IVd (2.3 g.) as described above, but with chloroform (15 cc.) as the solvent. The product was recrystallized from methanol (Norit) when it melted at 133.5° (dec.).

Anal. Calcd. for $C_{16}H_{22}OBr_2$: C, 49.25; H, 5.68. Found: C, 49.60; H, 5.85.

Hydroxylamino compound (VId) (1.16 g., 88%) was prepared from IVd (1.15 g.) and hydroxylamine hydrochloride as described above, and crystallized twice from methanol. It melted at 181.5–182.5°.

Anal. Calcd. for $C_{16}H_{25}O_2N$: C, 72.95; H, 9.57. Found: C, 73.36; H, 9.86.

Pentamethylbenzoic acid (VIId) (1.78 g., 40%) was prepared from IVd (4.6 g.) by permanganate oxidation as described above. The oxidation was sluggish, and 1.8 g. of the ketone was recovered unchanged. The acid, crystallized twice from 1:1 benzene–petroleum ether (B), melted at 203–207° alone or when mixed with an authentic specimen (m.p. 210–211°). The methyl ester, prepared from the acid by action of diazomethane, melted at 66–67° alone or when mixed with an authentic specimen (m.p. 68–70°); Jacobsen, ref. 13b, gives 67.5°.

MINNEAPOLIS 14, MINNESOTA RECEIVED MARCH 1, 1951

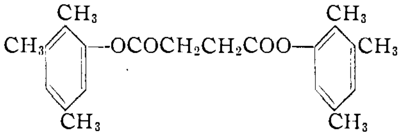
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

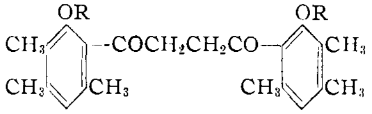
Fries Rearrangement of 2,3,5-Trimethylphenyl Succinate[1]

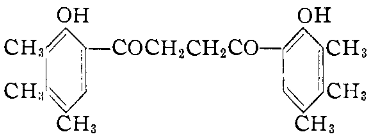
BY LEE IRVIN SMITH AND RICHARD REMSEN HOLMES

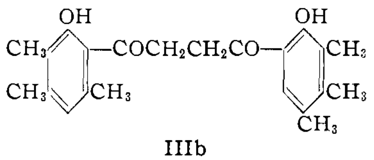
The Fries rearrangement of 2,3,5-trimethylphenyl succinate gives products resulting from a double rearrangement. These are the diorthohydroxy-1,4-diketone II, formed without rearrangement of methyl groups, and the isomeric diketone III, formed with rearrangement of one or more methyl groups. The diketone II has been converted into a diarylfuran X, and this into the bis-quinone XI.

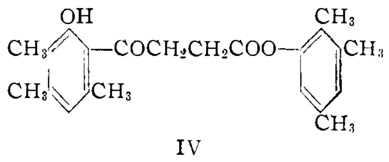
Fries rearrangements of phenolic esters of dibasic acids are considerably less satisfactory, with respect to yield and simplicity, than are the corresponding rearrangements of simple phenol esters, and few double Fries rearrangements are reported in the literature. Fries and Bartens[2] carried out such rearrangements of the succinate esters of *p*-cresol and *sym*-*m*-xylenol, but no yields were given. Schwenk and Priewe[3] carried out a double Fries rearrangement using the adipic ester of *m*-cresol; no yields were given, although the product was well characterized. Huebner and Link[4] reported that rearrangement of phenyl glutarate occurred, but the product of the double rearrangement was produced in very low yield. Recently Baddar and El-Assal[5] studied the action of aluminum chloride upon a mixture of phenol and succinic anhydride; they reported that the product was a mixture of *o*- and *p*-hydroxybenzoylpropionic acid.

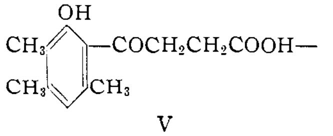

I


II, R = H
VI, R = CH_3
VII, R = Ac


IIIa


IIIb


IV


V

In connection with the studies of the reactions between quinones and metallic enolates, it was desired to prepare some bis-quinones with the two quinone nuclei joined by a chain of four carbon atoms, and as an approach to synthesis of such compounds, introduction of the four-carbon chain *via* a double Fries rearrangement of 2,3,5-trimethylphenyl succinate (I) was investigated. When the succinate I in tetrachloroethane was heated to 140° for several hours with two moles of aluminum chloride, a complex mixture resulted which could be separated—although with considerable difficulty—into the diketone II melting at 208–210°; an isomeric diketone melting at 246–248°, most likely having structure IIIa or IIIb; the keto ester IV; and the corresponding keto acid V; trimethylphenol and a considerable residue of an intractable tar. Formation of *o*-hydroxyketones by rearrangement of I at 140° is in agreement with the observations of Fries and Finck,[6] Auwers and Mauss,[7] Baddeley,[8] and others[9] who found that at temperatures above 100° meta substituted phenol esters rearrange almost exclusively to orthohydroxyketones in the

