Table I

Color Reactions

Compound	Concd. sulfuric acid	Dil. alkali
4-Chloro-2-nitrophenyl-4′-hydroxysulfuranilide	Violet solution, brown on standing	Greenish-brown precipitate
4-Chloro-2-nitrophenyl-2′,4′-dihydroxysulfuranilide	Clear, Bordeaux blue solution	Clear, olive-green solution
4-Chloro-2-nitrophenyl-2′-hydroxyquinonesulfurimine	Dissolved slowly to a brownish-red solution	Brown-red, turbid solution

After boiling the liquid for 45 minutes, the fibers were removed, washed with water and with soap solution. The material was found to be dyed a brown color. Wool was also dyed if the quinone were used as an acid dye in a bath containing 8% quinone, 10% sulfuric acid, 2% sodium sulfate, 0.5% sodium carbonate and water. The intensity of the resulting color was much less than before and the shade more yellowish.

The authors wish to express to Professor Lauder W. Jones their appreciation of his advice during this investigation.

Summary

It has been shown that the sulfur-nitrogen linkage of the *p*-hydroxyanilide of 4-chloro-2-nitrophenylsulfur chloride is split even by reduction in neutral solution with aluminum amalgam. The preparation of an anilide of 4-aminoresorcinol with 4-chloro-2-nitrophenylsulfur chloride, its oxidation product, the 4-chloro-2-nitrophenyl-2′-hydroxysulfurquinoneimine, and their properties have been reported. It has been shown that this oxidation product is a dye and represents a new type of indophenol dyes.

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ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. IV. CONDENSATION OF SOME SECONDARY ALCOHOLS WITH PHENOL

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The experiments described here constitute a continuation of our study of the dehydrating and catalytic effect of anhydrous aluminum chloride in the condensation of aromatic alcohols with aromatic compounds.

A previous article[1] describes the condensation of methylphenyl carbinol, ethylphenyl carbinol and benzhydrol with benzene with the formation of diphenylethane, diphenylpropane and triphenylmethane. We have now extended our studies to include the condensation of the same three alcohols with phenol.

[1] Huston and Friedemann, This Journal, **40**, 785 (1918).

The technique was essentially the same as that used in the preparation of *p*-benzylphenol from benzyl alcohol and phenol,[2] except that in the condensation of benzhydrol, carbon disulfide was substituted for petroleum ether.

Methylphenyl carbinol condensed with phenol, giving a 33–35% yield of *p*-hydroxy-1,1-diphenylethane: $C_6H_5CHOHCH_3 + C_6H_5OH = C_6H_5$-$C(CH_3)HC_6H_4OH + H_2O$; b. p., 168–170°, at 5 mm.; m. p., 57–58°. The benzoyl derivative melted at 82–83°. Koenigs and Carl[3] prepared this compound by condensing styrol and phenol by means of sulfuric and glacial acetic acids. They determined the configuration by oxidizing the methyl ether by means of potassium dichromate and sulfuric acid to *p*-methoxybenzophenone.

Ethylphenyl carbinol with phenol gave a somewhat smaller yield (27–30%) of *p*-hydroxy-1,1-diphenylpropane: $C_6H_5C(C_2H_5)HOH + C_6H_5OH = C_6H_5C(C_2H_5)HC_6H_4OH + H_2O$.

This compound boiled at 175–177° (6 mm.) and melted after crystallization from petroleum ether at 64.5°. The benzoyl derivative melted at 67°. Proof that the entering group takes the position *para* to the hydroxyl was obtained by oxidizing the methyl ether to *p*-methoxybenzophenone.

Benzhydrol with phenol gave a 40% yield of *p*-hydroxytriphenylmethane: $(C_6H_5)_2CHOH + C_6H_5OH = (C_6H_5)_2CHC_6H_4OH + H_2O$. This was identified by the melting point of the free phenol (110°) and its ethyl ether (70–71°) as the same compound which Bistrzycki and Herbst[4] prepared by reducing *p*-hydroxytriphenyl carbinol with zinc and acetic acid.

