorus pentoxide at 10 mm. overnight) was placed in the reaction vessel stirred with a mercury sealed Hershberg stirrer and heated under nitrogen for 30 minutes. It was then covered with 50 ml. of anhydrous ether (commercial anhydrous ether further dried over sodium wire). The mix-

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[11] Reference 8, p. 860.

[12] Microanalyses by Mr. J. Nemeth and associates, University of Illinois.

ture was stirred vigorously and treated with a crystal of iodine. π-Bromotricyclene (10 g., 0.046 mole) in 500 ml. of ether was added dropwise from a dropping funnel at a fairly even rate over 5 hr. at reflux temperature and, after all the bromide had been added, the solution was heated at reflux for 1 additional hr. The cooled Grignard reagent was then filtered through a glass-wool plug into the β,β-dimethylacrylyl chloride (16 g., 0.14 mole) in 25 ml. of ether at reflux temperature with stirring. The time required for the addition was 1.5 hr. The mixture was heated at reflux for another 15 minutes, then allowed to stand overnight.

The ethereal solution was treated with saturated ammonium chloride solution and stirred until both the aqueous and ethereal layers were clear. The ethereal layer was separated, washed with 5% sodium hydroxide then with water, dried over sodium sulfate and evaporated. The residue, a clear, mobile oil, was distilled. The main fractions (5.75 g., 57%) had b.p. 80–83° (0.15 mm.), $n^{25}\text{D}$ 1.4990–1.4998. The ketone had infrared absorption at 1680, 1620 and 858 cm.$^{-1}$ (chloroform); ultraviolet absorption 238 mμ (log ϵ 4.05) (95% ethanol), $[\alpha]^{26}\text{D}$ $-47.6°$ (absolute ethanol).

An analytical sample was prepared by filtering a portion of the above product through a column of alumina and redistilling through a Craig micro column.

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.42; H, 10.22.

Reduction of 250 mg. (1.15 × 10^{-3} mole) of the ketone over platinum catalyst in ethanol resulted in uptake of 1 mole of hydrogen. The product had an infrared spectrum identical with that of dihydro-α-santalene-11-one described below.

Dihydro-α-santalene-11-one.—This compound was prepared using the same procedure described above for α-santalene-11-one. The yield from 4.0 g. (0.018 mole) of π-bromotricyclene in 250 ml. of ether, 50 g. (2.1 moles) of magnesium covered with 20 ml. of ether and 6.4 g. (0.056 mole) of isovaleryl chloride in 10 ml. of ether was 1.5 g. (38%) after purification, b.p. 62–67° (0.25 mm.), $n^{21}\text{D}$ 1.4799. The crude product was purified by chromatography on alumina using pentane as eluent and distillation. The infrared spectrum had absorption at 1715, 858 cm.$^{-1}$ (carbon tetrachloride).

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.89; H, 11.00. Found: C, 81.89; H, 11.06.

α-Santalene-11-ol. A. By Sodium Borohydride Reduction.—α-Santalene-11-one (845 mg., 0.0039 mole) was reduced with sodium borohydride (1.0 g., 0.026 mole) in *ca.* 10 ml. of methanol for 24 hr. There was obtained 812 mg. (94%) of oil, infrared absorption at 3600, 3450 and 858 cm.$^{-1}$ (carbon tetrachloride).

B. By Lithium Aluminum Hydride–Aluminum Chloride Reduction.—To 855 mg. (0.025 mole) of lithium aluminum hydride in 35 ml. of ether was added 4.26 g. (0.032 mole) of aluminum chloride in 11 ml. of ether. The mixture was stirred for 30 minutes, then filtered into a three-necked flask equipped with stirrer, condenser and a dropping funnel. The unsaturated ketone (700 mg., 0.0032 mole) in 20 ml. of ether was added dropwise over 15 minutes and the solution stirred for 18 hr. The excess hydride was decomposed with 4 ml. of acetone in 15 ml. of ether. The ether solution was washed with 5% sodium hydroxide, then with water and dried over sodium sulfate. After evaporation of the solvent, the product crystallized as colorless needles (180 mg.) containing some oil. Sublimation on a steam-bath (10 mm.) yielded 100 mg. of material which was washed with pentane. The product had m.p. 103–108°, infrared absorption 3640 and 3460 cm.$^{-1}$.

