369. *Bromo- and Nitro-derivatives of Naphthalic Acid.*

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The bromination of naphthalic anhydride in a mixture of oleum and sulphuric acid leads, not to 4-bromonaphthalic anhydride as stated by Francesconi and Bargellini, but to 3-*bromonaphthalic anhydride*, m. p. 244°. This compound may also be prepared by bromination in nitric acid solution, or less satisfactorily by heating the anhydride with bromine in a sealed tube. Bromination in an alkaline medium, on the other hand, gives 4-bromonaphthalic anhydride, m. p. 222°. In the presence of iron filings, naphthalic anhydride may be brominated to a *tribromonaphthalic anhydride*, m. p. 232°, probably the 3 : 4 : 6 (or the 3 : 4 : 5)-compound.

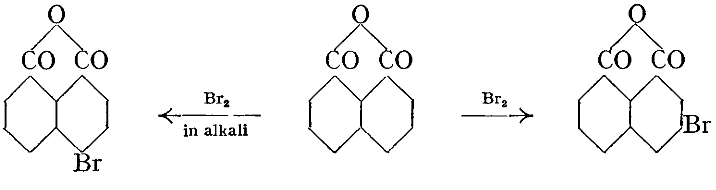
Homonuclear substitution occurs when 4-bromonaphthalic anhydride is nitrated, with formation of 4-*bromo*-3-*nitronaphthalic anhydride*. Further nitration of 4-nitronaphthalic anhydride, however, affords 4 : 5-dinitronaphthalic anhydride as the main product.

The mercuration of 3-bromonaphthalic anhydride, followed by hydrolysis with mineral acid, gives a mixture of bromo-acids from which 3-*bromo*-1-*naphthoic acid*, m. p. 231—232°, can be isolated. In a similar manner 5-bromo-1-naphthoic acid is obtained from the 4-bromo-anhydride.

THE only record of the direct bromination of naphthalic anhydride is by Francesconi and Bargellini (*Gazzetta*, 1902, **32**, 87), who prepared a number of halogeno- and nitro-derivatives; in all cases halogenation was carried out in a mixture of oleum and sulphuric acid, the use of bromine giving a product which could only be purified with difficulty and was assumed to be identical with 4-bromonaphthalic anhydride obtained by oxidation of 3-bromoacenaphthene.

During the present investigation naphthalic anhydride was first brominated by heating the reactants for a considerable time in a sealed tube, and a monobromo-compound, m. p. 244°, was isolated which differed from 4-bromonaphthalic anhydride and was shown to be 3-*bromonaphthalic anhydride* by its synthesis from 3-nitronaphthalic anhydride. Subsequent repetition of the bromination in oleum and sulphuric acid as described by Francesconi and Bargellini also led to the 3-bromo-compound. Owing to the troublesome experimental procedure and low yields, neither of these methods is satisfactory. Better results are obtained by carrying out the bromination in nitric acid solution : although the yield (20%) is still somewhat low, the preparation is rapidly effected and under the correct conditions (see experimental section) the product crystallises from the reaction mixture in the pure state.

When the bromination was carried out in an alkaline medium in presence of sodium hypobromite, 4-bromonaphthalic anhydride, m. p. 222°, was obtained in good yield.



Under more vigorous conditions, bromine and iron filings being used, a *tribromonaphthalic anhydride* was produced. As dinitration of the anhydride is known to lead to the formation of the symmetrical 3 : 6-dinitro-derivative (Rule and Brown, J., 1934, 171) and disulphonation has been found to take the same course (Rule and Douglas, unpublished work), it appears probable that the tribromo-compound contains bromine in the 3 : 4 : 6- or less likely in the 3 : 4 : 5-positions. The same compound may be obtained from acenaphthenequinone or its 3-bromo-derivative on bromination in the presence of iron, followed by oxidation (see preceding paper), but the yield by this method is smaller owing to the difficulty of removing other products which are formed during the bromination.

The nitration of 4-bromonaphthalic anhydride led somewhat unexpectedly to homonuclear substitution and the formation of 4-*bromo*-3-*nitronaphthalic anhydride*, the structure of which was proved by synthesis from 2-nitro-3-aminoacenaphthene. On the other hand, 4-nitronaphthalic anhydride on further nitration gave rise to the 4 : 5-dinitro-derivative.