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[1] Abstracted from a thesis by Richard Remsen Holmes, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, July, 1950. American Chemical Society Predoctoral Fellow, 1946–1950.

[2] K. Fries and K. Bartens, *Ann.*, **442**, 261 (1925).

[3] E. Schwenk and H. Priewe, THIS JOURNAL, **56**, 2101 (1934).

[4] C. F. Huebner and K. P. Link, *J. Biol. Chem.*, **138**, 529 (1941).

[5] F. G. Baddar and L. S. El-Assal, *J. Chem. Soc.*, 3606 (1950).

[6] K. Fries and G. Finck, *Ber.*, **41**, 4271 (1908).

[7] K. v. Auwers and W. Mauss, *Ann.*, **460**, 240 (1928).

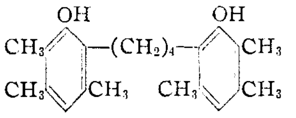
[8] G. Baddeley, *J. Chem. Soc.*, 273 (1943).

[9] L. I. Smith and J. W. Opie, *J. Org. Chem.*, **6**, 427 (1941).

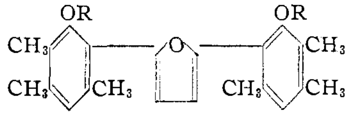
presence of aluminum chloride. The yield of ketones—II and III—was 30–45%, but the yield of pure II was considerably lower. Many variants in procedure were tried in the hope of improving the yield of II, but only two of these showed any promise. Use of stannic chloride as the solvent, and aluminum chloride as the catalyst, led to a clean product, chiefly II, in 24% yield; gradual addition of aluminum chloride to a boiling solution of I in tetrachloroethane with interruption of the reaction very soon after all the catalyst had been added led to II in 20% yield (pure product); almost identical results were obtained when the phenol and succinyl chloride were substituted for the ester I.

The ester IV could be hydrolyzed to a mixture of trimethylphenol and the ketoacid V, and this transformation served to characterize IV.

The 1,4-diketone II behaved as a cryptophenol; it was insoluble in aqueous alkali, but soluble in Claisen alkali with formation of a yellow solution; acidification of this solution precipitated II unchanged. The substance formed a dioxime, a dimethyl ether VI, and a diacetate VII; hydrolysis of the diacetate regenerated the diketone II. When II was subjected to a Clemmensen reduction, it was converted into a diarylbutane VIII. When dissolved in warm acetic anhydride containing a drop of sulfuric acid, II was converted into a mixture of VII and the diacetate (IX) of a diarylfuran; VII was also converted into IX by action of these reagents. Hydrolysis of IX led to the diarylfuran X, which could also be obtained directly from II by pyrolytic distillation.

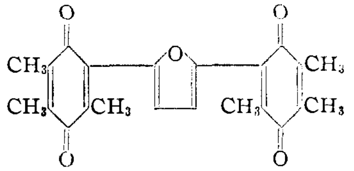


VIII



IX, R = Ac
X, R = H

The phenol-furan X underwent coupling with two moles of diazotized sulfanilic acid to give an azo dye. This dye was not isolated, but was reduced directly by action of stannous chloride to an aminophenol (also not isolated) which was oxidized to the diquinone XI.[10]



XI

The quinone XI was a stable red crystalline solid melting at 175–176°, soluble in most organic solvents, insoluble in water, alkali or acids, easily purified by recrystallization, chromatography or vacuum sublimation. Action of aqueous sodium bisulfite upon a benzene solution of XI converted it into the white bis-hydroquinone XII.

Formation of the *p*-quinone XI by this sequence of reactions establishes the presence of an open para position in each of the phenolic nuclei of X, and hence also in II, and this fact, together with the other reactions of II, show that both carbonyl groups in II are ortho to hydroxyl groups.

