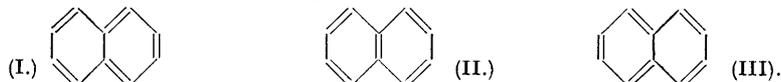


231. *The Structure of Naphthalene, Hydrindene, and Tetralin Derivatives.*

By (MISS) N. McLEISH and NEIL CAMPBELL.

THE structure of naphthalene has been the subject of many critical investigations, and has recently been attacked from several different standpoints (Challenor and Ingold, *J.*, 1923, **123**, 2066; Obermiller, *J. pr. Chem.*, 1930, **126**, 257; Bell, *J.*, 1932, 2732; Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1935, **57**, 1459; 1936, **58**, 2050; Sidgwick and Springall, *J.*, 1936, 1532; Ufimzew, *Ber.*, 1936, **69**, 2188; Baker and Carruthers, this vol., p. 479). The problem cannot be regarded as solved, for, while Ufimzew (*loc. cit.*) concludes that a modification of the Erdmann formula (*Annalen*, 1893, **275**, 191)—an equilibrium between structures (I), (II), and (III)—affords the most satisfactory explanation of the properties of naphthalene derivatives (cf. Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362), most of the evidence supports Fieser and Lothrop's conclusion (*loc. cit.*) that the Erlenmeyer formula (II) is the most acceptable to chemists. The chemical evidence rests chiefly on the reactivity of the 1-position and the non-reactivity of the 3-position in 2-substituted

naphthalene compounds. This is explained by the presence of a double bond between C_1 and C_2 , and a single bond between C_2 and C_3 . Many of the reactions used in the past, however, do not provide convincing proof of the formula, as they are not necessarily dependent on the presence of double bonds. For instance, the isolation of 5:6-benzoquinoline as the sole product of the Skraup reaction with β -naphthylamine (Knueppel, *Ber.*, 1896, **29**, 708), though showing the marked reactivity of the 1-position, does not necessarily mean that this is caused by a double bond between C_1 and C_2 . Such reactions are useful as indications,



but must not be taken as conclusive evidence. It is therefore very desirable that the properties and reactions used in such investigations should be known to involve one or more double bonds. For this reason the investigations of Baker and Carruthers (*loc. cit.*) and Fieser and Lothrop (*loc. cit.*) provide the best evidence so far advanced for the arrangement of the double bonds in condensed aromatic compounds. The present paper gives further evidence on somewhat similar lines for the structure of derivatives of naphthalene, hydrindene, and tetralin.

Fuson (*Chem. Reviews*, 1935, **16**, 1) in his theory of vinylogy has pointed out that the influence of one functional group on another is observed not only in cases such as nitromethane but also when the groups are separated by carbon atoms linked by a double bond or a system of conjugated double bonds. For example, the mobility of the bromine atom in *o*- and *p*-bromonitrobenzene is due to the presence in the ring of a double bond and two conjugated double bonds, just as the reactivity of the methyl group in nitromethane is also found in *o*- and *p*-nitrotoluene.

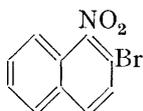


The reactivity of the bromine atom in aromatic bromonitro-compounds is therefore a method for detecting both the presence and the position of double bonds in aromatic compounds, and we have applied the method to bromonitro-derivatives of naphthalene, hydrindene, and tetralin. An analogous method was used by Mills and Smith (J., 1922, **121**, 2724) in the quinoline and isoquinoline series. Our work, like that of Fieser and Lothrop (*loc. cit.*) and Baker and Carruthers (*loc. cit.*), has the advantage that it overcomes the objections of Sutton and Pauling (*Trans. Faraday Soc.*, 1935, **31**, 939). It has also the advantage that semi-quantitative measurements can readily be made, and the reaction can be performed under mild conditions. The reactivity measurements were made by the piperidine method (cf. Le Fèvre and Turner, J., 1927, 1113), which proved to be the most suitable for the small quantities of compounds which were sometimes at our disposal. The measurements make no claim to accuracy, but are sufficient to show the relative reactivities of the bromine atom in the compounds examined. The results are in the table, and the details of the measurements in the experimental section.

