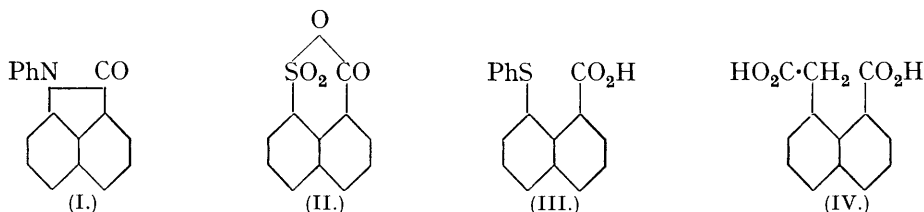


67. Reactivity of peri-Substituted Naphthalenes. Part III. Further Synthetic Reactions of 8-Halogeno-1-naphthoic Acids.

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THE reactivity of the halogen atom in 8-bromo-1-naphthoic acid is attested by the ease with which the compound may be converted, with the aid of copper-bronze catalyst, into alkoxy- and aryloxy-naphthoic acids, naphtholactone, and naphthastyril (Rule and Barnett, J., 1932, 2728; Rule and Brown, J., 1934, 137). As the bromo-acid is now obtainable in excellent yield from commercial naphthalic acid, its use in other syntheses of this type has been studied.

Among nitrogen derivatives it was found that sodioanilide reacted with 8-bromo-naphthoic acid to form *N*-phenylnaphthastyril (I). 8-Bromo-4 : 5-dinitronaphthoic acid



also reacted under pressure with ammonia to give 4 : 5-dinitronaphthastyril. The more basic compounds methylamine and piperidine, however, could not be brought into reaction with bromonaphthoic acid under any of the conditions employed, the only product obtained in the case of methylamine being a small amount of dinaphthyldicarboxylic acid, formed by the removal of bromine from two molecules of the acid.

Aqueous sodium bisulphite rapidly converted the bromo-acid into the corresponding sulphonic derivative, which was most conveniently treated with concentrated sulphuric acid and isolated as *naphthalene-1 : 8-carboxysulphonic anhydride* (II). This compound has been described in a patent by Cassella, G.m.b.H. (*Cent.*, 1927, II, 742), who obtained it from 8-aminonaphthalene-1-sulphonic acid by way of the cyano-derivative. The yields by the latter method are, however, poor owing to the preferential formation of naphthasultone from the diazonium salt. No reaction was observed when the bromo-acid was heated with aqueous sodium hydrosulphide, probably owing to the removal of the copper catalyst as sulphide. The use of sodium thiophenoxide, however, led to the formation of *phenyl 8-carboxy-1-naphthyl sulphide* (III). This compound was subsequently oxidised by hydrogen peroxide to the *sulphoxide*, which was resistant to further oxidation.

Earlier attempts to condense bromonaphthoic acid with sodiomalonic ester having failed (Rule and Barnett, *loc. cit.*), advantage was taken of the recent preparation of 8-iodonaphthoic acid from naphthastyril (Goldstein and Francey, *Helv. Chim. Acta*, 1932, **15**, 1364) to make use of the more reactive iodo-compound. In this way *homonaphthalic acid* (IV) was isolated in small yield. Here also part of the iodo-acid lost halogen with formation of the corresponding dinaphthyldicarboxylic acid.

EXPERIMENTAL.

4 : 5-Dinitronaphthastyril.—A solution of 2 g. of 8-bromo-4 : 5-dinitro-1-naphthoic acid (Rule, Pursell, and Brown, J., 1934, 170) in 30 c.c. of concentrated aqueous ammonia was heated with 0.04 g. of copper bronze, 0.04 g. of potassium chlorate, and 0.5 g. of ammonium nitrate (cf. Rule and Brown, *ibid.*, p. 137) in a glass-lined autoclave at 140—150° for 1 hour. The dark crystalline material was filtered off, washed with water, and recrystallised from glacial acetic acid, giving orange needles, m. p. 307—308°. Yield, 0.6 g.; 39% of the theoretical (Found : N, 16.1. $C_{11}H_5O_5N_3$ requires N, 16.2%).

N-Phenylnaphthastyril.—This was obtained by heating for 4 hours at 140° a mixture of 2 g. of 8-bromo-1-naphthoic acid, 1 g. of copper bronze, and a solution of 0.5 g. of sodium in excess of aniline. On pouring into water, a brown oil was formed, which solidified when the aniline was completely removed with acid. Two crystallisations from ligroin gave 0.5 g. of yellow needles (26% yield), m. p. 104—105° (Found : N, 5.6. $C_{17}H_{11}ON$ requires N, 5.7%). The *phenylnaphthastyril* is moderately easily soluble in the usual organic solvents and in hot concentrated hydrochloric acid. It dissolves in hot, but not in cold, aqueous sodium hydroxide, thus resembling naphthastyril.

8-Bromo-1-naphthanilide, prepared from the acid by use of thionyl chloride, followed by aniline, was found to be dimorphous, separating from benzene in long, fine, colourless needles, m. p. 125—126°, and from alcohol or ligroin in short thick prisms, m. p. 146—147°. Goldstein and Francey (*Helv. Chim. Acta*, 1932, **15**, 1364) record m. p. 151° (from alcohol) (Found : N, 4.4. Calc. for $C_{17}H_{12}ONBr$: N, 4.4%). A mixture of the two forms melted at 145—146°, a slight physical change unaccompanied by fusion occurring at 126°. The compound gave no appreciable yield of phenylnaphthastyril on being heated with copper bronze for 2 hours at 180°.

