3-(α-Carbamylisopropyl)-5,5-dimethylhydantoin.–The compound IVa (0.7 g., 0.0036 mole) in water (50 ml.) was heated under reflux for 8 hours. The water was removed *in vacuo* and the residue was extracted with acetone (20 ml.). The acetone solution was evaporated and the residue was crystallized from ethyl acetate, yield 0.22 g. (28.6%). The melting point was raised from 208–216° with dec. to 216–217° with dec. by further crystallizations from ethyl acetate.

Anal. Calcd. for $C_9H_{15}N_3O_3$: C, 50.70; H, 7.09; N, 19.71. Found: C, 50.11; H, 7.07; N, 19.81.

Method B. 3-(α-Carbamylisopropyl)-4-imino-5,5-dimethyl-2-imidazolidone Picrate.—A saturated solution (50 ml.) of picric acid was added to a solution of IVa (0.29 g., 0.00149 mole) in water (50 ml.) and the mixture was heated at 95° for 20 minutes. The clear solution on cooling deposited a crystalline picrate (m.p. 238–240°), yield 0.57 g. (87.2%). Two crystallizations from water raised the melting point to 242–242.5°.

Anal. Calcd. for $C_{15}H_{19}N_7O_9$: C, 40.81; H, 4.34; N, 22.22. Found: C, 40.93; H, 4.78; N, 21.78.

Method C. 3-(α-Carbamylisopropyl)-4-imino-5,5-dimethyl-2-imidazolidone Hydrochloride.—2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]-imidazole (2 g., 0.01 mole) was dissolved in 0.26 *N* ethanolic hydrogen chloride solution (39.6 ml.). The solution was evaporated to dryness *in vacuo* at room temperature after which the residual oil crystallized on standing, yield 2.42 g. (100%). Three crystallizations from methanol–ether solution raised the melting point from 249–250 to 253°.

Anal. Calcd. for $C_9H_{17}ClN_4O_2$: C, 43.47; H, 6.89; Cl, 14.26; N, 22.53. Found: C, 43.22; H, 6.86; Cl, 14.69; N, 22.49.

A sample of the hydrochloride on treatment with aqueous picric acid solution gave a picrate melting at 239–240°, yield 89%. A mixture melting point determination with the picrate (m.p. 242–242.5°) prepared by method B gave no depression.

Method D. 3-(α-Carboxyisopropyl)-5,5-dimethylhydantoin.—A solution of IVa (3 g., 0.0155 mole) in 3 *N* hydrochloric acid solution (100 ml.) was heated at 80° for 10 minutes. The solution was evaporated to dryness and the residue was extracted with water. The water-insoluble residue melted at 208–212°, yield 2.40 g. (72.2%). One crystallization from water raised the melting point of the 3-(α-carboxyisopropyl)-5,5-dimethylhydantoin to 215–216°.

Anal. Calcd. for $C_9H_{14}N_2O_4$: C, 50.47; H, 6.58; N, 13.08; neut. equiv., 214.22. Found: C, 50.25; H, 6.06; N, 13.19; neut. equiv., 214.5.

Method E. α-Aminoisobutyric Acid.—A solution of IVa (20 g., 0.13 mole) and barium hydroxide (19.5 g.) in water (300 ml.) was refluxed for 14 hours. The cooled solution was filtered and the precipitate washed with water. After the filtrate with washings was evaporated to dryness the residue was dissolved in water (30 ml.). This solution was acidified with glacial acetic acid and cooled. The precipitated solid (sublimes 280°) was recovered by filtration, yield 7.2 g. (68%). The infrared spectrum of this preparation was identical with the spectrum of a known commercial sample of α-aminoisobutyric acid.

Anhydride of 3-α-Carboxyisopropyl-5,5-dimethylhydantoin.—Benzoyl chloride (0.65 g., 0.0046 mole) was added dropwise to a cooled solution of 3-α-carboxyisopropyl-5,5-dimethylhydantoin and the solution was heated under reflux for 25 minutes. The reaction mixture was poured onto crushed ice and the precipitated product (m.p. 204-230°) was recovered by filtration, yield 0.51 g. (54%). Three crystallizations from absolute methanol (25 ml.) raised the melting point to 241–243°.

