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.

STATE COLLEGE, PA. RECEIVED DECEMBER 6, 1939

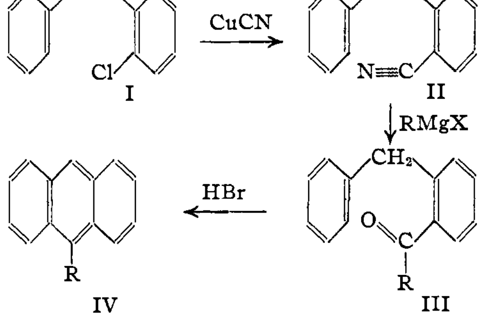
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

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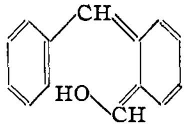
[1] E. Bergmann, *J. Org. Chem.*, **4**, 1 (1939).

o-benzylbenzonitrile (II) by the Grignard reaction. The nitrile (II) was prepared by two methods, the first of which, the action of lead thiocyanate on *o*-benzylbenzoic acid, did not seem capable of wide application and was discarded in favor of the action of cuprous cyanide on *o*-chlorodiphenylmethane (I). The latter compound was prepared by reduction of the benzohydrol obtained when phenylmagnesium bromide was allowed to react with *o*-chlorobenzaldehyde.[2] One would expect that Grignard reagents from a wide variety of aryl halides might be substituted for phenylmagnesium bromide, providing a means for the synthesis of a number of *o*-chlorodiphenylmethanes.

Three *o*-benzylphenyl ketones (III) were prepared, the phenyl, the methyl and the ethyl, of which only the first has been prepared previously.[1] Cyclization was effected by refluxing the ketones for four days in a mixture of hydrobromic and acetic acids. The expected hydrocarbons (IV) were obtained in yields ranging from 69% in the case of the ethyl ketone (III, R = C_2H_5) to 80% in the case of the methyl (III, R = CH_3). It is interesting to note that the phenyl ketone (IV, R = C_6H_5), despite the greater size of the phenyl group, cyclizes in a yield (75%) comparable with that of the alkyl ketones.

Bergmann[1] regarded the cyclization of *o*-benzylbenzaldehyde as a "modification of the Elbs synthesis of anthracene derivatives" and proposed a mechanism based on that advanced by Cook[3] for the latter reaction.

In our opinion, the cyclization of the aldehyde may be better understood if comparison is made instead with two other reactions which take place under similar conditions, *i. e.*, in boiling mineral acids. The first is the ring closure used by us in the synthesis of phenanthrene derivatives and for which we have recently proposed as an intermediate, a carbonyl compound of type VI[4] (here written in the enol form). The other comparable reaction is the formation of β-phenylnaphthalene from two molecules of phenylacetaldehyde. Carter and Van Loon[5] have suggested that the intermediate in this reaction is the enol VII. If *o*-benzylbenzaldehyde is represented in the enol form and this structure compared with those of the proposed intermediates, it will be seen that the feature common to all three is the β-(β-styryl)-vinyl alcohol system (VIII). It seems reasonable that the terminal hydroxyl on such a completely conjugated system would activate the *ortho* position of the aromatic ring so that cyclization could take place with the loss of water.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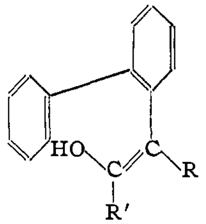
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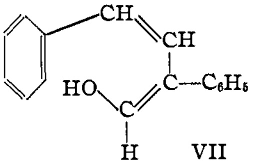
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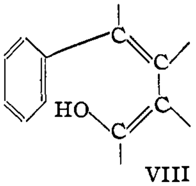
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Although perfectly aware that the sum of these speculations does not constitute a proof, we do consider that the assumption of such an intermediate forms a satisfactory working hypothesis. Further, by assuming that cyclization is preceded by enolization[6] we may explain the slow rate at which the anthracene hydrocarbons are formed since it would not be expected that *o*-benzylphenyl ketones would exist in the enolic form to any great extent.

A further study is being made of compounds containing the β-(β-styryl)-vinyl alcohol system, and work is in progress on the extension of the synthesis reported in this paper to the preparation of 1,2-benzanthracene derivatives.

Experimental

_o_-Chlorobenzohydrol was prepared by the action of phenylmagnesium bromide on *o*-chlorobenzaldehyde by a procedure essentially that of Tschitschibabin and Sheshler.[2] It was obtained as a colorless oil of b. p. 170–176° (5 mm.) and in a yield of 76%. The material crystallized on standing, m. p. 62–65°.

_o_-Chlorodiphenylmethane (I).—A mixture of 49.7 g. of *o*-chlorobenzohydrol, 10 g. of iodine, 10 g. of red phosphorus, 500 cc. of acetic acid and 50 cc. of water was refluxed for twenty-nine hours. The excess red phosphorus was then filtered off and the filtrate poured on ice and extracted with ether. The ethereal extract was washed with ice-cold 10% sodium hydroxide solution to remove the acids and the free iodine. The solution was dried, concentrated and the residue distilled under re-

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(2) This synthesis of *o*-chlorodiphenylmethane is essentially that used previously by Tschitschibabin and Sheshler, *J. Russ. Phys.-Chem. Soc.*, **56**, 149 (1925).

