

side. Interference figures indicated that the crystals were biaxial, hence they must belong to the monoclinic system. The trace of the optic plane was parallel to the shorter side of type B crystals.

Summary

2-Nitrofuran has been prepared by the decarboxylation of 5-nitro-furoic acid and has been shown to be identical with the nitrofuran obtained from furan by nitration. The latter had been incorrectly formulated by Marquis to be 3-nitrofuran.

Evidence is presented to support the view that the intermediate nitroacetates, produced in the nitration of various furan derivatives in acetic anhydride solution, are ring structures rather than open chain enols.

The mechanism of the nitration process is suggested tentatively to be a 1,4-addition to the furan ring, without scission of the oxygen bridge.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

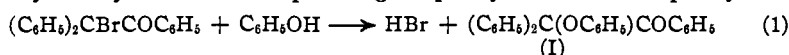
THE ACTION OF PHENOL ON BENZOYLDIPHENYLMETHYL BROMIDE

By C. FREDERICK KOELSCH¹

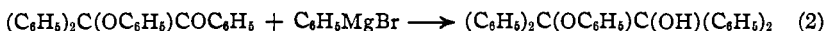
RECEIVED JANUARY 21, 1931

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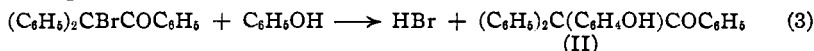
In a recent paper Schuster² reported that the reaction between benzoyldiphenylmethyl bromide and phenol gave phenylbenzoin monophenyl ether



Subsequent treatment of the resulting product with phenylmagnesium bromide was reported to give benzopinacolone monophenyl ether



A reaction such as that indicated in (1) would be remarkable indeed, since it is well known that phenol reacts in an acidic environment with certain compounds containing labile halogens to form nuclear substitution products; for example, phenol and triphenylchloromethane form *p*-hydroxytetraphenylmethane. It was then supposed that reaction (1) did not proceed as Schuster indicated, but rather



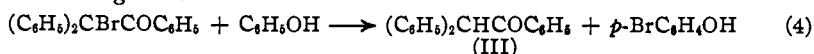
To test this supposition, Schuster's work was repeated in this Laboratory.

In the present paper it is shown that the reaction between benzoyldiphenylmethyl bromide and phenol proceeds neither according to (1) nor

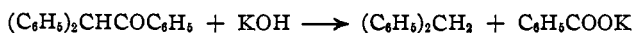
¹ Du Pont Fellow, 1930-1931.

² Schuster, *Ber.*, 63, 2397 (1930).

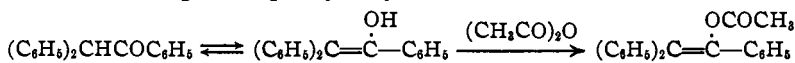
according to (3). Instead, it is shown that the reaction takes place in the following manner



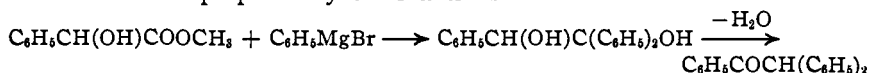
The first evidence that diphenylacetophenone (III) and not phenylbenzoin monophenyl ether (I) or hydroxytriphenylacetophenone (II) was produced in the reaction was obtained by treating the product with alcoholic potassium hydroxide, when potassium benzoate and diphenylmethane were formed



Later, it was found that the product, when treated with acetic anhydride and sulfuric acid, gave triphenylvinyl acetate

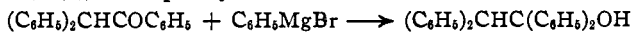


Finally, the identity of the product was proved by determining its melting point when mixed with a known specimen of diphenylacetophenone which had been prepared by the reactions³



Further evidence that the reaction proceeds according to Equation 4 was obtained by the isolation of *p*-bromophenol in considerable amounts from the reaction mixture. This compound was identified beyond question by its boiling point and by the melting point and neutral equivalent of the aryloxyacetic acid obtained from it by treatment with chloroacetic acid and sodium hydroxide.

