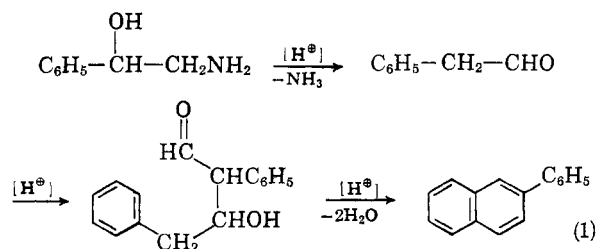


heating 2-hydroxy-2-phenylethylamine with 20% aqueous hydrochloric acid at 120–130° for 15 hours. The structure of the 1,3-diphenylcyclobutadiene was assigned on the basis of comparison of its melting point (and mixed melting point) with that believed to be of an authentic sample.¹ Because of present interest in the preparation and properties³ of cyclobutadienes, it was deemed advisable that the reported synthesis of 1,3-diphenylcyclobutadiene be investigated further.

It has been presently found that reaction of 2-hydroxy-2-phenylethylamine in a sealed tube at 135° for 15 hours in the presence of 20% hydrochloric acid gives 2-phenylnaphthalene (>50% yield) rather than 1,3-diphenylcyclobutadiene. All efforts to isolate a hydrocarbon corresponding to 1,3-diphenylcyclobutadiene failed.¹ The structure of the hydrocarbon obtained in the present research was assigned upon comparison of its melting point, mixed melting point, and infrared and ultraviolet spectra with that of unequivocal 2-phenylnaphthalene.⁴ The properties of the 2-phenylnaphthalene isolated compare favorably with that reported for 1,3-diphenylcyclobutadiene¹ with the exception of the extinction coefficient in the 247.5–249-m μ region. The results of the present study are in agreement with that reported previously⁵ in that 2-phenylnaphthalene is obtained in 80% yield by refluxing 2-hydroxy-2-phenylethylamine with 48% hydrobromic acid. It is apparent that 2-phenylnaphthalene is possibly formed from 2-hydroxy-2-phenylethylamine *via* phenylacetaldehyde and subsequent processes of the type illustrated in equation 1.⁶



Experimental

A solution of 2-hydroxy-2-phenylethylamine (0.5 g., 3.5 mmoles) in 20% aqueous hydrochloric acid (10 ml.) was

(2) The properties reported for 1,3-diphenylcyclobutadiene are: m.p. 97–98°; λ_{max} 249 (log ϵ 3.15) and 287.5 m μ (log ϵ 4.22) in 95% ethanol. *Anal. Calcd. for C₁₆H₁₂*: C, 94.1; H, 5.9; M, 204. Found: C, 94.2; H, 5.85; M, 202.

(3) G. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 147.

(4) The properties of 2-phenylnaphthalene (C₁₆H₁₂) presently obtained are: m.p. 102–103° (corr.); λ_{max} 247.5 (log ϵ 4.71) and 289 m μ (log ϵ 4.06) in 95% ethanol; lit., m.p. 102–103° [L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 940 (1938)]; λ_{max} 249 (log ϵ 4.7) and 288 m μ (log ϵ 4.07) in 95% ethanol [R. A. Friedel, M. Orchin, and L. Reggel, *ibid.*, **70**, 199 (1948)].

(5) H. E. Carter and E. J. Van Loon, *ibid.*, **60**, 1077 (1938).

(6) An alternate mechanism for formation of 2-phenylnaphthalene involving acetophenone¹ can be written. Such a reaction path appears improbable because of its complexity.

heated in a sealed tube for 15 hr. at 135°. The reaction mixture was extracted with ether. The ether extract was washed with water, 5% aqueous sodium bicarbonate, dried, and the solvents evaporated. The crude product (0.335 g.) upon crystallization from ethyl alcohol gave 2-phenylnaphthalene (0.185 g., 1.75 mmoles, 50% yield), m.p. 100–102°. Recrystallization of the 2-phenylnaphthalene raised its melting point to 102–103°. The infrared spectrum of the crude product of reaction was essentially identical with that of 2-phenylnaphthalene.