Naphthalene-1 : 8-carboxysulphonic Anhydride.—A solution of 2 g. of 8-bromo-1-naphthoic acid and 4 g. of sodium bisulphite in 15 c.c. of water was treated with 0.2 g. of copper bronze and boiled under reflux for 4 hours; it was then filtered and evaporated almost to dryness.* Cold concentrated sulphuric acid (about 20 c.c.) was added to the cold product till the whole was uniformly brownish-purple, the temperature rising to about 80°. After cooling, the addition of water threw out a white precipitate—the inorganic material being dissolved. The solid was filtered off, washed, and crystallised from a mixture (1 : 1) of water and glacial acetic acid. The *anhydride* formed colourless prisms, m. p. 152—153°. Yield, 0.85 g. (46%). It is soluble in alcohol and benzene, less soluble in ligroin and carbon tetrachloride (Found : S, 13.6. $C_{11}H_6O_4S$ requires S, 13.7%).

Phenyl 8-Carboxy-1-naphthyl Sulphide.—To 2 c.c. of thiophenol was added 0.5 g. of sodium, and the mixture heated to form sodium thiophenoxide. Thereafter, 5 g. of sodium 8-bromo-1-naphthoate, 0.5 g. of copper bronze, and 30 c.c. of xylene were added and the mixture was boiled under reflux for 40 hours, being vigorously shaken at intervals to break up the particles in suspension. The mixture was cooled, filtered, and extracted with sodium hydroxide. The aqueous layer was separated, and the excess of thiophenol oxidised to diphenyl disulphide by passing air through the solution. Insoluble disulphide was filtered off, and the filtrate acidified with hydrochloric acid. After standing over-night, the sticky material was extracted with hot water (400 c.c.) until hard and free from halogen. It then crystallised from ligroin in prisms, m. p. 131—132° (2 g., 35% yield). The *acid* is sparingly soluble in hot alcohol and ligroin, and in cold acetone, benzene, ether, chloroform and glacial acetic acid (Found : S, 11.4. $C_{17}H_{12}O_2S$ requires S, 11.4%).

Phenyl 8-Carboxy-1-naphthyl Sulphoxide.—A solution of the above sulphide in glacial acetic acid (2 g. in 15 c.c.) was heated on the steam-bath, and an equal volume of hydrogen peroxide ("20 vol.") added slowly. After $\frac{1}{4}$ hour a white crystalline solid began to deposit, and heating was continued for a further $\frac{3}{4}$ hour. The solid was filtered off and recrystallised from aqueous

* Better yields (85%) were subsequently obtained by boiling the dried salts for 4 hours with thionyl chloride, distilling off the reagent, and extracting the residue with benzene.

acetic acid (1 : 1), yielding 1.5 g. of colourless hexagonal plates (71% of the theoretical), m. p. 200—201°. The *sulphoxide* is fairly readily soluble in hot chloroform and in cold acetone, alcohol and acetic acid, but less soluble in hot ligroin, benzene and ether. It is insoluble in hot concentrated hydrochloric acid (Found: S, 10.6, 10.7; *M*, by titration with standard alkali, 295, 297. $C_{17}H_{12}O_3S$ requires S, 10.8%; *M*, 296. The sulphone, $C_{17}H_{12}O_4S$, requires S, 10.3%; *M*, 312). The customary method of preparing a sulphoxide with hydrogen peroxide in the cold (18 hours) yielded a mixture containing only a small amount of sulphoxide; a more vigorous oxidation of the sulphoxide in glacial acetic acid solution at 100° (3 hours) gave an oily mixture, which on purification from ethyl acetate gave only a trace of solid material, m. p. 197—198°. Mixed with the sulphoxide, this melted at 182—185°; it was possibly the sulphone, but could not be isolated in sufficient quantity for analysis, despite variations in the conditions and the use of other reagents.

Homonaphthalic Acid.—8-Iodo-1-naphthoic acid was prepared from naphthastyril (Rule and Brown, J., 1934, 137) by the method of Goldstein and Francey (*loc. cit.*), in 29% yield. To 0.5 g. of sodium dissolved in 5 c.c. of absolute alcohol was added 2 g. of iodonaphthoic acid, 0.2 g. of copper bronze, and 20 c.c. of ethyl malonate. The mixture was heated for 8 hours in an oil-bath at 120° and rendered alkaline, the excess of malonic ester removed in ether, and the aqueous layer acidified. The red oily precipitate was hydrolysed by boiling with sodium hydroxide for 1½ hours and then acidified. The red mass was extracted with 60 c.c. of chloroform, giving a red solution and leaving a brown insoluble powder (0.4 g.). On boiling the powder with benzene, filtering, and recrystallising the solid residue twice from ethyl acetate, it gave colourless plates of *homonaphthalic acid* (0.05 g.), m. p. 213—214° (decomp.). Mixed with 8-ethoxy-1-naphthoic acid (m. p. 210—211°), it melted at 194—196°. *Homonaphthalic acid* is practically insoluble in hot benzene, ligroin, or chloroform; but is moderately easily soluble in cold alcohol, ether, ethyl acetate and acetic acid (Found: C, 67.4; H, 4.3. $C_{13}H_{10}O_4$ requires C, 67.8; H, 4.4%. *peri*-Carboxynaphthylmalonic acid, $C_{14}H_{10}O_6$, requires C, 61.3; H, 3.7%).

On concentration of the above-mentioned chloroform mother-liquors a reddish powder was deposited (0.1 g.), soluble in sulphuric acid to a red-brown solution, turning green on warming. This was identified as carboxybenzobenzanthrone (an intermediate product in the formation of anthanthrone from 8 : 8'-dinaphthyl-1 : 1'-dicarboxylic acid) by mixed m. p. with an authentic specimen (Cassella, G.m.b.H., *Cent.*, 1928, I, 2311).

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