	Percentage removal of bromine.			Percentage removal of bromine.	
	0.5 Hour.	20 Hours.		0.5 Hour.	20 Hours.
1-Bromo-2-nitronaphthalene	91	101	2-Chloro-1-nitronaphthalene ...	46	—
2-Bromo-1-nitronaphthalene	65	100	4-Chloro-1-nitronaphthalene ...	43	—
4-Bromo-1-nitronaphthalene	60	98	8-Chloro-1-nitronaphthalene ...	—	0
5-Bromo-1-nitronaphthalene	—	0	4-Bromo-5-nitrohydrindene ...	—	< 5
6-Bromo-2-nitronaphthalene	0	0	6-Bromo-5-nitrohydrindene ...	—	72
5:8-Dibromo-1-nitronaphthalene	0	0	6-Bromo-7-nitrotetralin	5	51
3-Bromo-2-nitronaphthalene	0	0	6-Bromo-5-nitrotetralin	0	0
1-Chloro-2-nitronaphthalene	51	—			

If the Erlenmeyer formula is correct, the bromine atom in 1-bromo-2-nitronaphthalene,

2-bromo-1-nitronaphthalene, and 4-bromo-1-nitronaphthalene should be reactive, and in the other naphthalene compounds it should be non-reactive. The same applies to the corresponding chloronitro-compounds. If, on the other hand, the equilibrium formula of Erdmann ($I \rightleftharpoons II \rightleftharpoons III$) is correct, or an equilibrium between the structures (I) and (III) or (I) and (II) is accepted, 3-bromo-2-nitronaphthalene also must be reactive. In the naphthalene compounds studied (see table) a double bond exists between C_1 and C_2 , and a single bond between C_2 and C_3 . This rules out the equilibrium formulæ given above and confirms the Erlenmeyer formula. It is possible that the introduction of polar groups such as nitro- and bromo-groups into the naphthalene molecule, which is undoubtedly symmetrical (Kohlrausch, *Ber.*, 1935, **68**, 893), produces an unsymmetrical formula (Ufimzew, *loc. cit.*; Lesser, Kranepuhl, and Gad, *Ber.*, 1925, **58**, 2109) such as that inset, but the parallelism of our results with those of Fieser and other workers is strong evidence for the Erlenmeyer formula.

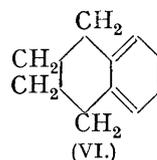
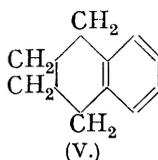
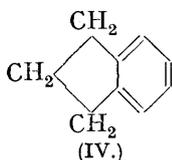


It might be expected that 6-bromo-2-nitronaphthalene would contain reactive bromine, as the bromine and the nitro-group are separated by a conjugated system of three double bonds. The fact that no reactivity was observed is another proof that the double bond shared by the two rings does not function normally. 8-Chloro-1-nitronaphthalene and 5:8-dibromo-1-nitronaphthalene also are of interest. In these compounds no reactivity was observed, although each contains a halogeno- and a nitro-group ortho to one another. It is clear that mere proximity of the groups is not sufficient to produce reactivity, and this fact confirms the correctness of Fuson's theory.

It must be stressed that all the chemical evidence for the structure of naphthalene rests on the properties and reactions of substituted naphthalene compounds. It is therefore possible that the polar effects of the substituents must be taken into account and what holds for one type of compound may not apply to others or to naphthalene itself. Thus the results of Baker and Carruthers (*loc. cit.*), as suggested by the authors themselves, may indicate in certain compounds an unsymmetrical distribution of bonds due to chelation between the substituents. Similarly there may be displacement of the double bonds by the use of vigorous conditions or reagents. This would account for the formation of 5:6-tetrahydrobenzindan-1-one from β -2-tetrahydronaphthylpropionyl chloride in presence of aluminium chloride (Darzens and Lévy, *Compt. rend.*, 1935, **201**, 902) and the formation of 2-hydroxy-3-naphthoic acid (Schmitt and Burkard, *Ber.*, 1887, **20**, 2702) by the action of carbon dioxide on sodium β -naphthoxide at a high temperature. The question of the mobility of the double bonds in naphthalene compounds can therefore only be settled by a thorough study of the reactions and properties of different types of naphthalene derivatives.

Attempts were made to prepare 8-bromo-1-nitronaphthalene in the same way as the chloro-compound, *i.e.*, action of the halogen on 1-nitronaphthalene, but 5-bromo-1-nitronaphthalene was invariably obtained. This may be due to an isomeric change caused by the hydrobromic acid liberated during the bromination converting the 8-bromo-1-nitronaphthalene first formed into the 5-bromo-compound in the same way that 1:8-dichloronaphthalene is converted into 1:5-dichloronaphthalene by the action of hydrochloric acid (Armstrong and Wynne, P., 1896—97, **13**, 154). For reactivity measurements 5:8-dibromo-1-nitronaphthalene and 8-chloro-1-nitronaphthalene were therefore used instead of 8-bromo-1-nitronaphthalene.