Anal. Calcd. for $C_{18}H_{26}N_4O_7$: C, 52.68; H, 6.39; N, 13.65. Found: C, 52.31; H, 6.48; N, 13.21.

Nitration of 2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole.—2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]-imidazole (3 g., 0.016 mole) was added over a period of 10 minutes to a stirred nitration mixture of ammonium chloride (1.98 g., 0.037 mole), nitric acid (10.5 g., 0.15 mole) and acetic anhydride (15.3 g., 0.15 mole) at 0°. The solution was allowed to warm up to 27° and the stirring was continued for 3 hours. This reaction mixture was poured onto ice (250 g.) and the insoluble precipitate (m.p. 202–207° dec.) was removed by filtration, yield 3.3 g. (77.3%). Four crystallizations from acetone–petroleum ether solution raised the melting point to 214–215° dec.

Anal. Calcd. for $C_9H_{12}N_6O_5$: C, 38.03; H, 4.26; N, 29.57. Found: C, 38.46; H, 4.61; N, 29.30.

2-Nitrimino-3,7-dimethyl-3,7-diethyl-5-oxo-6-nitro-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (m.p. 99–102°) was prepared in 69.5% yield under similar conditions. Several crystallizations from acetone–petroleum ether solution raised the melting point to 164–165° dec.

Anal. Calcd. for $C_{11}H_{16}N_6O_5$: C, 42.31; H, 5.17; N, 26.92. Found: C, 42.64; H, 5.21; N, 27.32.

Reaction of α-Aminoisobutyronitrile with Phosgene.—When phosgene was passed into a toluene solution of α-aminoisobutyronitrile following the method of Jacobson[4] a quantitative yield of crude product melting at 170–210° dec. was obtained. Repeated crystallizations from methanol raised the melting point to 240° dec. This product did not depress the melting point of a known sample of 2-imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz-[3,4-a]imidazole (m.p. 240° dec.) which was prepared as described above by heating 1,3-di-(α-cyanoisopropyl)-urea in ethanol under reflux for several hours.

Acknowledgment.—The infrared absorption spectra were determined by Dr. C. Sandorfy of the University of Montreal, Montreal, Quebec.

VILLE LASALLE, QUEBEC, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

8,10-Dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene: The Dienone–Phenol Rearrangement

BY STANLEY M. BLOOM

RECEIVED MAY 29, 1958

The synthesis of 8,10-dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene (IX) is reported. The phenol, 4,8-dimethyl-5-hydroxy-1,2,3,4-tetrahydronaphthalene (XII), obtained on dienone–phenol rearrangement of (IX) demonstrates the intermediacy of the spiran intermediate (X) in the reaction studied.

Woodward and Singh[1] first demonstrated that the acid-catalyzed rearrangement of cyclohexadienones does not always follow the course of santonin (I) in its conversion to desmotroposantonin (II).[2]

10-Methyl-2-keto-Δ-$^{1,9:3,4}$-hexahydronaphthalene (III) was synthesized and rearranged in acetic anhydride to 5-hydroxy-8-methyl-1,2,3,4-tetrahydronaphthalene (IV). Extending these data, Woodward and Singh suggested the structure VIa rather than VII for the phenol obtained from the acid-catalyzed rearrangement of steroid die-

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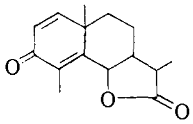
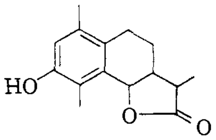
[1] R. B. Woodward and T. Singh, THIS JOURNAL, **72**, 494 (1950).

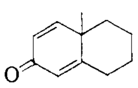
[2] Huang-Minlon, C. Lo and L. J. Chu, *ibid.*, **65**, 1780 (1943).