One of the difficulties encountered in working with the naphthalic anhydride group lies in the often considerable discrepancies in the melting points of these compounds recorded in the literature. For the better characterisation of the compounds under discussion a number of their more important derivatives have been prepared. Symmetrically substituted anhydrides are conveniently identified by conversion into the 1′ : 8′-naphthoylene-1 : 2-benziminazoles formed by union with *o*-phenylenediamine. Derivatives of this type have been prepared by Chakravarti (*J. Indian Chem. Soc.*, 1924, **1**, 19) and Bistrzycki and Risi (*Helv. Chim. Acta*, 1925, **8**, 810), who obtained them by heating the reactants together at a high temperature. It has now been found that a simpler method is to effect the condensation in boiling acetic acid solution. When heated with nitrobenzene as solvent, the starting materials were recovered largely unchanged.

The mercuration of 3-bromonaphthalic anhydride gave rise to a mixture of anhydromercuri-naphthoic acids, from which no pure dibromonaphthoic acid could be prepared by treatment with bromine. From the mixture of bromonaphthoic acids formed on boiling the mercurated compound with hydrochloric acid, a small yield (23%) of 3-*bromo*-1-*naphthoic acid* was isolated, this structure being proved by the synthesis of the compound from 3-nitro-1-naphthoic acid. In a similar manner the mercuration of 4-bromonaphthalic anhydride led to the production of a mixture of naphthoic acids, from which 5-bromo-1-naphthoic acid was separated by fractional crystallisation.

EXPERIMENTAL.

Naphthalic anhydride, m. p. 272—273°, forms a benziminazole derivative, m. p. 206°, which is pale yellow, and remains unchanged after 2 hours' heating at 215° (Chakravarti, and Bistrzycki and Risi, *locc. cit.*, give m. p. 198° and 189° respectively).

Bromination of Naphthalic Anhydride.—(a) The anhydride (5 g.) was heated with bromine (2 c.c.) for 18 hours at 150°. After extraction of unchanged material with hot alcohol (75 c.c.), a second extraction removed 3-*bromonaphthalic anhydride*, m. p. 244° after recrystallisation from alcohol or sublimation (Found : C, 52·0; H, 1·8; Br, 29·0. $C_{12}H_5O_3Br$ requires C, 51·9; H, 1·9; Br, 28·9%); mixed m. p. with the 4-bromo-derivative (m. p. 222°) 190—200°.

(b) Naphthalic anhydride (20 g.) was brominated in a mixture of oleum and sulphuric acid as described by Francesconi and Bargellini (*loc. cit.*), giving a product which on crystallisation from acetic anhydride melted at 238—241° (yield, 6·3 g.; 25%), not depressed by admixture with the above compound, m. p. 244° (F. and B. record m. p. 211—212° for their purest product and state no yield).

(c) Naphthalic anhydride (5 g.) was dissolved in concentrated nitric acid (100 c.c.) by rapid heating to 70°. Bromine (3 g.) was added, the temperature being maintained at 60—70°, and after ½ hour the mixture was cooled in water and kept overnight; fine colourless needles (1·4 g.; 20%) of 3-bromonaphthalic anhydride crystallised, m. p. 242—243°. When the acid filtrate was poured into water, less than 1 g. of solid separated, from which a further small amount of the bromo-anhydride was isolated by recrystallisation.

3-Nitronaphthalic anhydride was converted through the amino- into the bromo-derivative, which sublimed in colourless needles, m. p. 244° alone or mixed with the above-mentioned specimens.

3-*Bromonaphthalimide*, prepared from the anhydride and concentrated aqueous ammonia, melted at 316° (Found : N, 4·95. $C_{12}H_6O_2NBr$ requires N, 5·1%). *Methyl* 3-*bromonaphthalate* was prepared by use of methyl sulphate and 10% aqueous sodium carbonate; crystallised from alcohol, it melted at 105° (Found : Br, 25·1. $C_{14}H_{11}O_4Br$ requires Br, 24·8%). 3-Bromonaphthalophenylhydrazide, crystallised from acetic acid, melted at 223—224°. This m. p. was recorded by Francesconi and Bargellini (*loc. cit.*) for the phenylhydrazide prepared from a crude bromo-anhydride incorrectly assumed to be the 4-bromo-compound.