(3) Cook, *J. Chem. Soc.*, 487 (1931).

(4) Bradsher, THIS JOURNAL, **61**, 3131 (1939).

(5) Carter and Van Loon, *ibid.*, **60**, 1077 (1938).

(6) It should be pointed out that the Bergmann mechanism likewise involves enolization as its first step.

duced pressure. The fraction boiling at 144° (5 mm.) weighed 37.4 g. (81%) and was water-white.

o-**Benzoylbenzonitrile (II).** (a) **From *o*-Benzoylbenzoic Acid.**—The nitrile was prepared by the method of Bergmann[1] in yields of 35–50%.

(b) **From *o*-Chlorodiphenylmethane.**—By heating *o*-chlorodiphenylmethane with 10.8 g. of cuprous cyanide for twenty-three hours at 250°, and working up the product in the usual manner, the nitrile was obtained as a colorless oil, b. p. 160–164° (4 mm.); yield 10.3 g. (54%). A fore-run of *o*-chlorodiphenylmethane (4.6 g.) was recovered.

o-**Benzylacetophenone (III, R = CH_3).**—A Grignard reagent was prepared in ether from 28.4 g. of methyl iodide and 5.4 g. of magnesium. Most of the ether was distilled off, 14.6 g. of *o*-benzylbenzonitrile added in 100 cc. of dry benzene, and the solution refluxed overnight. The mixture was decomposed by the addition of 20% ammonium chloride solution and the benzene layer separated. This layer was extracted with ice-cold 2 *N* hydrochloric acid, the acid layer separated, refluxed for one hour to hydrolyze the imine hydrochloride, cooled and extracted with ether. The ethereal extract was evaporated and the residue distilled under reduced pressure. The ketone, a yellow oil, b. p. 167° (5 mm.), crystallized on standing; yield 11.5 g. (72%). A sample recrystallized from petroleum ether was obtained as white needles, m. p. 49–50°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.5.; H, 6.8.

9-Methylanthracene (IV, R = CH_3).—A mixture of 2 g. of *o*-benzylacetophenone, 20 cc. of acetic acid and 20 cc. of 34% hydrobromic acid was refluxed for four days. Upon cooling, the product solidified and was collected and recrystallized from methanol. It was obtained as flat yellow needles, m. p. 80–81°; yield 1.45 g. (80%). The melting point was not raised by repeated recrystallization.

Anal. Calcd. for $C_{15}H_{12}$: C, 93.7; H, 6.3. Found: C, 93.4; H, 6.4.

o-**Benzylpropiophenone (III, R = C_2H_5).**—This ketone was prepared by the action of an excess of ethylmagnesium bromide on *o*-benzylbenzonitrile in a manner analogous to that employed in the synthesis of *o*-benzylacetophenone. The product was a yellow oil, b. p. 156° (3 mm.), and was obtained in a yield of 73%.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.2. Found: C, 85.6; H, 7.3.

The phenylhydrazone was prepared by refluxing the ketone for three hours with phenylhydrazine in alcohol. Recrystallized from alcohol, it was obtained as white needles, m. p. 97–98°. These were unstable and decomposed on standing for two days.

9-Ethylanthracene.—This hydrocarbon was obtained by refluxing 2.05 g. of the above ketone with acetic and hydrobromic acids in a manner analogous to that employed in the synthesis of 9-methylanthracene. The product, recrystallized from methanol, was obtained as yellowish irregular plates, m. p. 58–59°; yield 1.3 g. (69%).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.2; H, 6.8. Found: C, 93.0; H, 7.1.

o-**Benzylbenzophenone** was prepared by the method used in the preparation of the other two ketones, except that hydrolysis of the imine hydrochloride required two hours of refluxing. The product was obtained as a yellow, very slightly fluorescent oil,[7] b. p. 199–200° (3 mm.) and in a yield of 82%. On seeding, the ketone crystallized to a yellowish solid, m. p. 50–52°.

9-Phenylanthracene was prepared by refluxing 2.06 g. of the above ketone with acetic and hydrobromic acids as in the preparation of the other hydrocarbons. The product formed fluorescent plates on crystallization from ethanol, m. p. 154–155°; yield 1.44 g. (75%). Upon concentration of the mother liquor, an additional 0.1 g. was obtained, m. p. 153–155°.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.5; H, 5.5. Found: C, 94.4; H, 5.8.

Summary

A new and general method has been found for the synthesis of 9-substituted anthracene hydrocarbons.

The theory has been presented that the cyclization involved is one characteristic of the β-(β-styryl)-vinyl alcohol system.

DURHAM, NORTH CAROLINA
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[7] Bergmann, ref. 1, who prepared this ketone by refluxing the imine hydrochloride for *six* hours with dilute hydrochloric acid, reported that the oil had an intense green fluorescence. This difference undoubtedly is due to the formation of more 9-phenylanthracene during the longer period of refluxing.