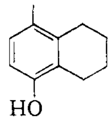
I



II

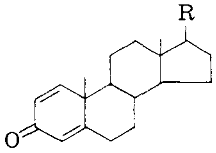


III

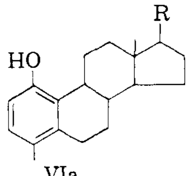


IV

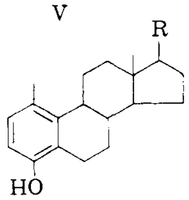
nones of the type V. Inhoffen, *et al.*,[3] earlier had postulated VII to agree with the result of the santonin rearrangement. To arrive at VIa the authors proposed a mechanism for the conversion proceeding through the hypothetical intermediate VIII. A 1,2-shift of the more highly substituted carbon atom in VIII led to the product VIa rather than VIb obtainable through the migration of the least substituted carbon atom.[4] Woodward, *et al.*,[5] in a latter paper, proved the validity of the new assignment.



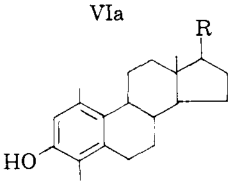
V



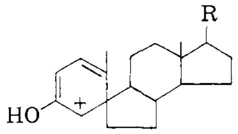
VIa



VIb

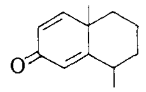


VII



VIII

In the course of other work under way in this Laboratory, we had need of 8,10-dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene (IX),[6] and the compound was accordingly synthesized (*vide infra*)



IX

As this cyclohexadienone IX is ideally suited to provide a demonstration of the existence of a spiran intermediate X analogous to VIII in the dienone–phenol rearrangement, its rearrangement was studied. The phenol XII would result if path A (Fig. 1) is followed, while in contrast, path B proceeding through XI would result in the phenol XIII.[7,8]

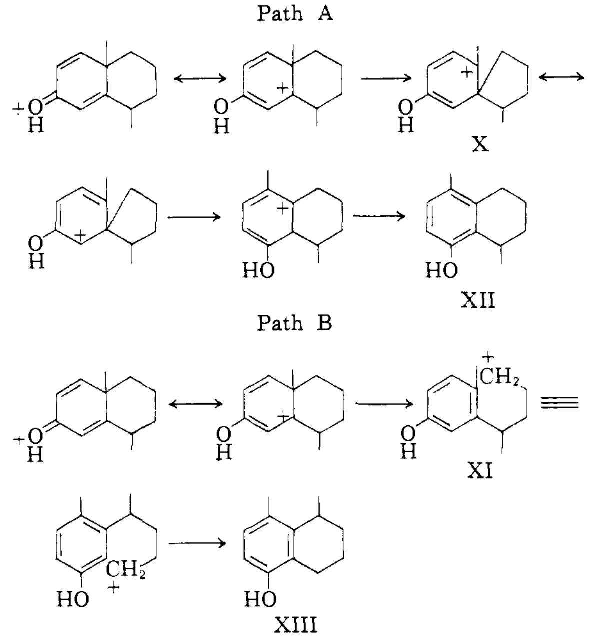


Fig. 1.

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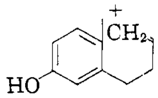
[3] H. H. Inhoffen and G. Zuhladorff, *Ber.*, **74**, 604, 1911 (1941).

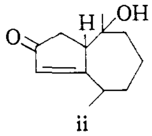
[4] Two mechanisms were originally considered by Woodward and Singh[1] to account for the rearrangement of III to IV. The possibility that it is first formed from III and then closed to IV by internal electrophilic substitution at the unblocked *o*-position was eliminated on the basis of later work. See R. B. Woodward, "Perspectives in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 178, for the data providing proof of the existence of a spiran intermediate in a case studied.



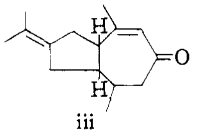
i

[5] R. B. Woodward, H. H. Inhoffen, H. O. Larson and K. Menzel, *Ber.*, **86**, 594 (1953).

