683. *Diaryls. Part II.*[1] *The Rearrangement of* 1,2′-*Hydrazonaphthalene.*

By E. R. Ward and B. D. Pearson.

1,2′-Hydrazonaphthalene rearranges in acid media to give 1′,2-diamino-1,2′-binaphthyl. This result is compared with the analogous rearrangement of the two isomeric hydrazonaphthalenes, and a general mechanism involving a π-complex transition state is formulated.

Ultraviolet spectra of four dinitrobinaphthyls are interpreted in relation to the possible steric effects within such molecules.

Pyrolyses of 1,2′-binaphthyl-1′,2-iodonium iodide failed to yield 1,2:5,6-dibenzobiphenylene.

A new preparation of 2-nitro-1-naphthylamine from naphthionic acid is described.

After reaction of ethereal 1-bromo-2-iodonaphthalene with magnesium Ward and Pearson [1] were able to isolate, in minute yield, a hydrocarbon which may have been 1,2:5,6-dibenzobiphenylene. We have now attempted to prepare this from 1,2′-binaphthyl-1′,2-iodonium iodide, but pyrolyses of the latter under varying conditions (cf. Ward and Pearson,[1] Curtis and Viswanath [2]) failed.

The iodonium iodide was obtained from 1′,2-diamino-1,2′-binaphthyl. This compound was prepared by Cook *et al.*[3] by reduction of 1,2′-azonaphthalene to 1,2′-hydrazonaphthalene and subsequent rearrangement, but they did not orientate it. We have now established its constitution by obtaining it by catalytic reduction of 1′,2-dinitro-1,2′-dinaphthyl, the latter being isolated in 40% yield from a crossed Ullmann reaction between 2-iodo-1- and 1-iodo-2-nitronaphthalene (which also produced a small amount of 1,1′-dinitro-2,2′-dinaphthyl but apparently no 2,2′-dinitro-1,1′-dinaphthyl). This new route is rendered impracticable by the difficulty in preparing 2-nitro-1-naphthylamine on a large scale. An attractive route to the nitro-amine appeared to be nitration of *N*-acetylnaphthionic acid (the sulphonic acid group acting as a blocking group), followed by hydrolysis and desulphonation of the 4-acetamido-3-nitronaphthalene-1-sulphonic acid. Although the last stages can be satisfactorily performed in a combined process the nitration gives erratic results.

Cook *et al.* prepared 1,2′-azonaphthalene by deamination of the product obtained by coupling diazotised 2-naphthylamine with 1-naphthylamine hydrochloride in water. This deamination was originally carried out by Nietzki and Gottig [4] and has been repeated by

---

[1] The Paper by Ward and Pearson, *J.*, 1959, 1676, is regarded as Part I.

[2] Custis and Viswanath, *J.*, 1959, 1670.

[3] Cook, Hewett, and Kennaway, *Amer. J. Cancer*, 1940, **40**, 62.

[4] Nietzki and Gottig, *Ber.*, 1887, **20**, 612.

