[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. X.[1] Rearrangements

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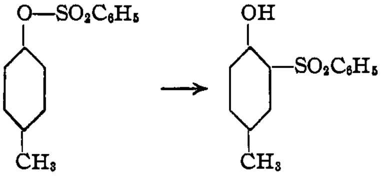
It has been found that a number of rearrangements commonly catalyzed by other condensing agents are also promoted by hydrogen fluoride. A few examples are reported here.

The exchange of alkyl groups by two aromatic compounds has been demonstrated repeatedly when aluminum chloride is employed.[2] Thus, polyamylbenzenes react with benzene to give monoamylbenzene.[3] We have found that *t*-butylbenzene reacts with phenol in the presence of hydrogen fluoride at 0° to give benzene and *t*-butylphenol, the latter in yields of about 10%. No attempt was made to carry out this conversion at higher temperatures, although it has been reported that disproportionation increases with temperature, when cymene is treated with aluminum chloride.[4]

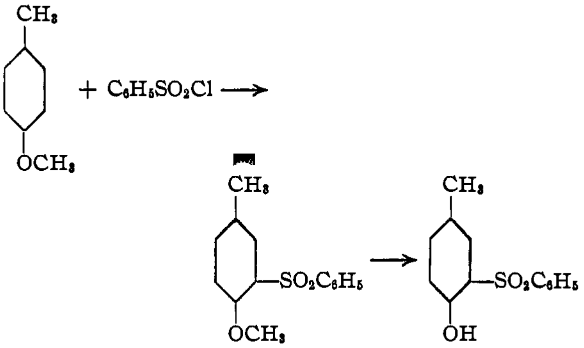
The conversion of a ketoxime to an anilide has been carried out in the cold using an acetic acid–hydrogen fluoride mixture, and also an ether–hydrogen fluoride mixture. Benzophenone oxime undergoes the Beckmann rearrangement with phosphorus pentachloride almost quantitatively, whereas with hydrogen fluoride under the conditions we employed only a 72% yield of benzanilide was obtained.

It has been reported previously that hydrogen fluoride would not effect a Fries rearrangement at room temperature.[5] This statement was amply confirmed by our observations of the behavior of phenyl acetate. A mixture of the ester and hydrogen fluoride gave no appreciable amounts of rearranged product. However, when warmed to 100° it was found that rearrangement to the *p*-acylphenol did take place, although there was much to be desired with respect to smoothness and yield.

A reaction similar to the Fries is the conversion of a phenol sulfonate to an hydroxy sulfone. Thus, in the presence of hydrogen fluoride at 100° *p*-cresyl benzenesulfonate was converted to 2-hydroxy-4-methyl-diphenyl sulfone in yields of 10%.



The hydroxy sulfone was synthesized by allowing *p*-cresyl methyl ether to react with benzenesulfonyl chloride in the presence of aluminum chloride to give I. The methoxy sulfone was then treated with aluminum chloride at an elevated temperature to produce the hydroxy sulfone II.



I II

Due to the strong ortho directing tendency of the methoxy group it is reasonably certain that the sulfonyl radical entered the position ortho rather than meta to the methoxyl. At any rate, the synthesized sulfone was identical with the one obtained from the rearrangement.

We wish to thank Prof. E. H. Cox of Swarthmore College for a sample of *p*-cresyl sulfonate.

Experimental

Reaction of Phenol with *t*-Butylbenzene.—One-half molar quantities of phenol and the alkylbenzene were mixed and added to 70 g. of hydrogen fluoride at 0°. The reaction was allowed to proceed with stirring for a period of thirteen hours, after which time it was poured onto ice, neutralized, taken up in ether, and dried. There was isolated from the reaction mixture, 2.6 g. of benzene, identified by conversion to a dinitro derivative, and 7.5 g. of *p*-*t*-butylphenol, m. p. and mixed m. p. 98–99°.

Beckmann Rearrangement of Benzophenone Oxime.—Five grams of the ketoxime was dissolved in 75 cc. of acetic acid and the solution then was added slowly to 86 g. of hydrogen fluoride at 0°. After standing overnight the mixture was warmed on the steam-bath to remove the more volatile acid. Upon cooling the solution was diluted with water, the precipitate filtered and washed, and then

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(1) For the previous paper of this series see THIS JOURNAL, **62**, 45 (1940).

(2) Calloway, *Chem. Rev.*, **17**, 336 (1935).

(3) Boedtker and Halse, *Bull. soc. chim.*, **19**, 444 (1916).

(4) Schorger, THIS JOURNAL, **39**, 2671 (1917).

(5) Fieser and Hershberg, *ibid.*, **61**, 1272 (1939).

recrystallized from dilute ethanol. The melting point and mixed melting point was 161–162°. The yield was 3.6 g. (72%). A mixture of 145 g. of hydrogen fluoride, 7 g. of the oxime, and 150 cc. of dry ether was made at 0° and then kept at room temperature for twenty-four hours. After removal of hydrogen fluoride and subsequent recrystallization from a methanol–water solvent, 5 g. of benzanilide representing a 72% yield was obtained. When the reaction was carried out using phosphorus pentachloride as the agent for the isomerization, 8 g. of the oxime gave 7.2 g. of the anilide.

