23. *Reactivity of* peri-*Substituted Naphthalenes. Part I. Displacement of the Nitro-group in* 8-*Nitro*-1-*naphthoic Acid by Thionyl Halides to form* 8-*Chloro- and* 8-*Bromo-naphthoic Acids.*

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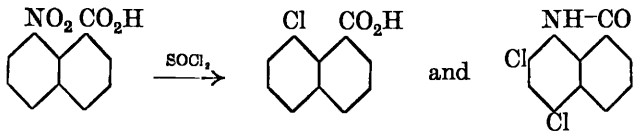
IT was observed by H. Meyer (*Monatsh.*, 1915, **36**, 723) that when certain aromatic nitro-compounds were treated with thionyl chloride under pressure and at high temperatures the nitro-groups became replaced by halogen. More recently, an attempt to prepare the menthyl ester of 8-nitro-1-naphthoic acid by way of the acid chloride led instead to the isolation of the 8-chloro-ester (Rule, Spence, and Bretscher, J., 1929, 2521), since notwithstanding the moderate experimental conditions the nitro-group had been displaced under the influence of the thionyl chloride employed. As considerable interest attaches to the 8-halogenated 1-naphthoic acids owing to the mobility of the group in position 8, it was thought possible that thionyl chloride and bromide might provide a useful means of preparing these compounds from the nitro-derivative.

The 8-chloro-acid has been obtained by Eckstrand (*J. pr. Chem.*, 1888, **38**, 150) from the corresponding nitro-acid by reduction to the amino-compound, followed by the Sandmeyer reaction. This process, however, gives very poor yields and is of little value as a preparative method. In a communication dealing with the mercuration of naphthoic acids, Whitmore and Fox (*J. Amer. Chem. Soc.*, 1929, **51**, 3363; see also Leuck, Perkins, and Whitmore, *ibid.*, p. 1831) remark that " in the course of the study, anhydro-8-hydroxymercuri-1-naphthoic acid obtained from naphthalic acid was changed to the 8-chloro- and the 8-bromo-acids. This is the best available way to obtain the 8-halogen-1-naphthoic acids in quantity and in a high degree of purity." No further details are given, although the previously unknown 8-bromo-acid was apparently obtained in small amount (no analysis is recorded) from the mercuration product of 1-naphthoic acid by treatment in glacial acetic acid solution with bromine at room temperature.

It has now been found that when 8-nitro-1-naphthoic acid is treated with thionyl chloride two reactions occur simultaneously. On the one hand chlorine displaces the nitro-group to form 8-chloro-1-naphthoic acid, and on the other the reducing and chlorinating properties of the reagent convert some of the nitro-acid into dichloronaphthostyril in which the halogen atoms probably occupy the 5- and 7-positions. In this connexion it may be noted that H. Meyer (*loc. cit.*) observed the formation of dichloronaphthalene

when naphthalene was heated with thionyl chloride in a sealed tube at high temperatures. The best conditions for the formation of the



chloro-acid obtain when the reaction is carried out in benzene solution, the yield of pure acid being 26% (or 38% allowing for nitro-acid recovered unchanged). In a similar manner the use of thionyl bromide gave 8-bromo-1-naphthoic acid, although only in 9% yield.

Sulphuryl chloride, which also behaves as a chlorinating agent, differs from thionyl chloride in possessing no reducing properties. In agreement with this difference in chemical nature, when the 8-nitro-acid was heated with sulphuryl chloride no dichloronaphthostyril was formed. The yield of 8-chloro-acid was also very much reduced, despite the more vigorous treatment necessitated by the lower solubility of the nitro-compound in the reagent. In this case much of the nitro-acid was recovered unchanged.

No perceptible esterification occurred when the bromo-acid was heated for 8 hours with methyl alcohol in the presence of hydrogen chloride. This increased steric hindrance offered by *peri*-substituents, as compared with *o*-substituents in benzoic acids, confirms the observations previously made with the nitro- and methoxy-acids (Rule, Spence, and Bretscher, *loc. cit.*). Eckstrand also failed to obtain any esterification under these conditions with the 8-chloro-acid.

Various attempts were made to prepare the iodo-acid by the above method and also by submitting the amino-acid to the Sandmeyer reaction, but in each case without success.

The mobility of the group in the *peri*-position is apparently conditioned by the spatial proximity of the carboxyl group, since 5-nitro-1-naphthoic acid was recovered unchanged after vigorous treatment with thionyl chloride at the boiling point. *o*-Nitrobenzoic acid also remained unaffected by the reagent at the dilution and temperature employed.

For the preparation of the 8-chloro- and 8-bromo-1-naphthoic acids in quantity, however, by far the most satisfactory method is to make use of the mercuration process indicated by Whitmore and Fox. In the hands of the present authors the yields, based on the naphthalic acid used, were 26% for the chloro-acid and 20% for the bromo-derivative. The very low price of the starting material thus renders these interesting compounds readily accessible.

EXPERIMENTAL.

Contrary to the finding of Whitmore and Fox (*J. Amer. Chem. Soc.*, 1929, **51**, 3367) no difficulty was experienced in obtaining moderately good yields of α-naphthonitrile by the Sandmeyer reaction, thus confirming the conclusions of Clarke and Read (*ibid.*, 1924, **46**, 1001) and J. McRae (*ibid.*, 1930, **52**, 4550). For preparation in quantity, however, better yields (33%) were secured by distilling a dry mixture of sodium α-naphthalenesulphonate and potassium ferrocyanide (Eckstrand, *J. pr. Chem.*, 1888, **38**, 139). The nitrile may be converted almost quantitatively into the pure acid by hydrolysis with aqueous-alcoholic potash in an autoclave at 160°.

