Anal. Calcd. for $C_{18}H_{14}S$: C, 82.40; H, 5.38; S, 12.22. Found: C, 82.64; H, 5.52; S, 12.21.

The **picrate** was prepared from the above purified sample and crystallized from alcohol. It formed purplish black microneedles, m. p. 135.5–137°.

Anal. Calcd. for $C_{18}H_{14}S \cdot C_6H_3O_7N_3$: N, 8.55. Found: N, 8.33.

When the synthesis was repeated using the quinone resulting from cyclization of the pure higher melting keto acid (II), the same dimethyl compound was produced; melting point and mixed melting point, 157–159° (found: C, 82.17; H, 5.70).

Methylmethoxymethylbenzthiophanthrene.—This substance was first encountered in an early experiment in which the solution obtained from methylmagnesium iodide and the benzthiophanthrenequinone mixture was treated at 0° with methanol and a few drops of concentrated hydrochloric acid. Processing of the tarry reaction mixture afforded a small amount of a solid product which after purification from methanol formed pale yellow needles, m. p. 121–122°.

Anal. Calcd. for $C_{19}H_{16}OS$: C, 78.05; H, 5.51. Found: C, 78.12; H, 5.44.

An ether of the same melting point and mixed melting point was later obtained in 25% yield from the quinone by treatment of the iodo compound with sodium methoxide in hot methanol. The most likely structure is that of 4-methyl-9-methoxymethyl-5,6-benzthiophanthrene.

Summary

A novel sequence of reactions which provides a very convenient route to 9,10-dimethyl-1,2-benzanthracene and related compounds was encountered in the course of an unsuccessful attempt to apply known methods of synthesis to the problem of preparing thiophene isologs of certain carcinogenic hydrocarbons. The Grignard derivative resulting from the action of methylmagnesium iodide on 1,2-benzanthraquinone, when treated directly with methanol, hydriodic acid and acetic acid, affords 9-methyl-10-iodomethyl-1,2-benzanthracene, and this can be reduced very smoothly to the hydrocarbon with stannous chloride in dioxane.

The intermediate 10-iodomethyl compound was also synthesized in 90% yield by a second novel reaction consisting in the iodomethylation of 9-methyl-1,2-benzanthracene.

The first series of reactions was applied successfully to the synthesis of 4,9-dimethyl-5,6-benzthiophanthrene, although some complications arose from the occurrence of a keto acid rearrangement in the cyclization reaction employed for the preparation of the benzthiophanthrenequinone required as starting material.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Alkylation of Benzene with *d*-*s*-Butyl Alcohol

BY CHARLES C. PRICE AND MARION LUND

The purpose of the present investigation was to determine the stereochemical course for certain cases of alkylation of the Friedel–Crafts type involving reactions at an asymmetric carbon atom. The boron fluoride and aluminum chloride catalyzed alkylations of benzene with *s*-butyl alcohol were chosen since, in each case, the reaction has been reported to proceed without isomerization of the alkyl group.[1]

The alkylation of benzene with *dl*-*s*-butyl alcohol in the presence of one equivalent of either of these catalysts gave *dl*-*s*-butylbenzene in yields of 50–60%. In two experiments using *d*-*s*-butyl alcohol ($[\alpha]^{20}D$ +11.05° and +11.36°) with boron fluoride as the catalyst, the *s*-butylbenzene formed was levorotatory ($[\alpha]^{20}D$ −0.15° and −0.16°) but with aluminum chloride as the catalyst the product was a racemic mixture.

