[CONTRIBUTION FROM THE NEW PRODUCT DEVELOPMENT LABORATORY, CHEMICAL DIVISION, GENERAL ELECTRIC COMPANY]

REACTION OF DIMETHYLOLUREA WITH PHENOLS

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The reaction of mono- and di-methylolurea with phenols has been reported by von Diesbach (1, 2). Depending on whether one or two moles of the phenol was used mono- or di-N-(hydroxybenzyl) derivatives of urea were obtained. The reactions were usually carried out in alcoholic solutions, and acidic catalysts were employed. It has now been found that when dimethylolurea reacts with an excess of a phenol, dihydroxydiphenylmethanes are obtained in good yield.

The hydroxybenzylureas found by von Diesbach are probably formed under our conditions (reaction a) but react further with more phenol to give dihydroxydiphenyl methane as shown in reaction b.



Reactions similar to (b) are common. For example, bis(hydroxybenzyl)amine or tris(hydroxybenzyl)amine react with phenols to give the corresponding dihydroxydiphenylmethanes and ammonia (3). Likewise hydroxybenzyl alcohols or bis(hydroxybenzyl) ethers react with phenols, particularly in the presence of acids, to give dihydroxydiphenylmethanes and water (4-6).

The comparatively high yield of 4,4'-dihydroxydiphenylmethane, combined with the small amount of the corresponding 2,4'-isomer obtained, indicates a strong tendency for reaction at the *para* position on the phenol. However, reaction will occur at the *ortho* position when the *para* position is blocked as was shown by reaction of 2,4-dimethylphenol with dimethylolurea to give bis(2hydroxy-3,5-dimethylphenyl)methane.

EXPERIMENTAL

Dimethylolurea was prepared from formaldehyde and urea according to D'Alelio (7). It was recrystallized twice from alcohol, m.p. 125-126°; lit. (8) m.p. 126°.

Reaction of dimethylolurea with phenol. Phenol (3000 g.) and 10 ml. of concentrated hydrochloric acid were heated to 45° . The phenol was stirred rapidly while a slurry of 300 g. of dimethylolurea in 600 ml. of water was added over a period of one hour. The temperature was held at $45-50^{\circ}$ for $1\frac{3}{4}$ hours and at 60° for one-half hour. Then 200 ml. of concentrated hydrochloric acid was added and the solution was boiled for one hour. After removal of the acid and excess phenol, by heating to 130° at 20-25 mm., the residue was extracted repeatedly with boiling water and then with boiling toluene. On cooling the extracts 898.5 g. of crude crystalline product was obtained. Recrystallization from water yielded 479 g. of snow-white crystals, m.p. $154-157^{\circ}$. A portion of the product was distilled, b.p. $237-243^{\circ}/$ 12-13 mm., m.p. $159.5-161.5^{\circ}$. The product was identified as 4,4'-dihydroxydiphenylmethane by running a mixture melting point with an authentic sample of the compound and by comparison of infrared absorption spectra; lit. (9) m.p. 158° , (10) m.p. $162-163^{\circ}$.

Also separated from the extracts was 7.5 g. of a material, m.p. 110–113°, which appeared to be impure 2,4'-dihydroxydiphenylmethane, as well as a residue of unknown structure amounting to 215 g.

Reaction of 2,4-dimethylphenol with dimethylolurea. First, 30 g. of 2,4-dimethylphenol was dissolved in 30 ml. of glacial acetic acid and 5 ml. of concentrated hydrochloric acid. The solution was heated to 80-90° and 3 g. of dimethylolurea in 25 ml. of water was added in small portions. The reaction mixture was boiled 50 minutes. On cooling crystals formed which were extracted with ether. The ether extract was dried and diluted with petroleum ether. Snow-white crystals separated, m.p. 148-150°. The product was shown to be bis(2-hydroxy-3,5-dimethylphenyl)methane by running a mixture melting point with an authentic sample of the compound prepared by condensation of 2,4-dimethylphenol with formaldehyde, m.p. 148-149°; lit (11), m.p. 148°.

Anal. Calc'd for C₁₇H₂₀O₂: C, 79.90; H, 7.83. Found: C, 79.79, 80.33; H, 7.80, 7.92.

SUMMARY

The reaction of dimethylolurea with an excess of phenol and with 2,4-dimethylphenol gave the corresponding dihydroxydiphenylmethane.

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