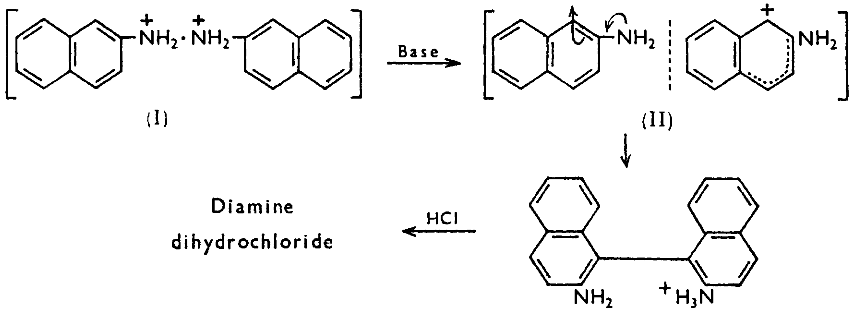
Badger and Lewis.[5] Since none of these workers separated the 4-amino-1,2′-azonaphthalene before its deamination it appeared to us that the reported differences in m. p. of the deamination product might be due to the presence, in varying amount, of the isomeric 2,2′-azonaphthalene. However the product we obtained by deaminating the mixed azo-compounds proved identical with that obtained by deaminating pure 4-amino-1,2′-azonaphthalene (separated from the coupling product by chromatography on alumina [6]). This confirms Turner's suggestion [7] that in the diazotisation and deamination of the mixed aminoazo-compounds arising from coupling a diazo-compound with 1-naphthylamine the 1-amino-2-azonaphthalenes are converted into naphthotriazoles in the diazotisation and subsequently eliminated in working up the product. Attempts to prepare 1,2′-azonaphthalene by desulphonation of 1′,2-azonaphthalene-5-sulphonic acid (Acilan Braun 4G,C.I. 13,000), with 50% or 70% aqueous sulphuric acid, were not successful.

The yield of 1′,2-diamino-1,2′-dinaphthyl was improved from the 20% claimed by Cook *et al.*, who used sodium dithionite as reducing agent, to 95% by using zinc powder and ammonia (cf. Vecera, Petranek, and Gasparic [8]). Paper chromatography showed that the crude rearrangement product from 1,2′-hydrazonaphthalene contained no component in addition to the identified 1′,2-diamino-1,2′-dinaphthyl.

For the first time the rearrangements of the three hydrazonaphthalenes can be studied qualitatively. The results are summarised in Table 1. The results are similar to the electrophilic substitution of naphthalene derivatives containing an electron-releasing group (*e.g.*, NH_2). The most reactive positions in 1-naphthylamine derivatives are the 2- and the 4-position, and in 2-naphthylamine derivatives the 1-position. One scheme for formulating intramolecular attack by an electrophilic entity on an electron-releasing entity by using the doubly protonated transition state (I) identified by Hammond and Shine [12] is as annexed. Hughes and Ingold [13] pointed out that the transition state (I) offers an exceptional amount of extra resonance energy and owing to the proximity of the two planar naphthalene molecules a π-complex, as proposed by Dewar,[14] may be favoured. Removal of a proton from the transition state, accomplished by a suitable base (cf.

TABLE 1.

Hydrazonaphthalene	Product
2,2′-	1,1′-Diamino-2,2′-binaphthyl [9, 10]
1,2′-	1′,2-Diamino-1,2′-binaphthyl
1,1′-	2,2′- and 4,4′-Diamino-1,1′-binaphthyl (about equal amounts) [11]



---

[5] Badger and Lewis, *J.*, 1953, 2154.

[6] Ward, Wells, and Pearson, *J. Soc. Dyers and Colourists*, in the press.

[7] Turner, *J.*, 1949, 2282.

[8] Vecera, Petranek, and Gasparic, *Chem. Listy*, 1957, **51**, 911.

[9] Meisenheimer and Witte, *Ber.*, 1903, **36**, 4159.

[10] Cumming and Howie, *J.*, 1932, 528.

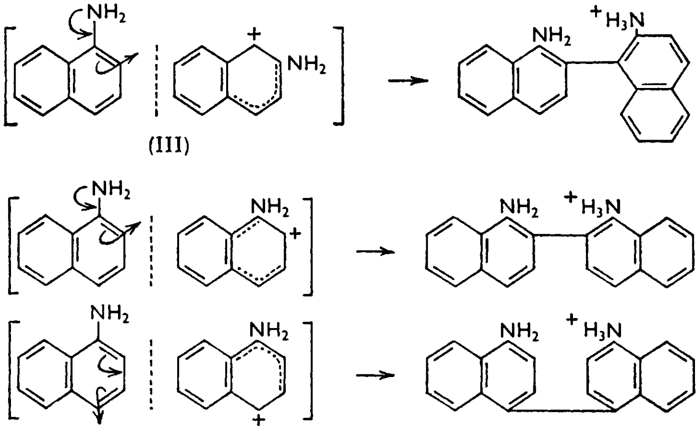
[11] Hodgson and Habeshaw, *J.*, 1947, 77.