Santonin and Related Compounds. XXIV.¹ The Rearrangement of the $\Delta^{1,4}$ -3-Dienone Possessing a Lactone Ring

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In paper XXII³ of this series, it was disclosed that in the $\Delta^{1,4}$ -3-dienone systems (as I), the conformation alternation of the acetic acid side chain at the 6-position exerted an important effect on the course of the migration. It was also indicated that the properties of the acidic reagents used had a significant bearing on a feature of the dienone rearrangement. In the four patterns cited therein, the migration of *trans*-9-methyl-3-keto- $\Delta^{1,4}$ -hexahydronaphthalene-6-acetic acid (II) in acetic anhydride-sulfuric acid afforded the unexpected phenol, 4-methyl-*ar*-2-tetralol-6-acetic acid (III). In view of this abnormal result, it was of interest to explore the aromatization of a similar dienone carrying a lactone at the position corresponding to II.

Previous attempts were made by Gunstone and Tulloch⁴ to prepare the dienone-lactone IV by introduction of an additional double bond into the corresponding monoene-lactone V. However, their efforts to form the cross-conjugated dienone by bromination-dehydrobromination of V, whose configuration remained ambiguous at that time,⁵ were unfruitful. In the present work, the synthesis of IV was achieved in the same way as projected by the British workers.⁴ *trans*-9-methyl- $\Delta^{1,4}$ -3-octalone-6-acetic acid VI (R = H) possessing the established configuration, as reported previously,⁴ was monobrominated with N-bromosuccinimide to give the bromo compound VI (R = Br), which is stereochemically stable in the presence of hydrobromic acid and thus must have the

(1) Part XXIII, S. Inayama, and M. Yanagita, *J. Org. Chem.*, **27**, 1465 (1962).

(2) Present address: Tokyo Research Laboratory, Tanabe Seiyaku Co., Ltd., Saitama-ken, Toda, Japan; to whom inquiries regarding this article should be directed.

(3) M. Hirakura, M. Yanagita, and S. Inayama, *J. Org. Chem.*, **26**, 3061 (1961).

(4) F. D. Gunstone and A. P. Tulloch, *J. Chem. Soc.*, 1130 (1955).

(5) M. Yanagita, S. Inayama, M. Hirakura, and F. Seki, *J. Org. Chem.*, **23**, 690 (1958).

bromine atom equatorial.⁶ The reaction solution without isolation of the product was directly subjected to acetolysis with sodium acetate to afford the same bromine-free product as formed earlier by alkaline hydrolysis of the same bromide.⁴ Product V, whose structure has already been verified by the light absorption spectra comparison,⁴ may be deemed to arise through an unimolecular nucleophilic substitution (S_N1). In VI (R = Br) the bromine atom first ionizes as an anion; the positive charge left at the 5-position (VII) might be attacked by the negatively charged oxygen atom of the carboxyl group from the less hindered α -side⁷ to form the most stable C-5 equatorial *cis*-lactone V.

Dehydrogenation of V was carried out by the usual selenium dioxide oxidation⁵ to afford the desired dienone-lactone IV, m.p. 136–137°, in 32% yield. This lactone possesses a maximum at 239 m μ (ϵ 15,600), in good agreement with those reported for the $\Delta^{1,4}$ -3-dienone moiety.³ In the infrared region, it exhibits a medium strong band at 1028 cm.⁻¹, corresponding to the preceding equatorial lactone in the santonin series.⁸ This value gives additional support for the axial character of the acetic acid residue in IV (hence in II).

