chloride was added in small portions and after all had been added, the reaction mixture was allowed to stand at room temperature for sixteen hours. The solution was poured onto excess ice and carefully acidified with concentrated hydrochloric acid. The white, viscous product which separated was stirred mechanically until it became solid. It was then filtered, washed with water and recrystallized from 95% alcohol; after drying at 80° *in vacuo*, it had a m. p. 130°.

Anal. Calcd. for $C_{19}H_{23}O_9N$: C, 55.74; H, 5.66; N, 3.42. Found: C, 55.98; H, 5.69; N, 3.39.

1-(*p*-Aminobenzoyl)-2,3-4,6-diacetone-*l*-sorbose (III).—A suspension of 25 g. of 1-(*p*-nitrobenzoyl)-2,3-4,6-diacetone-*l*-sorbose in 450 cc. of absolute alcohol was reduced by hydrogen in the presence of Adams catalyst. The reduction was complete in ten minutes at 30-lb. pressure. The solution was then filtered and evaporated to a small volume when the crystalline product separated. After crystallization was complete, the product was recrystallized from absolute alcohol. It was dried at 100° in vacuum and had a m. p. 168 to 169°.

Anal. Calcd. for $C_{19}H_{25}O_7N$: C, 60.15; H, 6.64; N, 3.69. Found: C, 60.03; H, 6.58; N, 3.79.

1-(*p*-Aminobenzoyl)-2,3-monoacetone-*l*-sorbose (IV).—A suspension of 1.1 g. of 1-(*p*-aminobenzoyl)-2,3-4,6-diacetone-*l*-sorbose in 14 cc. of 50% acetic acid was warmed on the steam-bath for one hour. During this time, the crystalline compound slowly went into solution. The solution was then concentrated in vacuum at 60° to about 4 cc. and cooled. Upon neutralization with sodium hydroxide a solid was precipitated. This was filtered, washed with water and then twice recrystallized from boiling water to yield a colorless crystalline compound upon cooling. The filtered substance was washed and dried at 100° *in vacuo* over phosphorus pentoxide; m. p. 171 to 172°. The compound does not reduce Fehling solution.

Anal. Calcd. for $C_{16}H_{21}O_7N$: C, 56.61; H, 6.24; N, 4.13. Found: C, 56.61; H, 6.48; N, 4.18.

1-(*p*-Aminobenzoyl)-*l*-sorbose (V).—Ten grams of the *p*-aminobenzoyl diacetone-*l*-sorbose was suspended in 150 cc. of 0.1 *N* sulfuric acid and heated on the steam-bath for three hours. The solution was then cooled and stirred with an excess of moist barium carbonate for about thirty minutes. The precipitate which formed was removed by centrifugation. The aqueous solution was concentrated *in vacuo* at 25 to 30° to about 20 cc. when a small amount of a crystalline product (the monoacetone derivative) separated. After separating these few crystals, the solution was again concentrated and the small volume obtained was dissolved in a benzene–alcohol solution and again evaporated. This procedure was repeated until a dry, amorphous residue was obtained. The amorphous compound was dissolved in methanol and the solution treated dropwise with dry ether until a faint turbidity appeared. The solution was then set in the refrigerator when a small amount of an oil was deposited. This procedure was continued until crystals began to separate from the solution. At this point, the clear liquid was decanted from the oil and when treated with dry ether, as previously described, a solid precipitate was obtained. This product was then recrystallized from a mixture of 95% alcohol and absolute alcohol and after standing in the refrigerator for several days, gave a crop of small crystals. These crystals were collected, washed with absolute alcohol and ether and dried in a vacuum desiccator over phosphorus pentoxide. The m. p. was 159 to 160°; $[\alpha]^{20}D$ −5.0° (*C*, 2.52%; water).

Anal. Calcd. for $C_{13}H_{17}O_7N$: C, 52.17; H, 5.74; N, 4.68. Found: C, 52.17; H, 5.78; N, 4.85.

The insoluble material obtained from the barium carbonate treatment contains a great deal of the monoacetone derivative. Therefore, the entire residue was refluxed with alcohol and the alcohol evaporated to dryness. The monoacetone derivative so obtained was then hydrolyzed as above. This recovery process was continued until all of the monoacetone compound was hydrolyzed.

