hydrogen saturated with formaldehyde by passing the hydrogen through aqueous 40% formalin. The reduction was carried out for forty-five minutes at 270° and then for forty-five minutes at temperatures slightly above those at which the dehydrogenation run was to be conducted.

Catalytic Synthesis of 2-Methylbenzofuran.—The following is an example of a typical dehydrogenation run for the preparation of 2-methylbenzofuran.

o-Allylphenol[5] (50.2 g.) was processed over 5 ml. of palladium catalyst at a temperature of 550 ± 4° over a period of one hundred thirty minutes. A total of 47.6 g. of condensate was collected and the catalyst tube gained 1.2 g. weight. About 0.3 g. of material remained in the seed system. A total of 3330 ml. of gas was given off during the course of the reaction as measured by a wet test meter. The rate of gas evolution was 40 ml./min. at the end of the first fifteen minutes at which time the catalyst reached a relatively steady activity. This rate gradually fell until it reached a constant value of 16 ml./min. at seventy minutes. This rate then held until the end of the reaction. On longer runs of four hours or more the rate sometimes fell as low as 12 ml./min.

The condensate was made alkaline with 20% sodium hydroxide and the 2-methylbenzofuran extracted with petroleum ether. After drying over sodium sulfate the extract was distilled through a 20-plate, 30", "spinning band" distilling column. Distillation gave 14.6 g. of 2-methylbenzofuran, b. p. 190–196° (730 mm.), 3.3 g., 170–190° (730 mm.) which was mainly benzofuran, a residue and hold back of 1.7 g. remaining in the distilling flask.

The alkali-soluble portion of the condensate was acidified with hydrochloric acid, extracted with ether, the extract dried over calcium chloride and then distilled. Nine and four-tenths grams of material, mainly *o*-allylphenol, was collected between 200–216° (730 mm.). Three and seven-tenths grams was obtained, boiling at 175–200°, and consisting of a mixture of phenol, *o*-cresol and a trace of *o*-allylphenol.

Tables I and II summarize the results of the run with *o*-allylphenol and *o*-ethylphenol.[6] All of the runs were made and worked up as described above except where indicated.

(5) D. S. Tarbell, "Organic Reactions," John Wiley and Sons Inc., New York, N. Y., 1944, Vol. II, p. 26.

(6) The *o*-ethylphenol was supplied through the courtesy of Dale Robertson of this Laboratory. It was prepared by vapor-phase alkylation of phenol and had a b. p. of 203.1–205.1° (730 mm. cor.) after two distillations through a 20-plate distilling column.

Discussion

In all of the catalytic runs made in this research using both *o*-ethylphenol and *o*-allylphenol, very little charring occurred on the catalyst or on the quartz chips used as preheater. The catalyst gained 0.6 g. to 1.2 g. depending on the size of the run and the temperature. The condensate was clear and light brown in color.

It should be noted that the catalyst activity as measured by the rate of gas evolution fell off after about the first hour to about 50% of the fifteen minute value. An attempt to use a chromium oxide on alumina catalyst was unsuccessful because of excessive decomposition of the phenols At present work is in progress to find a more stable and more active catalyst. It was discovered that the activated charcoal[4] itself possessed considerable ability to bring about the dehydrocyclization. This may be due to the charcoal itself or possibly to impurities in it.

As noted in Table I, a considerable amount of benzofuran was formed in the preparation of 2-methylbenzofuran. This same phenomenon has been observed in the preliminary investigation of the preparation of other 2-methylbenzofurans and also with the corresponding sulfur analogs.

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Summary

A vapor phase catalytic method for the dehydrogenation of *o*-ethylphenol to benzofuran and *o*-allylphenol to 2-methylbenzofuran is described.

CLAREMONT, CALIFORNIA RECEIVED AUGUST 4, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE VICK CHEMICAL COMPANY]

Attempted Synthesis of β-2,6-Dihydroxybenzoyl- and β-2,4,6-Trihydroxybenzoyl-acrylic Acids

BY CHARLES I. JAROWSKI,[1a] WILLIAM J. MORAN[1b] AND BETTY JANE CRAMER[1c]

The most active bacteriostatic agent in a series of β-aroyl acrylic acids was β-2,4,6-triethylbenzoylacrylic acid.[2] The preparation of β-2,6-dihydroxy- (I) and β-2,4,6-trihydroxybenzoyl acrylic acid (II) was attempted to determine the effect of ortho hydroxyl groups. The formula chart shows the method used for I.