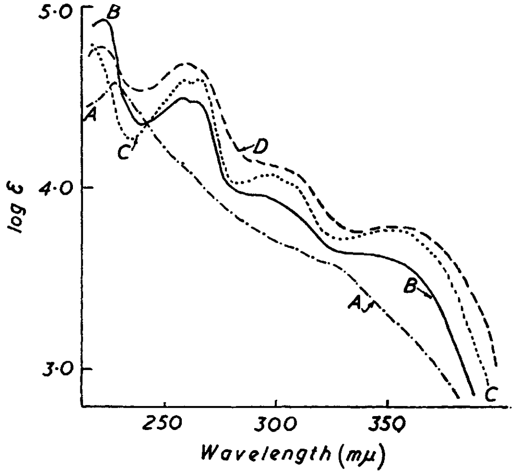
[12] Hammond and Shine, *J. Amer. Chem. Soc.*, 1950, **72**, 220.

[13] Hughes and Ingold, *J.*, 1941, 608.

[14] Dewar, " Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 236.

Dewar[14]), would then lead to a second π-complex (II) in which an intramolecular carbonium-ion attack takes place on the adjacent naphthalene nucleus. This attack forms the diaminobinaphthyl and liberates a second proton for salt formation. That carbonium ion will be formed which has the greatest stabilisation energy. The positions of highest electron-density on the other naphthalene nucleus will be adjacent to the positively charged atom (provided the polarisibility and localisation energy of the carbon atoms are suitable).


(III)



Ultraviolet spectra of (*A*) 1,1′-*dinitro*-2,2′-, (*B*) 1′,2-*dinitro*-1,2′-, (*C*) 2,2′-*dinitro*-1,1′-, *and* (*D*) 3,3′-*dinitro*-2,2′-*binaphthyl in ethanol.*

Whereas in the benzene series within the π-complex relative nuclear rotation can occur (leading to the formation of diphenylines) in the naphthalene series this rotation may be prevented by an electrostatic locking effect initiated by the second nucleus (due to charge transference). In the case of the unsymmetrical hydrazonaphthalene it is assumed that the carbonium ion (III) predominates, the steric arrangement then causing formation of the 1,2′-bond, formation of the 1,4′-bond being impossible without molecular rotation within the complex (III).

The ultraviolet spectra of the four dinitrobinaphthyls (Table 2) can be interpreted in terms of steric hindrance to conjugation within the binaphthyl molecule. Friedel, Orchin, and Reggel[15] deduced from the spectra of the binaphthyls that although there was steric hindrance to conjugation in 1,1′-binaphthyl, and to a small extent in 1,2′-dinaphthyl, 2,2′-binaphthyl was comparatively free from steric hindrance and hence planar.

[15] Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

The spectrum of 1,1'-dinitro-2,2'-binaphthyl, as is usual for a large conjugated molecule, has little fine structure; only the band at 228 mμ can be identified with a bathochromic shift of the band at 212 mμ in the spectrum of 2,2'-dinaphthyl.

The spectra of 2,2'-dinitro-1,1'- and 3,3'-dinitro-2,2'-binaphthyl are very similar to the spectrum of 2-nitronaphthalene, indicating that there is little conjugation between the naphthalene nuclei in these two binaphthyls. 1',2-Dinitro-1,2'-binaphthyl also possesses a spectrum quite like that of 2-nitronaphthalene, but there is some smoothing out of the fine structure, which suggests that a small measure of conjugation is present.