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Summary

A series of reactions for the synthesis of 1-(*p*-aminobenzoyl)-*l*-sorbose has been described.

RAHWAY, NEW JERSEY RECEIVED MARCH 29, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Indirect Phenol–Aldehyde Condensations[1]

BY JOSEPH B. NIEDERL AND IRVING W. RUDERMAN[2]

Introduction

In an effort further to elucidate the mechanism of the phenol–formaldehyde condensation, the study of the condensation of *p*-alkylated phenol dialcohols with both *p*-alkylated and *o,p*-dialkylated phenols was continued.

Since an *o,p*-dialkylated phenol, or "blocked" phenol, has only one open reactive position, its condensation with a *p*-alkylated phenol dialcohol can only yield a tri-nuclear linear compound. The condensation of a *p*-alkylated phenol with a *p*-alkylated phenol dialcohol may, however, theoretically at least, proceed beyond the tri-nuclear stage. Morgan,[3] Megson and Drummond[4] and Koebner[5] have reported the isolation in high yield of a tri-nuclear linear compound from the condensation of *p*-cresol and *p*-cresol dialcohol, but there is no report in the literature of how other *p*-alkylated phenols react under similar conditions.

Accordingly, in this investigation 4-*tt*-octyl-

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(1) Abstracted in part from the thesis of I. W. Ruderman presented to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science, *June, 1944.* This paper was presented before the Division of Paint, Varnish and Plastics Chemistry at the 108th meeting of the American Chemical Society in New York, N. Y., September, 1944.

(2) Present address: Research Department, Panelyte Division, St. Regis Paper Co., Trenton, N. J.

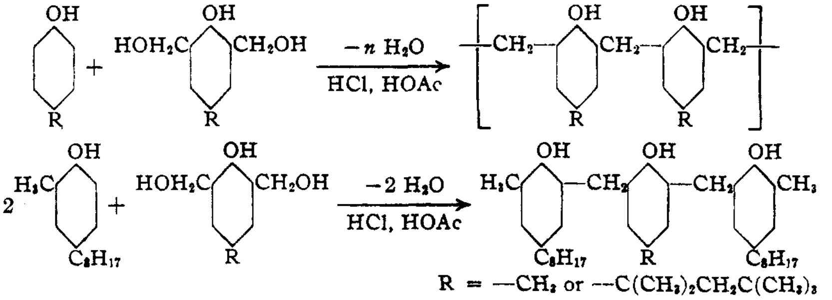
(3) J. Morgan, *J. Soc. Chem. Ind.*, **49**, 245T (1930).

(4) Megson and Drummond, *ibid.*, **49**, 251T (1930).

(5) M. Koebner, *Chem. Ztg.*, **54**, 619 (1930); *Angew. Chem.*, **46**, 252 (1933).

phenol ("diisobutylphenol")[6] was condensed with *p*-cresol dialcohol, and 4-*tt*-octylphenol dialcohol was condensed with *p*-cresol. Similarly, 4-*tt*-octyl-*o*-cresol,[6a] a blocked phenol, was condensed with *p*-cresol dialcohol and with 4-*tt*-octylphenol dialcohol.[6a] The condensations were carried out in glacial acetic acid saturated with hydrogen chloride according to the method of Niederl and McCoy.[7]

It was found that the condensations of the *p*-alkylated phenols with the *p*-alkylated phenol dialcohols yielded polymers rather than tri-nuclear compounds. The molecular weights of the acetates of these polymers were determined by the ebullioscopic method of Menzies and Wright,[8] using benzene as the solvent. With the blocked phenols, however, the condensation products analyzed correctly for tri-nuclear linear compounds. The equations for the reactions involved may be represented as



Experimental Details

Condensation of 4-*tt*-Octylphenol with 2,6-Dimethylol-*p*-cresol

Ten and three-tenths grams (0.05 mole) of 4-*t*-octylphenol and 8.4 g. (0.05 mole) of 2,6-dimethylol-*p*-cresol, prepared according to Auwers[9] and Ullmann and Brittner,[10] were dissolved in 50 ml. of glacial acetic acid. Dry hydrogen chloride gas was passed into this solution for two hours, after which the solution was poured into a separatory funnel, stoppered, and allowed to stand for two days. The oily layer which formed was separated and poured into water. A white solid was precipitated and it was filtered off, washed with water, and dried; yield, 15.3 g. The crude product was purified by repeatedly dissolving it in glacial acetic acid, filtering, and reprecipitating the solid by dilution with water. The purified product was dried at 56° *in vacuo* over solid sodium hydroxide; m. p. 118–120°.