The spectra in the infrared of the bis-phenol II and its diacetate VII were determined[11]; they indicate that both keto groups in II are ortho to hydroxyl groups. One strong carbonyl band, present in the spectrum of II at 1605–1610 cm.$^{-1}$, was shifted to 1700 cm.$^{-1}$ in the spectrum of the acetate VII. This behavior is diagnostic for the presence of the "conjugated chelate" system —COCH=CH—OH found in ortho hydroxy ketones.[12] Moreover, the spectrum of II showed no band in the usual region of 3200–3500 cm.$^{-1}$ arising from the presence of a free hydroxyl group; this is also characteristic of "conjugated chelate" systems. On the other hand, the spectrum of the diarylbutane VIII does show the characteristic hydroxyl band at 3200–3600 cm.$^{-1}$.

With the structure of II established, it appeared probable that the isomeric diketone III formed concurrently with II, had one of the structures shown for it. The substance was a cryptophenol, insoluble in aqueous alkali but soluble in Claisen alkali. It formed a diacetate, isomeric with VII, and regenerating III upon hydrolysis. Reduction of III by the method of Clemmensen produced a diarylbutane isomeric with VIII but, curiously enough, III was not converted into a diarylfuran by action of acetic anhydride. The infrared absorption spectra[11] of III and its diacetate indicated that III was a di-orthohydroxyketone. A strong carbonyl band present in the spectrum of III at 1605–1610 cm.$^{-1}$ was shifted to 1670 cm.$^{-1}$ in the spectrum of the diacetate, and the spectrum of III showed no band at 3200–3600 cm.$^{-1}$ in the region of the free hydroxyl group; but the spectrum of the related diarylbutane does show this band. The spectra of II and III were similar, but not identical, over the entire range covered, from 650 to 3600 cm.$^{-1}$, and they indicated that II and III were closely related structurally.

Experimental Part[13]

2,3,5-Trimethylphenyl Succinate (I).—A solution of 2,3,5-trimethylphenol (75 g., 0.48 mole) and succinyl chloride (130 g., 0.96 mole)[14] in benzene (200 cc.) was heated for 14 hours on a steam-bath. The warm solution was washed with aqueous sodium hydroxide (5%) and then with water. On cooling to room temperature, the benzene solution deposited the ester (153 g., 90%) melting at 82–86°. The product was crystallized from aqueous methanol and

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[10] L. I. Smith, J. W. Opie, S. Wawzonek and W. W. Prichard, *ibid.*, **4**, 318 (1939).

[11] We wish to express our thanks to Mr. John Lancaster, Mr. Bert Zaslow and to Dr. Bryce L. Crawford, Jr., of this Laboratory, for the determination of these absorption spectra and for aid in the interpretation of the curves. The complete curves may be found in the Ph.D. thesis of R. R. Holmes, ref. 1.

[12] (a) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949); (b) I. M. Hunsberger, *ibid.*, **72** 5626 (1950).

[13] Microanalyses by R. Amidon, J. Buckley, W. Cummings, W. Hunter, R. Kelly, F. Robinson and H. Turner. All melting points are uncorrected.

[14] (a) D. Vorländer, *Ann.*, **280**, 183 (1894); (b) L. P. Kyrides, THIS JOURNAL, **59**, 206 (1937).

then from petroleum ether (b.p. 60–68°), when it melted at 86–87°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.40. Found: C, 74.44; H, 7.79.

1,4-Di-(2-hydroxy-3,4,6-trimethylphenyl)-butane-1,4-dione (II) (A).—Of the many variants in the general procedure for conducting the rearrangement of I to II, the following was found to involve the least time and effort, and to give a product which was readily purified. A 5-l. round-bottomed flask was equipped with a Y-tube adapter to which were fitted a long upright air condenser and a dropping funnel. The top half of the flask was wrapped with aluminum foil, and the flask was heated by means of three infrared lamps placed one-half inch from the bottom of the flask. A solution of 2,3,5-trimethylphenol (1060 g., 8 moles) in tetrachloroethane (1.5 l.) was placed in the flask and heated to the boiling point while succinyl chloride (600 g., 4 moles) was added dropwise (four hours). The mixture was boiled until no more hydrogen chloride was evolved (three hours); the dropping funnel was then replaced by a funnel for addition of solids and fitted with a long, stiff wire reaching to the junction of the arms of the Y-tube. Powdered aluminum chloride (1.1 kg., 8.7 moles) was added gradually (four hours) to the vigorously boiling solution, using the stiff wire as a poker. Evolution of hydrogen chloride was very vigorous. When about half of the aluminum chloride was added, more tetrachloroethane (1.5 l.) was introduced to keep the mixture fluid. After addition of aluminum chloride was complete, the mixture was heated for 30 minutes and then poured, *while still hot*, into a stirred mixture of ice (10 kg.) and hydrochloric acid (2 l.). The mixture was stirred occasionally and was allowed to stand overnight. The suspension of semi-solid material was warmed on the steam-bath until fluid; the top (aqueous) layer was decanted and discarded. The residue was transferred to the original apparatus, enough tetrachloroethane was added to bring the volume to 3 l., and the mixture was boiled vigorously to dissolve the brown solid and to distil the water out through the air condenser. While still hot, the clear brown solution was decanted from the slight sludge of alumina, and set aside to cool. The solid was removed, washed on the filter with several small portions of cold chloroform, and dried in an oven. The cream-colored material weighed 300 g. (20%), melted at 205–207°, and was essentially pure. For purification, this material (280 g.) was dissolved in boiling pyridine (1.5 l.) and the hot solution was allowed to cool slowly. The pale yellow needles (260 g.), after drying at 100°, melted at 207–209°. The various filtrates, residues, etc., from this experiment were not processed to recover the by-products.