We also applied our methods to derivatives of hydrindene and tetralin. The work of Mills and Nixon (J., 1930, 2510) indicated that in hydrindene and tetralin the bonds were



stabilised, and formulæ (IV) and (V) were advanced. Recent work by Fieser and Lothrop (*loc. cit.*), Sidgwick and Springall (*loc. cit.*), and Baker (this vol., p. 476) has confirmed

structure (IV) for hydrindene derivatives. Our results also are in agreement with this formula, as a double bond is shown to exist between C₅ and C₆ and a single bond between C₄ and C₅. The stabilised form for tetralin (V) may hold for the hydrocarbon as advocated by Mills and Nixon, but it apparently does not hold for all its derivatives. Thus, while the bromination and coupling reactions of 6-hydroxytetralin point to structure (V) (cf. Mills and Nixon, *loc. cit.*), the Skraup reaction on 6-aminotetralin (v. Braun and Gruber, *Ber.*, 1922, 55, 1710) indicates a preponderance of form (VI). The fact that in all the reactions mixtures were obtained, and the work of Fieser and Lothrop (*loc. cit.*) and Sidgwick and Springall (*loc. cit.*) provides evidence that the bonds in tetralin derivatives are not fixed. Our observation that 6-bromo-5-nitrotetralin is completely non-reactive and 7-bromo-6-nitrotetralin reactive indicates structure (VI). It may be that the presence of the bromo- and the nitro-group does stabilise the molecule in this way, or it is possible that the reduced ring has some inhibiting effect on the bromine reactivity (cf. Lindemann and Pabst, *Annalen*, 1928, 462, 24). It is impossible at present to decide between these alternatives.

Borsche and Bodenstein (*Ber.*, 1926, 59, 1909) claimed to have obtained 6-bromo-5-acetamidohydrindene and 4-nitro-5-acetamidohydrindene by the bromination and nitration respectively of 5-acetamidohydrindene. From these two compounds we obtained the corresponding bromonitrohydrindenes by hydrolysis to the amino-compounds and replacement of the amino-group by the nitro-group in 6-bromo-5-aminohydrindene and by the bromo-group in the nitroaminohydrindene. The two bromonitrohydrindenes so obtained were found to be identical by a mixed melting-point determination and by measurements of the bromine reactivity. The nitro-compound obtained by Borsche and Bodenstein must therefore have been the 6-nitro- and not the 4-nitro-compound. It also follows that their product of the nitration of 5-acetylhydrindene must have been 6-nitro-5-acetylhydrindene and not 4-nitro-5-acetylhydrindene as they claimed. Doubt on some of the results of Borsche and Bodenstein had been cast by Lindner and Bruhin (*Ber.*, 1927, 60, 439).

In one case, 4-bromo-5-nitrohydrindene, we were unable to purify the compound thoroughly, but quantitative analysis showed it to be sufficiently pure for a rough estimation of the bromine reactivity to be made.

EXPERIMENTAL.

Unless otherwise stated, the methods of preparation and the properties of the compounds used are those given in the literature. Many of the bromonitro-compounds were prepared from the corresponding nitroamines, the method of Hodgson and Walker (*J.*, 1933, 1620) always being used. The identity and purity of the nitroamino-compounds were checked by the preparation of acetyl or benzoyl derivatives or of molecular compounds with *s.*-trinitrobenzene. The bromonitro-compounds in most instances were analysed quantitatively (Dr. Weiler, Oxford).

