44. *Derivatives of* 8-*Bromo- and* 8-*Chloro*-1-*naphthoic Acids and their Orientation by Dehalogenation and Decarboxylation.*

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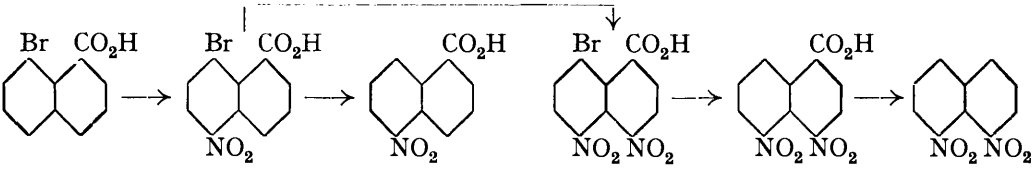
THE task of orienting derivatives of the *peri*-halogenated naphthoic acids has now been much facilitated by the discovery that the 8-halogenated naphthoic acids may be dehalogenated to the corresponding naphthoic acids in good yields (generally 55—75%) in boiling toluene containing copper-bronze. Halogen atoms or nitro-groups attached to other points in the molecule remain unaffected, with the probable exception of halogen ortho to carboxyl (compare Hurtley, J., 1929, 1870). In this reaction the required hydrogen appears to be derived from the carboxyl group by interaction with copper, since the latter rapidly loses its metallic lustre and no displacement of halogen by hydrogen was observed with the corresponding esters or salts, in which no carboxylic hydrogen is available. In various test experiments with different solvents, these were recovered unchanged : there is thus no question of the solvent acting as a hydrogen donor as in the reactions examined by Lesslie and Turner (J., 1932, 281).

The process, often found advantageous, of eliminating carbon dioxide by boiling acids of this type with dry quinoline in the presence of copper-bronze (Shepard, Winslow, and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 2084; Davies, Heilbron, and Irving, J., 1932, 2715) proved ineffective when applied directly to acids containing halogen in the *peri*-position to carboxyl and was therefore employed after dehalogenation. By the application of one or both of these reactions it is an easy matter to determine the orientation of a substituted 8-halogeno-1-naphthoic acid by converting it into a simpler naphthalene derivative of known structure.

On treatment with nitric acid the 8-bromo-acid passes into 8-*bromo*-5-*nitro*- and thence into 8-*bromo*-4 : 5-*dinitro*-1-*naphthoic acid.* The conversion of the latter compound into 4 : 5-*dinitro*-1-*naphthoic acid* and, by loss of carbon dioxide, into 1 : 8-dinitronaphthalene confirms the structure proposed for the dinitro-1-naphthoic acid of m. p. 265° by Ekstrand (*J. pr. Chem.*, 1888, **38**, 263), who found it among the nitration products of α-naphthoic acid.

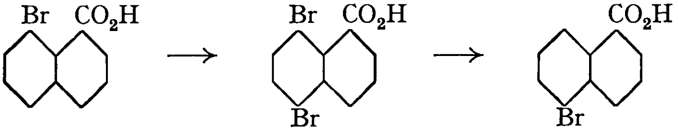


Ekstrand's nitration of 8-chloro-1-naphthoic acid (*loc. cit.*) was repeated, yielding a chloronitro-acid which on dehalogenation with copper-bronze was converted into 5-nitro-1-naphthoic acid. The nitration product is thus 8-chloro-5-nitro-1-naphthoic acid.

Earlier attempts to eliminate carbon dioxide from the dinitronaphthoic acid by heating the compound above its melting point proved unsuccessful, and in the hope of obtaining information as to the position of the second nitro-group an examination was made of the comparative reactivities of the halogen atom in 8-bromo-, 8-bromo-5-nitro-, and 8-bromo-dinitro-naphthoic acid. The acid (0·05 g. of the bromo-acid or equivalent proportions of its nitro-derivatives) was dissolved in 10 c.c. of methyl alcohol, and 0·2 g. of copper-bronze added, followed by 10 c.c. of standardised sodium methoxide solution. Liberated bromide was titrated with silver nitrate and ammonium thiocyanate. The following figures indicate the percentage conversion into methoxy-acid effected by boiling the solutions for 15 minutes (65°) : Sodium methoxide, 0·115*N* : 8-Bromo-acid, 34·8%; 8-bromo-5-nitro-acid, 74·7%. The following determinations with the bromo- and the bromodinitro-acid, carried out at a much later date with a different sample of copper-bronze, illustrate the manner in which the catalytic influence varies with the sample of catalyst employed; despite the higher concentration of alkali, the bromo-acid reacted much more slowly : Sodium methoxide, 0·231*N* : 8-Bromo-acid, 16·8%; bromodinitro-acid, 84·8%.