TABLE 2. *Ultraviolet spectral maxima* (log ε *in parentheses*) *for ethanol solution.*

Dinitrobinaphthyl					
1,1'-NO_2	-2,2'- (*A*)	228(4·59)			
1',2-	-1,2'- (*B*)	222(4·92)	258(4·46) 264(4·44)	293(3·95) †	350(3·6) †
2,2'-	-1,1'- (*C*)		258(4·57), 266(4·58)	297(4·07)	350(3·74)
3,3'-	-2,2'- (*D*)	221(4·77)	269(4·68)	305(4·11)	355(3·75)
Binaphthyls [18]					
1,1'-		220(4·95)		283(4·12), 293(4·10)	
1,2'-		219(5·10)		282(4·20)	
2,2'-		212(4·65)		254(5·0)	
Nitronaphthalenes [19]					
2-			258(4·40)	306(3·93)	352(3·44)
1-			243(4·02)		343(3·60)
1',2-Diamino-1,2'-binaphthyl			244(3·74)	283(4·09), 293(4·04)	335(3·92)
2,2'-Diamino-1,1'-binaphthyl [17]			241(4·97)	273(4·08), 282(4·14), 293(4·02) †	346(3·75)
2-Naphthylamine [17]			236(4·78)	280(3·82), 292(3·73)	340(3·28)

† Inflexion.

It is interesting that 3,3'-dinitro-2,2'-binaphthyl exhibits a large amount of steric hindrance whilst 1,1'-dinitro-2,2'-binaphthyl is unhindered. Steric models (Catalin) indicate that, while a completely planar structure for 1,1'-dinitro-2,2'-binaphthyl is unlikely, the hindrance between the 1-nitro-group and the 8-hydrogen atom will rotate the nitro-group out of the plane of the ring, thus allowing the two naphthalene systems to become nearly coplanar. In 3,3'-dinitro-2,2'-dinaphthyl, however, the nitro-groups' being in the plane of the aromatic ring leads to more steric hindrance and it may be that it is energetically more favourable for the nitro-group to be in this planar position rather than that the binaphthyl itself should become more planar. However, it is well known that the onset of spectrally detectable effects occurs somewhere between the covalent and the van der Waals distances (cf. Braude [16]) and so different types of model can give different results.

Jones [17] found that the ultraviolet spectrum of 2,2'-diamino-1,1'-binaphthyl closely resembled that of 2-naphthylamine, indicating little conjugation between the naphthalene nuclei. This parallels the case of the above dinitrobinaphthyls, and again the unsymmetrical 1',2-diamino-1,2'-binaphthyl shows rather less fine structure than the more sterically hindered, symmetrical 2,2'-diamino-1,1'-binaphthyl (Table 2).

EXPERIMENTAL

Preparation of 2-Nitro-1-naphthylamine from Naphthionic Acid (*With* C. D. JOHNSON).—Naphthionic acid (5 g.), pyridine (2·25 g.), and acetic anhydride (9·5 g.) were refluxed together for 1 hr. After cooling to *ca.* 40° hydrochloric acid (*d* 1·18; 25 c.c.) in water (10 c.c.) was added with stirring. Precipitation of 4-acetamidonaphthalene-1-sulphonic acid began immediately and next morning it was collected, washed with acetic acid, and dried at 100°. The yield is

---

[16] Braude in " Progress in Stereochemistry," Vol. I, ed. Klyne, Butterworths, London 1954, p. 146.

[17] Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127.

[18] Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," Wiley and Sons, New York, 1951.

[19] Coulson, Thesis, London, 1955.

almost quantitative and the product gave a satisfactory assay with N-sodium hydroxide (phenolphthalein as indicator). It is essential at this stage to have a very fine crystalline material, otherwise the subsequent nitration is extremely difficult.

The acetyl derivative (5 g.) was suspended in acetic acid (10 c.c.), and nitric acid (*d* 1·5; 2·5 g.) was added together with boron trifluoride–acetic acid complex (20 g.; 40% of BF_3) in acetic acid (75 c.c.). A crystal of sodium nitrite was added and, with very good stirring, the temperature was raised to 75° and maintained there for 30 min. (at lower temperatures nitration was incomplete, whereas at 80° large amounts of by-products were produced). Yields varied from 40 to 70%.