11-Chloro-α-santalene.—To the crude α-santalene-11-ol (800 mg.) in 8 ml. of anhydrous ether and 0.5 ml. of pyridine cooled to 0–5° was added thionyl chloride (0.4 ml.) in 8 ml. of ether over 15 minutes. The mixture was stirred vigorously for 1.5 hr. with cooling in an ice-bath and then was diluted with ether and washed with water. From the ether solution was obtained 710 mg. (81.5%) of an oil which showed neither hydroxyl nor carbonyl absorption in the infrared.

***trans*-$\Delta^{11,12}$-Iso-α-santalene.**—11-Chloro-α-santalene (742 mg., 0.0031 mole) was heated under reflux with 1.2 g. (0.03 mole) of lithium aluminum hydride in tetrahydrofuran for 48 hr. The excess lithium aluminum hydride was destroyed with water and the solvent was evaporated. The residue was suspended in ether and water and acidified with 3 *N* hydrochloric acid. The crude santalene which was obtained from the ether solution was dissolved in pentane and passed through a column of alumina. There was obtained 360 mg. of oil (negative Beilstein halogen test) which after distillation in a micro distilling apparatus gave 250 mg. of *trans*-$\Delta^{11,12}$-iso-α-santalene, $n^{20}\text{D}$ 1.4872; infrared absorption 1647, 975 and 858 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{24}$: C, 88.15; H, 11.84. Found: C, 87.70; H, 11.83.

α-Santalene.—π-Tricyclylmagnesium bromide was prepared as described previously. π-Bromotricyclene (10 g., 0.046 mole) in 500 ml. of absolute ether was added to 70 g. (2.9 moles) of magnesium in 100 ml. of ether during 7 hr. The mixture was heated at reflux for an additional 1.5 hr. The Grignard reagent was filtered through a glass-wool plug into γ,γ-dimethylallyl mesitoate (12.8 g., 0.055 mole, b.p. 95–100° (0.1 mm.)) in 50 ml. of ether. The time required for the addition was 2 hr. The excess magnesium was rinsed with 100 ml. of ether and the washing also was added to the ester. The mixture was allowed to stand at room temperature for 96 hr. At the end of this time a fine white precipitate appeared in considerable quantity. To the ether solution was added with stirring a saturated ammonium chloride solution, and stirring was continued until both aqueous and ether layers were clear. The ether solution was washed with 10% sodium hydroxide, water and dried over sodium sulfate. The crude oil (12 g.) after evaporation of ether was dissolved in pentane and chromatographed on alumina. The product was eluted with pentane and distilled to give two fractions: no. 1, 1.29 g., b.p. 56–130° (15–20 mm.), $n^{25}\text{D}$ 1.4496; no. 2, 2.81 g., b.p. 130–140° (15–20 mm.), $n^{25}\text{D}$ 1.4820. The residue from the distillation which solidified was largely bi-π-tricyclyl (see below). Fraction 2 was redistilled, dissolved in pentane and chromatographed on alumina. The eluate was distilled and yielded 1.7 g. of oil, b.p. 116–120° (8 ± 2 mm.), $n^{25}\text{D}$ 1.4822; infrared absorption at 1670, 858 and 840 cm.$^{-1}$; $\alpha^{26}\text{D}$ $+18.4°$, $+17.2°$ (pure liquid).

Anal. Calcd. for $C_{15}H_{24}$: C, 88.15; H, 11.84. Found: C, 88.06; H, 12.17.

The above constants for synthetic α-santalene agree well with those reported for the purest sample yet isolated from natural sources which had b.p. 116 (6 mm.), $n^{24.8}\text{D}$ 1.4855, $\alpha^{24.8}\text{D}$ $+6.60°$.[13]

Dihydro-α-santalene.—(A) α-Santalene (102 mg., 0.5 millimole) was hydrogenated over platinum catalyst in alcohol, 11.2 ml. (83%) of hydrogen being absorbed (calculated 13.5 ml. at 26°, 747.5 mm.). Distillation from a micro apparatus gave 51.2 mg. of oil, $n^{25}\text{D}$ 1.4660.

(B) *trans*-$\Delta^{11,12}$-iso-α-santalene (51.2 mg., 0.25 millimole) was hydrogenated over platinum in alcohol, 6.8 ml. (99%) of hydrogen being absorbed (calculated 6.85 ml. at 26°, 747.5 mm.). Distillation in a micro apparatus yielded 35 mg. of oil, $n^{25}\text{D}$ 1.4640. The infrared spectra of the above preparations were superimposable.