(d) A solution of naphthalic anhydride (20 g.) in hot aqueous potassium hydroxide (28 g. in 120 c.c.) was cooled in ice and treated with bromine (48 g., added during 2½ hours). The temperature was then raised to 60° and maintained for 24 hours, an excess of sulphuric acid added, and the mixture boiled for a short time. The 4-bromonaphthalic acid obtained was recrystallised from nitrobenzene; yield, 12 g. (43%); m. p. 214—216°. The pure anhydride melts at 222°. Melting points observed for the methyl ester and the imide were in agreement with those already recorded by Dziewonski and Koewa (*Bull. Acad. Polonaise*, 1928, *A*, 405), but the phenylhydrazide was found to melt at 231° (Dziewonski records 223—224°). A mixed m. p. of the phenylhydrazides prepared from the 3- and the 4-bromonaphthalic anhydride showed strong depression.

(e) Iron filings (2 g.) were added to a suspension of naphthalic anhydride (10 g.) in bromine (20 c.c.), the mixture being then boiled under reflux for 15 hours. The product was poured into water (1 l.) acidified with sulphuric acid, and the excess of bromine boiled off. Filtration gave a solid, which was extracted with a boiling solution of sodium carbonate. The filtered extract deposited on cooling the sodium salt of the tribromo-acid, sodium chloride being added to make the separation more complete. After crystallisation from water (lustrous plates, 18 g.), treatment with acid and crystallisation from acetic anhydride afforded *tribromonaphthalic anhydride*, m. p. 232°. Yield, 13 g. (60%) (Found : Br, 54·9. $C_{12}H_3O_3Br_3$ requires Br, 55·1%).

Nitration of 4-Bromonaphthalic Anhydride.—The anhydride (3 g.), dissolved in sulphuric acid (20 c.c.), was treated gradually at 15—20° with a mixture of nitric acid (0·5 c.c., *d* 1·51) and sulphuric acid (10 c.c.), and the whole heated for 1 hour at 100°. The product was precipitated with water and crystallised from acetic anhydride. Yield, 1·4 g. (40%); m. p. 229—230°. Further crystallisation from nitric acid gave colourless needles of *4-bromo-3-nitronaphthalic anhydride*, m. p. 231—232° (Found : N, 4·5. $C_{12}H_4O_5NBr$ requires N, 4·35%). The orientation of the nitro-group was proved by the following synthesis : 2-nitro-3-aminoacenaphthene (Morgan and co-workers, *J. Soc. Chem. Ind.*, 1924, 343 T; 1925, 493 T; 1930, 413 T) (5 g.) was dissolved in 85% sulphuric acid (40 c.c.) and glacial acetic acid (50 c.c.), sodium nitrite (3·5 g.) and ice (200 g.) added, and the diazo-solution poured into a solution of cuprous bromide (10 g.) in 20% hydrobromic acid. The temperature was slowly raised to 60°, and the mixture kept overnight. The solid deposit (6 g.) was filtered off and extracted with light petroleum, the extract yielding orange crystals, m. p. 130—135° (2·5 g.). Further crystallisation from light petroleum afforded long rectangular prisms of *3-bromo-2-nitroacenaphthene*, m. p. 143° (Found : Br, 29·1. $C_{12}H_8O_2NBr$ requires Br, 28·8%). Sodium dichromate (10 g.) was gradually added to a solution of 3-bromo-2-nitroacenaphthene (2 g.) in glacial acetic acid (25 c.c.) at 70—80°. After further heating for 30 minutes on a water-bath the mixture was poured into water acidified with sulphuric acid and the anhydride was extracted from the precipitated solid with aqueous sodium carbonate. After recrystallisation from nitric acid fine colourless needles of 4-bromo-3-nitronaphthalic anhydride (0·4 g.) were obtained, m. p. 232° alone or mixed with the product obtained by nitrating 4-bromonaphthalic anhydride.

Nitration of 4-Nitronaphthalic Anhydride.—The anhydride (5 g.) was treated with concentrated sulphuric acid (30 c.c.) and sodium nitrate (2 g.), and the temperature slowly raised to 100°. Crystals of 4 : 5-dinitronaphthalic anhydride soon began to separate and after 15 minutes the pasty mass was allowed to cool. Yield, 2·2 g.; m. p. 320—322°, raised to 323—325° on crystallisation from nitric acid. The m. p. of a specimen of 4 : 5-dinitronaphthalic anhydride prepared from acenaphthenequinone (Rowe and Davies, J., 1920, **117**, 1344; Mayer and Kaufmann, *Ber.*, 1920, **53**, 289) rose to 327—329° after several recrystallisations from nitric acid (Mayer and Kaufmann record m. p. about 310°, not sharp). Mixed with the above nitro-compound, this substance melted at 326—328° and each sample under the microscope showed the same crystalline form of elongated rectangular plates.