3-Bromo-2-nitronaphthalene.—1: 3-Dibromo- β -naphthylamine was prepared as described by Bell (*loc. cit.*) and from it 3-bromo- β -naphthylamine was obtained as described by Conden and Kenyon (*J.*, 1935, 1591). Attempts to oxidise the amino-group to the nitro-group by the methods of Meisenheimer and Hesse (*Ber.*, 1919, 52, 1172) and Bigiavi and Albanese (*Centr.*, 1935, 1348) were unsuccessful. The compound was therefore converted into the nitro-compound by the method of Hantzsch and Blagden (*Ber.*, 1900, 33, 2554). Copper sulphate crystals (10 g.) were dissolved in water (100 c.c.), and 2*N*-sodium hydroxide added until all the copper was precipitated as the hydroxide. The mixture was cooled in ice, and sulphur dioxide passed in until a dark green solution was obtained. When this was warmed, a red precipitate of cupro-cupri-sulphite (5 g.) was obtained. The amine (6 g.) was converted into the sulphate by the addition of sulphuric acid, water (25 c.c.) added to the paste, and the amine diazotised. A mixture of cupro-cupri-sulphite (10 g.), sodium nitrite (32 g.), and water (120 c.c.) was stirred mechanically, and the diazo-solution added drop by drop. The mixture was stirred at room temperature until the brisk evolution of gas had ceased, and then distilled with superheated steam. This method of separation was tedious owing to the low volatility of the 3-bromo-2-nitronaphthalene. The product (0.5 g.) crystallised from alcohol in pale yellow needles, m. p. 84° (Found: N, 5.7; Br, 33.4. Calc. for C₁₀H₆O₂NBr: N, 5.6; Br, 31.7%). Hodgson (*J.*, 1936, 1151) gives the same m. p.

5-Bromo-1-nitronaphthalene.—This compound was prepared by a modification of Scheufelin's method (*Annalen*, 1885, 231, 185). A mixture of α -nitronaphthalene (20 g.) and ferric chloride

(0.5 g.) was liquefied on a water-bath, and bromine passed through it for 1 hour, hydrogen bromide being evolved. The product was poured into water, washed with sodium carbonate solution, and crystallised repeatedly from alcohol (charcoal), 4 g. of yellow needles, m. p. 121° (lit., 122.5°), being obtained (Found: N, 5.3; Br, 31.5. Calc. for $C_{10}H_6O_2NBr$: N, 5.6; Br, 31.7%).

6-Bromo-2-nitronaphthalene.—6-Bromo- β -naphthylamine, prepared by the method of Saunders and Hamilton (*J. Amer. Chem. Soc.*, 1932, **54**, 636), crystallised from glacial acetic acid in yellow plates, m. p. 206—207° (lit., 203°). After diazotisation it yielded 6-bromo-2-nitronaphthalene, which crystallised from glacial acetic acid in brown-yellow needles, m. p. 190° (Found: N, 5.6; Br, 31.3. $C_{10}H_6O_2NBr$ requires N, 5.6; Br, 31.7%).

5:8-Dibromo-1-nitronaphthalene.—This compound was prepared by a modification of Salkind's method (*Ber.*, 1931, **64**, 958), 1:4-dibromonaphthalene (19 g.) and concentrated nitric acid (110 c.c.) being stirred together at 65° for 4 hours. The precipitate obtained on cooling was crystallised repeatedly from glacial acetic acid, yielding 6.5 g. of pale yellow needles, m. p. 118° (lit., 116—117°).

4:6-Dibromo-5-p-toluenesulphonamidohydrindene.—6-Bromo-5-aminohydrindene (Borsche and Bodenstein, *loc. cit.*) (18 g.) was dissolved in pyridine (50 c.c.), and *p*-toluenesulphonyl chloride (16.5 g.) added. The solution was boiled for 20 minutes and cooled, bromine (4.5 c.c.) added slowly, and the mixture kept overnight and poured into water. The sticky mass obtained solidified on trituration with cold alcohol (100 c.c.). **4:6-Dibromo-5-p-toluenesulphonamidohydrindene** (12 g.) crystallised from alcohol in colourless prisms, m. p. 199—200° (Found: Br, 36.7; S, 7.2. $C_{16}H_{15}O_2NBr_2S$ requires Br, 35.9; S, 7.2%).

4:6-Dibromo-5-aminohydrindene.—The preceding compound (11 g.) was dissolved in warm concentrated sulphuric acid (120 c.c.), and the solution poured into a large volume of water, 4:6-dibromo-5-aminohydrindene separating. It crystallised from alcohol in colourless needles, m. p. 71° (Borsche and Bodenstein, *loc. cit.*, record 70°) (Found: Br, 53.8. Calc. for $C_9H_9NBr_2$: Br, 54.9%).

4-Bromo-5-aminohydrindene.—4:6-Dibromo-5-aminohydrindene (8 g.) was heated for 1 hour with alcohol (40 c.c.), concentrated hydrochloric acid (40 c.c.), and tin (8 g.). After 40 minutes the solution was filtered hot and poured into 2*N*-sodium hydroxide (250 c.c.), and the dark grey compound extracted with alcohol. Water was added to the alcoholic solution until it became milky; after 12 hours, long white needles (2 g.) of 4-bromo-5-aminohydrindene separated, m. p. 50—51° (Found: N, 6.4; Br, 39.5. $C_9H_{10}NBr$ requires N, 6.6; Br, 37.6%). An oil was obtained by mixing the compound with 6-bromo-5-aminohydrindene, showing that the reduction had removed the 6-bromine atom.