The rearrangement of IV was effected with acetic anhydride and concentrated sulfuric acid by the usual procedure.³ The oily product, which could not be induced to crystallize, was hydrolyzed directly with dilute sodium carbonate solution in aqueous ethanol to a phenolic lactone, m.p. 174–175°, in a 69% yield from IV. The infrared spectrum possesses bands at 3317 (OH), 1738 (γ -lactone) and 816 and 809 cm.⁻¹ (adjacent hydrogens on a benzene ring),^{3,9} indicative of the *p*-cresol derivative with a lactone ring. In the light of the absorption data and the analytical figures, the structure X or X' may possibly be assigned to the present lactone.

According to the mechanisms previously suggested for the dienonephenol rearrangement,¹⁰ the migration mentioned above can be assumed to proceed through either of two possible routes (A and B); see Fig. 1. On reaction with acetic anhydride, IV would be first converted to the acetate cation of a spiran structure, formulated as VIII. In the spiran, if the bond a is cleaved (the path A), a transition cation IX would result,

in which a resonance between the bonds $\text{CH}_2\text{—O}^+$ and $\text{CH}_2\text{=O}^+$ can occur, the former contributing more than the latter. The cationic center in IX would attack the ring in the position *ortho* to the

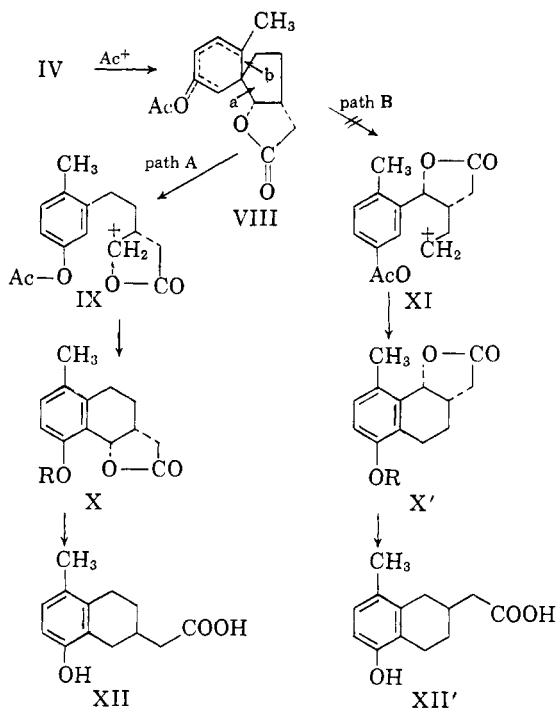
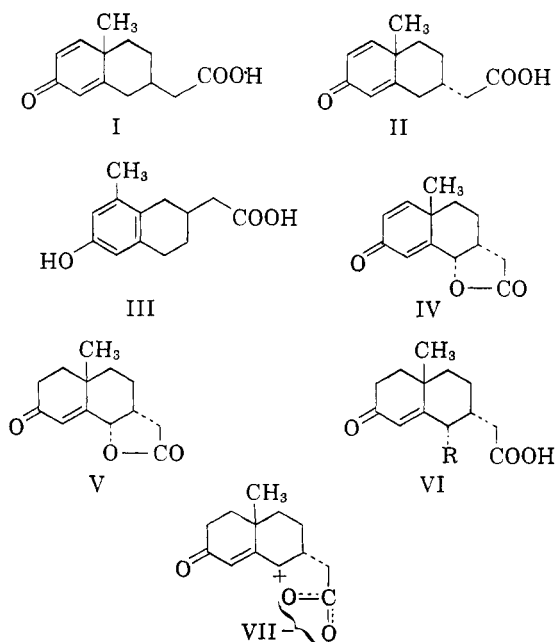


Figure 1

acetoxy group to form X (R = COCH₃). On the other hand, the rupture of the bond b (the path B) would lead to the isomeric acetate X' (R = COCH₃) *via* the alternative cation XI, in which such a resonance involving the cationic center is impossible. Clearly IX is more stable than XI and therefore it may be inferred that in the rearrangement, path A is preferred to B, leading to the predomi-



(6) Cf. Y. Abe, T. Harukawa, H. Ishikawa, T. Miki, M. Sumi, and T. Toga, *J. Am. Chem. Soc.*, **78**, 1422 (1956).