[6] The compound IX on irradiation with ultraviolet light is expected to give ii, an intermediate in a projected synthesis of vetivone (iii). This work is presently in progress in this Laboratory (see D. H. R. Barton, P. de Mayo and M. Shafiq, *J. Chem. Soc.*, 929 (1957), for an analogy).

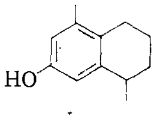


ii



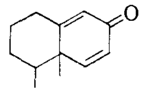
iii

[7] A simple 1,2-methyl shift which was found in the santonin rearrangement but excluded for the steroid dienones on the basis of Woodward's work, would lead to iv.



iv

[8] The dienone v would not allow a choice between path A and B for both pathways would give the phenol XII. The compound v is the prototype for the steroid dienones which are not suited for the test provided by the present work. In path A, the spiran X is opened in the manner found in the steroid dienone rearrangement, *i.e.*, the more highly substituted carbon atom migrates preferentially (*vide supra*).



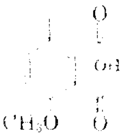
v

Rearrangement of IX in acetic anhydride to which a trace of sulfuric acid had been added (*vide infra*) led to the isolation of the phenol XII. This finding is in accord with the work of Woodward and Singh[1,4] and reaffirms the intermediacy of the spiran in the dienone–phenol rearrangement.[4,9]

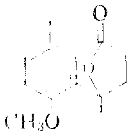
The 8,10-dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene (IX) necessary for the study was synthesized in an over-all yield of 10% starting from 2-methylcyclohexanone. The method was an adaptation of that of Wilds and Djerassi[10] employed[1] previously. 2,6Dimethyl-6-formylcyclohexanone[11] on condensation with acetone, with piperidine acetate as catalyst, then ring closure by methanolic potassium hydroxide gave IX as a solid, m.p. 59.5-60.5°, λ_{max} 243.5 mμ (log ϵ 4.07), $\lambda_{max}^{CCl_4}$ 6.03 and 6.17 μ.

The cyclohexadienone IX on rearrangement in acetic anhydride, to which a trace of sulfuric acid had been added, gave an oily phenol acetate. On hydrolysis a 40% yield of a crystalline phenol was obtained, m.p. 93-94.5°, whose analysis was in accord with the formulation $C_{12}H_{16}O$. The compound was tentatively assigned the structure XII on the basis of the previous discussion. The validity of the assignment was proved by the unambiguous synthesis of XII.

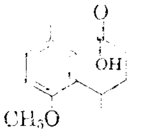
γ-(2-Methoxy-5-methylbenzoyl)-propionic acid[12] (XIV) on reaction with methylmagnesium iodide gave the lactone XV as an oil in 56% yield.[13] Hydrogenolysis of the lactone XV led to XVI in virtually quantitative yield. Ring closure to the α-tetralone XVIII was effected with polyphosphoric acid.[14] Hydrogenation and hydrogenolysis of the crystalline tetralone and cleavage of the resulting phenolic ether gave on chromatography the crystalline phenol XII. The phenol so synthesized was found to be identical with the phenol obtained on rearranging the cyclohexadienone IX by comparison of infrared spectra and by mixed melting point determination. The phenol is cryptophenolic in character, being insoluble in 5% sodium hydroxide solution.



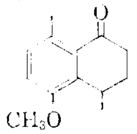
XIV



XV



XVI



XVII

Experimental Part[15]

