

imum of 285° was used. All compounds except the *t*-butyl-naphthylalkene VI gave only one observable peak (*vide supra*). Data on relative retention times are presented in Table II.

Polarography.—The solvent-electrolyte mixture, 0.1 *M* tetra-*n*-butylammonium iodide in 75% (by volume) dioxane in water, was pre-electrolyzed in an H-type cell for 80–110 min. at 3.0 v. in an atmosphere of pre-purified (>99.99%) nitrogen. Polarography proper was conducted using a Sargent Model XXI polarograph; an attached potentiometer for measuring *E*, the applied potential, to an accuracy of ±0.2 mv.; Sargent S-29417 capillary tubing (*m*, 0.67 mg. per sec.; *t*, 9.9 sec. at *E* = 0), and a thermostated (25.0 ± 0.1°) H-cell with a fine sintered glass disk separating anode compartment (containing a saturated aqueous solution of tetra-*n*-butylammonium iodide in water) from cathode compartment. Two saturated potassium chloride salt bridges (containing filter paper plugs in the

ends toward the H-cell and joined in series *via* a test tube containing the same solution) connected the anode compartment with a saturated calomel electrode (S.C.E.). Solutions *ca.* 3.5, 6.3, and 8.3 × 10⁻⁴ *M* in hydrocarbon were run for each alkene. The current *i* was obtained from the maxima of the pen oscillations. Values of *E*_{1/2} were corrected for *iR* drop (*R* ≈ 8000 ohms, measured during each run and at maximum drop size by means of a General Radio Co. impedance bridge Type 650-A using a 1000 c.p.s. current and an attached oscilloscope) across the cell and were within ±3 mv. of the average value for the various runs on naphthalene and on each of the compounds I–VI. Polarographic data are presented in Table II.

Acknowledgment.—The authors gratefully acknowledge helpful discussions on interpretations of our data with Dr. John B. Bush of this laboratory.

The Partial Reduction of Thujic Acid

D. J. PASTO

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

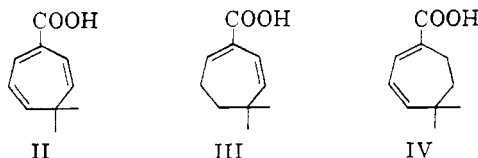
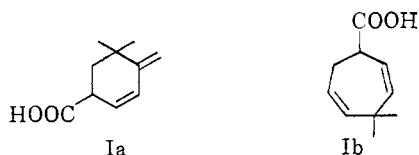
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The partial reduction of thujic acid has been shown to give 4,4-dimethyl-2,6-cycloheptadienecarboxylic acid (V). The isomerization of V was studied and the structures of the isomerization products determined using spectral, chemical, and photochemical evidence. The possible identity of the isomerization products of V with naturally occurring acids isolated from *Libocedrus formosana* is indicated.

The essential oil of *Libocedrus formosana*, found throughout the region surrounding the Pacific Ocean, has been investigated by Ichikawa¹ and was found to contain three crystalline C₁₀H₁₄O₂ acids with melting points of 40–41°, 78–81°, and 103°. Of these acids, only the lower melting acid, termed shonanic acid, was studied in any detail and structure Ia was proposed.² In reviewing the earlier work, Erdtman³ suggested that structure Ib is more reasonable for shonanic acid based on its reported chemistry. Lo and Lin⁴ reinvestigated the

was identical with hexahydrothujic acid. Ichikawa² reported that shonanic acid could be converted to isoshonanic acid (m.p. 44–46°) on treatment with base. Lo and Lin⁴ confirmed this isomerization but reported a melting point of 87–87.5° with absorption in the ultraviolet at 278 mμ (log ε 4.56).

Lin, Lo, and Lin⁵ reported that the reduction of thujic acid with sodium amalgam in a boric acid buffer followed by distillation gave isoshonanic acid. These authors proposed that isoshonanic acid could be represented by either of the formulas III or IV with the former seemingly more probable.



acidic residue from *Libocedrus formosana* and isolated two acids, one melting at 40–41° (C₁₀H₁₄O₂, no absorption between 220 and 340 mμ in the ultraviolet) apparently identical with Ichikawa's shonanic acid and the second acid melting at 89–90° and identified as thujic acid (II). Shonanic acid could be hydrogenated to tetrahydroshonanic acid, which

It seemed unlikely to the present author that sodium amalgam reduction of thujic acid should give either III or IV, since both III and IV are still α,β-unsaturated acids and should undergo further competitive reduction. This would result in a complex mixture of mono-, di-, and triunsaturated acids. It was felt that shonanic acid, represented as Ib, or the previously unmentioned acid V, was the prime reduction product which underwent isomerization during distillation. (Reduction of thujic

(1) N. Ichikawa, *J. Chem. Soc. Japan*, **53**, 353 (1932); *Bull. Chem. Soc. Japan*, **11**, 759 (1936).

