Experimental

Skraup Reaction with *m*-Trifluoromethylaniline.—To a mixture of 64.4 g. (0.40 mole) of *m*-trifluoromethylaniline[1] and 120 g. (1.3 moles) of glycerol was added 56.5 g. (0.40 mole) of arsenic acid and 110 g. (1.1 moles) of concentrated sulfuric acid. The reaction mass was shaken well before being placed under a reflux condenser. The mixture was heated cautiously until the reaction started, and then the burner was removed. When the initial reaction had subsided, the mixture was refluxed for four hours by heating on a sand-bath. After cooling, the contents were poured into one liter of cold water and allowed to stand overnight. The solution was partially neutralized with 65 g. of solid sodium hydroxide, filtered, and after complete neutralization extracted three times with ether. The total volume of the ether extracts was 800 cc. After drying the ether solution over calcium chloride, and removing the ether by distillation, the quinoline compounds distilled over the range 80–100° (3 mm.), and the yield was 44.5 g. (56.5%).

7-Trifluoromethylquinoline.—Upon redistillation at atmospheric pressure, the fraction (10 g., 12.7%) distilling between 205–218° consisted chiefly of 5-trifluoromethylquinoline; and the fraction (34 g., 43%) distilling over at 218–225° was largely 7-trifluoromethylquinoline. When the latter, higher-boiling fraction was cooled, crystallization set in. Recrystallization from 60% ethanol gave a product melting at 66–68°. Redistillation of these crystals gave 7-trifluoromethylquinoline which boiled at 219–221° (731 mm.). The yield of pure compound was 25 g. or 31.8%.

Anal. Calcd. for $C_{10}H_6NF_3$: N, 7.11. Found: N, 6.91 and 7.01.

The compound was hydrolyzed by refluxing 0.5 g. in 10 cc. of 80% sulfuric acid for three hours on a sand-bath.[2] After neutralization with sodium hydroxide and recrystallization from water the 7-quinolinecarboxylic acid melted at 246–247° (cor.). The melting point reported by Skraup and Brunner[3] is 247°.

5-Trifluoromethylquinoline.—The fraction distilling between 205–218° was first partially purified by forming the oxalic acid salt in ethanol. To the salt (which melted between 120–126°) was added water and ether, and then 20% potassium hydroxide. The ether layer was separated, dried over calcium chloride, and the ether removed by distillation. The 5-trifluoromethylquinoline distilled at 214–215° (732 mm.); d^{32}_4 1.272; n^{32}_D 1.528. The yield of pure product was 4.5 g. or 5.7%.

Anal. Calcd. for $C_{10}H_6NF_3$: N, 7.11. Found: N, 7.07.

Hydrolysis, by the procedure used with the 7-isomer, gave 5-quinolinecarboxylic acid which melted at 341–343°. The melting point reported by V. Jakubowski[4] is 338–340°.

2-*p*-Tolyl-7-trifluoromethylquinoline.—To 16.8 g. (0.085 mole) of 7-trifluoromethylquinoline dissolved in 50 cc. of dry ether was added, over a two-hour period with stirring, 64 cc. of an ether solution containing 0.093 mole of *p*-tolyllithium.[5] The mixture was refluxed gently for three hours, and then cooled and poured into 35 g. of ice-water. The ether layer was separated, the water layer was extracted three times with ether, and to the 350 cc. of ether solution was added 10 cc. (0.098 mole) of nitrobenzene. This ether solution was added dropwise to a Claisen flask heated by a boiling water-bath. After the ether was removed, reduced pressure was applied and the nitrobenzene and any initial quinoline compound was separated by distillation. The fraction distilling between 188–195° (6 mm.) was collected (20.2 g. or 83% yield of crude material). Recrystallization from 350 cc. of 95% ethanol gave 15.1 g. or a 61% yield of compound melting at 131–133°.

Anal. Calcd. for $C_{17}H_{12}NF_3$: N, 4.88. Found: N, 4.74.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED AUGUST 19, 1943

---

[1] The *m*-trifluoromethylaniline was prepared by a modification of the method outlined by Swarts, *Bull. acad. roy. Belg.*, [3] **35**, 390 (1898).

[2] This was done in accordance with general directions of Simons and Ramler, THIS JOURNAL, **65**, 389 (1943).

[3] Skraup and Brunner, *Monatsh.*, **7**, 519 (1886).

[4] V. Jakubowski, *Ber.*, **43**, 3027 (1910). Our melting point determination, carried out in a sealed tube, was probably accurate to ±3°.