The nitro-amide (10 g.) was refluxed with a 1 : 1 : 1 v/v mixture (300 c.c.) of ethanol, water, and sulphuric acid (*d* 1·84) for 30 min. Any solids remaining at this stage were filtered off and the filtrate was poured on ice. The solids were collected, washed with water, and basified by further trituration with water, yielding almost pure 2-nitro-1-naphthylamine (*ca.* 70%; overall from naphthionic acid 30—50%). Very pure material may be obtained by chromatographing this product (in 5 g. portions) on alumina in benzene.

Crossed Ullmann Reaction between 1-*Iodo*-2-*nitronaphthalene and* 2-*Iodo*-1-*nitronaphthalene.*—The iodo-compounds were prepared by diazotising the amines by Hodgson and Walker's method,[20] and decomposing the diazonium solutions by addition to aqueous potassium iodide and iodine. The yields of almost pure material (which were used directly without recrystallisation) were 80 and 98% respectively. The intimately mixed iodo-compounds (5 g. of each) were heated at 155° in a constant-temperature heater, and copper bronze (8 g.) was added slowly with stirring. The inner vessel was occasionally removed and allowed to cool to 150° before replacement, to prevent the temperature of the mixture from exceeding 175°. Heating was then continued for 1 hr. The cooled solids were extracted with boiling benzene (3 × 100 c.c.), and the extracts concentrated and filtered through alumina (2·5 × 20 cm.). Further concentration and cooling yielded 1,1'-dinitro-2,2'-binaphthyl (*A*) (0·15 g., 2·6%), m. p. 283° (Cumming and Howie [21] give m. p. 284°). The remainder of the benzene was evaporated, yielding a semicrystalline material which was stirred with light petroleum (b. p. 60—80°) (15 c.c.) and benzene (6 c.c.); filtration yielded 1',2-*dinitro*-1,2'-*binaphthyl* (*B*) (2·3 g., 40%, m. p. 170—172°). Crystallised from 1 : 1 v/v ethanol–ethyl acetate this had m. p. 174—176° (Found: C, 70·1; H, 3·6; N, 8·1. $C_{20}H_{12}O_4N_2$ requires C, 69·8; H, 3·5; N, 8·1%). Concentration of this mother-liquor gave further amounts of compound (*A*) (0·15 g., 2·6%). Evaporation of the original mother-liquor gave a tar from which nothing crystallised. Compound (*B*) was orientated by the fact that it was different from both (*A*) and 2,2'-dinitro-1,1'-binaphthyl (mixed m. p.s., ultraviolet and infrared spectra).

1',2-*Diamino*-1,2'-*binaphthyl.*—1',2-Dinitro-1,2'-binaphthyl (1 g.) in ethanol (10 c.c.) and ethyl acetate (100 c.c.), containing B.D.H. stabilised Raney nickel (1 g.), was reduced with hydrogen at 70—80° (atmospheric pressure). Reduction appeared to be complete in about 12 hr. Then the nickel was filtered off and the filtrate concentrated to 20 c.c. The crude diamine was collected and crystallised three times from ethanol, giving white needles (0·71 g., 86%), m. p. 149° (Cook *et al.*[3] give 150—151°) (Found: C, 83·2; H, 5·7; N, 9·2. Calc. for $C_{20}H_{16}N_2$: C, 84·5; H, 5·6; N, 9·9%).