The sign of rotation of the active *s*-butylbenzene does not necessarily indicate the configuration of the asymmetric carbon atom involved, although the change of sign during alkylation would at least lead one to suspect the possibility of a Walden inversion. It is interesting to note in this connection that Sprung and Wallis[2] observed no change in the sign of rotation after the rearrangement of the *s*-butyl group in *d*-*s*-butyl phenyl, *m*-cresyl and *p*-cresyl ethers by mixtures of sulfuric and acetic acids or zinc chloride and acetic acid. Here again, of course, the sign of rotation may have no relation to the configuration of the asymmetric carbon atom. Both cases,

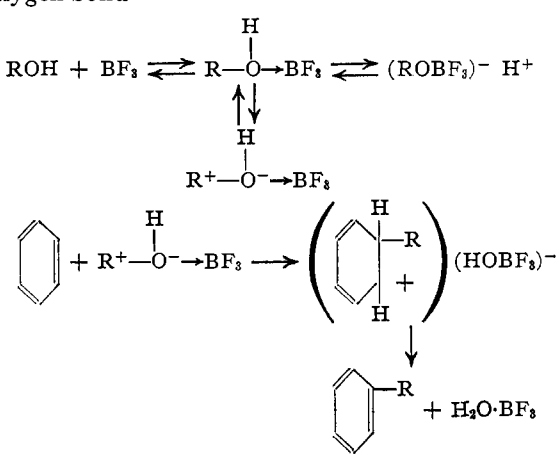
(1) (a) McKenna and Sowa, THIS JOURNAL, **59**, 470 (1937); (b) Huston and Hsieh, *ibid.*, **58**, 439 (1936).

(2) Sprung and Wallis, *ibid.*, **56**, 1715 (1934); Gilbert and Wallis, *J. Org. Chem.*, **5**, 184 (1940).

however, involve scission of an alkyl-oxygen bond followed by substitution of the alkyl group on a carbon atom of an aromatic ring.

In the rearrangements of the aralkyl ethers, Sprung and Wallis were able to conclude that racemization occurred during the rearrangements since samples from different reactions showed varying degrees of activity. In our case, since the samples of active hydrocarbon showed the same activity, a final decision as to the extent of racemization must await the preparation of pure optically active *s*-butylbenzene.

The preservation of the activity of the asymmetric carbon atom of *d*-*s*-butyl alcohol during the boron fluoride catalyzed alkylation of benzene cannot be accounted for on the basis of the intermediate formation of an olefin,[1a,3] a possibility which, it has already been pointed out, does not exist in the case of methylation and benzylation.[4] It would also seem improbable that the alcohol–catalyst complex could actually ionize to give a free alkyl cation[4b]; the activating effect of the catalyst must serve rather to polarize the carbon–oxygen bond



The complete lack of optical activity when aluminum chloride was used as the catalyst may indicate a significant difference in mechanism from that outlined above. It has been suggested by Norris and Sturgis[5] that in this case the reaction proceeds through the intermediate formation of an alkyl halide.

$$ROH + AlCl_3 \longrightarrow HCl + ROAlCl_2 \quad (1)$$

$$ROAlCl_2 \longrightarrow RCl + AlOCl \quad (2)$$

$$RCl + C_6H_6 \xrightarrow{AlCl_3} RC_6H_5 + HCl \quad (3)$$

Since step (3) frequently involves isomerization of the alkyl group, *e. g.*, *s*-butyl to *t*-butyl, it must also obviously result in racemization. Presumably the second step could also result in racemization since it, too, involves reaction at the asymmetric carbon atom.

In an attempt to test whether steps (1) or (2) might lead to racemization, *s*-butyl alcohol was treated with a molar ratio of aluminum chloride at room temperature for fifteen hours, conditions identical with those used in alkylation. After addition of water, however, only traces of alcohol and no alkyl halide were obtained, in contrast to the results reported for the simpler alcohols.[5] The chief product in the present case was a dark brown non-volatile polymer. This suggests that, in spite of the evidence presented by Norris and Sturgis,[5] alkylation using an alcohol with aluminum chloride may proceed by a mechanism other than that outlined by these authors.