The product of the action of phenylmagnesium bromide on diphenylacetophenone, which melts at 232–233° and not at 219° as Schuster reported, is $\alpha,\alpha,\beta,\beta$ -tetraphenylethanol⁴



On treatment with alcoholic potassium hydroxide it gave a mixture of diphenylmethane and benzophenone



Schuster noted and was unable to explain the resistance of the hydroxyl group to substitution by bromine on treatment with hydrogen bromide in the compound which he obtained by the action of phenylmagnesium bromide on his supposed phenylbenzoin monophenyl ether. Since it has been pointed out that this reaction product is really $\alpha,\alpha,\beta,\beta$ -tetraphenylethanol, and since unreactivity toward such a reagent as hydrogen bromide is apparently a characteristic property of polyphenylethanol,⁵ this behavior of the compound in question is not surprising.

³ Orekhoff, *Bull. soc. chim.*, [4] 25, 189 (1919).

⁴ McKenzie and Boyle, *J. Chem. Soc.*, 119, 1140 (1921).

⁵ Cf. Schmidlin, *Ber.*, 43, 1146 (1910).

Experimental

Benzoyldiphenylmethyl Bromide and Phenol.—The procedure of Schuster for carrying out the reaction between these two compounds was followed closely. Eight grams of benzoyldiphenylmethyl bromide⁶ was heated at 100° for three hours with 3.2 g. of phenol. The product, after triturating with dilute sodium hydroxide solution, was crystallized from alcohol, giving 5.25 g. of diphenylacetophenone melting at 135–136°, uncorr. (On heating with concentrated sulfuric acid, diphenylacetophenone gives a deep green solution. The color becomes reddish-brown on dilution.)

The oil obtained on acidification of the sodium hydroxide extract was taken up in ether, dried, and the ether removed. Distillation of the residue at 23 mm. gave two main fractions, both of which solidified. The first (1.2 g.), which boiled at 80–85°, was phenol; the second (1.9 g.), which boiled at 127–130°, was identified as *p*-bromophenol by the preparation of *p*-bromophenoxyacetic acid from it, which melted at 156–158° and had a neutral equivalent of 228.⁷

Cleavage of Diphenylacetophenone by Potassium Hydroxide.—Three grams of the ketone obtained above was refluxed for twenty hours with a solution of 2 g. of potassium hydroxide in 50 ml. of alcohol. The solvent was removed in a current of air at reduced pressure, water was added, and the mixture was steam distilled. From the distillate was obtained 1.6 g. of diphenylmethane boiling at 145–150° at 25 mm., and melting at 21–23°, which gave benzophenone on oxidation with chromic acid. The residue from the steam distillation gave on acidification 1.02 g. of benzoic acid melting at 120–121°; neutral equivalent, 120.

Triphenylvinyl Acetate.—A mixture of 0.5 g. of diphenylacetophenone with 5 ml. of acetic anhydride and 3 drops of concentrated sulfuric acid was heated at 60–70° for twelve hours. The product, on crystallization from dilute acetic acid, melted at 102–104°,⁸ and gave diphenylacetophenone on warming with alcoholic sodium hydroxide.

Only unchanged diphenylacetophenone was recovered when an attempt was made to methylate the compound with dimethyl sulfate and alkali in methyl alcohol.