8,10-Dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene.—2-Methylcyclohexanone, b.p. 164–166° (64%), from the oxidation[16] of technical grade 2-methylcyclohexanol, was converted by the procedure of Johnson[11] to 2,6-dimethyl-2-formylcyclohexanone, b.p. 106–112° at 17 mm. (distilled through a 20 cm. Vigreux column), *via* 2-methyl-6-hydroxy methylenecyclohexanone, b.p. 85–87° at 15 mm. (29% over-all). The procedure used by Woodward[1] to convert 2-methyl-2-formylcyclohexanone to 10-methyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene was employed to obtain the cyclohexadienone IX. 2,6-Dimethyl-6-formylcyclohexanone, 91.3 g., was dissolved in 800 ml. of dry acetone. Distilled piperidine, 53 g., and glacial acetic acid, 37.5 g., were added carefully with swirling. The reaction mixture was refluxed 84 hours. The reaction was concentrated on the steam-bath. Residual volatile materials were removed at water-pump pressure and water and ethyl ether added. The water layer was discarded. The ether layer was washed with dilute hydrochloric acid, water, 5% potassium bicarbonate solution, and water, respectively. The ether layer, after drying with anhydrous sodium sulfate, was evaporated *in vacuo* (water aspirator) with external warming for a few minutes. The orange oil so obtained was added to 750 ml. of dried methanol (distilled from magnesium methoxide). Potassium hydroxide, 45 g., in 45 ml. of water was added to the above solution. The reaction mixture which immediately turned red was refluxed 6.5 hours. The methanol was taken off on the steam-bath and water and ethyl ether added. The water layer was extracted with three portions of ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. On concentration of the ether an orange oil was obtained. When a small amount of petroleum ether (b.p. 30–60°) was added and the solution seeded, 24.0 g. of 8,10-dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene was obtained, m.p. 50–52°. The residual oil was concentrated and distilled. After a forerun of 9.5 g. of material boiling from 35–40° at 1.5 mm., the cyclohexadienone distilled, b.p. 104–105° at 0.65 mm. The slightly yellow liquid, weighing 9.5 g., crystallized on standing. The total yield was 33.5 g. (32%). The compound on recrystallization from petroleum ether (b.p. 30–60°) three times gave a m.p. 59.5–60.5°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.92; H, 9.30.

The compound possessed an ultraviolet maximum at 243.5 mμ, log ϵ 4.07, and maxima in the infrared at 6.03 and 6.17 μ in carbon tetrachloride. The 2,4-dinitrophenylhydrazone on crystallization from ethanol–chloroform and from ethyl acetate–cyclohexane melted at 167–168.5°. An additional crystallization from ethanol–chloroform gave red-orange platelets, m.p. 171.5–172.5°.

Anal. Calcd. for $C_{18}H_{20}N_4O_4$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.85; H, 5.64; N, 15.49.

Hydrogenation of 8,10-Dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene.—The cyclohexadienone IX was hydrogenated under the conditions described by Woodward and Singh.[1] The oil obtained gave a 2,4-dinitrophenylhydrazone which crystallized from absolute ethanol, m.p. 115–117°. On crystallization from absolute ethanol, cyclohexane and finally twice from ethanol the m.p. 129.5–131.5° was obtained.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.29; H, 6.80; N, 15.82.

Rearrangement of 8,10-Dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene.—Analytical grade cyclohexadienone IX, 462 mg., was dissolved in 20 ml. of acetic anhydride. Concentrated sulfuric acid, 5 drops, and 3 ml. of acetic anhydride, previously mixed, were added with swirling, and the flask stoppered and allowed to stand for 6 hours. The reaction mixture was added to 80 ml. of water and allowed to stand at room temperature until the excess acetic anhydride

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(9) The author wishes to thank one of the referees for pointing out that the work described herein provides the first detailed experimental evidence for the existence of a spiran intermediate in the dienone–phenol rearrangement. The elegant proof of Woodward has yet to be published in full.

(10) A. L. Wilds and C. Djerassi, This Journal, **68**, 1716 (1946).

(11) W. S. Johnson and H. Posvic, *ibid.*, **69**, 1361 (1947).

(12) K. W. Rosenmund and D. Shapiro, *Arch. Pharm.*, **272**, 313 (1934); also, J. Herran, O. Mancera, G. Rosenkranz and C. Djerassi, *J. Org. Chem.*, **16**, 899 (1951).

(13) See R. C. Petterson and M. C. Kloetzel, This Journal **80**, 1416 (1958), for another example of the direct addition of methylmagnesium iodide to a keto-acid.

(14) See F. D. Popp and W. E. McEwen, *Chem. Revs.*, **58**, 321 (1958), for a review on the use of polyphosphoric acid in ring closures.