Preparation and Pyrolysis of 1,2'-*Dinaphthyl*-1',2-*iodonium Iodide.*—The above diamine (1 g.) was dissolved in warm water (15 c.c.) and hydrochloric acid (*d* 1·18; 8 c.c.). This was treated, at 0°, with sodium nitrite (0·6 g.) in water (4 c.c.) and after 15 min. added to potassium iodide (9 g.) and iodine (2 g.) in water (4 c.c.). After 2 hr. the solids were collected, washed with water, and kept overnight in aqueous 10% (w/v) sodium thiosulphate; the semiliquid product solidified. This crude product (2·1 g.) was used for pyrolyses which were carried out as described by Ward and Pearson.[1]

1-*Amino*-2,2'-*azonaphthalene and* 4-*Amino*-1,2'-*azonaphthalene.*—These compounds were prepared by coupling diazotised 2-naphthylamine with 1-naphthylamine hydrochloride in water at pH 3·5, with subsequent chromatographic separation of the mixed azo-dyes.[6] 1-*Amino*-2,2'-*azonaphthalene* was obtained as red plates [from 1 : 1 v/v benzene–light petroleum (b. p. 60—80°)], m. p. 193—194° (Found: C, 81·2; H, 5·3; N, 13·6. $C_{20}H_{15}N_3$ requires C, 80·8; H, 5·1; N, 14·1%), and 4-amino-1,2'-azonaphthalene as orange-red needles (from the same solvents), m. p. 144—145° (cf. m. p. 152°, Nietzki and Gottig; [4] 136°, Cook *et al.*[3]).

---

[20] Hodgson and Walker, *J.*, 1933, 1620.

[21] Cumming and Howie, *J.*, 1931, 3176.

Deamination of 4-Amino-1,2′-azonaphthalene.—The azo-compound (5 g.) was dissolved in warm ethanol (250 c.c.), the solution cooled to 0°, and sulphuric acid (*d* 1·84; 8·5 c.c.) added. Sodium nitrite (1·16 g., 1 mol.) in water (5 c.c.) was slowly added, at 0°, and the mixture allowed to warm to room temperature, nitrogen being evolved. After 72 hr. the mixture was poured into water (1 l.), and the solid collected and dried *in vacuo* at 70°. This was extracted with light petroleum (b. p. 60—80°) (200 c.c., Soxhlet), and the extract concentrated to 50 c.c. and filtered through alumina (3 × 20 cm.). From the filtrate almost pure 1,2′-azonaphthalene (1·9 g., 40%) was obtained, forming orange needles (from ethanol), m. p. 143—144° (Badger and Lewis[5] give 145°). Similar yields were obtained when the mixed azo-dyes were deaminated. Deamination by diazotisation in a mixture of sulphuric and hypophosphorous acid gave only 27% yield. Hodgson–Walker diazotisation followed by addition of cuprous oxide, or addition to methanol–cuprous oxide, did not give this product.

Preparation and Rearrangement of 1,2′-Hydrazonaphthalene.—1,2′-Azonaphthalene (1 g.) was dissolved in refluxing acetone (85 c.c.), and the hot solution was treated with zinc powder ("AnalaR," 1·5 g.) and ammonia (*d* 0·88; 15 c.c.). After 15 minutes' refluxing, this treatment was repeated and in a further 10 min. the solution was colourless. The solution was filtered hot to remove zinc, the zinc was extracted by hot acetone (15 c.c.), and the combined filtrates were cooled in a closed vessel to minimise oxidation. Hydrochloric acid (*d* 1·8) was then added (until the pH was $\not>$2) and after 3 hr. at room temperature the solution was basified by ammonia (*d* 0·88). The 1′,2-diamino-1,2′-binaphthyl slowly separated and after 24 hr. was collected as a white solid (0·95 g., 95%; m. p. 137—140°); crystallised from ethanol it had m. p. 149° and was identical (ultraviolet spectra) with the diamine prepared as above.

Ultraviolet spectra were recorded by a Unicam S.P. 500 photoelectric spectrophotometer for ethanol solutions. The infrared spectra of the four dinitrobinaphthyls will be made available through the Documentation of Molecular Spectroscopy punched-card collection.

The authors are indebted to the Department of Scientific and Industrial Research for a special grant and to Dr. D. H. Whiffen (University of Birmingham) for the infrared spectral measurements.

LEICESTER COLLEGE OF TECHNOLOGY AND COMMERCE,
LEICESTER.

[*Received, April* 15*th*, 1959.]