(2) N. Ichikawa, *J. Chem. Soc. Japan*, **55**, 85, 95, 105, 111, 1074, 1124 (1934); *Bull. Chem. Soc. Japan*, **12**, 233, 243, 253, 258, 267 (1937).

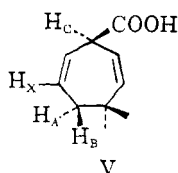
(3) H. Erdtman, "Progress in Organic Chemistry," Vol. 1, J. W. Cook, ed., Academic Press Inc., New York, N. Y., 1952, p. 51.

(4) T. B. Lo and Y. T. Lin, *J. Chinese Chem. Soc.*, **3**, #3, 30 (1956).

(5) Y. T. Lin, T. B. Lo, and T. H. Lin, *ibid.*, **3**, #3, 36 (1956).

acid by 1,2-addition of hydrogen would give Ib and by 1,4-addition would give V.) With this in mind and with the availability of nuclear magnetic resonance for unambiguous identification of the isomeric acids, a reinvestigation of the sodium amalgam reduction of II was undertaken.

The sodium amalgam reduction of II was carried out exactly as described in the literature⁵ but gave a crystalline product on removing the extraction solvent *in vacuo*. Repeated low temperature recrystallization from petroleum ether gave an extremely unstable crystalline acid with melting point of 58–59.5° (infrared absorption at 5.85 μ with low intensity end absorption in the ultraviolet). The n.m.r. spectrum confirmed the structure of the acid as being that of V. Centered at 7.76 p.p.m. were two overlapping quartets corresponding to two protons. Analysis of this region showed it to be the AB part of an ABX system^{6a} where $\Delta\delta_{AB}$ is 16.4 ± 0.5 c.p.s., J_{AB} is 13.5 ± 0.5 c.p.s., and $J_{AX} \approx J_{BX} \approx 6.2$ c.p.s. The X proton absorption is buried beneath complex vinyl proton absorption centered at 4.03 and 4.55 p.p.m. A broad single proton peak corresponding to H_c appeared at 5.87 p.p.m. The methyl proton absorption appeared as two singlets at 8.97 and 8.95 p.p.m. The n.m.r. spectrum is compatible only with structure V where the asym-



metry of the carboxyl bearing carbon produces the chemically different methylene protons, H_A and H_B, and methyl groups. The n.m.r. spectrum of the crude reduction product indicated that it was composed of at least 95% of V.

Treatment of V with strong base for short periods of time produced a very rapid isomerization to give a crystalline mixture of two acids (5.95 μ , $\lambda_{\max}^{95\% \text{ C}_2\text{H}_5\text{OH}}$ 262 m μ). Reduction of the isomerized acid mixture with lithium aluminum hydride produced a mixture of alcohols which showed absorption in the 248–252-m μ region of the ultraviolet consistent with the presence of an alkyl substituted 1,3-cycloheptadiene.^{7,8} This, along with other evidence to be

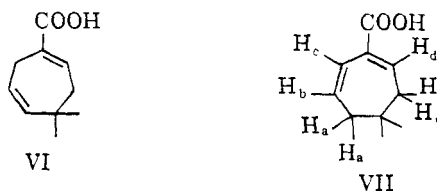
(6)(a) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 90; (b) *ibid.*, p. 60 and 121.

(7) The ultraviolet spectrum of 1,3-cycloheptadiene has been reported to show a maximum at 248 m μ (7400) in isoctane solution [E. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5756 (1950)]. The present author has observed a maximum at 241 m μ (5300) in 95% ethanol (D. J. Pasto, Ph.D. dissertation, Iowa State University of Science and Technology, Ames, Iowa, 1960, p. 195) and 3,5-cycloheptadiene-1-ol has been reported to have a maximum at 242–245 m μ (log ϵ 3.80) in ethanol solution (J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *J. Am. Chem. Soc.*, **77**, 4401 (1955)).