[5] Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

Sulfonation of Some Naphthalene Derivatives in the Presence of Boron Trifluoride[1]

BY G. F. HENNION AND CLAUDE J. SCHMIDLE

The pronounced catalytic effect of boron trifluoride in the sulfonation of several aromatic compounds was reported some time ago.[2] Since boron trifluoride is one of the strongest acceptor reagents known, it was deemed important to determine whether this new method might result in unusual orientations of the —SO_3H group in typical aromatic donor compounds. Both of the naphthylamines and *β*-naphthol were selected for this purpose to establish the orientation effects of the groups —NH_2:BF_3 and —OH:BF_3.

We wish to report now that the sole function of boron trifluoride in these cases appears to be that of a strong dehydrating catalyst since the ordinary sulfonic acid derivatives were formed. Thus while no unusual directing influence was observed, improved yields of clean products were obtained quickly at somewhat lower temperatures than ordinarily used.

Experimental

Sulfonation of *α*-Naphthylamine.—Thirty-six grams of the amine was sifted into 144 g. of concentrated sulfuric acid in a three-necked flask equipped with a mechanical stirrer, thermometer and inlet tube. Boron trifluoride (26 g.) was admitted at 75–80°, the absorption requiring about one hour. The product was diluted with 300 cc. of cold water. The crystalline deposit left only 5 g. of unreacted amine when extracted with 2 *N* sodium hydroxide, indicating about 86% sulfonation. The product was essentially naphthionic acid as shown by comparison with an authentic sample.[3]

A control experiment, performed in exactly the same manner but without boron trifluoride, showed 60% sulfonation.

Sulfonation of *β*-Naphthylamine.—Forty-eight grams of the amine sulfate was treated with 134 g. of concentrated sulfuric acid and allowed to absorb 85 g. of boron trifluoride at 50–55° during thirty minutes. After another thirty minutes, sulfonation was 95% complete. The crude dry sodium salts were fractionated by extraction with boiling alcohol. The insoluble portion (48%) was identified as the 8-sulfonic acid.[4] The alcohol soluble material proved to be the 5-sulfonic acid (52%). The benzyl-iso-thiouronium salts melted at 102–103° and 172–174°, respectively.

---

[1] Paper XXIX on organic reactions with boron trifluoride; previous paper, *ibid.*, **65**, 1603 (1943).

[2] Thomas, Anzilotti and Hennion, *Ind. Eng. Chem.*, **32**, 408 (1940).

[3] The benzyl-iso-thiouronium derivative melted at 103–104° and the mixed m. p. with a sample made from authentic naphthionic acid was 102–104°. Since these compounds were not analyzed, it should be noted that Chambers and Watt, *J. Org. Chem.*, **6**, 376 (1941), report 195° for the melting point.

[4] Green and Vakil, *J. Chem. Soc.*, **113**, 35 (1918).

Sulfonation at 20° gave a product which was about 56% 8-sulfonic acid and 44% the 4-isomer; at 80° the composition was 33% of 8- and 67% 5-acid.

A control experiment without boron trifluoride at 75–80° indicated 52% sulfonation based on recovered β-naphthylamine.

Sulfonation of β-Naphthol.—Twenty-nine grams was sifted into 116 g. of sulfuric acid previously saturated with boron trifluoride. The naphthol was added during ten minutes and the treatment with boron trifluoride continued for two hours at 80–90° when 22 g. had been absorbed. Dilution with water gave a clear orange-red solution. Examination of the sodium, barium and β-naphthylamine[5] salts indicated that the chief material is the 3,6-disulfonic acid.

---

[5] Forster and Keyworth, *J. Soc. Chem. Ind.*, **46**, 26T (1927).

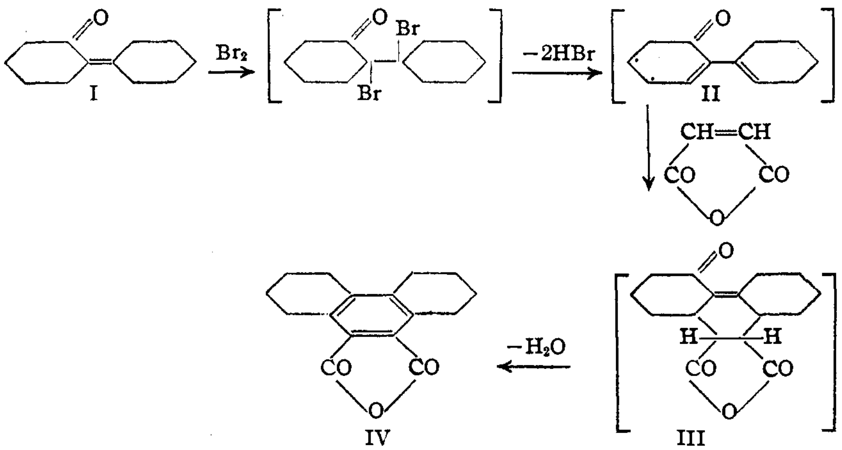
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