(7) The α,β stereochemical designation are patterned after the now widely adapted steroid convention; see L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, 1959, p. 2.

(8) T. Kanzawa, H. Kamio, M. Sumi, and M. Nishikawa, *J. Am. Chem. Soc.*, **80**, 3705 (1958).

(9) J. L. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley & Sons, Inc., New York, 1958, p. 78.

(10) R. B. Woodward and T. Singh, *J. Am. Chem. Soc.*, **72**, 494 (1950); S. M. Bloom, *ibid.*, **80**, 6280 (1958).

nant formation of X. That such was the case was established by the zinc reduction of the chief product from the rearrangement, affording only 4-methyl-*ar*-2-tetralol-7-acetic acid XII, identified by comparison with an authentic sample recently prepared in this laboratory.³ No evidence for the alternative possible product XII' from X' (R = H) could be found in the reduction, excluding the possibility of path B. Since, in the migration of IV, positions 5 and 6 do not appear to be directly involved, the configurations at these positions may be considered to remain untouched, as shown in X. It is notable that such a lactone ring in the dienone has a remarkable effect on the migration course in forming X, in which the acetic acid residue occupies position (7) dissimilar from that (6) predicted from the migration paths of the dienone-acetic acids (I).³ The variety of the rearrangement courses, including the present result, can hardly be rationalized on the available data.

Experimental¹⁴

All temperatures are uncorrected. Infrared absorption spectra were measured with a Perkin-Elmer Model 21 double beam spectrophotometer.

Lactone of 9-Methyl-5 α -hydroxy- Δ^4 -3-octalone-6 α -acetic Acid (V).—Under the same conditions as reported previously,⁴ *trans*-9-methyl- Δ^4 -3-octalone-6-acetic acid (II, 3.0 g.)⁵ was monobrominated with *N*-bromosuccinimide (2.5 g.) in carbon tetrachloride (200 cc.), except under exposure to diffused sunlight in the absence of peroxide. After removal of the succinimide, the reaction containing the product was mixed with acetic acid (15 cc.) and fused sodium acetate (16 g.). The mixture was heated at 90–100° on a water bath with occasional shaking. The reaction was diluted with water, extracted with ethyl acetate, and the acetate layer washed with saturated aqueous bicarbonate and water. Evaporation of the dried acetate solution furnished 1.21 g. (40%) of the lactone V as colorless crystals, m.p. 132–134°, from ethyl acetate-petroleum ether. Two further crystallizations from benzene-petroleum ether raised the melting point to 134–135°; $\lambda_{\text{max}}^{\text{EtOH}}$ 234.5 μm (ϵ 10,300). Reported,⁴ m.p. 136–137°; $\lambda_{\text{max}}^{\text{EtOH}}$ 235 μm ($\log \epsilon$ 4.14).

Lactone of 3-Keto-9-methyl-5 α -hydroxy- Δ^1 -4-hexahydro-naphthalene-6 α -acetic Acid (IV).—Under the same conditions as described previously for the oxidation of the dimethyl-octalone,⁵ 0.82 g. of the above monoenolactone V was heated to reflux with selenium dioxide (0.50 g.) in a mixture of *tert*-butyl alcohol (110 cc.) and glacial acetic acid (1 cc.). The product, a red-brown sirup, was dissolved in ethyl acetate, and, after washing with aqueous bicarbonate and water, the acetate was evaporated to leave a viscous mass which could not be crystallized. The mass was chromatographed on an alumina column (10 g.) and the elutions with benzene gave 0.26 g. (32%) of the dienone-lactone IV, m.p. 133–136°, from ethyl acetate-petroleum ether. Two further crystallizations from benzene formed yellowish plates, m.p. 136–137°; $\lambda_{\text{max}}^{\text{EtOH}}$ 239 μm (ϵ 15,600); $\nu_{\text{max}}^{\text{Nujol}}$ 1785 (γ -lactone), 1663 (Δ^1 -3-dienone) and 1629 (double bond).⁵

Anal. Calcd. for C₁₃H₁₄O₃: C, 71.54; H, 6.47. Found: C, 71.03; H, 6.11.