(B).—The succinate I (35.5 g., 0.1 mole) and aluminum chloride (26.6 g., 0.2 mole) were heated for 1.5 hours to 140–150° in tetrachloroethane (200 cc.). The mixture was poured into iced hydrochloric acid (1 l., 1:1) and the organic layer was removed and distilled with steam to remove the solvent. 2,3,5-Trimethylphenol (1.1 g., m.p. 93–94°) was removed from the distillate by extraction with alkali. The residue from the steam distillation was boiled with acetone (150 cc.) for two hours. The undissolved solid (10 g., 31%) was removed and crystallized first from benzene and then from dioxane, when it formed a white powder melting at 205–207°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.40. Found: C, 74.37; H, 7.46.

The following variants in procedure for rearrangement of I were tried: action of aluminum chloride, 2 moles, upon I, no solvent, gave II in about 10% yield; action of 3 moles of aluminum chloride upon I, no solvent, gave no II; action of less than 2 moles of aluminum chloride upon I gave II in 8% yield and the bulk of the product was the ester IV; rearrangement of I in the nitrobenzene gave no II; rearrangement in *o*-dichlorobenzene gave very impure II in about 20% yield; action of boron trifluoride etherate upon a mixture of succinic acid and the phenol gave II in 9% yield; rearrangement of I by action of aluminum chloride in stannic chloride gave II in 24% yield melting at 200–204° and easily purified. A Friedel–Crafts reaction between succinyl chloride and the methyl ether of 2,3,5-trimethylphenol produced only alkali soluble materials; no methyl ether VI of II was obtained.

4-(2-Hydroxy-3,4,6-trimethylphenyl)-4-ketobutanoic Acid (V).—The acetone extract of the crude rearrangement product (see B above) was added to ether (200 cc.) and aqueous sodium hydroxide (200 cc., 10%). The layers were separated; the ether layer, on evaporation, left a black gum from which no pure substance could be isolated. The aqueous alkaline layer was boiled to remove acetone and then was acidified. The dark, gummy solid was removed, dissolved in ether (150 cc.) and the solution was extracted with aqueous sodium bicarbonate (5%). Acidification of the alkaline extract produced V (1.2 g.) which, after crystallization from benzene, melted at 170–171°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83; neut. equiv., 236. Found: C, 66.36; H, 7.19; neut. equiv., 228.

2,3,5-Trimethylphenyl 4-(2-Hydroxy-3,4,6-trimethylphenyl)-4-ketobutanoate (IV).—The above ether solution, after removal of V by alkaline extraction, was evaporated to a small volume and cooled. The solid (2.2 g.) was removed and crystallized twice from petroleum ether (b.p. 60–68°); it then melted at 134–135°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.40. Found: C, 74.46; H, 7.58.

Hydrolysis of IV (1 g.) by action of aqueous methanolic potassium hydroxide led to trimethylphenol (0.15 g.) melting at 93–95°, and the ketoacid V (0.4 g.), m.p. and mixed m.p., 170–171°.

Diacetate VII of II.—The crude diketone II (120 g., m.p. 193–200°) and acetic anhydride (250 cc.) were boiled for two hours in pyridine (1 l.). The cooled solution was poured into ice-water (5 l.) and the solid was removed and recrystallized from acetic acid (200 cc.) (Norit). A second crystallization from a mixture of ethyl acetate and petroleum ether (b.p. 60–68°) gave VII (80 g., 60%) melting at 150–154°. The analytical sample, crystallized again from the same solvent pair, melted at 154–156°.