RECEIVED SEPTEMBER 13, 1943

A Novel Preparation of *sym*-Octahydrophenanthrene-9,10-dicarboxylic Anhydride

BY CHARLES C. PRICE, MARTIN KNELL AND JAMES P. WEST

The ready availability of 2-cyclohexylidenecyclohexanone (I) through the hydrogen chloride-catalyzed condensation of cyclohexanone with itself[1] suggested the possibility that this compound might be a useful raw material for the synthesis of hydrophenanthrene derivatives. For example, the addition of bromine to the double bond[2] followed by dehydrohalogenation[3] should form 2-ketobicyclohexenyl (II).



Since the diene system of bicyclohexenyl itself is capable of undergoing a normal Diels–Alder condensation with maleic anhydride,[4] it was anticipated that treatment of II with maleic anhydride should yield 4-keto-*sym*-dodecahydro-9,10-phenanthrenedicarboxylic anhydride (III).

All attempts to isolate 2-ketobicyclohexenyl from the bromination and dehydrohalogenation of 2-cyclohexylidenecyclohexanone have failed. Evidently the compound is susceptible to polymerization, even at room temperature, since the only product obtainable was a non-volatile, pale tan, thermoplastic resin.

It was possible to carry out the Diels–Alder reaction with II only as formed in the reaction mixture. 2-Cyclohexylidenecyclohexanone was brominated in the cold (dry ice–acetone bath), maleic anhydride was then added and the mixture was allowed to warm slowly to room temperature. By this procedure, 2-cyclohexylidinecyclohexanone was converted to *sym*-octahydrophenanthrene-9,10-dicarboxylic anhydride (IV, 16% yield) identical with the material reported by Weidlich.[5]

A blank experiment showed the bromine to be essential since, in its absence, the starting materials, 2-cyclohexylidenecyclohexanone and maleic anhydride, were recovered unchanged.

Since the expected keto-anhydride III was not isolated, the initial addition of maleic anhydride to II may well have followed some other course than that indicated in the equations.

Experimental

2-Cyclohexylidenecyclohexanone (I).—Dry hydrogen chloride was passed into freshly distilled cyclohexanone (320 g.) cooled in an ice-bath and the resulting crystalline mass was shaken with 10% sodium hydroxide according to Rapson's directions.[1b] Ether extraction and vacuum distillation yielded 200 g. (70%) of 2-cyclohexylidenecyclohexanone, b. p. 149–150° (22 mm.). The semicarbazone melted at 187–188° (lit., 189–190°).[1a]

Addition of Halogen.—Attempts to add bromine or chlorine, directly or by means of sulfuryl chloride, at temperatures ranging from 25 to −78° under air or nitrogen atmosphere and in chloroform or ether solution gave essentially the same results. Hydrogen halide was eliminated spontaneously and a viscous, deep purple-red oil was formed. On addition of a base such as piperidine or aqueous alkali, the color faded to pale tan but acidification with aqueous hydrochloric acid regenerated the deep purple-red color. The material, either before or after treatment with a base, was non-volatile; even attempts at molecular distillation under 10^{-3} mm. pressure failed. The residue from all attempted distillations was a pale tan, red-green fluorescent, thermoplastic resin. This resin was insoluble in water, phosphoric acid, hydrochloric acid and alkali, sparingly soluble in alcohol and ether and soluble in sulfuric acid. It was essentially halogen-free; one sample was found to contain 0.67% chlorine.

***sym*-Octahydrophenanthrene-9,10-dicarboxylic Anhydride (IV).**—A solution of 13 ml. (0.25 mole) of bromine in 100 ml. of anhydrous ether was added slowly to a stirred solution of 50 ml. (0.25 mole) of 2-cyclohexylidenecyclohexanone in 200 ml. of anhydrous ether. The solution was stirred vigorously and cooled by means of a dry ice–methanol bath. The color of the bromine was discharged instantly, even at this temperature. After the addition of

---

[1] (a) Zelinsky, Schuikin and Fatejew, *J. Gen. Chem.*, U. S. S. R., **2**, 671 (1932). (b) Rapson, *J. Chem. Soc.*, 15 (1941).

[2] See, *e. g.*, Claisen and Claparete, *Ber.*, **14**, 2460 (1881).

[3] See, *e. g.*, Zelinsky and Gorsley, *ibid.*, **41**, 2479 (1908).

[4] Gruber and Adams, THIS JOURNAL, **57**, 2555 (1935).

[5] Weidlich, *Ber.*, **71**, 1208 (1938).