Treatment of the alcohol with boron fluoride under the conditions used for alkylation yielded only polymeric material, in agreement with the observation of Whitmore and Laucius[6] that isopropyl alcohol formed a polymer with boron fluoride. It is interesting to note, however, that cyclohexanol, which is as effective an alkylation agent as isopropyl or *s*-butyl alcohol, can be recovered in practically quantitative yield after even more vigorous treatment with boron fluoride.[4b]

Experimental

d-*s*-**Butyl alcohol** was prepared according to the method of Viditz[7] using the modifications suggested by Sprung and Wallis.[2] The brucine salt of *s*-butyl hydrogen phthalate melting above 156° was hydrolyzed to give satisfactory samples of the *d*-alcohol, b. p. 99°, $[\alpha]^{20}D$ +11.05° to +11.46°.[8]

dl-*s*-**Butylbenzene.**—Forty grams (0.3 mole) of aluminum chloride and 170 cc. of thiophene-free benzene were stirred in an ice–salt-bath while 30 cc. (23 g., 0.32 mole) of *dl*-*s*-butyl alcohol (b. p. 99°) was added at such a rate that the temperature of the reaction mixture did not rise above 5° (about forty-five minutes was required). After two hours, the mixture was allowed to warm to room temperature for twelve hours and then decomposed with ice and hydrochloric acid. The pale yellow benzene layer was washed, dried, and fractionally distilled to give 25.0 g. (58.2%) of *s*-butylbenzene, b. p. 61–62° (18 mm.), $n^{20}D$ 1.4892.

A parallel experiment with 23 g. of *d*-*s*-butyl alcohol ($[\alpha]^{20}D$ +11.46°) gave 21.3 g. (49.7%) of *dl*-*s*-butylbenzene, b. p. 61° (18 mm.), $n^{20}D$ 1.4893, $[\alpha]^{20}D$ 0.00°.

(3) McKenna and Sowa, THIS JOURNAL, **59**, 1204 (1937).

(4) (a) Bowden, *ibid.*, **60**, 645 (1938); (b) Price and Ciskowski, *ibid.*, **60**, 2499 (1938).

(5) Norris and Sturgis, *ibid.*, **61**, 1413 (1939).

(6) Whitmore and Laucius, *ibid.*, **61**, 973 (1939).

(7) Viditz, *Biochem. Z.*, **259**, 194 (1933).

(8) All rotations recorded were observed with the pure liquids in a 2-dm. tube.

When 23 g. of *dl*-*s*-butyl alcohol in 100 cc. of ordinary benzene was treated with boron fluoride, the mixture turned lavender. After 16 g. of catalyst had been absorbed, a vigorous reaction occurred and two layers separated. After standing overnight, the mixture was washed, dried and fractionaly distilled; yield, 24 g. (55.9%), b. p. 61–62° (18 mm.), $n^{20}D$ 1.4880. The discrepancy in refractive index seems to arise from impurity in the benzene (thiophene), since using thiophene-free benzene or washing the impure product with cold concentrated sulfuric acid gave material with the correct physical properties. Fractional distillation was ineffective in removing the impurity from the product, and it is interesting to note that the impurity does not alter the molecular refractivity of the *s*-butylbenzene.

l-*s*-**Butylbenzene.**—When 23.0 g. of *d*-*s*-butyl alcohol ($[\alpha]^{20}D$ +11.36) was condensed with thiophene-free benzene as above, using boron fluoride as the catalyst, 20.3 g. (48%) of *l*-*s*-butylbenzene was obtained, b. p. 61° (18 mm.), $n^{20}D$ 1.4891, $[\alpha]^{20}D$ −0.16° (observed rotation −0.27°). The properties of this material were unaffected by washing with cold concentrated sulfuric acid, by refractionation or by standing for over a month.

A preliminary experiment using ordinary benzene and *d*-*s*-butyl alcohol ($[\alpha]^{20}D$ +11.05) gave optically active material, but, as with the other products using ordinary benzene, it had a low index of refraction ($n^{20}D$ 1.4848, d^{20}_4 0.8558, $M^{20}D$ (calcd.) 44.79, $M^{20}D$ (found) 44.86, $[\alpha]^{20}D$ −0.16). Washing with cold concentrated sulfuric acid raised the index of refraction without affecting the optical activity ($n^{20}D$ 1.4880, d^{20}_4 0.8612, $M^{20}D$ (calcd.) 44.79, $M^{20}D$ (found) 44.82, $[\alpha]^{20}D$ −0.15°).