It appears that the introduction of a nitro-group into position 5 increases the reactivity of the bromine atom, and that two such groups, in positions 4 and 5, produce a still greater effect. These results are in general agreement with those of Salkind (*Ber.*, 1931, **64**, 289), who found that the halogen in 1-bromonaphthalene was much more strongly activated by two nitro-groups in positions 4 and 5 than by either of these groups separately.

The bromination of 8-bromo-1-naphthoic acid in a sealed tube at 150° led to the formation of 5 : 8-dibromo-1-naphthoic acid, identical with the compound prepared by Goldstein and Francey from 5-bromonaphthastyril (*Helv. Chim. Acta*, 1932, **15**, 1362). Further interaction was accompanied by loss of carbon dioxide and production of a neutral solid, which appeared to be a mixture of tribromo- and tetrabromo-naphthalenes, although



no pure compound could be isolated. The structure of the 5 : 8-dibromo-acid was confirmed by partial debromination to give 5-bromonaphthoic acid.

EXPERIMENTAL.

8-Bromo-1-naphthoic Acid.—A solution of naphthalic acid (50 g.) and sodium hydroxide (31 g.) in 1200 c.c. of hot water was filtered, and heated under reflux while yellow mercuric oxide (55 g.), dissolved in warm glacial acetic acid (40 c.c.) and water (150 c.c.), was added. The whole was made distinctly acid with acetic acid (a light brown suspension formed) and boiled for 96 hours until evolution of carbon dioxide ceased. A test portion dissolved completely in aqueous sodium hydroxide and deposited no mercury on a clean copper wire. The cold liquid was filtered, and the precipitate washed with water, alcohol, and ether (compare Leuck, Perkins, and Whitmore, *J. Amer. Chem. Soc.*, **1929**, **51**, 1831).

The hydroxymercuri-compound (94 g.) thus obtained was suspended in a mixture of 300 c.c. of glacial acetic acid and 50 c.c. of water cooled externally with ice, and a solution of 34 g. of bromine in 150 c.c. of concentrated aqueous sodium bromide added slowly with efficient stirring during 2—3 hours. After being slowly heated to 90°, the mixture was poured with stirring into 3 l. of cold water. The solid precipitate was boiled out with successive quantities (3 l.) of water until no more acid was deposited by the cold filtrate. Yield, 37 g.; m. p. 169—172°. A final crystallisation from benzene gave 33 g. of pure acid, m. p. 177—178° (57% of the theoretical yield, based on the naphthalic acid used). Alternatively * the reaction mixture after bromination may be poured into 3 l. of boiling water, boiled for a further 5 minutes, and filtered. The filtrate on cooling deposits 30 g. of crude acid and an additional 12 g. is obtained by extracting the solid residue on the filter-paper twice with 3 l. of boiling water. The crude acid in this case contains a little dibromo-acid, but is obtained pure after two recrystallisations from benzene. Yield, 33 g.

The actual yield obviously varies with the purity of the naphthalic acid employed. The crude bromo-acid obtained from 46 g. of pure naphthalic anhydride (B.D.H. product, m. p. 272—273°) weighed 53 g. and had m. p. 171—172° with softening at 158°. After crystallisation from benzene this gave 40 g. (68% of the theoretical) of pure acid, m. p. 177° with slight softening at 170°.

Ethyl 8-bromo-1-naphthoate separates from light petroleum in colourless plates, m. p. 52° (Found: C, 55·7; H, 4·0. $C_{13}H_{11}O_2Br$ requires C, 55·9; H, 3·9).

8-Bromo-5-nitro-1-naphthoic Acid.—The bromo-acid (10 g.) was mixed with concentrated nitric acid (15 c.c.) and maintained at 65° with occasional shaking. After 3—4 hours the mixture was poured into 50 c.c. of water. The precipitate obtained separated from alcohol as a yellow powder, m. p. 245°, practically insoluble in benzene, ligroin or toluene, soluble in cold alkali and in hot acetone or alcohol (Found: N, 4·9. $C_{11}H_6O_4NBr$ requires N, 4·7%).

The position of the nitro-group was established by boiling the acid (0·5 g.) for 1 hour in decalin containing copper-bronze (0·5 g.) in suspension. The cold liquid was shaken with aqueous sodium hydroxide, and the extract on acidification deposited 5-nitro-1-naphthoic acid; recrystallised from aqueous alcohol, this had m. p. 238°, alone or mixed with an authentic specimen.

Methyl 8-bromo-5-nitro-1-naphthoate separated from light petroleum in aggregates of rod-shaped crystals, m. p. 97° (Found: N, 4·3. $C_{12}H_8O_4NBr$ requires N, 4·5%). The *ethyl* ester was deposited from acetone in highly twinned prisms, m. p. 103° (Found: N, 4·4. $C_{13}H_{10}O_4NBr$ requires N, 4·3%).