4-Bromo-5-nitrohydrindene.—4-Bromo-5-aminohydrindene was converted into 4-bromo-5-nitrohydrindene by the method used for preparing 3-bromo-2-nitronaphthalene (see above). The reaction mixture on steam distillation gave a pale yellow oil, but attempts to crystallise it met with no success. As in all cases of preparations of nitro-compounds by this method, the yield was exceedingly small, and we had little more than was sufficient for reactivity measurements and analysis (Found: N, 4.3; Br, 35.2. $C_9H_8O_2NBr$ requires N, 6.0; Br, 33.0%).

6-Bromo-5-nitrohydrindene.—6-Bromo-5-aminohydrindene (3.5 g.), m. p. 46—47° (Borsche and Bodenstein, *loc. cit.*, record 43°), was converted into 6-bromo-5-nitrohydrindene by the method just mentioned. The reaction mixture was steam-distilled for 6 hours, and an oil obtained which was dissolved in ether-methyl alcohol. When the ether was allowed to evaporate at room temperature, the solution deposited 6-bromo-5-nitrohydrindene in yellow needles (0.5 g.), m. p. 42°. The compound was also prepared by standard methods from the nitro-5-acetamidohydrindene of Borsche and Bodenstein (*loc. cit.*) and purified by dissolving it in methyl alcohol and cooling the solution in a freezing mixture; m. p. 44—45°. The compound was shown to be identical with 6-bromo-5-nitrohydrindene by mixed m. p. determination and bromine reactivity (Found: N, 6.0; Br, 32.8. $C_9H_8O_2NBr$ requires N, 6.0; Br, 33.0%).

6-Bromo-7-nitrotetralin.—6-Acetyltetralin was converted into 6-acetamidotetralin by Scharwin's method (*Ber.*, 1902, **35**, 2513), but, as phosphorus pentachloride was found to be unsatisfactory for the Beckmann rearrangement involved, benzenesulphonyl chloride (cf. Blatt and Barnes, *J. Amer. Chem. Soc.*, 1934, **56**, 1150) was used. The oxime of 6-acetyltetralin (10 g.) was dissolved in pyridine (100 c.c.), and benzenesulphonyl chloride (12 c.c.) slowly added, the temperature being kept below 15°. After 3 hours the solution was poured into ice and dilute hydrochloric acid. After several hours 6-acetoamidotetralin separated and was crystallised from ligroin, m. p. 107°; yield, 6 g. If larger quantities of oxime were used, charring occurred and the yield diminished. The compound was nitrated (Schroeter, *Annalen*, 1921, **426**, 66), and

from the resulting 7-nitro-6-acetoamidotetralin 6-bromo-7-nitrotetralin was prepared by standard methods; it formed prisms from methyl alcohol, m. p. 53—54° (Found: N, 5.3; Br, 31.3, $C_{10}H_{10}O_2NBr$ requires N, 5.5; Br, 31.3%).

6-Bromo-5-nitrotetralin.—Prepared by the usual methods from 5-nitro-6-acetoamidotetralin (Schroeter, *loc. cit.*), this formed golden-yellow plates from alcohol, m. p. 103—104° (Vesely and Chudozilow, *Chem. Abs.*, 1925, 128, 1056, record 101—102°) (Found: N, 5.7; Br, 30.6. Calc. for $C_{10}H_{10}O_2NBr$: N, 5.5; Br, 31.3%).

Quantitative Method.—The method followed was that of Salkind (*Ber.*, 1931, 64, 289), as it was found to be suitable for small quantities of material. About 0.1 g. of the bromo(chloro)-compound was accurately weighed in a glass tube provided with a ground glass stopper. Piperidine (1 c.c.) was added, and the tube immersed in a thermostat at approximately 45°. After a definite interval of time the contents of the tube were washed into a separating funnel with water (50 c.c.), and the solution shaken with pure benzene, which removed coloured organic matter from the aqueous layer but no halogen. The aqueous layer was now almost colourless. The halogen present was determined by Volhard's method by titration with silver nitrate (*N/50*) and potassium thiocyanate (*N/50*), ferric alum being used as indicator. All determinations were done in duplicate.

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