

there has never appeared in the literature any simple, clear cut, synthetic procedure for it. Since this compound was needed for further work, it was desirable to find a convenient method of preparation that would afford the compound in reasonable yield and high purity.

Among the earliest preparations of this compound is that involving the reaction of mucic or saccharic acids (or their salts) with concentrated hydrobromic acid solution. This reaction does not give the desired product in good yield (20–30%) and furthermore, involves a tedious work-up to afford pure material. Many papers appear in the literature² which describe the preparation of dehydromucic acid by oxidation of compounds such as aldehydopyromucic acid, 5-acetoxymethylfurfural, 5-chloromethylfurfural, 5-formyloxy-methylfuroic acid, and 5-methoxymethylfurfural. In each case the authors either do not report any yield or fail to identify properly their product. Often, the starting materials are not easily obtainable.

A study of the action of nitric acid on derivatives of 5-hydroxymethyl-2-furoic acid was carried out with the hope that oxidation of one of these substances would lead to the desired dicarboxylic acid in good yield. Moldenhauer, *et al.*,³ reported that oxidation of methyl 5-formyloxymethyl-2-furoate with 65% nitric acid gave a 74% yield of the diacid. The compound was identified merely by its failure to melt up to 220°.

No analysis or neutralization equivalent was reported, and in many attempts to prepare the diacid by this method, we consistently obtained grossly impure product (neutralization equivalent 105–115).

The best results that could be obtained involved the use of 60% nitric acid and a reaction time of two days. The product obtained from these reactions had a neutralization equivalent of 82–84 and even this material could not be purified, without great loss, through simple recrystallization. It was found convenient to esterify this crude material, distil, and then saponify the dimethyl ester obtained. On several occasions we were able to isolate 5-hydroxymethyl-2-furoic acid (m.p. 168–169°, neut. equiv. 142.6, reported⁴ m.p. 166–167°, neut. equiv. 142) at this point which indicates the contaminant present in the dibasic acid obtained by Moldenhauer's procedure.

Experimental

Methyl 5-Acetoxymethyl-2-furoate.—Methyl 5-chloromethyl-2-furoate was prepared essentially according to the

(1) The authors gratefully acknowledge the interest of Mr. Andrew P. Dunlop and the financial assistance of The Quaker Oats Co. in support of this and other work.

(2) Dunlop and Peters, "The Furans," A.C.S. Monograph series No. 119, Reinhold Publishing Corp., New York, N. Y., 1953, pp. 572–573.

(3) O. Moldenhauer, G. Trautmann, R. Pflüger, and H. Doser, *Ann.*, **580**, 179 (1953).

(4) T. Reichstein, *Helv. Chim. Acta*, **9**, 1066 (1926).

method of Moldenhauer.³ Yields of product boiling at 117–124° at 7 mm. varied between 80 and 87%.

One hundred grams (0.57 mole) of the chloromethyl compound and 70 g. (0.86 mole) of anhydrous sodium acetate were refluxed in 143 ml. of glacial acetic acid for 2 hr. in a 500-ml. flask fitted with reflux condenser and stirrer. After this time, the flask was set for distillation and about 100–125 ml. of acetic acid was distilled under diminished pressure. The solution was kept stirred during this distillation in order to prevent bumping. The remaining solution was cooled and poured into 200 ml. of ice-cold water. A solid mass formed within the flask and was taken up into 150 ml. of ether by stirring and warming the solution. The ether layer was then removed, and the aqueous layer was extracted four times with 50-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and then distilled to remove the solvent. The residue was distilled at reduced pressure and the product collected at 135–137°/5 mm., m.p. 142–143°. The yields in this reaction were 80–90% based on the chloromethyl compound used (in six runs).

Anal. Calcd. for C₉H₁₀O₅: C, 54.5; H, 5.05. Found: C, 54.6; H, 5.15.

Furan-2,5-dicarboxylic Acid.—One hundred grams of methyl 5-acetoxymethyl-2-furoate was heated with a solution of 100 ml. of water and 450 ml. of concentrated nitric acid (70%) in a 2-l. one-neck flask fitted with a reflux condenser. The reflux condenser was connected to a trap containing 10% sodium hydroxide solution. Heating was continued until the exothermic reaction began, and then the flask was cooled in an ice water bath to control the vigorous oxidation. When the reaction subsided, heat was again applied and the solution was refluxed for 48 hr. After the first few hours of refluxing, a white solid began to separate. At the end of the reflux time the reaction mixture was cooled in an ice bath and then filtered. The product collected was washed well with water and then dried in an oven at 110°. The yield was 55.0 g. of material having a neutralization equivalent of 82 (calcd. neut. equiv. 78). Purification of this material by recrystallization from water or acetic acid could not be effected without seriously affecting the yield.

The crude diacid was next esterified by refluxing with 400 ml. of absolute methanol containing 10 ml. of concentrated sulfuric acid for a total of 5 hr.

After this time about 300–325 ml. of alcohol was distilled and the remaining solution was poured into 500 ml. of cold water. The solid which separated was filtered off and washed by slurring with 10% sodium bicarbonate solution and then with water. This product amounted to 60.0 g. after drying overnight in a desiccator over sodium hydroxide. Distillation of this solid gave 41.5 g. of product, b.p. 140–145°/10 mm. A residue of 12 g. of the monomethyl ester was recovered, re-esterified, and combined with the distilled portion. Saponification with 10% sodium hydroxide gave 35 g. (45%) of the desired product having neut. equiv. 78.7–79.0 after being crystallized once from water.

Investigation of a Reported Synthesis of 1,3-Diphenylcyclobutadiene

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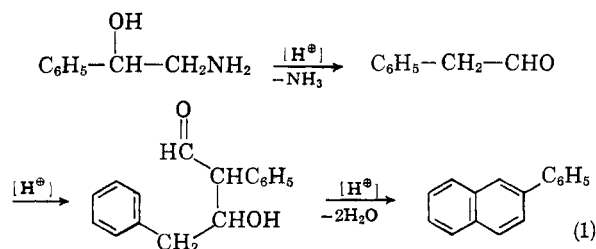
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It has been recently reported¹ that 1,3-diphenylcyclobutadiene² is obtained in good yield by

(1) A. Chatterjee, S. K. Srimany, and (Miss) B. Chaudhury, *J. Chem. Soc.*, 4576 (1961).

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).

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(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).