(8) An alkyl substituent on a diene chromophore results in a bathochromic shift of 5 m μ (L. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 17).

presented later, eliminates from consideration as a constituent of the mixture a structure such as VI which, precluding rearrangement during the hydride reduction, would not give a substituted 1,3-cycloheptadiene.

Repeated low temperature fractional recrystallization of the mixture from petroleum ether gave a pure crystalline acid with m.p. 79–80° [infrared absorption 5.95 μ ; and $\lambda_{\max}^{95\% \text{ C}_2\text{H}_5\text{OH}}$ 262 m μ (log ϵ 3.55)]. The n.m.r. spectrum identified the acid as having the structure shown as VII.



The allylic protons H_a and H_e appear as two overlapping doublets at 7.99 and 7.86 p.p.m. with J_{ab} of 6.6 and J_{ce} of 6.1 c.p.s. Proton H_c appears as a doublet at 3.56 p.p.m. with J_{cb} of 12.2 c.p.s. Proton H_b, being spin-coupled with H_c (12.2 c.p.s.) H_a (6.1 c.p.s.) appears as a five peak pattern resulting from two overlapping triplets at 3.97 p.p.m. Proton H_a appears as a triplet at 2.70 p.p.m. (J_{ae} of 6.4 c.p.s.).

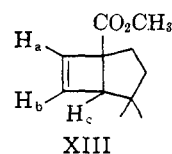
Evaporation of the mother liquors from the isolation and purification of VII, gave a mixture of acids which could not be further separated by fractional recrystallization, fractional distillation, column chromatography on Fluorisil or by vapor phase chromatography (VPC) of the corresponding methyl esters. Analysis by n.m.r. indicated approximately 60% VII still present in the mixture. Although the other isomeric acid could not be isolated in a pure state, indirect evidence was obtained to indicate that its structure is that shown as III. The ultraviolet maximum of the mixture, left after removing part of VII that was present, was still positioned at 262 m μ indicating that the same chromophore was present in both of the acids. Subtraction of the n.m.r. spectrum of VII from that of the mixture revealed multiplets centered at 8.36 and 7.50 p.p.m. characteristic of methylene protons in a saturated and allylic environment, respectively. The remainder of the spectrum showed two doublets at 4.27 and 4.03 p.p.m. (J of 13 c.p.s.) and a triplet at 2.81 p.p.m. (J of 6 c.p.s.). The n.m.r. spectrum thus obtained is compatible with structure III.

As it appeared that it would be impossible to effect separation of the acid mixture into its pure components by purely physical means, another method had to be found either to effect separation or to provide more evidence as to the respective structures. Due to the apparent very facile double bond migration under acidic, basic, and thermal conditions, the method of separation would have to depend on prior conversion of the acidic components, or their methyl esters, into entities in which

isomerization could not occur. A method fulfilling this requirement is the photochemical isomerization of 1,3-cycloheptadienes to bicyclo[3.2.0]hept-6-ene systems, a reaction which has been well documented⁹ and is suitable for aiding in structure proofs. Although alkyl group migration has been observed during irradiation,^{9a,d} the migration of double bonds during irradiation has not been observed. As the double bonds in the acids being studied were very prone to migration it was first necessary to determine whether or not double bond migration could occur in these systems under irradiative conditions. Irradiation of an ethereal solution of pure VII gave a photoisomer which was too unstable to characterize. The corresponding methyl ester of VII, VIII, when irradiated gave a reasonably stable photoisomer IX which was shown to be homogeneous by n.m.r. and VPC. The infrared spectrum of IX showed peaks at 5.83 and 6.24 μ in carbon tetrachloride solution with absorption in the ultraviolet at 226 m μ ($\log \epsilon$ 3.73). The n.m.r. spectrum confirmed the structure as IX. The n.m.r. spectrum showed a single proton resonance at 3.23 p.p.m. characteristic of beta proton resonances in α,β -unsaturated systems.^{6b} The bridgehead protons appear as a complex multiplet at 6.61 with the methylene protons appearing as two apparent doublets at 8.44 and 8.54 p.p.m. and a complex multiplet centered at 8.69 p.p.m. The appearance of such a pattern is due to the non-equivalence of the two protons on each methylene group caused by different spatial orientation imposed by the rigid system. The chemically different methylys appear at 9.00 and 9.92 p.p.m.