(15) All melting points are corrected and boiling points uncorrected. Analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Ultraviolet absorption spectra were determined in 95% ethanol and infrared spectra in the solvent indicated.

(16) The method of K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946), was employed.

had decomposed. The solution, so obtained, was extracted with four 30-ml. portions of ethyl ether. The combined ether extracts were washed successively with two portions of saturated common salt solution, three 30-ml. portions of saturated sodium bicarbonate solution, once again with the saturated brine solution and dried over anhydrous sodium sulfate. On evaporation of the dried ether layer, 490 mg. (82%) of a yellow oil was obtained. The oily phenol acetate was hydrolyzed employing the method of Woodward and Singh.[1] The acetate was taken up in 40 ml. of absolute ethanol, 3 ml. of concentrated hydrochloric acid was added and the solution refluxed 6 hours. On removal of the ethanolic hydrochloric acid *in vacuo* (water aspirator) an oil was obtained which was taken up in dichloromethane, dried using anhydrous sodium sulfate, and concentrated *in vacuo* (water aspirator) to a yellow oil, weight 325 mg. (70%), which partially crystallized on seeding. On crystallization from petroleum ether (b.p. 30–60°) the phenol was obtained, m.p. 87–89°, weight 147 mg. An infrared absorption spectrum of the mother liquor taken in carbon disulfide was substantially the same as the isolated crystalline material. On comparison of the spectrum with that of a sample of synthesized XII (*vide infra*) a slight difference became apparent. The spectrum of the mother liquor had a slight hump at 11.8 μ which did not occur in the spectrum of the synthetic material. Compound XII probably is contaminated to the extent of about 5 to 10% with iv.[17]

Another 37 mg. of phenol, m.p. 87–89°, was isolated by chromatographing the mother liquor in the manner described below for the purification of synthetic XII (total yield 184 mg., 40%). For analysis the phenol was crystallized once from petroleum ether (b.p. 30–60°) and finally from ligroin (b.p. 90–100°), m.p. 93–94.5°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.22; H, 9.29.

In an earlier reaction an effort was made to crystallize the intermediate phenol acetate. Chromatography of the acetate employing Alcoa F-20 activated alumina was to no avail. Petroleum ether (b.p. 30–60°) eluted the phenol acetate as a colorless oil. An infrared spectrum taken in carbon disulfide showed a single peak in the carbonyl region at 5.67 μ. No hydroxyl absorption was apparent.

Synthesis of 4,8-Dimethyl-5-hydroxy-1,2,3,4-tetrahydronaphthalene (XII).—Five grams of γ-(2-methoxy-5-methylbenzoyl)-propionic acid[12] was finely powdered and suspended in 60 ml. of dry ethyl ether. A solution of methylmagnesium iodide previously made from 1.3 g. of magnesium and excess methyl iodide, was added dropwise to the suspension under nitrogen. After addition was complete the reaction was stirred 15 hours under nitrogen. An ice-hydrochloric acid mixture was added carefully to decompose the precipitated magnesium salts. The ether layer was separated and washed with water. Extraction of the ether layer with 5% sodium carbonate solution did not remove all of the product which had lactonized on work-up. The sodium carbonate solution, on acidification with hydrochloric acid, extraction with ethyl ether, drying over anhydrous magnesium sulfate, and evaporation gave an oil whose infrared absorption spectrum was substantially the same as the material isolated below. The ether layer remaining after sodium carbonate extraction was washed with water and dried over anhydrous magnesium sulfate. On evaporation the same oil as obtained above was isolated. The two fractions were combined and distilled. The lactone XV was obtained as a pale yellow oil, b.p. 180–186° at 27 mm., weight 2.8 g. (56%), which darkened on standing. An infrared spectrum taken in methylene chloride gave a sharp maximum at 5.70 μ in the carbonyl region and no apparent absorption in the hydroxyl region.