α-Santalene Nitrosochloride.—A stream of dry nitrosyl chloride was passed into a solution of 137 mg. of synthetic α-santalene in 1 ml. of methylene chloride at $-70°$, and the solution was stored at that temperature for 45 minutes. The excess nitrosyl chloride was removed by flushing the cold ($-70°$) solution with nitrogen, and the solvent was removed under aspirator pressure to constant weight to give 173 mg. (95%) of colorless crystals, m.p. 109–112.5°. Recrystallization from benzene (0.8 ml.) afforded 57 mg. (31.5%) of crystalline nitrosochloride derivative, m.p. 123.5–124.5° (lit.[14] m.p. 122°). Repeated recrystallization of this material gave 50% recovery of analytically pure nitrosochloride derivative, m.p. 127–127.5°; infrared absorption: 855 and 3050 cm.$^{-1}$ (tricyclene system), 1375 cm.$^{-1}$, 1200 cm.$^{-1}$, no. OH, C=C, C=O.

Anal. Calcd. for $C_{15}H_{24}NOCl$: C, 66.77; H, 8.97; N, 5.19. Found: C, 66.50; H, 8.97; N, 5.32; (material is probably $(C_{15}H_{24}NOCl)_2$).

α-Santalene and π-[α,α-Dimethylallyl]-tricyclene.—The Grignard reagent from 3.5 g. (0.016 mole) of π-bromotricyclene in 350 ml. of ether was allowed to react with 6.5 g

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[13] B. B. Ghatgey and S. C. Bhattacharyya, *Perfumery and Ess Oil Record*, **47**, 353 (1956).

[14] M. Guerbet, *Compt. rend.*, **130**, 1324 (1900).

(0.0435 mole) of γ,γ-dimethylallyl bromide for 36 hr. at room temperature. An ether solution of the crude product was shaken with pyridine followed by water to remove the excess allylic bromide. Distillation gave 926 mg. of material, b.p. 112–118° (10 mm.). This was filtered through a column of alumina with pentane and redistilled through a 20-cm. Holzmann column to give two fractions: (a) 272 mg., b.p. 110–115° (10 mm.), $n^{25}\text{D}$ 1.4926, $[\alpha]^{25}\text{D}$ +1.5° (alcohol); and (b) 613 mg., b.p. 115–120° (10 mm.), $n^{25}\text{D}$ 1.4858, $[\alpha]^{25}\text{D}$ +8° (alcohol). That both (a) and (b) were mixtures of two similar and probably C_{15} components in different ratios was shown by vapor phase chromatography. The elution times of these components were 15.8 minutes and 20.4 minutes on a 2-meter column type "C" (Perkin-Elmer) at 178°. For comparison π-bromotricyclene was eluted in ten minutes.

Dihydro-α-santalene and π-*t*-Amyltricyclene.—Catalytic reduction of 186 mg. of fraction (a) above over platinum gave 134 mg. (71%) of distilled dihydro-(a), $n^{25}\text{D}$ 1.4793. Vapor phase chromatography of this product at 180° and otherwise identical conditions as above gave two components having elution maxima at 15 and 16 minutes. The ratio of the components in fraction (a) and dihydro-(a) was about 1:1 in both cases. The infrared spectrum of dihydro-(a) manifested tricyclene absorption at 3055 and 855 cm.$^{-1}$ and no absorption characteristic of olefins.

Bi-π-tricyclyl.—From the Grignard reactions of π-bromotricyclene with magnesium there was obtained invariably *ca.* 20% of a neutral crystalline compound, m.p. *ca.* 98–106° crude, which on two recrystallizations from ethanol and sublimation had m.p. 113.5–114.5°. The analytical values indicated a bitricyclyl formula.

Anal. Calcd. for $C_{20}H_{30}$: C, 88.82; H, 11.18; mol. wt., 270.4. Found: C, 89.08; H, 11.17; mol. wt., 286 (Rast).

