tempt to attribute deviations to a change in "a" with solvent or to ion associations which might change the factor $\mathfrak{z}_A\mathfrak{z}_B$ from 2 to 1. Considering all of the limitations imposed in obtaining equations (1) and (2) from the theory, one must conclude that the agreement is as good as could reasonably be expected.

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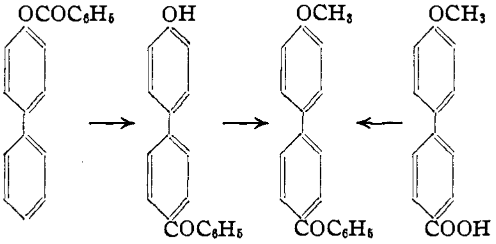
The Fries Rearrangement of 4-Benzoyloxydiphenyl

BY L. F. FIESER AND CHARLES K. BRADSHER

Having recently reported that the Fries rearrangement of 4-acetoxydiphenyl yields a mixture of 4-hydroxy-3-acetyldiphenyl and 4-hydroxy-4′-acetyldiphenyl,[1] we were interested to note that, in a paper published prior to ours but after the completion of our work, Hey and Jackson[2] obtained only 4-hydroxy-3-benzoyldiphenyl on heating 4-benzoyloxydiphenyl with aluminum chloride in tetrachloroethane solution at 140° and found no evidence of the heteronuclear migration of the benzoyl group. No trace of the alkali-soluble product, m. p. 193–195°, claimed by Blicke and Weinkauff[3] to be produced under identical conditions was observed. The latter investigators had assigned to their product, albeit without satisfactory evidence, the structure of 4-hydroxy-4′-benzoyldiphenyl and had regarded this as a case of heteronuclear rearrangement.

In view of the discrepancy in these two reports and the divergence of our results with the acetate from those of Hey and Jackson with the benzoate, we investigated the rearrangement of the latter ester under conditions similar to those employed with the former.[1] The reagents were brought together in the presence of carbon bisulfide, the solvent was distilled, and the residue heated at 160°. From the resulting mixture a substance identified as 4-hydroxy-4′-benzoyldiphenyl (II), m. p. 194–195° when pure, was isolated in 22% yield. As in other cases, the 4′-derivative is easily separated by virtue of its relatively low solubility. The structure of the substance was established by conversion to the methyl ether (III), which was compared with a sample synthesized by the condensation of the chloride of 4-methoxy-4′-carboxydiphenyl[1] (IV) with benzene. The two samples were found to be identical. The same substance resulted from the Friedel and Crafts reaction of 4-methoxydiphenyl with benzoyl chloride, as stated by Blicke and Weinkauff and by Hey and Jackson, but our results differed from those of the previous investigators in that we isolated not only the 4′-benzoyl derivative (37% yield) but also 4-methoxy-3-benzoyldiphenyl (39% yield).



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We are in agreement with both pairs of investigators regarding the properties of the various compounds, and the differences in the results appear to be due to variations in the conditions of the reactions and the methods of separating the products. We are inclined to believe that the conditions for the Fries rearrangement specified by Blicke and Weinkauff are not very satisfactory, for although these workers undoubtedly obtained 4-hydroxy-4′-benzoyldiphenyl, we were no more able to duplicate their results, at least in one small-scale experiment, than were Hey and Jackson.

That under slightly different conditions the benzoyl group migrates to an appreciable and unmistakable extent to the 4′-position is consistent with the findings regarding the acetyl migration.[1] We do not, however, regard these examples of heteronuclear migration as having any great theoretical significance, for the evidence available indicates that the Fries reaction is not a true rearrangement but an intermolecular acylation.[4]

Experimental Part

Fries Rearrangement.—4-Benzoyloxydiphenyl (5 g.) was mixed thoroughly with finely powdered aluminum chloride (4.7 g.) and carbon bisulfide (25 cc.) and the solvent was removed by distillation from the steam-bath. The residue was heated for thirty minutes in an oil-bath maintained at 160°, and after cooling and adding ice and

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[1] Fieser and Bradsher, THIS JOURNAL, **58**, 1738 (1936).

[2] Hey and Jackson, *J. Chem. Soc.*, 802 (1936).

[3] Blicke and Weinkauff, THIS JOURNAL, **54**, 330 (1932).

[4] Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928); Cox, THIS JOURNAL, **52**, 352 (1930).

dilute hydrochloric acid the product was taken up in ether. The ethereal solution was washed with dilute acid and with water and extracted with 2.5% sodium hydroxide, and on acidifying the alkaline extract there was obtained 4 g. of grayish material. On two crystallizations from benzene this afforded nearly pure **4-methoxy-4′-benzoyldiphenyl**, m. p. 193–195°, yield 1.1 g. (22%). A small amount of a highly colored impurity was removed on reprecipitation from an alkaline solution, and further crystallization from benzene gave round, faintly yellow crystal-clusters, m. p. 194–195°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.18; H, 5.14. Found: C, 83.42; H, 5.14.