The freshly distilled lactone XV, 2.65 g., was dissolved in 30 ml. of glacial acetic acid and 760 mg. of 10% Pd–C (Baker) added. Hydrogenation was carried out in a Parr shaker at 12 lb./in.^{2} for 3.5 hours. The catalyst was filtered off and the solution concentrated *in vacuo* (water aspirator). The oily residue, on cooling and scratching, completely crystallized. Crystallization from cyclohexane gave the acid XVI as fine white needles, m.p. 92–93°. For analysis the compound was again crystallized from cyclohexane, white rods, m.p. 93.5–94.0°.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.47; H, 8.18.

The crystalline acid XVI, 1.60 g., was added to 75 g. of polyphosphoric acid (Victor). The reaction mixture was stirred and the temperature was brought to 98° slowly. As the solution became red the temperature was reduced to 75–85° for the remainder of the 1.75-hour reaction period. The polyphosphoric acid solution was cooled externally and ice-water added. The reaction was extracted with four 50-ml. portions of ethyl ether. The ether extracts were combined and washed with water until the wash water was colorless. The ethyl layer was washed with a saturated sodium bicarbonate solution, water, and dried over anhydrous magnesium sulfate. On evaporation of the ether a yellow oil was obtained which crystallized on cooling and scratching. The α-tetralone XVII, m.p. 45–47°, weighed 1.16 g. (78%). On crystallization from petroleum ether (b.p. 30–60°) three times (Norite) flattened white prisms were obtained, m.p. 50–51°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.65; H, 7.81.

The tetralone XVII, m.p. 45–47°, 871 mg., was dissolved in 25 ml. of glacial acetic acid to which 222 mg. of 10% Pd–C (Baker) had been added. Hydrogenation at 15 lb./in.^{2} for 21 hours was necessary to obtain a product which no longer had carbonyl absorption in the infrared. The catalyst was filtered off and the acetic acid solution concentrated *in vacuo* (water aspirator) to a thick oil. The oil was taken up in 8 ml. of glacial acetic acid. Hydrobromic acid (48%), 2.75 ml., was added and the mixture was refluxed for 6 hours. The reaction was concentrated *in vacuo* (water aspirator) to an oily, reddish residue. The residue was taken up in ethyl ether and washed successively with water, saturated sodium bicarbonate solution, water, and 5% sodium hydroxide solution. The sodium bicarbonate and the sodium hydroxide extracts contained little material on work-up by acidification, extraction with ethyl ether and evaporation of the dried ether layers. The neutral ether layer on drying with anhydrous magnesium sulfate and evaporation gave up 480 mg. of a heavy reddish oil. The oil was purified by chromatography on 10 g. of Alcoa F-20 activated alumina contained in a standard Kimble acid buret. The oil was applied to the column with petroleum ether (b.p. 30–60°) to which a trace of ethyl ether had been added. Elution with 50 ml. of petroleum ether (b.p. 30–60°) gave 20 mg. of an oil which was discarded. Petroleum ether (b.p. 30–60°)–ethyl ether, 1:1, 100 ml., eluted 187 mg. of a reddish oil that soon crystallized. Finally 200 ml. of ethyl ether eluted 195 mg. of a very thick oil which did not crystallize and was discarded. The crystalline fraction on recrystallization from petroleum ether (b.p. 30–60°) (Norite) gave white compact crystals (XII), m.p. 93–94°. Mixed melting point determination with the phenol obtained from the rearrangement of IX gave m.p. 93–94.5°. The infrared spectra of the synthetic material and the phenol from IX taken in carbon disulfide were identical.

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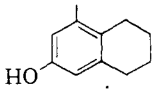
[17] A. S. Dreiding, *et al.*, THIS JOURNAL, **75**, 3159 (1953), reported that IV and vi may be distinguished by spectral differences in the fingerprint region of the infrared: IV possesses a maximum at 12.40 μ



vi

and vi at 11.76 μ (both in mineral oil). The hump at 11.8 μ in the spectrum of the mother liquor may be accounted for by the presence of a small amount of iv. The main band in the fingerprint region is at 12.50 μ, close to that found by Dreiding, *et al.*, for IV.