As the photoisomerization of VIII gave a single product without double bond migration, the method appeared suitable for attempted separation or identification of the components in the acid mixture. The mixture of acids, remaining after partial separation of VII, was esterified with diazomethane giving the corresponding methyl esters VIII and X, and irradiated to give a mixture of photoisomers which could not be resolved by VPC. Reduction to the corresponding primary alcohols with lithium aluminum hydride followed by VPC also failed to effect separation. The n.m.r. spectrum of the photo ester mixture showed, in addition to peaks corresponding to IX which could be clearly distinguished, a finely split single proton resonance at 3.33 p.p.m. consistent with the beta proton of XI (there were no peaks characteristic of the photoisomer XIII discussed in a subsequent paragraph). The *gem*-dimethyls appeared at 9.11 and 8.95 p.p.m. with the ethereal methyl appearing at 6.35 p.p.m. thus indicating the probable presence of XI.

More drastic treatment of V with base, *i.e.* refluxing with base for long periods of time, resulted in a shift of the maximum in the ultraviolet to 272 m μ . The recovered acid mixture contained at least three isomeric acids which again could not be separated by fractional recrystallization, fractional distillation, column chromatography, or by VPC of the mixture of the corresponding methyl esters. Again, photoisomerization was turned to in order to achieve separation or identification of the components of the mixture. The mixture of methyl esters was irradiated giving a mixture of photoisomers which could be partially separated by VPC techniques. The vapor phase chromatogram indicated the presence of three fractions. The first fraction showed a peak in the infrared at 5.80 μ in carbon tetrachloride solution indicating the presence of a β,γ -unsaturated ester.¹⁰ The ultraviolet spectrum showed only end absorption (220 m μ , $\log \epsilon$ 2.91). The structure of fraction one was unambiguously shown to be that of XIII by its n.m.r. spectrum. The n.m.r. spectrum showed two doublets, representing



protons H_a and H_b , in the vinyl region at 4.00 and 3.87 p.p.m. (J of 2.5 c.p.s.), the doublet representing H_b being further split (< 0.5 c.p.s.) due to additional coupling with the bridgehead proton H_c . The bridgehead proton H_c appears as an unresolved doublet at 7.22 p.p.m. with the methylene protons appearing as a complex multiplet centered at 8.28 p.p.m. The *gem*-dimethyls appear as two singlets at 9.03 and 9.02 p.p.m. The n.m.r. spectrum is compatible only with XIII and must have been formed from the methyl ester of IV, XII. The shift to longer wave length in the ultraviolet during the base-catalyzed isomerization is consistent with the presence of IV, as it would be expected to show a longer wave length maximum than III or VII. The second fraction was identified as a mixture of IX and XI and the third fraction was identified as unreacted starting material. Analysis of the acid mixture formed after varying lengths of time in refluxing base, by methylation, irradiation, and n.m.r. and VPC analysis indicated the existence of a base-catalyzed equilibrium containing approximately 13% III, 58% IV, and 29% VII.

As the earlier report of the sodium amalgam reduction of II indicated that isoshonanonic acid was formed,⁵ a finding contrary to the present results, the possibility that the primary reduction product