Anal. Calcd. for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 71.27; H, 6.98.

Hydrolysis of the acetate VII (80 g.) by action for 48 hours of boiling aqueous (200 cc.) methanol (400 cc.) containing hydrochloric acid (20 cc.) led to II (50 g., 79%) melting after crystallization from pyridine, at 208–210°. The acetate VII was much more readily soluble in the common organic solvents than was the parent diketone II, and the easy formation, purification and hydrolysis of VII offered the quickest way for separating II from the isomeric diketone III.

Dimethyl Ether VI of II.—Sodium (1 g.) was added to a suspension of the diketone II (7 g.) in dry xylene (200 cc.) and the mixture was stirred and refluxed until the metal dissolved completely. Methyl iodide (10 g.) was added slowly (four hours) and the mixture was then washed with water, Claisen alkali, and again with water. The xylene was removed by distillation under atmospheric pressure and the residual oil was dissolved in petroleum ether (20 cc., b.p. 60–68°) and set aside at 0°. The solid (3.8 g., 50%, m.p. 110–123°) was removed, dissolved in a mixture of benzene and petroleum ether (1:1) and chromatographed on a column (2 × 30 cm.) of alumina (Alcoa F). The material obtained this way, after crystallization from methanol, melted at 124–125°.

Anal. Calcd. for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.46; H, 8.03.

Dioxime of II.—The diketone II (5 g.) and hydroxylamine hydrochloride (2 g.) were boiled for 12 hours in a mixture of pyridine (15 cc.) and ethanol (15 cc.). The high melting (312°) solid (0.3 g.) deposited during the reaction was removed and the filtrate was poured into water. The dioxime was removed and crystallized several times from ethanol. It weighed 0.5 g. and melted at 239–240° (dec).

Anal. Calcd. for $C_{22}H_{28}O_4N_2$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.48; H, 7.55; N, 7.02.

1,4-Di-(2-hydroxy-3,4,6-trimethylphenyl)-butane (VIII).—A solution of the diacetate VII (10 g.) in ethanol (75 cc.) containing hydrochloric acid (75 cc.) was boiled for 24 hours with amalgamated zinc (50 g.) with addition of more hydrochloric acid (20 cc.) every few hours. The mixture was cooled and the solids were removed and extracted with boiling ethyl acetate (100 cc.). The extract, on cooling, deposited VIII (1.2 g.) which, after two crystallizations from ethyl acetate, melted at 199–201°.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.99; H, 9.51.

2,5-Di-(2-acetoxy-3,4,6-trimethylphenyl)-furan (IX).—A solution of the diketone II (9 g.) in acetic anhydride (100 cc.) containing a drop of sulfuric acid was warmed for 20 minutes on a steam-bath and then poured over ice (600 g.) and allowed to stand overnight. The product was removed and crystallized once from ethanol and once from petroleum ether (b.p., 60–68°); this gave the diacetate VII (3 g.) melting at 155–156°. The mother liquors, on concentration, gave IX (5.2 g.) which, after crystallization from petroleum ether (b.p. 60–68°) melted at 114–116°. The experiment was duplicated, substituting the diacetate VII (0.5 g.) for the diketone II; the product (0.4 g.) was IX.

Anal. Calcd. for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.15; H, 6.87.

2,5-Di-(2-hydroxy-3,4,6-trimethylphenyl)-furan (X). A.—The diacetate IX (5 g.) was warmed with aqueous hydrochloric acid (5%) for several hours. The solid (3.1 g.) was removed and crystallized first from ethanol and then from petroleum ether (b.p. 60–68°) when it formed long white needles melting at 130–131°.

B.—The diketone II (50 g.) was distilled from a sausage flask (free flame) under 20 mm. A mixture of water and a phenol distilled first, followed by a high-boiling substance which was crystallized from ethanol. It weighed 10 g. (21%) and melted at 116–124°; after a second crystallization from ethanol, the substance melted at 130–131°, alone or when mixed with the product from A above.

Anal. Calcd. for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.62; H, 7.38.

The furan was readily soluble in aqueous alkali (5%) in contrast with the behavior of II. Acidification of the alkaline solution regenerated X unchanged.