Condensation of III with diethyl oxalate in the presence of sodium ethoxide gave IV. The crude product was heated under reflux with a mixture of glacial acetic and concentrated hydrochloric acids to give V. This in turn was esterified and hydrogenated to VII.

It had been previously shown that 2-carbethoxy-γ-chromanone was easily converted to β-(*o*-hydroxybenzoyl)-acrylic acid by treatment with dilute alkali. Hence treatment of VII with alkali gave either I or VIII.

It was expected that the reaction between maleic anhydride and phloroglucinol would result in the formation of II and 2-carboxy-5,7-dihydroxy-γ-chromanone (IX), for a similar reaction using

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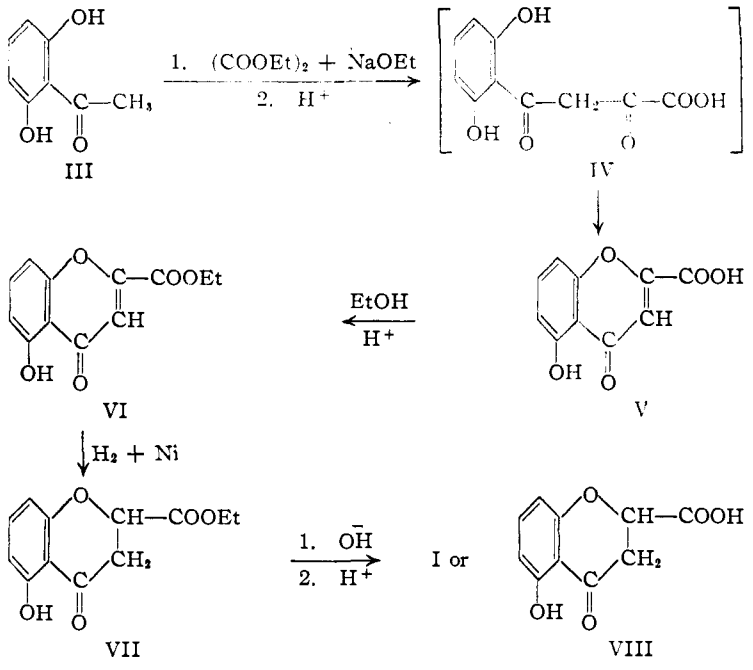
(2) Cramer, Schroeder, Moran, Nield, Edwards, Jarowski and Puetzer, *J. Am. Pharm. Assoc.*, **37**, 439 (1948)



cinnamoyl chloride led to the formation of a mixture of a chalcone and γ-chromanone derivative.[3] When the reaction mixture was worked up however only one acid was isolated.

The two acids are almost white in color whereas all the other β-aroylacrylic acids prepared were highly colored. They both failed to abolish the nitroprusside reaction of cysteine, a test designed for the detection of α,β-unsaturated ketones.[4] All the β-aroylacrylic acids previously prepared readily added cysteine.[2] The two compounds were ineffective as antibacterial agents. Treatment of the supposed β-2,6-dihydroxybenzoylacrylic acid with excess diazomethane in ether gave the methyl ester exclusively. The failure to methylate the phenolic group was not surprising for more drastic conditions are needed as a general rule to alkylate such a group ortho to a carbonyl.[5] The complete absence of any pyrazoline derivative was an argument against I. According to the work of Lutz and Scott[6] diazomethane reacts with β-aroylacrylic acids to give substituted pyrazolines.

From the above it was felt that the correct structures of the two acids prepared are most likely VIII and IX.

Experimental[7]

2-Carboxy-5-hydroxy-γ-chromone (V).—Alcohol-free sodium ethoxide was prepared by adding 25 cc. of absolute ethanol to 8 g. (0.345 gram atom) of metallic sodium sanded in 350 cc. of dry xylene at 105–115° and distilling off the excess alcohol. The stirred suspension was cooled to 20° and a mixture of 16.1 g. (0.11 mole) ethyl oxalate and 15.2 g. (0.1 mole) of 2,6-dihydroxyacetophenone in 75 cc. of anhydrous ether was added during 15 minutes. The mixture was kept at 20–25° for 0.5 hr., heated under reflux for 1.5 hr., cooled and filtered. The sodium salt was dissolved in cold water and extracted twice with 200 cc. of ether. The aqueous solution was acidified to congo paper with 10% hydrochloric acid and extracted with 500 cc. of ether. The dried ethereal extract (sodium sulfate) was deprived of solvent and the residual red oil was dissolved in 90 cc. of 5 to 1 glacial acetic–concentrated hydrochloric acid and heated under reflux one hour. The reaction mixture was cooled and the insoluble solid (12 g.) was collected. Recrystallization from 75% acetic acid gave 10.3 g. (46%) of bright yellow crystals of V with a melting point of 264°.