$\alpha, \alpha, \beta, \beta$ -Tetraphenylethanol.—To the filtered solution of phenylmagnesium bromide prepared from 20 g. of phenyl bromide in 50 ml. of ether was added 8 g. of diphenylacetophenone. The solution, after refluxing for half an hour, was worked up as described by Schuster, giving a product which on one crystallization from toluene melted at 218–223°. On repeated recrystallization from toluene, this was separated into $\alpha, \alpha, \beta, \beta$ -tetraphenylethanol melting at 227–229° uncorr. (2.4 g.), and unchanged diphenylacetophenone (4.6 g.).⁴

Cleavage of $\alpha, \alpha, \beta, \beta$ -Tetraphenylethanol by Potassium Hydroxide.—One gram of the alcohol was refluxed for two hours with 1 g. of potassium hydroxide dissolved in 20 ml. of alcohol. Water was added after removing the alcohol under reduced pressure, and the mixture was steam distilled. The residue contained only a negligible amount of organic material. The oil in the distillate was taken up in ether; this solution was dried with calcium chloride and treated with the filtered Grignard solution from 3.0 g. of phenyl bromide. Dilute sulfuric acid was added, the ether was removed, and the residue was steam distilled. The distillate contained 0.27 g. of diphenylmethane (calcd. 0.48 g.) identified by oxidation to benzophenone. The non-volatile organic substance was identified as triphenylcarbinol by its melting point (159–160°, uncorr.) and its characteristic color reaction with concentrated sulfuric acid; it weighed 0.65 g., corresponding to 0.45 g. of benzophenone (calcd. 0.52 g.).

⁶ Löwenbein and Schuster, *Ann.*, **481**, 106 (1930).

⁷ Koelsch, *THIS JOURNAL*, **53**, 305 (1931).

⁸ Biltz, *Ann.*, **296**, 245 (1897).

The assistance of Professor S. M. McElvain is gratefully acknowledged.

Summary

The reaction between phenol and benzoyldiphenylmethyl bromide gives *p*-bromophenol and diphenylacetophenone.

The compounds described as phenylbenzoin monophenyl ether and benzopinacone monophenyl ether by Schuster² are in reality diphenylacetophenone and $\alpha,\alpha,\beta,\beta$ -tetraphenylethanol.

Diphenylacetophenone and $\alpha,\alpha,\beta,\beta$ -tetraphenylethanol are smoothly cleaved by alcoholic potassium hydroxide, giving in the one case benzoic acid and diphenylmethane, and in the other benzophenone and diphenylmethane.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

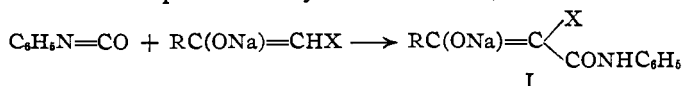
THE COURSE OF ADDITION OF SODIUM ENOL ALKYL MALONIC AND SODIUM ENOL ALKYL CYANACETIC ESTERS TO UNSATURATED ESTERS

BY ARTHUR MICHAEL AND JOHN ROSS

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According to the law of chemical neutralization,¹ the course of an addition reaction involving the use of an enolic sodium derivative will be such as to produce a compound in which the sodium is in a better neutralized state. The attainment of the maximal heat of formation in the addition reaction depends upon the neutralization of the positive energy of the metal and this energy factor determines the utmost possible degradation of chemical energy. This generalization is well illustrated in the reactions of sodium enol derivatives with phenyl isocyanate.² With the sodium enol derivatives of acetoacetic, malonic, formyl, acetic, benzoylacetic esters and diacylmethane, the reaction takes place smoothly to give in most cases almost quantitative yields of anilides, thus



In these derivatives the α -hydrogen atoms of the enolic sodium mother substances are replaced by the negative $-\text{CONHC}_6\text{H}_5$ group, and, hence, the sodium atoms are better neutralized in the C-addition products (I). When there is no α -hydrogen atom in the sodium compound, this simple reaction cannot take place. For example, with the sodium enol derivatives of ethylmalonic and ethylacetoacetic esters maximal possible energy degradation is attained by the phenyl isocyanate polymerizing mainly

¹ Michael, *J. prakt. Chem.*, 60, 293 (1899); THIS JOURNAL, 32, 990 (1910).

² Michael, *Ber.*, 38, 22 (1905).