45. *Constitution of Dinitroacenaphthenequinone and of Dinitronaphthalic Acid. Preparation of a New Dinitronaphthalene.*

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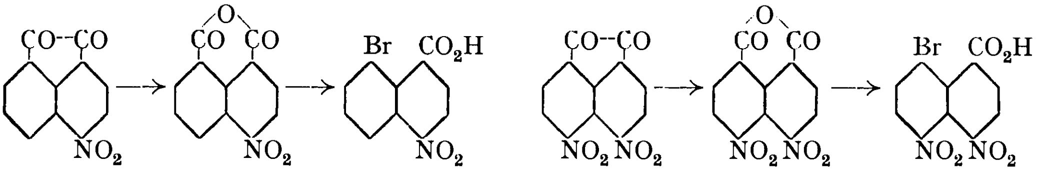
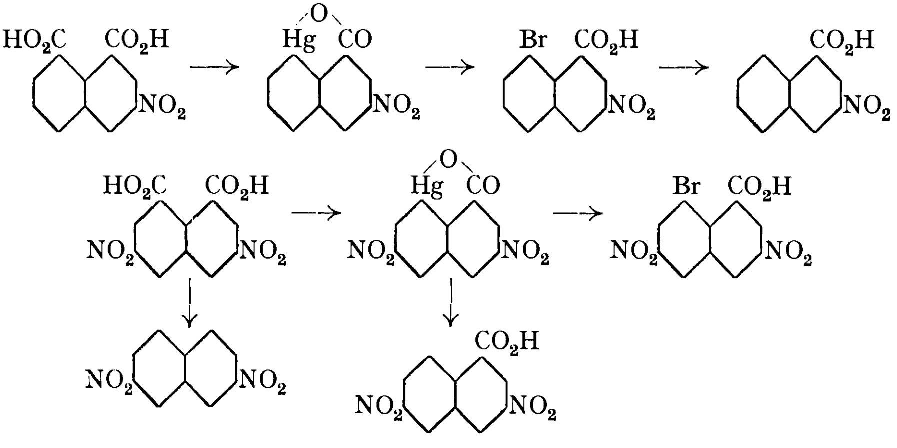
When acenaphthenequinone is nitrated, the reagent first attacks one of the free *peri*-positions to form the 3-nitro-compound (Rowe and Davies, J., 1920, **117**, 1349; Mayer and Kaufmann, *Ber.*, 1920, **53**, 296). More vigorous treatment yields a dinitro-compound, described as the 3 : 4-derivative by Mayer and Kaufmann, who compared the melting point of the dinitronaphthalic anhydride obtained from it on oxidation with that of the corresponding anhydride prepared by direct oxidation of 5 : 6-dinitroacenaphthene. The anhydrides were found to melt unsharply at about 310° and the proof of their identity was apparently not regarded as entirely conclusive (compare pp. 292, 298). In this respect, however, the results of Rowe and Davies were more definite.

Naphthalic anhydride on nitration forms first a 3-nitro-derivative (Graebe and Briones, *Annalen*, 1903, **327**, 84) and then a dinitro-compound, in which the position of the second nitro-group has not yet been established.

The present communication deals with the oxidation of mono- and di-nitroacenaphthenequinones to the corresponding naphthalic anhydrides by the method of Rowe and Davies (*loc. cit.*), followed by mercuration and bromination. This treatment leads to the isolation of *8-bromo-4-nitro-1-naphthoic acid* and of 8-bromo-4 : 5-dinitro-1-naphthoic acid (see preceding paper) respectively, thus confirming the structure given to dinitroacenaphthenequinone by the above authors.



Similarly, the successive application of mercuration and bromination to 3-nitronaphthalic acid, followed by dehalogenation with copper-bronze in boiling toluene, led to the formation of *8-bromo-3-nitro-1-naphthoic acid* and of the known 3-nitronaphthoic acid. The mercuration compound prepared from dinitronaphthalic acid, when treated with bromine, gave *8-bromo-3 : 6-dinitro-1-naphthoic acid*, and when heated with hydrochloric acid was hydrolysed to *3 : 6-dinitro-1-naphthoic acid*. The structure of the last two acids was proved by boiling the original dinitronaphthalic acid with quinoline and carefully adding copper-bronze. Under these conditions decarboxylation occurred, with formation of the previously unknown *2 : 7-dinitronaphthalene* in 27% yield. The latter, on reduction with tin and hydrochloric acid, was converted into 2 : 7-diaminonaphthalene, which in this way becomes for the first time a comparatively readily accessible compound.



Experimental.