Anal. Calcd. for $C_{10}H_6O_5$: C, 58.3; H, 2.9; neut. eq., 206. Found: C, 58.15; H, 2.97; neut. eq., 202.

2-Carbethoxy-5-hydroxy-γ-chromone (VI).—Concentrated sulfuric acid (5 cc.) was added to a suspension of 7.3 g. (0.035 mole) of V in 50 cc. of absolute ethanol and heated under reflux on a steam-bath. The insoluble chromone acid gradually went into solution. After one hour the reaction mixture was poured into 300 cc. of ice water with stirring. The solid was filtered off and washed free of acid with cold sodium bicarbonate solution. The ester was recrystallized from benzene to give 6.3 g. (76%) of yellow crystals melting at 148°.

Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.6; H, 4.3. Found: C, 61.88; H, 4.42.

2-Carbethoxy-5-hydroxy-γ-chromanone (VII).—A mixture of 4.7 g. (0.02 mole) of VI, 100 cc. of absolute ethanol and one-half teaspoonfull of a suspension of freshly prepared nickel catalyst[8] was heated to 80° under hydrogen at 30 lb. pressure. In ten minutes the pressure fell two pounds (theory, 1.6 lb.). The catalyst was filtered off and the filtrate was concentrated to 50 cc. and cooled. The less soluble VI was filtered off and identified by a mixture melting point. The filtrate was further concentrated and cooled. The yellow crystals obtained were recrystallized from absolute ethanol; m. p. 72–74°; 2.1 g. (44%).

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 61.23; H, 5.18.

Alkaline Hydrolysis of VII.—Two grams (0.0084 mole) of VII was added to 25 cc. of 10% sodium hydroxide and heated to 75° for five minutes. The solution was acidified with 10% sulfuric acid and cooled. The tan product was recrystallized from 95% ethanol; m. p. of gray acid 191°; yield 0.95 g. (54%).

Anal. Calcd. for $C_{10}H_8O_5$: C, 57.7; H, 3.87; neut. eq., 208; mol. wt., 208. Found: C, 57.49; H, 4.03; neut. eq., 214; mol. wt., 240 (Rast method).

2-Carbomethoxy-5-hydroxy-γ-chromanone.—To an ethereal solution of 1.1 g. (0.0053 mole) of VIII was added a 5-fold (0.0265 mole) molar concentration of diazomethane in ether. The solution was allowed to stand overnight at room temperature. The excess diazomethane and solvent were distilled off and the sirupy residue was washed with sodium bicarbonate solution. The insoluble material was dissolved in ether and dried (sodium sulfate). Removal of the ether left a solid which was recrystallized from methanol; m. p. 78.5°; 0.74 g. (63%). The compound still gave a positive test for the phenolic group with ferric chloride solution.

(3) Shinoda and Sato, *J. Pharm. Soc. Japan*, **48**, 791–801 (1928); *C. A.*, **23**, 836 (1929).

(4) Geiger and Conn, THIS JOURNAL, **67**, 112 (1945).

(5) Houben, "Die Methoden der organischen Chemie," Vol. III, G. Thieme, Leipzig, 153.

(6) Lutz and Scott, *Virginia Acad. Sci. Proc.*, **2**, 195 (1944).

(7) All melting points are uncorrected.

(8) Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

Anal. Calcd. for $C_{11}H_{10}O_5$: C, 59.41; H, 4.53. Found: C, 59.17; H, 4.36.

5,7-Dihydroxy-2-carboxy-γ-chromanone (IX).—A mixture of 5.04 g. (0.022 mole) of phloroglucinol and 3.96 g. (0.04 mole) of maleic anhydride in 45 cc. of nitrobenzene was cooled to 10°. During the course of 15 minutes 17.42 g. (0.13 mole) of anhydrous aluminum chloride was introduced with mechanical stirring. External cooling was needed to keep the temperature at 30°. After 0.5 hr. the exothermic reaction subsided and the mixture was stirred at room temperature for 0.75 hr. The aluminum complex was decomposed in a mixture of ice and concentrated hydrochloric acid. The crude acid (4 g.) was recrystallized from water; m. p. of light colored acid 262.5° (dec.).