These experiments give additional evidence of the effect of unsaturation of the *alpha* carbon on the reactivity of the alcoholic hydroxyl group.[5] As was the case when these same alcohols were condensed with benzene,[1] benzhydrol in which both *alpha* carbons are members of the unsaturated benzene ring gave a much larger yield of condensation product than did methylphenyl carbinol or ethylphenyl carbinol.

There is evidently a strong tendency on the part of the phenolic hydroxyl group to direct the entering group to the *para* position. The formation of the *ortho*-substitution product is not precluded and was expected, but in no case was it formed in sufficient quantity for isolation.

Experimental Part

Methylphenyl Carbinol and Phenol with Aluminum Chloride.—In the same manner as described in a previous article[2] of this series, 17.7 g. of phenol, 21 g. of methylphenyl

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[2] Huston, THIS JOURNAL, **46**, 2775 (1924).

[3] Koenigs and Carl, *Ber.*, **24**, 3889 (1891).

[4] Bistrzycki and Herbst, *Ber.*, **35**, 3137 (1902).

[5] Huston and Sager, THIS JOURNAL, **48**, 1955 (1926).

carbinol and 11.5 g. of aluminum chloride, added in small portions, were stirred together. The temperature was kept below 40°. After decomposition of the dark red product with ice and hydrochloric acid, and extraction with ether, the ether was distilled off and the residue fractionated; 11.9 g. of phenol was recovered at 100–120° (5 mm.); 3 g. distilled at 120–150° (5 mm.); 24.5 g. at 150–170° (mostly 165–170°) (5 mm.).

Eighteen and five-tenths g. of this final fraction was dissolved in sodium hydroxide, extracted with petroleum ether and reprecipitated with hydrochloric acid. The oil was dissolved in ether and dried over sodium carbonate, and after recovery of the ether the residue was again distilled. Practically all of it distilled at 165–173° as a thick, slightly yellow oil. After standing in the ice box for several months, this solidified and was purified by recrystallization from petroleum ether. It came down in clusters of short, bluish-white prisms; m. p., 57–58°.[3]

The benzoyl derivative was prepared by the Schotten-Baumann reaction. It crystallized from dil. alcohol in very fine, flat needles; m. p., 82–83°.

Ethylphenyl Carbinol and Phenol with Aluminum Chloride.—Sixteen g. of ethylphenyl carbinol, 47.3 g. of phenol and 36 g. of aluminum chloride were allowed to react under the usual conditions, the temperature being kept below 25°. The product was fractionated four times at 10 mm. Twelve g. of phenol was recovered below 150°, 6 g. distilled at 150–183°, 25 g. at 183–185°, 4 g. at 185–200° and 6 g. at 200–300°.

The 183–185° fraction was a viscous, yellowish liquid which crystallized upon standing for several weeks in an ice box. After six recrystallizations from petroleum ether, the white, silky crystals melted at 64.5°. The purified compound boiled at 175–177° (6 mm.).

Anal. Subs., 0.1057: CO_2, 0.3293; H_2O, 0.0729. Calcd. for $C_{15}H_{16}O$: C, 84.886; H, 7.568. Found: C, 85.005; H, 7.650.

The benzoyl derivative crystallized from alcohol in long, flat, needle-like prisms; m. p., 67–68°. Two g. of the phenol was dissolved in methyl alcohol and converted into the methyl ether by means of methyl iodide and sodium. This was purified by steam distillation and oxidized by boiling for eight hours with potassium dichromate and sulfuric acid. The product, when extracted with ether, distilled with steam and recrystallized from alcohol, gave the proper melting point for *p*-methoxybenzophenone (61–62°).