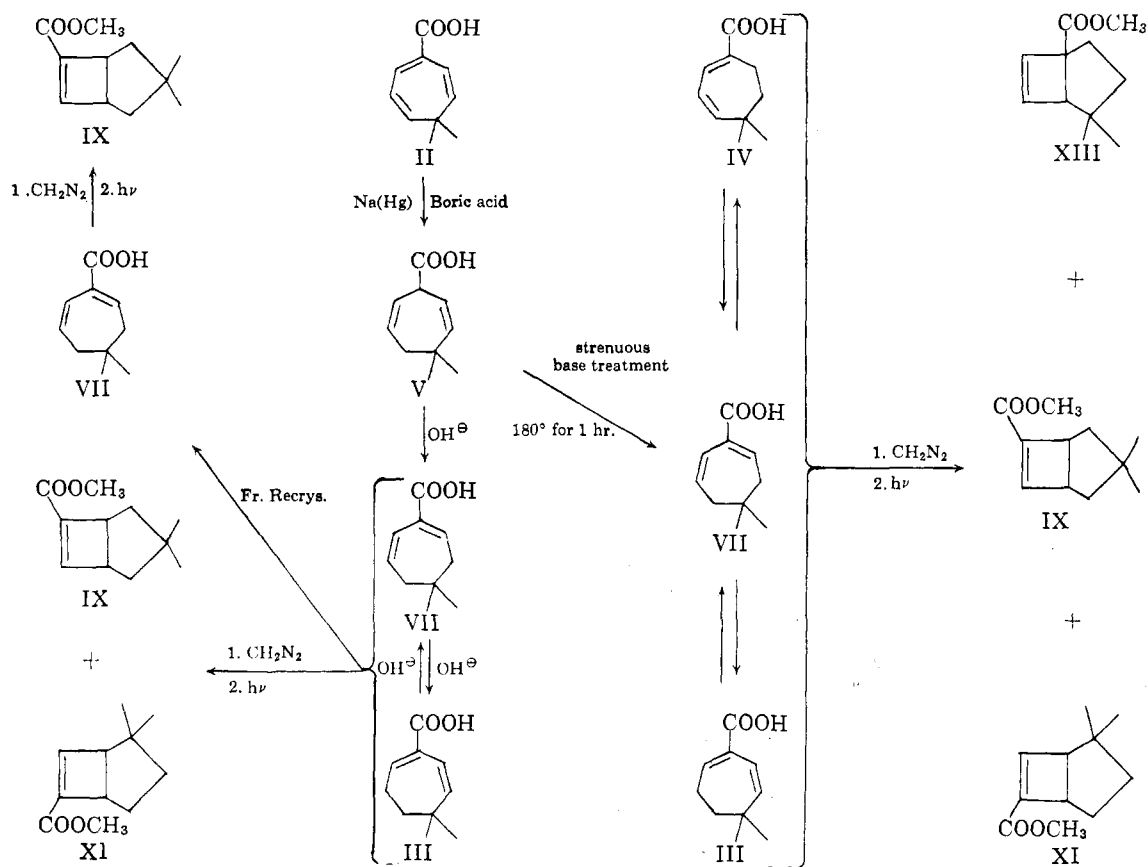
(9) (a) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960); (b) O. L. Chapman and D. J. Pasto, *Chem. Ind. (London)*, 53 (1961); (c) J. Rigaudy and P. Courtot, *Tetrahedron Letters*, **3**, 95 (1961); (d) J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 116 (1961); (e) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, #3, 186 (1961); (f) G. J. Fonken, *Chem. Ind. (London)*, 1575 (1961).

(10) β,γ -Unsaturation produces a slight shift to longer wave length in the case of ketones [R. Mecke and K. Noack, *Angew. Chem.*, **18**, 150 (1956); N. Fuson, M-L. Josien, and E. M. Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954)] and a similar effect would be expected in the case of esters although the shift observed in the case of XIII is larger than those reported with ketones.

V underwent isomerization on distillation was investigated. The present author found that V could be distilled at 110–115° at 0.5 mm. without rearrangement.¹¹ Heating at higher temperatures for longer periods of time (180° for 1 hour) caused extensive decomposition but gave a mixture of acids which displayed a 272 m μ maximum in the ultraviolet. Trituration with petroleum ether and chromatography on Fluorasil gave in poor yield (17%) an acid mixture virtually identical with the mixture obtained by strenuous base treatment of V. Esterification with diazomethane followed by irradiation and analysis by VPC indicated the acid mixture contained 37% of a mixture of III and VII and 63% of IV. The above transformations are illustrated in the following scheme.

zation of VII ($\lambda_{\max}^{95\% \text{ C}_2\text{H}_5\text{OH}} 262 \text{ m}\mu$) indicates that isoshonanac acid ($\lambda_{\max}^{95\% \text{ C}_2\text{H}_5\text{OH}} 278 \text{ m}\mu$) must have a longer conjugated system such as that appearing in IV. (Structure III cannot be considered for isoshonanac acid as it would be expected to absorb in the ultraviolet at 262 m μ as does VII.) Additional evidence for the structure of IV for isoshonanac acid is that in a reaction from which isoshonanac acid has been isolated,⁵ *i.e.* heat isomerization during distillation of the crude reduction product, the ultraviolet absorption has moved to longer wave length and the photoisomer XIII can be isolated from the mixture after methylation and irradiation. This evidence strongly points to IV as the structure for isoshonanac acid.

At this point one may only conjecture as to the



Although shonanac acid was not encountered during the present investigation and isoshonanac could not be isolated in pure form, evidence was obtained which would allow one to assign structures for both acids. As there are only two 4,4-dimethylcycloheptadiene carboxylic acids which are totally unconjugated, those being I_b and V, the isolation and characterization of V, having physical properties different from those reported for shonanac acid, gives added support for the structure of shonanac acid as that being I_b. The isolation and characteri-

identity of the acids reported by Ichikawa¹ with melting points of 78–81° and 103°. The similarity of the melting point of VII (79–80°) with the unknown acid of melting point 78–81° may indicate this unknown acid has the structure VII. The 103° melting acid may be III. Although no direct comparison of Ichikawa's acids with those isolated in the present investigation was possible, the procedure for the production of III and VII *via* a base-catalyzed isomerization of V parallels the original extraction procedure employing aqueous base for the isolation of the natural acid mixture containing predominantly I_b.