8-Chloro-5-nitro-1-naphthoic acid was prepared from 2·5 g. of 8-chloronaphthoic acid and 3 c.c. of fuming nitric acid (compare Ekstrand, *loc. cit.*, p. 170). It crystallised from alcohol in rhombic leaflets (1·25 g.), m. p. 225—226°. Ekstrand records m. p. 227°. On dehalogenation with copper-bronze in boiling toluene for 3 hours, this acid gave 5-nitro-1-naphthoic acid, confirmed by mixed melting point.

8-Bromo-4 : 5-dinitro-1-naphthoic Acid.—This was obtained from 7·5 g. of the mononitro-acid and a mixture of 3 c.c. of concentrated sulphuric acid, 4 c.c. of concentrated nitric acid, and 4 c.c. of fuming nitric acid. The reaction mixture was heated for 6 hours at 100°, poured into water, and kept over-night. The separated *bromodinitro-acid* (5 g.) was first purified by deposition from aqueous alcohol (3 : 1); m. p. 238—240° (decomp.). From hot acetone–benzene it was then thrown out by the addition of light petroleum in aggregates of needles, m. p. 249—252°. For the following purposes the crude acid (9 g.) was more readily purified by boiling out impurities with benzene (15 c.c.). The insoluble acid was filtered off and washed with light petroleum. As so obtained, it was a powder, m. p. 250—252° (decomp.), the tint

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* A more rapid method suggested by Dr. L. A. Bigelow.

of which varied inexplicably from greyish-white to yellow (Found : N, 8·1. $C_{11}H_5O_6N_2Br$ requires N, 8·2%).

The *methyl* ester separated from alcohol in colourless plates, m. p. 155° (Found : N, 8·0. $C_{12}H_7O_6N_2Br$ requires N, 7·9%), and the *ethyl* ester in prisms, m. p. 127—128° (Found : N, 7·7. $C_{13}H_9O_6N_2Br$ requires N, 7·6%).

Attempts to decarboxylate the bromo-dinitro-acid by use of copper-bronze to give 1-bromo-4 : 5-dinitronaphthalene gave a mixture of products which could not be purified, but the position of the nitro-groups was proved in the following manner, as well as by the synthesis from acenaphthenequinone described in the succeeding paper.

The acid (2 g.) was first dehalogenated by boiling it vigorously for 7 hours in toluene (15 c.c.) containing copper-bronze (2 g.) in suspension. The recovered acid (1·3 g.) was purified from aqueous alcohol (animal charcoal), forming a buff-coloured microcrystalline powder (0·7 g.), m. p. 257—259° (decomp.) (yield, 45%). Pure 4 : 5-*dinitro*-1-*naphthoic acid* melts at 265° (Found : N, 10·8. $C_{11}H_6O_6N_2$ requires N, 10·7%). *Ethyl* 4 : 5-*dinitronaphthoate*, precipitated from hot benzene solution by addition of light petroleum, formed yellow needles, m. p. 143—144° (Found : N, 9·8. $C_{13}H_{10}O_6N_2$ requires N, 9·7%). Ekstrand (*loc. cit.*, p. 256) records m. p. 143°.

The dinitronaphthoic acid (0·5) in dry boiling quinoline (1 c.c.) was treated carefully with copper-bronze (0·25 g.). Carbon dioxide was evolved, and heating maintained for 15 minutes. The cooled mixture was extracted with ether, and the extract washed in turn with mineral acid and aqueous alkali. After removal of the ether, and recrystallisation of the residual neutral solid (0·15 g.) from benzene, colourless crystals of 1 : 8-dinitronaphthalene were obtained, m. p. 166—169°, and 167—169° in admixture with purified 1 : 8-dinitronaphthalene (m. p. 169°).

5 : 8-*Dibromo*-1-*naphthoic Acid*.—This was obtained in 57% yield by heating the 8-bromo-acid (2 g.), glacial acetic acid (5 c.c.), and bromine (0·7 c.c.) in a sealed tube at 150° for 2 hours. The resulting acid, after separation from a small amount of neutral product and several recrystallisations from alcohol, formed colourless microcrystalline plates which had a reddish-brown tint in bulk. M. p. 232° (Goldstein and Francey, *loc. cit.*, record m. p. 227·5°).

The dibromo-acid was boiled in toluene solution with copper-bronze. The recovered acid separated from alcohol in colourless needles (0·25 g.), m. p. 257°, and 258° in admixture with 5-bromo-1-naphthoic acid (m. p. 260°).

SUMMARY.

1. The orientation of a substituted 8-halogeno-1-naphthoic acid may be determined by (*a*) dehalogenation by boiling the acid in toluene solution with addition of copper-bronze, followed if necessary by (*b*) decarboxylation in boiling quinoline with the aid of copper-bronze.

2. The 8-halogeno-1-naphthoic acids are nitrated first in position 5 and eventually in the 4 : 5-positions. Halogenation only occurs readily in position 5.

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