Bromonitronaphthoic Acids from Acenaphthenequinone.—Acenaphthenequinone was mononitrated, and the product oxidised to 4-nitronaphthalic anhydride (Rowe and Davies, *loc. cit.*). The latter compound (10 g.) gave 15 g. of dry mercuration product (Leuck, Perkins, and Whitmore, *J. Amer. Chem. Soc.*, 1929, **51**, 1835), which were suspended in 150 c.c. of glacial acetic acid at 0° and slowly treated (during 1 hour) with bromine (5·8 g.) dissolved in 40 c.c. of concentrated aqueous sodium bromide. After being heated at 90° for 15 minutes, the yellow-brown solution was poured into 500 c.c. of cold water. The brownish product (6 g.), m. p. 130—170°, after six recrystallisations from acetic acid, gave 0·5 g. of a yellow crystalline bromonitronaphthoic acid, m. p. 201—203°, readily soluble in alcohol, acetic acid, or acetone (Found : N, 4·7. $C_{11}H_6O_4NBr$ requires N, 4·7%). As 8-bromo-5-nitro-1-naphthoic acid melts at 247° (see previous paper), the compound, m. p. 201—203°, must have the only alternative structure compatible with that of the initial material, and is therefore 8-*bromo*-4-*nitro*-1-*naphthoic acid*. A mixture of these two acids melted several degrees below 200°.

Dinitroacenaphthenequinone was oxidised to dinitronaphthalic anhydride (Rowe and Davies, *loc. cit.*). The latter compound (10 g.), dissolved in a hot solution of 3 g. of sodium hydroxide in 200 c.c. of water, was mixed with a hot solution of 7·5 g. of yellow mercuric oxide in 30 c.c. of water, to which 10 c.c. of glacial acetic acid had been added. The mixture was made distinctly acid with glacial acetic acid (a yellow suspension formed) and boiled under reflux for 100 hours. The dark mercuration product was washed with water, alcohol, and ether, and dried. Yield, 11 g.

The mercuri-compound was suspended in 150 c.c. of glacial acetic acid and brominated as described above, with 4 g. of bromine. Crystallisation of the bromo-compound from acetic acid (animal charcoal) and eventually from concentrated nitric acid gave yellow crystals (2 g.), m. p. 248—252° (decomp.) (27% yield). The product was identical with the 8-bromo-4 : 5-dinitro-1-naphthoic acid prepared by direct nitration of 8-bromonaphthoic acid (see preceding paper); mixed m. p. 248—252°.

By way of further confirmation the dinitromercuri-compound, when heated with concentrated hydrochloric acid, gave colourless needles of 4 : 5-dinitro-1-naphthoic acid, m. p. and mixed m. p. 265° (see preceding paper).

Bromonitronaphthoic Acids from Naphthalic Anhydride.—Resublimed naphthalic anhydride, m. p. 270—271°, was converted into 3-nitronaphthalic acid (Graebe and Briones, *loc. cit.*), and the latter mercurated. The mercuration compound (15 g.), on treatment with bromine (6 g.) as described above, gave a yellow acid (9 g.), m. p. 200—225°. This was apparently a mixture of isomerides, which after several recrystallisations from acetic acid gave colourless microcrystalline plates (3 g.), m. p. 240—242°, unchanged by further crystallisation (Found : N, 4·9. $C_{11}H_6O_4NBr$ requires N, 4·7%). The initial material employed might be expected to lead to the formation of either 8-*bromo*-3-*nitro*-1-*naphthoic acid* or the 6-nitro-isomeride. Of these two structures, the former was established by boiling the acid (0·5 g.) for 2 hours with toluene in the presence of copper-bronze. This treatment yielded a nitronaphthoic acid (0·2 g.), m. p. 268—269°. Leuck, Perkins, and Whitmore (*J. Amer. Chem. Soc.*, 1929, **51**, 1833) record 3-nitronaphthoic acid, m. p. 270·5—271·5°, and 6-nitronaphthoic acid, m. p. 227°.

Methyl 8-*bromo*-3-*nitro*-1-*naphthoate*, prepared by use of thionyl chloride, deposited from ligroin in crystals, m. p. 173°, only sparingly soluble in cold ether or benzene (Found : N, 4·6. $C_{12}H_8O_4NBr$ requires N, 4·5%). The *ethyl* ester (from ligroin) had m. p. 155—156° (Found : N, 4·3. $C_{13}H_{10}O_4NBr$ requires N, 4·4%).