Fries Rearrangement of Phenyl Acetate.—A solution of 33 g. of the ester in 75 cc. of pentane was placed in a copper bomb; 20 g. of hydrogen fluoride was added, the vessel sealed and heated for twenty-four hours at 100°. The mixture was then poured onto ice and neutralized. The dark red organic layer was ether extracted, dried, and distilled; 11 g. of an impure solid fraction was obtained which after recrystallization from ligroin melted at 108–110°. It was converted to the semicarbazone in the usual way. The derivative melted at 195–198°. When admixed with a sample of the semicarbazone of *p*-hydroxyacetophenone, m. p. 198–199°, there was no depression in melting point.

Rearrangement of *p*-Cresyl Benzenesulfonate.—Ten grams of the ester was dissolved in 400 cc. of ligroin and placed in a copper bomb; 140 g. of hydrogen fluoride was added, the bomb closed and heated at 100° for fourteen hours. The mixture was processed in the previously described manner, the ether solution finally being extracted with a 10% sodium hydroxide solution. Acidification of the latter precipitated 1 g. of the hydroxy sulfone, m. p. 135–136°.

Preparation of 2-Methoxy-4-methyl-diphenyl Sulfone (I).—One-tenth of a mole of *p*-cresol methyl ether and one-tenth mole of benzenesulfonyl chloride were dissolved in 50 cc. of carbon disulfide. To this solution, 15 g. of aluminum chloride was added gradually. When the catalyst had all been added, the mixture was refluxed on the steam-bath for five hours, and the solvent was removed. The residue was cooled and dilute hydrochloric acid was added cautiously. The organic solid which remained was washed with water by decantation, filtered, washed again, and then recrystallized from dilute ethanol to give 18.5 g. of the sulfone, m. p. 137–138°. The yield was 71% of the theoretical.

Anal. Calcd. for $C_{14}H_{14}O_3S$: S, 12.21. Found: S, 11.84.

Preparation of 2-Hydroxy-4-methyl-diphenyl Sulfone (II).—Six grams of aluminum chloride was intimately mixed with 3 g. of the methoxy sulfone (I), placed in a 50-cc. round-bottomed flask, and heated in an oil-bath to 140°. The temperature was maintained at 140–150° for two hours. Upon cooling, the mixture was treated with dilute hydrochloric acid and thoroughly freed from attendant salts. The mass was then dissolved in 10% sodium hydroxide, the solution filtered, and then acidified. The precipitated hydroxy sulfone was recrystallized from diluted ethyl alcohol to give 2.6 g. of pure sulfone, m. p. 137–138°. From the mother liquor there was obtained another 0.1 g. of pure sulfone, making the total yield 95% of the theoretical.

A mixed m. p. determination with the sulfone obtained from the rearrangement was 136–137°. A mixture of the hydroxy and methoxy sulfones (I and II) melted at 105–112°.

Summary

Hydrogen fluoride has been used to effect a number of exchange reactions or rearrangements of organic compounds. The following are examples: *t*-butylbenzene reacted with phenol to form *t*-butylphenol and benzene. Benzophenone oxime rearranged to benzanilide. Phenyl acetate rearranged to *p*-hydroxyacetophenone. *p*-Cresyl benzenesulfonate rearranged to 2-hydroxy-4-methyl-diphenyl sulfone.

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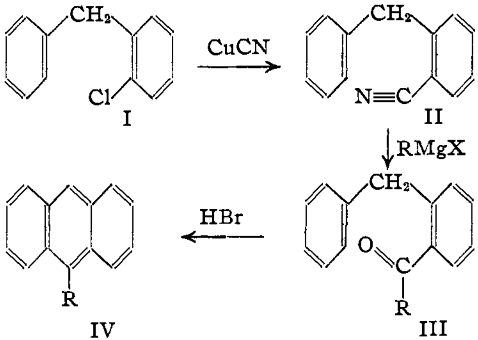
A New Route to 9-Alkyl- and 9-Arylanthracenes

BY CHARLES K. BRADSHER

Recently Bergmann[1] observed that hydrolysis of the acetal of *o*-benzylbenzaldehyde in boiling hydrochloric acid gave not only the expected aldehyde (III, R = H), but also a small amount of anthracene. From this observation and from considerations which we shall discuss later, we concluded that *o*-benzyl phenyl ketones (III) should cyclize to form 9-alkyl- and 9-arylanthracenes (IV).

The required ketones were obtained from



(R = CH_3, C_2H_5, C_6H_5)

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(1) E. Bergmann, *J. Org. Chem.*, **4**. 1 (1939).