Benzhydrol and Phenol with Aluminum Chloride.—Twenty-five g. of benzhydrol, 14.2 g. of phenol and 8 g. of aluminum chloride were allowed to react as above, except that carbon disulfide (200 cc.) was used instead of petroleum ether. The temperature was maintained below 25°. The intermediate compound was a dark red, semi-solid mass which decomposed slowly in ice water. Upon fractionally distilling the product at 5–6 mm. the temperature rose rapidly to above 200°. No phenol was recovered. After the third fractionation (5–6 mm.) 15.2 g. was obtained at 215–220° (mostly 217–218°), and 5.1 g. at 220–240°.

The 215–220° fraction was dissolved in the smallest possible quantity of ether and then diluted largely with petroleum ether. This solution evaporated slowly in the ice box, depositing queer, nodular masses of yellowish crystals. After five crystallizations it melted at 110°.[4]

The ethyl ether was prepared by treating 1 g. of the phenol in ethyl alcohol with molecular equivalents of sodium and ethyl iodide. It crystallized from alcohol in short, glistening needles; m. p., 70–71°. The benzoyl derivative was prepared by the Schotten-Baumann reaction and recrystallized from alcohol. It came down in prisms; m. p., 125°.

Summary

1. Methylphenyl carbinol, ethylphenyl carbinol and benzhydrol were condensed with phenol by means of anhydrous aluminum chloride

according to the equation $C_6H_5C(R)HOH + C_6H_5OH = C_6H_5C(R)HC_6H_4OH$ (*p*) + H_2O, where R is methyl, ethyl or phenyl.

2. A relatively large yield from benzhydrol further confirms the hypothesis that unsaturation of carbon atoms adjacent to the alcoholic group increases the reactivity of the hydroxyl group.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOBART COLLEGE]

METHYLPHENYL-STANNANES

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Introduction

Derivatives of tetramethyl-stannane are for the most part, liquids or solids of low melting point and are, on the whole, rather reactive. Derivatives of tetraphenyl-stannane, however, are solids of high melting point and, as a rule, are less reactive than the corresponding methyl compounds. From the three mixed methylphenyl-stannanes, $CH_3Sn(C_6H_5)_3$, $(CH_3)_2Sn(C_6H_5)_2$ and $(CH_3)_3SnC_6H_5$, we might expect derivatives having chemical and physical properties intermediate between those of the corresponding derivatives of tetramethyl- and tetraphenyl-stannane. It was for the purpose of later preparing and studying some of these compounds that the preparation of the mixed stannanes was undertaken.

One of the general methods of preparing mixed stannanes consists in treating a solution of sodium alkyl or aryl stannide in liquid ammonia with alkyl or aryl halide as represented by the following equation:[1] $R_3SnNa + R'X = R_3SnR' + NaX$. This is often a most satisfactory method because of the ease of preparation and purification of the product and also because of the high yields obtainable. The success of this type of reaction is dependent upon the nature of the radicals attached to the tin and the halogen atoms. For example, in preparing dimethyldiphenylstannane by the reaction $Na_2Sn(C_6H_5)_2 + 2CH_3I = (CH_3)_2Sn(C_6H_5)_2 + 2NaI$, yields of the purified product as high as 85% of that calculated were obtained. On treating disodium-dimethyl stannide with two molecules of iodobenzene, however, practically no stannane was obtained but a compound was formed which on hydrolysis yielded dimethylstannyl oxide, $(CH_3)_2SnO$. Furthermore, methyl triphenyl-stannane could be made in practically quantitative yields by the reaction $NaSn(C_6H_5)_3 + CH_3I = CH_3Sn(C_6H_5)_3 + NaI$, while treating sodium-trimethyl stannide with iodobenzene gave a product containing approximately 14% of the stannane and 86% of the nitride, $[(CH_3)_3Sn]_3N$. The main reaction in this case is $3NaSn(CH_3)_3 + 3C_6H_5I + NH_3 = [(CH_3)_3Sn]_3N + 3C_6H_6 + 3NaI$.

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[1] Kraus and Sessions, THIS JOURNAL, 47, 2365 (1925).