Dinitronaphthalic acid, m. p. 208—210°, was obtained from naphthalic anhydride in 67% yield by the method of Francesconi and Bargellini (*Gazzetta*, 1902, **32**, 94). The acid (10 g.) gave 12·5 g. of the mercuri-derivative (1·5 g. of initial material recovered), which was brominated with 4·5 g. of bromine. The product, crystallised from acetic acid (at first with addition of animal charcoal), gave colourless microcrystalline plates (2·5 g.) of 8-*bromo*-3 : 6-*dinitro*-1-*naphthoic acid*, m. p. 273—275°. The acid dissolves readily in cold acetone, and in hot alcohol, acetic acid, or benzene. It has a very bitter taste (Found : N, 8·3. $C_{11}H_5O_6N_2Br$ requires N, 8·2%). The *methyl* ester formed rectangular prisms, m. p. 137—138°, from alcohol (Found : N, 8·1. $C_{12}H_7O_6N_2Br$ requires N, 7·9%). The *ethyl* ester (from alcohol) had m. p. 205—207° (Found : N, 7·6. $C_{13}H_9O_6N_2Br$ requires N, 7·6%).

Another portion (12 g.) of the mercuri-derivative from dinitronaphthalic acid was warmed with dilute sodium hydroxide solution (50 c.c.), and the suspension treated with concentrated hydrochloric acid (120 c.c.) and boiled for 4 hours. The brown solid deposited from the cooled mixture was decolorised in alcoholic solution with animal charcoal and recrystallised twice from acetic acid, giving buff-coloured crystals of 3 : 6-*dinitro*-1-*naphthoic acid* (4 g.), m. p. 273·5—274° (yield, 59%) (Found : N, 10·6. $C_{11}H_6O_6N_2$ requires N, 10·7%). The *methyl* ester, m. p. 196—197°, was deposited from alcohol in colourless needles, only sparingly soluble in cold ether (Found : N, 10·0. $C_{12}H_8O_6N_2$ requires N, 10·15%). The *ethyl* ester (from alcohol) had m. p. 145—146° (Found : N, 9·6. $C_{13}H_{10}O_6N_2$ requires N, 9·7%).

Preparation of 2 : 7-*Dinitronaphthalene.*—The orientation of the nitro-groups in the above derivatives is dependent upon the structure of dinitronaphthalic acid. This was determined by decarboxylation with copper-bronze and boiling quinoline, a preliminary experiment with naphthalic acid having shown that the procedure was applicable to dicarboxylic derivatives.

Dinitronaphthalic acid (2 g.) was dissolved in dry boiling quinoline (4 c.c.), and copper-bronze (2 g.) added carefully in small portions. After 15 minutes' boiling, the cooled product was extracted with ether, and the filtered extract washed successively with dilute hydrochloric acid, aqueous sodium carbonate, and water. After evaporation of the solvent, the residual yellow solid was recrystallised from acetic anhydride, giving a dinitronaphthalene (0·4 g.), m. p. 234° (Found : N, 12·8. $C_{10}H_6O_4N_2$ requires N, 12·8%). The compound dissolves readily in acetic acid and benzene, is less soluble in alcohol and only sparingly in ether.

Disregarding any theoretical considerations, and in view of the known structure of the mononitronaphthalic acid, the possible positions for the nitro-groups in the dinitronaphthalene are 1 : 2, 1 : 7, 2 : 6, 2 : 7, or 2 : 3. Of these, the melting point eliminates the first three, leaving the unknown 2 : 7- and 2 : 3-derivatives. The diaminonaphthalenes corresponding to the 2 : 3-, 2 : 6-, and 2 : 7-structures are, however, all known. The above dinitro-compound was therefore reduced with tin and hydrochloric acid, giving a diamino-compound which crystallised from water in colourless plates, m. p. 159°. In van der Kam's " Naphtalin Derivate " 2 : 7-diaminonaphthalene is listed as melting at 159° (2 : 3-compound, m. p. 191° ; 2 : 6-compound, m. p. 216—218°). The new dinitronaphthalene is thus the 2 : 7-*derivative*, and the dinitronaphthalic acid is the 3 : 6-compound, leading to the constitutions given above for the derivatives prepared from the latter source.

The substituted 8-bromonaphthoic acids described in this and in the foregoing paper are being used in the preparation of substituted benzanthrones and anthranthrones.

SUMMARY.

Mono- and di-nitroacenaphthenequinones have been converted into bromonitronaphthoic acids by oxidation to the corresponding naphthalic anhydrides, followed by mercuration and bromination. The results confirm the structure assigned to the dinitroquinone by other workers.

Mono- and di-nitration products of naphthalic anhydride have been successively mercurated and brominated to give new bromonitronaphthoic acids and 3 : 6-dinitronaphthoic acid. The structures of these compounds are established by the decarboxylation of dinitronaphthalic acid to give the previously unknown 2 : 7-dinitronaphthalene, which reduces to 2 : 7-diaminonaphthalene.

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