The most satisfactory yield of 8-nitro-1-naphthoic acid was given by conducting the nitration as follows. α-Naphthoic acid (120 g.) was mixed to a cream with concentrated nitric acid (450 c.c.) and transferred to a 2-litre flask fitted with stirring apparatus. The temperature was raised to 60° for 2 hours, and stirring continued for 2—3 hours after the temperature had fallen to normal. The product was then poured into a large volume of water, stirred, and filtered. Finally the 8-nitro-acid was isolated according to the directions of Eckstrand (*loc. cit.*, p. 156). Yield of pure acid, m. p. 214—215°, 35 g.

Interaction of Thionyl Chloride and 8-Nitro-1-naphthoic Acid.—The nitro-acid (10 g.) was first heated under reflux with thionyl chloride (50 g.) for 10 hours. On cooling, a crystalline solid deposited, which was filtered off and washed with benzene. After being twice crystallised from chloroform, the pale yellowish-green needles (3 g.) melted at 269—270°, and readily sublimed. This neutral substance contained chlorine and nitrogen and was found to be dichloronaphthostyril. A sample of the latter prepared by heating 8-nitro-1-naphthoic acid with fuming hydrochloric acid in a sealed tube at 140—160° for 2 hours melted at 265—266°, and admixed with the above product at 267° (Eckstrand, *loc. cit.*, p. 174, records m. p. 264—265°).

Dichloronaphthostyril also deposited in smaller yield when the nitro-acid was allowed to remain in contact with thionyl chloride for 36 hours at room temperature, thus illustrating the ease with which the *peri*-substituent is attacked under mild experimental conditions.

Interaction in benzene solution. The nitro-acid (10 g.) was mixed with thionyl chloride (30 g.) and benzene (150 c.c.) in a flask under a reflux condenser. A steady evolution of hydrogen chloride was maintained by heating, and after the acid had dissolved the mixture was left over-night. The mixture was then boiled for ½ hour and the benzene and excess of thionyl chloride were distilled off

under diminished pressure (on two occasions sudden decomposition occurred at this point). The dark product was boiled out with successive small quantities of water, which on cooling deposited yellowish-brown crystals of crude 8-chloro-1-naphthoic acid (4·5 g.). After being dried, the acid was recrystallised from ligroin until pure. Yield 2·5 g., m. p. 167—168°. No increase in the amount of chloro-acid was obtained when heating was continued for a longer period. The brown tarry residue remaining after the above extractions contained unchanged nitro-acid, which was removed by treatment with aqueous alkali. Further recrystallisation gave the nitro-acid, 3 g., m. p. 211—212°. From the alkali-insoluble residue, by extraction with hot alcohol, was obtained dichloronaphthostyril, 1·5 g., m. p. 264—265°.

It appears probable that the main replacement of nitro-group by halogen in the above reaction occurs during the removal of excess thionyl chloride by heating under diminished pressure, since little chloro-acid was isolated by the alternative method of pouring the benzene solution on ice.

Interaction with thionyl bromide. The method used for the preparation of thionyl bromide was a modification of that employed by Besson (*Compt. rend.*, 1896, **122**, 320). Hydrogen bromide was passed into a Woulff's bottle containing thionyl chloride, the bottle being surrounded by water at 60—75° and the second neck being provided with an upright condenser, fitted at its upper end with a calcium chloride tube. An excess of hydrogen bromide was passed in, and the product fractionated. An almost quantitative yield of thionyl bromide, b. p. 78—80°/86 mm., was obtained. Besson records b. p. 68°/40 mm.

Thionyl bromide and 8-nitro-1-naphthoic acid (10 g.) were allowed to react in benzene solution as described above, giving 8-*bromo*-1-*naphthoic acid* (1 g.), m. p. 178° (Found : Br, 32·1. $C_{11}H_7O_2Br$ requires Br, 31·9%).

The bromo-acid was converted into its *amide*, m. p. 179—180° (when mixed with the pure acid the product melted from 135° upwards) (Found : Br, 32·2. $C_{11}H_8ONBr$ requires Br, 32·0%). The acid dissolves readily in alcohol and to a smaller extent in hot water or benzene. It is only sparingly soluble in hot ligroin.

Methyl 8-*bromo*-1-*naphthoate* prepared by way of the acid chloride was obtained as an oil which solidified on standing for several days in a vacuum desiccator. Crystallised from petroleum (b. p. 80—100°), it melted at 33° (Found : Br, 30·4. $C_{12}H_9O_2Br$ requires Br, 30·2%).

8-*Chloro*-1-*naphthoic Acid from Naphthalic Acid.*—The naphthalic acid was converted into the mercuration product according to the

method of Leuck, Perkins, and Whitmore (*loc. cit.*). The dried chloromercuri-compound (20 g.) in glacial acetic acid suspension (250 c.c.) was then treated with a solution of chlorine (4 g.) in glacial acetic acid (50 c.c.). After the mixture had been brought to the boiling point, it was cooled, poured into ice-cold water (500 c.c.), and kept at 0° for several hours. The brown precipitate was filtered off and extracted with boiling water, which deposited the crude chloro-acid on cooling. After several recrystallisations from water the latter gave the pure chloro-acid (3 g.), m. p. 168—169°.

8-Bromo-1-naphthoic acid was obtained in a similar manner by heating the chloromercuri-compound (20 g.) in acetic acid with bromine (9 g.) dissolved in aqueous sodium bromide. The acid after recrystallisation from water melted at 176—177°. Yield, 2·5 g.

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