Summary

The alkylation of benzene with *d*-*s*-butyl alcohol using boron fluoride as a catalyst yielded *s*-butylbenzene which was levo-rotatory. With aluminum chloride as a catalyst the product was racemic.

URBANA, ILLINOIS RECEIVED AUGUST 1, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AND CHEMISTRY, WORCESTER POLYTECHNIC INSTITUTE]

Indicator Properties of 8-Hydroxyquinoline-5-sulfonic Acid and its Derivatives

BY HARRY B. FELDMAN AND ARNET L. POWELL[1]

Van Urk[2] has investigated the indicator properties of 7-iodo-8-hydroxyquinoline-5-sulfonic acid, a compound used in medicine. It acts as a monochromatic amphoteric indicator with a maximum color intensity at *p*H 4. The decrease in color intensity with increase or decrease in *p*H suggests the application of indicators of this type in the field of *p*H measurements.

In the present work the indicator properties of 8-hydroxyquinoline-5-sulfonic acid, the parent acid of the above compound, as well as some of its derivatives were determined.

Experimental

Materials.—8-Hydroxyquinoline-5-sulfonic acid was prepared by sulfonation of 8-hydroxyquinoline in the cold using the method of Claus and Posselt.[3] The final product, after recrystallization from dilute hydrochloric acid, was washed free of chlorides and dried at 98°. Its decomposition point was found to be 300°.

7-Iodo-8-hydroxyquinoline-5-sulfonic acid was obtained from the Eastman Kodak Co., who stated that its purity, based on the iodine content, was 98–99.5%.

7-Bromo-8-hydroxyquinoline-5-sulfonic acid and 7-chloro-8-hydroxyquinoline-5-sulfonic acid were prepared by bromination and chlorination, respectively, of 8-hydroxyquinoline-5-sulfonic acid.[4] *Anal.* Calcd. for $C_9H_6O_4NSBr$: Br, 26.28. Found: Br, 25.07. Calcd. for $C_9H_6O_4NSCl$: Cl, 13.66. Found: Cl, 12.63.

6-Methyl-8-hydroxyquinoline-5-sulfonic acid was prepared starting with 6-methylquinoline. The latter was sulfonated using the method of Lubavin[5] to form 6-methylquinoline-8-sulfonic acid which was converted to 6-methyl-8-hydroxyquinoline by fusion with sodium hydroxide according to Fischer and Willmack.[6] Isolation of the product from the fusion mass by crystallization from alcohol was found unsatisfactory but was accomplished by depositing the product by sublimation on the bottom of a beaker filled with cold water. Sulfonation of this product by the method of Claus and Posselt[3] yielded 6-methyl-8-hydroxyquinoline-5-sulfonic acid which had a melting point of 210°, identical with that given in the literature.[7]

Buffer solutions in the range of *p*H less than 2 were prepared by dilution of 0.1 *N* hydrochloric acid. McIlvaine's standard buffer solutions prepared from citric acid and disodium phosphate were used for the *p*H range 2.2 to 8.0 and solutions of *p*H 9.2, 10.0, and 11.0 were prepared from Kolthoff and Vlesschhouwer's alkaline soda–borax buffers. The *p*H of each buffer solution below *p*H 9 was checked electrometrically with the quinhydrone electrode.

(1) The material presented in this paper constitutes a portion of the thesis presented by Arnet L. Powell to the Faculty of Worcester Polytechnic Institute in partial fulfillment of the requirements for the degree of Master of Science.

(2) H. W. van Urk, *Z. anal. Chem.*, **77**, 12 (1929).

(3) Claus and Posselt, *J. prakt. Chem.*, [2] **41**, 33 (1889).

(4) German Patent 73,145; *Friedlaender, Fortschritte der Theerfarbenfabrikation*, **3**, 966.

(5) Lubavin, *Ber.*, **2**, 400 (1869).

(6) Fischer and Willmack, *ibid.*, **17**, 441 (1884).

(7) German Patent 84,063; *Friedlaender, Fortschritte der Theerfarbenfabrikation*, **4**, 1146.