(11) The original authors (see ref. 5) distilled the acid at 130–132° at 1.5 mm.

Experimental¹²

Sodium Amalgam Reduction of Thujic Acid.—A suspension of 6.7 g. (0.04 mole) of thujic acid and 11.4 g. of boric acid in 114 ml. of water was cooled to 0° in an ice bath and 2.2 g. (0.095 mole of active hydrogen) of sodium in 125 g. of mercury was added slowly with stirring. Stirring was continued until the evolution of hydrogen had ceased. The solution was acidified with hydrochloric acid and then was extracted with two portions of ether. The ether extract was washed with water, dried over sodium sulfate, and the solvent was immediately removed under reduced pressure leaving 6.1 g. (0.037 mole, 93%) of a pale yellow oil which crystallized on standing in a freezer overnight. Recrystallization from petroleum ether at -70° gave unstable, colorless needles with m.p. 58–59.5°. The infrared spectrum showed a peak at 5.87 μ with only low intensity end absorption in the ultraviolet (215 $m\mu$, $\log \epsilon$ 2.98).

Base-Catalyzed Isomerization of V and Isolation of VII.—A solution of 1.0 g. of V in 20 ml. of 20% sodium hydroxide was heated at reflux for 1 hr. The solution was acidified with hydrochloric acid and was extracted with two 50-ml. portions of ether. The extract was dried over sodium sulfate. The solvent was removed under reduced pressure leaving a pale yellow residue which crystallized on standing. Repeated low temperature fractional recrystallization from petroleum ether gave colorless needles of VII with m.p. 79–80° [5.95 μ and $\lambda_{\max}^{95\% \text{ C}_2\text{H}_5\text{OH}}$ 262 $m\mu$ ($\log \epsilon$ 3.55)].

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_2$: C, 72.26; H, 8.49. Found: C, 72.00; H, 8.52.

The mother liquors from the separation and recrystallization of V were combined and evaporated leaving a pale yellow, viscous liquid which could not be induced to crystallize. The mixture showed a peak at 5.95 μ in the infrared with absorption in the ultraviolet at 262 $m\mu$. The mixture could not be further separated by fractional recrystallization, fractional distillation or by column chromatography on Fluorisil. Esterification with ethereal diazomethane followed by analysis by VPC on a silicone GE SF-96 column at 180° produced a single symmetrical peak with a retention time of 15.7 min.

Esterification of VII.—A solution of 500 mg. of V in 15 ml. of ether was treated with a slight excess of freshly distilled diazomethane. The solvent was removed under reduced pressure. The residue was purified by molecular distillation at 45–50° at 0.1 mm. giving a colorless, mobile liquid VIII, n_D^{25} 1.4974. The infrared spectrum showed a peak at 5.88 μ with ultraviolet absorption at 267 $m\mu$ ($\log \epsilon$ 3.68). The n.m.r. spectrum in carbon tetrachloride showed *gem*-dimethyls at 8.99 p.p.m. (relative to tetramethylsilane), overlapping doublets at 8.03 (*J* of 5.7 c.p.s.) and 7.91 p.p.m. (*J* of 6.6 c.p.s.), ethereal methyl at 6.29 p.p.m., two overlapping triplets producing a quintet centered at 3.99 p.p.m. (*J* of 5.3 c.p.s.), doublet at 3.60 p.p.m. (*J* of 11.2 c.p.s.), and a triplet at 2.88 p.p.m. (*J* of 6.0 c.p.s.).

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.95. Found: C, 73.35; H, 8.77.

Photoisomerization of Ester VIII.—A solution of 240 mg. of VIII in 400 ml. of anhydrous ether was irradiated with a 200-watt Hanovia immersion lamp, using a 250 $m\mu$ cut-off filter, until the absorption at 267 $m\mu$ had disappeared. The ether was removed under reduced pressure and the residue

was purified by molecular distillation at 50° at 1 mm. giving a colorless liquid IX, n_D^{25} 1.4717. The infrared spectrum showed peaks at 5.83 and 6.24 μ in carbon tetrachloride with ultraviolet absorption at 226 $m\mu$ ($\log \epsilon$ 3.73). The vapor chromatogram at 180° on a silicone GE SF-96 column showed a single sharp symmetrical peak with a retention time of 11.7 min. The material slowly polymerized on standing at room temperature for several days.