No pure products were isolated from the mother liquor. On conducting the rearrangement according to Blicke and Weinkauff[3] the alkali-soluble product amounted to only about 2% of the ester used and it consisted largely of 4-hydroxydiphenyl.

The acetate formed colorless plates, m. p. 127–128°, from methyl alcohol.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72; H, 5.09. Found: C, 80.00; H, 5.39.

The methyl ether, prepared with the use of dimethyl sulfate and alkali, crystallized from benzene as colorless needles, m. p. 165–166°. It was identified by comparison with the samples described below.

Friedel and Crafts Reaction.—A solution of 10 g. of 4-methoxydiphenyl and 6.9 cc. of benzoyl chloride in 130 cc. of tetrachloroethane was cooled to −10° and 8 g. of aluminum chloride was added all at once. The mixture was stirred mechanically and allowed to come to room temperature. After eighteen hours ice and acid were added, the solvent was removed with steam, and the moist product was taken up in benzene. On concentrating the solution to a volume of 50 cc. and cooling, 5.8 g. of nearly pure **4-methoxy-4′-benzoyldiphenyl**, m. p. 165–167°, crystallized. The mother liquor was concentrated to a volume of 25 cc. and treated with petroleum ether. The material which separated on one crystallization from methyl alcohol gave 6.1 g. of a product melting at 91–92° (flat needles). This substance is insoluble in alkali and depresses the melting point of 4-methoxydiphenyl; it is undoubtedly 4-methoxy-3-benzoyldiphenyl, which Hey and Jackson[2] prepared by a synthesis establishing the structure and for which they report the melting point 93°.

Synthesis of 4-Methoxy-4′-benzoyldiphenyl.—A solution of 0.5 g. of 4-methoxy-4′-carboxydiphenyl[1] in 10 cc. of thionyl chloride was refluxed gently for one hour and the excess reagent was removed at reduced pressure. The residue was dissolved in 25 cc. of thiophene-free benzene, 0.3 g. of aluminum chloride was added and the mixture was refluxed for one hour. The reaction product, recovered in the usual way, crystallized from alcohol or benzene as colorless needles, m. p. 165–166°. Mixed melting point determinations of this 4-methoxy-4′-benzoyldiphenyl with both of the samples obtained above indicated the identity of all three preparations.

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A New Synthesis of Morpholine

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Morpholine was first prepared by L. Knorr[1] by heating diethanolamine and an excess of concentrated hydrochloric acid in a sealed tube and then refluxing the reaction mass with potassium hydroxide. Because of low yields Knorr abandoned this method for the sulfuric acid method.[2] In both cases he failed to state his yields. However, Jones and Burns[3] have shown that morpholine is formed in about a 10% yield by the action of sulfuric acid on diethanolamine following the directions of Knorr. Therefore the yield using hydrochloric acid and potassium hydroxide must have been considerably lower. The only other methods for the preparation of morpholine are indirect ones and need not be reviewed here.

In his first preparation Knorr assumed the chlorohydrin of diethanolamine to be formed. Ring closure with loss of hydrogen chloride was then effected by refluxing in potassium hydroxide solution. He based this assumption on the fact that he was able to isolate the chlorohydrin of N-phenyldiethanolamine in a similar reaction; however, he was unable to isolate the chlorohydrin of diethanolamine because of its similarity in properties to the parent substance.

We have shown in this investigation that the chlorohydrin does not necessarily have to be formed and that no dehydrating agent other than that of heat on the hydrochloride is necessary for the formation of morpholine from diethanolamine. This was surprising in view of the work of Knorr.

Preparation.—Diethanolamine (2 moles) is placed in a round-bottomed flask fitted with a thermometer and an air-cooled condenser. Concentrated hydrochloric acid is added slowly until the solution is acid to litmus. The solution is then heated rapidly until the water is driven off, and the temperature of the solution is kept at 200–210° for fifteen hours. The reaction mass is now allowed to cool, an excess of calcium oxide is added, and the mixture subjected to dry distillation. The resulting liquid is dried over solid sodium hydroxide and refluxed over metallic sodium for thirty minutes; it is then subjected to fractionation. The entire product boils at from 126–129° and is practically anhydrous. The yield is around 48%. This procedure offers a rapid

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(1) Knorr, *Ber.*, **22**, 2081 (1889).

(2) Knorr, *Ann.*, **301**, 1 (1898).

(3) Jones and Burns, THIS JOURNAL, **47**, 2966 (1925).