Anal. Calcd. for $C_{10}H_8O_6$: C, 53.56; H, 3.57; neut. eq., 224. Found: C, 53.14; H, 3.58; neut. eq., 230.

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Summary

An attempt was made to prepare β-(2,6-dihydroxybenzoyl)-acrylic acid and β-(2,4,6-trihydroxybenzoyl)-acrylic acid. The failure of these compounds to add cysteine and their almost white color indicate that cyclization has occurred to give the corresponding 2-carboxy-γ-chromanone.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY AND PURDUE RESEARCH FOUNDATION]

The Chemical Behavior of Hexachlorocyclopentadiene. I. Transformation to Octachloro-3a,4,7,7a-Tetrahydro-4,7-methanoindene-1,8-dione[1]

BY J. S. NEWCOMER[2] AND E. T. McBEE

During the course of extensive studies conducted in this Laboratory on the chlorination of organic compounds, it was discovered that the pentanes, with the exception of neopentane, can be readily converted to hexachlorocyclopentadiene. The results of preliminary investigations concerning the chemical behavior of this chlorocarbon are shown diagrammatically in Fig. 1.

In view of the recent publication of Prins,[3] the authors were prompted to report[4] the results of concurrent investigations on this versatile chemical intermediate. Since this report,[4] Krynitsky and Bost[5] have described the preparation of tetrachloro-5,5-diethoxycyclopentadiene by the reaction of hexachlorocyclopentadiene with sodium ethoxide.

Prins[3] reported the conversion of hexachlorocyclopentadiene to (a) nonachloromethylcyclopentene by the addition of chloroform, (b) a compound, $C_{10}Cl_{12}$, by the action of aluminum chloride, (c) 3,4,5-trichloro-3-cyclopentene-1,2-dione and 2,3,4,4,5-pentachloro-2-cyclopentenone by the action of sulfuric acid, and (d) octachlorocyclopentene by the addition of chlorine. Recently, Prill[6] described the use of hexachlorocyclopentadiene in the diene synthesis.

The ketals (II), tetrachloro-5,5-dimethoxy- and -diethoxycyclopentadiene, were prepared by the action of the appropriate sodium alkoxides or alcoholic potassium hydroxide on hexachlorocyclopentadiene (I). The ketals were shown to contain a diene system by effecting condensations with maleic anhydride. The adducts, 1,4,5,6-tetrachloro-7,7-dialkoxybicyclo(2.2.1)5-heptene-2,3-dicarboxylic acids (XIV), were converted to 4,5-dichlorobenzene-1,2,3-tricarboxylic acid (XV) upon treatment with sulfuric acid. The position of the two alkoxy groups on the same carbon atom was also established by hydrolysis of II with sulfuric acid to form tetrachlorocyclopentadienone, which immediately dimerized to form an indefinite hydrate of octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione. Recrystallization of the latter from aqueous acetic acid produced the tetrahydrate (III), which was identified by dehydration to the anhydrous form (IV) and by conversion to hexachloroindone (V) upon treatment with water. The anhydrous form (IV) was shown by the method of mixed melting points to be identical to that prepared as described by Zincke[7] and Meyer by the reduction of a hexachlorocyclopentenone (m. p. 28°) with stannous chloride. Although not reported by Zincke, the initial product isolated from the reaction mixture is an indefinite hydrate of IV. The hydrate is readily differentiated from the anhydrous form by the insolubility of the former in non-polar solvents at room temperature. However, if the hydrate is boiled with such solvents until solution is effected, the product obtained by cooling the solution is the anhydrous form. The reduction of an isomeric hexachlorocyclopentenone (m.p. 92°) with stannous chloride has been reported[5] to form a compound having the molecular formula $C_5H_2Cl_4O$. This material has now been found to be a hydrate of indefinite composition of IV, containing approximately two molecules of water.

Octachlorocyclopentene (VI) was prepared by the addition of chlorine to I at atmospheric pressure and in the presence of a catalytic amount of aluminum chloride. The rapid absorption of

(1) Abstracted from the doctoral thesis of J. S. Newcomer.

(2) Present address: Sharples Chemicals, Inc., Wyandotte, Michigan.

(3) H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946).

(4) Presented before the Division of Organic Chemistry at the 111th Meeting of the American Chemical Society, April, 1947.

(5) J. A. Krynitsky and R. W. Bost, THIS JOURNAL, **69**, 1918 (1947).

(6) E. A. Prill, *ibid.*, **69**, 62 (1947).

(7) T. Zincke and K. H. Meyer, *Ann.*, **367**, 9 (1909).