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.95. Found: C, 73.32; H, 8.75.

Photoisomerization of the Mixture of Esters VIII and X.—The acid mixture remaining after isolation of VII was esterified with ethereal diazomethane. A solution of 750 mg. of the ester mixture in 400 ml. of ether was irradiated as above until the absorption at 267 $m\mu$ had disappeared. The ether was removed under reduced pressure, and the residue molecularly distilled at 60° at 1 mm. The infrared spectrum showed peaks at 5.83 and 6.24 μ with ultraviolet absorption at 227 $m\mu$ ($\log \epsilon$ 3.82). The vapor phase chromatogram showed two overlapping peaks on a silicone GE SF-96 column at 180° with retention times of 11.8 and 12.4 min. The n.m.r. spectrum showed the following peaks which were not found in the n.m.r. spectrum of IX: *gem*-dimethyls at 9.11 and 8.95 p.p.m., ethereal methyl at 6.35 p.p.m., and a doublet at 3.33 p.p.m. (*J* of 0.6 c.p.s.). The n.m.r. spectrum indicated that the acid mixture contained approximately 60% of VII and 40% of III.

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.95. Found: C, 73.29; H, 8.93.

Base-Catalyzed Isomerization of V to the Mixture of III, IV, and VII and Irradiation of the Corresponding Ester Mixture.—A solution of 3.0 g. of V in 30 ml. of 20% sodium hydroxide was refluxed for 22 hr. The solution was acidified and extracted with two portions of ether. The extract was dried over sodium sulfate. The solvent was removed under reduced pressure leaving a pale yellow residue which crystallized on standing. The infrared spectrum showed a peak at 5.95 μ with ultraviolet absorption at 272 $m\mu$. The n.m.r. spectrum indicated the presence of III and VII plus an additional acid. The mixture could not be separated by fractional recrystallization, fractional distillation or by column chromatography on Fluorisil.

The mixture of acids was converted to the corresponding mixture of methyl esters with ethereal diazomethane. The ester mixture (750 mg.) was dissolved in 400 ml. of ether and irradiated as above. The ether was removed under reduced pressure. Analysis by VPC on a silicone GE SF-96 column at 180° showed a symmetrical peak with a retention time of 9.2 min. (fraction one), two overlapping peaks with a retention time of 13.2 min. (fraction two) and a peak with a retention time of 15.2 min. (fraction three). Fractions one and two were collected using preparative scale VPC techniques. Fraction two was identified as a mixture of IX and XI, and fraction three was identified as starting material by comparison of retention times and admixture.

Fraction one was molecularly distilled at 50° at 1 mm. giving a colorless, mobile liquid XIII. The infrared spectrum showed a peak at 5.80 μ in carbon tetrachloride solution with only low intensity end absorption in the ultraviolet (225 $m\mu$ and below, $\log \epsilon$ 2.91).

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.95. Found: C, 73.27; H, 9.07.

A portion of V was refluxed in 20% sodium hydroxide. Aliquots were removed periodically and the acid mixture isolated. The mixture was esterified with ethereal diazomethane and the ester mixture irradiated. The resulting mixture of photoisomers was analyzed by VPC and n.m.r. indicating the existence of an equilibrium between III, IV, and VII containing approximately 13% III, 58% IV, and 29% VII.

Thermal Isomerization of V.—A 1-g. sample of V was heated under nitrogen at 180° (no solvent) until there was no further change observed in the ultraviolet. The material

(12) All melting points and boiling points are uncorrected. Microanalysis were carried out by Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside, N. Y.

(13) The recorded melting point represents the temperature range in which a majority of the sample melted. The material underwent rapid decomposition and required filtration after each recrystallization. Acceptable analysis could not be obtained: a sample analyzed within 48 hr. showed carbon 3% low, after 10 days 10% low. The material could be stored for several days without appreciable decomposition at -20°.

was triturated with petroleum ether and chromatographed on a short column of Fluorasil giving 174 mg. of crystalline material (5.95μ and $\lambda_{max}^{96\% \text{ C}_2\text{H}_5\text{OH}}$ 272 $m\mu$). The n.m.r. was identical with that of the strenuous base-isomerized mixture containing III, IV, and VII. Esterification with ethereal diazomethane followed by irradiation and analysis by

VPC showed the presence of 70% of IV and 30% of a mixture of III and VII.