Condensation of Naphthalic Anhydride with o-Phenylenediamine.—The anhydride (2 g.), dissolved in boiling acetic acid (60 c.c.), was treated with *o*-phenylenediamine (1·2 g.) in acetic acid (10 c.c.). After being boiled for ½ hour, the liquid on cooling deposited fine yellow crystals of 1′ : 8′-naphthoylene-1 : 2-benziminazole, which were washed with a little cold acetic acid. Yield, 2·2 g.; m. p. 204—205°, raised to 206° on recrystallisation from chlorobenzene (Found : N, 10·3. Calc. for $C_{18}H_{10}ON_2$: N, 10·4%). *4′ : 5′-Dinitro-1′ : 8′-naphthoylene-1 : 2-benziminazole*, obtained in a similar manner from 4 : 5-dinitronaphthalic anhydride, separated in fine bronze needles, m. p. 370° (Found : N, 15·5. $C_{18}H_8O_5N_4$ requires N, 15·55%).

3 : 6-Dinitronaphthalic acid was prepared by the method of Francesconi and Bargellini (*loc. cit.*; see also Rule and Brown, J., 1934, 173). It was observed that the acid, m. p. 210°, deposited unchanged after being boiled with nitrobenzene. In this respect it differs from naphthalic acid, which undergoes conversion into the anhydride. Francesconi and Bargellini state that the anhydride, m. p. 266° (decomp.), may be obtained by crystallising the dinitro-

acid from nitric acid. During the present work a sample of 3 : 6-dinitronaphthalic acid which had been purified from nitrobenzene was recrystallised from nitric acid, giving long colourless needles, m. p. 330°, without any sign of decomposition (Found : N, 10·0. Calc. for $C_{12}H_4O_7N_2$: N, 9·7%). Condensation with *o*-phenylenediamine afforded 3′ : 6′-*dinitro*-1′ : 8′-*naphthoylene*-1 : 2-*benziminazole* in orange crystals, m. p. 301° (Found : N, 15·2. $C_{18}H_8O_5N_4$ requires N, 15·55%).

Mercuration of Substituted Naphthalic Anhydrides.—This was effected by the method of Whitmore and Fox (*J. Amer. Chem. Soc.*, 1929, **51**, 3363). The mercuration product from 4-bromonaphthalic anhydride (10 g.), when boiled for 3 hours with 5N-hydrochloric acid, gave an almost quantitative yield of bromonaphthoic acids, from which, on crystallisation from acetic acid, 2 g. (35%) of 5-bromo-1-naphthoic acid were isolated, m. p. 256—258°, not depressed by the product (m. p. 260°) obtained by the direct bromination of naphthoic acid.

The mercuration of 3-bromonaphthalic anhydride (8·3 g.), followed by hydrolysis with mineral acid, gave a mixture of bromonaphthoic acids (6·7 g.), from which, after four recrystallisations from acetic acid, 3-*bromo*-1-*naphthoic acid* (1·6 g., 23%) was isolated, m. p. 231—232°, not changed by sublimation. The position of the bromine atom was proved by synthesis, 3-nitronaphthalic acid being mercurated and the product hydrolysed to give a mixture from which 3-nitro-1-naphthoic acid was obtained (cf. Leuck, Perkins, and Whitmore, *J. Amer. Chem. Soc.*, 1929, **51**, 1833). The last-named acid (2 g.) was reduced with sodium hyposulphite and the amino-acid, without being isolated, was diazotised and treated with cuprous bromide in hydrobromic acid. The crude 3-bromonaphthoic acid was mixed with graphite (4 parts) and sublimed, giving 0·3 g., m. p. 237—238° alone or when mixed with the above specimen, m. p. 234—236° (Found : C, 52·2; H, 2·9; Br, 31·4. $C_{11}H_7O_2Br$ requires C, 52·6; H, 2·8; Br, 31·8%). More conclusive proof of identity was obtained by converting each sample of bromo-acid into *methyl* 3-*bromo*-1-*naphthoate* by the thionyl chloride method; after crystallisation from aqueous alcohol the products melted at 59° alone or mixed (Found : Br, 30·6. $C_{12}H_9O_2Br$ requires Br, 30·2%).

The mercuration of the above-mentioned tribromonaphthalic anhydride was also effected, but hydrolysis led to a mixture of tribromonaphthoic acids which could not be separated. In none of the above cases could any definite compounds be isolated by brominating the mercury compounds.

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