Anal. Calcd. for $(C_{23}H_{30}O_2)_x$: C, 81.61; H, 8.93. Found: C, 81.34; H, 8.85.

Acetate.—Ten grams of the above condensation product was refluxed with 50 ml. of acetic anhydride for two hours. The solution was poured into water, whereupon an oil separated out. Upon standing overnight the oil changed to a white solid, which was filtered off, washed with water, and dried. The crude product was purified in the manner described above; m. p. 94–96°.

Anal. Calcd. for $(C_{27}H_{34}O_4)_x$: C, 76.74; H, 8.11. Found: C, 76.64; H, 7.92; mol. wt., 1509.

Condensation of *p*-Cresol with 2,6-Dimethylol-4-*tt*-octylphenol.—Five and four-tenths grams (0.05 mole) of *p*-cresol and 13.3 g. (0.05 mole) of 2,6-dimethylol-4-*tt*-octylphenol were condensed in glacial acetic acid saturated with hydrogen chloride as in the previous condensation. The yield of crude condensate was 18.1 g.; m. p. after purification, 121–122°; mixed m. p. with the condensation product of 4-*tt*-octylphenol and 2,6-dimethylol-*p*-cresol, 119–121°.

Anal. Calcd. for $(C_{23}H_{30}O_2)_x$: C, 81.61; H, 8.93. Found: C, 81.51; H, 8.82.

Acetate.—Prepared as described above by refluxing the condensation product with acetic anhydride; m. p. 86–88°; mixed m. p. with the acetate of the condensation product of 4-*tt*-octylphenol and 2,6-dimethylol-*p*-cresol, 91–93°.

Anal. Calcd. for $(C_{27}H_{34}O_4)_x$: C, 76.74; H, 8.11. Found: C, 76.89; H, 8.02; mol. wt., 1420.

Condensation of 4-*tt*-Octyl-*o*-cresol with 2,6-Dimethylol-*p*-cresol

Twenty-two grams (0.1 mole) of 4-*tt*-octyl-*o*-cresol and 8.4 g. (0.05 mole) of 2,6-dimethylol-*p*-cresol were condensed using the procedure given above. Twenty-eight and two-tenths grams of crude condensate was obtained; m. p. after purification, 56–59°.

Anal. Calcd. for $C_{39}H_{56}O_3$: C, 81.77; H, 9.85; mol. wt., 572. Found: C, 81.64; H, 9.95; mol. wt., 677.

Condensation of 4-*tt*-Octyl-*o*-cresol with 2,6-Dimethylol-4-*tt*-octylphenol

Twenty-two grams (0.1 mole) of 4-*tt*-octyl-*o*-cresol and 13.3 g. (0.05 mol.) of 2,6-dimethylol-4-*tt*-octylphenol were condensed as described above. The yield of crude condensate was 34.0 g.; m. p. after purification, 55–57°.

Anal. Calcd. for $C_{46}H_{70}O_3$: C, 82.33; H, 10.52; mol. wt., 670. Found: C, 82.12; H, 10.35; mol. wt., 653.

Summary

Both blocked and partially blocked phenols were condensed with *p*-alkylated phenol dialcohols in glacial acetic acid saturated with hydrogen chloride.

It was found that the condensations of *p*-alkylated phenols, 4-*tt*-octylphenol and *p*-cresol, with *p*-cresol dialcohol and 4-*tt*-octylphenol dialcohol, respectively, unexpectedly proceeded beyond the tri-nuclear stage to form polymers.

The condensation of 4-*tt*-octyl-*o*-cresol, a blocked phenol, with *p*-cresol dialcohol and with 4-*tt*-octylphenol dialcohol yielded, however, the expected tri-nuclear linear compounds.

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