Acknowledgment.—The author wishes to acknowledge Crown Zellerbach Corp. of Camas, Washington, for generous amounts of thujic acid.

Terpenoids. XXXIII. Transformations in the Santalene Series

SURYAKUMARI RAMASWAMI, S. K. RAMASWAMI, AND S. C. BHATTACHARYYA

Contribution No. 499 from the National Chemical Laboratory, Poona-8, India

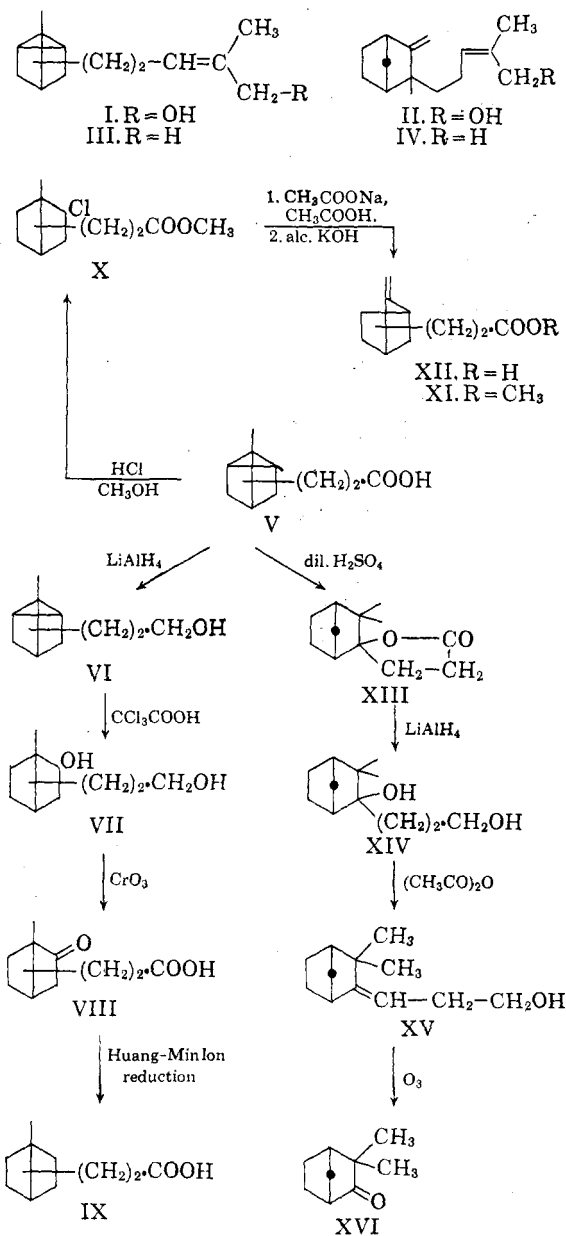
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Starting from the crystalline tricyclic derivative tricycloekasantalic acid, several compounds having different bicyclic ring systems have been obtained. Some of these are of use in the synthesis of compounds of the bornane and camphene series.

α -Santalol (I), β -santalol (II), and the corresponding hydrocarbons, α -santalene (III) and β -santalene (IV), are the main constituents of East Indian sandalwood oil. The chemistry of these interesting compounds and allied products has been investigated by several workers.¹ Some of the earlier investigations² have been extended by us with a view to having a better understanding of the nature of the molecular rearrangements in this series and the results are presented in this communication. We were specially prompted to put our results on record because of a very recent publication.³

α -Santalene gives, on ozonization or permanganate oxidation, the crystalline tricycloekasantalic acid (V), which can be conveniently reduced with lithium aluminum hydride to tricycloekasantalol (VI), previously prepared⁴ by reduction of the corresponding ester with sodium and alcohol. Hydration of VI with trichloroacetic acid and subsequent hydrolysis gave the crystalline diol (VII). Formic acid, dilute sulfuric acid, and trifluoroacetic acid⁵ were found to be less convenient for this purpose. The secondary nature of the ring hydroxyl group was confirmed by chromic acid oxidation of the diol to a crystalline ketocarboxylic acid (VIII) which on Huang-Minlon reduction gave dihydroekasantalic acid (IX).

On treatment with gaseous hydrogen chloride in methanolic solution, tricycloekasantalic acid was converted to the methyl ester (X). Somewhat contrary to the findings of Semmler,⁴ this chloro ester



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