2,5-Di-(3,5-6-trimethyl-1,4-quinonyl)-furan (XI).—Sulfanilic acid (21 g.) was diazotized in the usual manner, and the solution of the diazonium compound was poured slowly into a well-stirred solution of the furan X (15 g.) in water (100 cc.) containing a large excess of potassium hydroxide (28 g.). The mixture, after standing at room temperature overnight, was acidified with hydrochloric acid (50 cc.). The solid dark red azo dye was not isolated; instead, the suspension was boiled for 30 minutes with a solution of stannous chloride dihydrate (45 g.) in hydrochloric acid (40 cc.). Most of the solid dissolved and the red color faded to a light tan. More stannous chloride (10 g.) was added, heating was continued for 15 minutes, and then ferric chloride hexahydrate (200 g.) was added with vigorous stirring. Heating was continued for 40 minutes, the red solid was removed and the filtrate was extracted with 100-cc. portions of benzene. The solid and the benzene extracts were combined, heated to the boiling point, filtered, and the benzene was removed from the filtrate. The residual red solid (11.5 g., 65%) melted at 170–173°. The solid was crystallized twice from a mixture of chloroform and petroleum ether (b.p. 30–60°), when it formed tiny red needles melting at 175–176°.

Anal. Calcd. for $C_{22}H_{20}O_5$: C, 72.51; H, 5.53. Found: C, 72.52; H, 5.83.

The quinone was soluble in all the common organic solvents except petroleum ether. It was insoluble in water, aqueous acid or alkali. It sublimed readily at 150° under reduced pressure (2–3 mm.), and also chromatographed readily from chloroform onto anhydrous magnesium sulfate; the best solvent for development and elution was petroleum ether (b.p. 30–60°) containing 5% of chloroform.

2,5-Di-(3,5,6-trimethyl-1,4-dihydroxyphenyl)-furan (XII).—A solution of the quinone XI (2 g.) in benzene (5 cc.) was shaken with saturated aqueous sodium bisulfite (5 cc.). The red color gave way to purple, which persisted for several hours at room temperature. But when the mixture was heated to the boiling point, the color faded and the cooled benzene layer deposited tiny white crystals of the hydroquinone, which melted at 225–228°.

Anal. Calcd. for $C_{22}H_{24}O_5$: C, 71.7; H, 6.6. Found: C, 72.06; H, 6.98.

Diketone III.—The Fries rearrangement was carried out as described under A above, except that the mixture was heated at 144° for eight hours after addition of the aluminum chloride. After decomposition of the reaction mixture, it was distilled with steam until no further organic material came over. The residue was boiled with acetone, and the crude mixture of diketones II and III was removed. This material (80 g.) was dissolved in hot pyridine (500 cc.) and the solution was allowed to cool slowly. The first crop of material (III) (19 g.) melted at 218–240°; after crystallization twice from pyridine and once from ethyl acetate, it melted at 246–248°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.40. Found: C, 74.53; H, 7.57.

The filtrate from crude III, evaporated to dryness, left a residue (60 g.) which melted at 195–200°. When this material (20 g.) was boiled with pyridine (200 cc.) and the solution was allowed to cool slowly, the first crop of crystals (10 g.) melted at 225–243°; the filtrate from this deposited a second crop (8 g.) melting at 195–200°. To make sure that II was not being converted into III by action of boiling pyridine, pure II (10 g., m.p. 208–210°) was boiled with pyridine for several days; there was no change and the recovered material weighed 10 g. and melted at 208–210°.

Diacetate of III.—The diketone III (3 g.) was dissolved in pyridine (50 cc.) and acetic anhydride (20 cc.). The solution was boiled for two hours, poured into water, and the product was removed and crystallized from ethyl acetate. It weighed 3 g. (85%) and melted at 213–214°.

Anal. Calcd. for $C_{26}H_{30}O_6$: C, 71.21; H, 6.90. Found: C, 70.96; H, 7.15.

When hydrolyzed by action of boiling methanol (50 cc.) and hydrochloric acid (50 cc.) for 72 hours, the diacetate (3.4 g.) gave III (2.05 g.) melting at 246–248° and a residue (1 g.) of unchanged diacetate.

Diarylbutane from III.—The diacetate of III (8 g.), zinc (50 g.), ethanol (175 cc.) and hydrochloric acid (100 cc.) were refluxed for 36 hours. The hot mixture was filtered, and the filtrate was cooled. The white solid was removed and crystallized from a mixture of ethyl acetate and petroleum ether (b.p. 30–60°); it then melted at 146–148°.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.75; H, 9.50.

No furan, corresponding to X, could be obtained from III by either of the procedures used successfully for conversion of II into X. In both cases, unchanged starting material (or the diacetate) was quantitatively recovered.

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