Rearrangement of the Above Dienone-Lactone (IV) in Acetic Anhydride.—This reaction was carried out under the customary conditions.³ IV (0.16 g.) was dissolved in acetic anhydride (1 cc.) containing a trace of concentrated sulfuric acid and kept at room temperature for 6 hr. The reaction

was not exothermic and the color changed from a pale yellow to an orange yellow. The mixture was poured into ice water and no crystals separated even after standing in a refrigerator overnight. The aqueous solution was extracted with ether and the ethereal layer washed with aqueous bicarbonate and water. Drying and evaporation of the ether left a neutral sirup (0.15 g.), which could not be induced to crystallize. The sirup was heated to reflux in a mixture of ethanol (5 cc.) and 10% aqueous sodium carbonate (3 cc.) for 30 min. After evaporation of the alkaline solution *in vacuo*, the residue was mixed with water, acidified, and extracted with ethyl acetate. The acetate extract was washed as usual, and evaporated to leave 0.11 g. (69%) of lactone of 4-methyl-8 α -hydroxy-1-*ar*-tetralol-7 α -acetic acid X (R = H), m.p. 168°, from ethyl acetate-petroleum ether. Two further crystallizations from the same solvents furnished microscopic white plates, m.p. 174–175°; $\lambda_{\text{max}}^{\text{EtOH}}$ 289 μm (ϵ 3430); $\nu_{\text{max}}^{\text{Nujol}}$ 3317 (OH), 1738 (γ -lactone),¹² and 816 and 809 (adjacent hydrogens on a benzene ring).^{3,9}

Anal. Calcd. for C₁₃H₁₄O₃: C, 71.54; H, 6.47. Found: C, 71.65; H, 6.34.

Reduction of the Above Tetralol-Lactone (X) with Zinc.—As described for the reduction of the acetoxytetrahydro-santonin,¹³ a solution of 50 mg. of X (R = H) in 5 cc. of acetic acid was heated with 0.5 g. of zinc dust on a water bath for 6 hr. Worked up as usual, the bicarbonate soluble portion of the product afforded 30 mg. of the crude acid (XII), m.p. 118–120°, from benzene-petroleum ether. Two further crystallizations from the same solvents formed prisms, m.p. 121–122°, showing no depression on admixture with an authentic sample of 4-methyl-1-*ar*-tetralol-7-acetic acid (XII).³ The light absorption spectra are practically identical with those reported for XII; $\lambda_{\text{max}}^{\text{EtOH}}$ 280 μm (ϵ 2140); $\nu_{\text{max}}^{\text{Nujol}}$ 3330 (OH), 1700 (COOH), and 817 and 804 (adjacent hydrogens on a benzene ring).^{3,9}

Acknowledgment.—The authors wish to thank Dr. T. Kotera, Tanabe Seiyaku Co., Ltd., Osaka, Japan, for the infrared spectroscopic analyses.

(12) Ref. 7, p. 186.

(13) K. Yamakawa, *J. Org. Chem.*, **24**, 897 (1959).

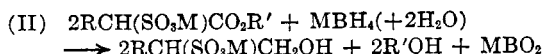
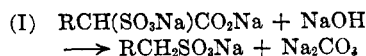
Alkanesulfonates and Hydroxyalkane-sulfonates from α -Sulfo Fatty Acids¹

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Continuation of research on long chain α -sulfo fatty acids has led to a decarboxylation (I) and a reduction method (II) as shown by the equations:



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(2) Eastern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

(11) Microanalyses were carried out by Miss K. Shimamura and ultraviolet measurement by Miss M. Suzuki, both of this school.