The infrared spectrum of bi-π-tricyclyl determined in carbon tetrachloride differs from the spectrum of tricyclene in the C–CH_3 region (single peak 1380 cm.$^{-1}$) and in having a single medium peak at 855 cm.$^{-1}$. Otherwise the curves are very similar. There is no absorption in the 1650 cm.$^{-1}$ region and the dimer gives a negative tetranitromethane test. The bi-π-tricyclyl structure seems probable for this compound.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Reactions of Hindered α-Substituted Acids. V. The Effect of a β-Methyl Group on the Acid-Catalyzed Rearrangement[1,2]

BY WYMAN R. VAUGHAN AND A. CHARLES SCHOENTHALER[3]

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The role of the methyl group in promoting the acid-catalyzed rearrangement of 2-hydroxy-3-methyldibenzo[2.2.2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (Ia) to 2-*exo*-hydroxy-6-methyl-3,4,7,8-dibenzo[3.2.1]bicycloöctadiene-1-*cis*-6-dicarboxylic acid-2,6-lactone (IIa) is considered in the light of the failure of the desmethyl analog to undergo the rearrangement. The possibility of participation by the methyl group in the rearrangement is ruled out by the rearrangement of an optically pure sample of Ia to a correspondingly pure sample of IIa. Other examples in similar compounds wherein the methyl group facilitates rearrangement are also considered.

The rearrangement of 2-hydroxy-3-methyldibenzo[2.2.2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (Ia) to 2-*exo*-hydroxy-6-methyl-3,4,7,8-dibenzo[3.2.1]bicycloöctadiene-1-*cis*-6-dicarboxylic acid-2-6-lactone (IIa) and of the desmethyl bromoanalog (Ic) to the analogous lactone (IIb) or diacid (IIc) have been described in previous papers in this series.[4–6]

A review of the data presented in these papers indicates one salient feature of the rearrangement: it can compete best with concurrent reactions when the method of inducing reaction is one which favors S_N1–E_1 type behavior. Thus the action of 48% aqueous hydrogen bromide on Ia affords but one product, IIa, the rearranged lactone-acid.[4] Consequently it appeared that the most information about the rearrangement could be gained from a careful examination of the latter reaction. The comparatively more readily accessible desmethyl analog Ib seemed an attractive starting point for such an investigation in spite of an observation that it did not appear to react with 48% hydrobromic acid under the usual conditions[7]; but unfortunately numerous attempts to effect rearrangement afforded only the starting material or the starting material plus completely intractable tars, abundant confirmation for the earlier observation.

Since the expected lactone-acid IIb and the corresponding diacid IIc were both known to exist,[5] it appeared that the methyl group in Ia was in some manner influencing the course of the reaction. It already had been pointed out[2] that a methyl group is capable of promoting the rearrangement in the *cis*-chloroanhydride system, but in the latter the absence of the methyl group did not lead to complete inhibition of rearrangement or suppression of other recognizable reactions.

At this juncture another instance of similar behavior due to the methyl group was encountered: in the course of investigating methods for the synthesis of a series of monobasic haloacids structurally related to the dibasic acids already studied, hydrogen bromide in toluene was added to dibenzo[2.2.2]-bicycloöctatriene-2-carboxylic acid (IIIb) to produce *cis*-3-bromodibenzo[2.2.2]bicycloöctadiene-2-carboxylic acid (IVa),[8,9] but when the same reaction was attempted with the 3-methyl analog of IIIb (IIIa), none of the expected product was isolated. Instead there was obtained a very poor yield of a bromoacid V isomeric with the desired

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[1] Abstracted from a portion of the Ph.D. dissertation of A. C. Schoenthaler, University of Michigan, 1955.

[2] Preceding paper in this series, W. R. Vaughan and R. Q. Little, Jr., THIS JOURNAL, **76**, 4130 (1954).

[3] Allied Chemical and Dye Corporation Fellow, 1954–1955.

[4] W. R. Vaughan and K. M. Milton, THIS JOURNAL, **74**, 5623 (1952).

[5] W. R. Vaughan, M. V. Andersen, Jr., and R. Q. Little, Jr., *ibid.*, **76**, 1748 (1954).

[6] W. R. Vaughan and R. Q. Little, Jr., *ibid.*, **76**, 2952 (1954).

[7] R. Q. Little, Jr., Ph.D. dissertation, University of Michigan, 1953, p. 63.

[8] For the stereospecific character of this addition *cf.* W. R. Vaughan, R. L. Craven, R. Q. Little, Jr., and A. C. Schoenthaler, THIS JOURNAL, **77**, 1594 (1955).

[9] When hydrogen bromide–acetic acid was used the epimer IVb was obtained. Presumably the usual steric course of addition was followed to give IVa which is demonstrably epimerizable in hydrogen bromide–acetic acid to IVb.