## **1,8-Dehydronaphthalene.** Part II.<sup>1</sup> Generation of **1,8-Dehydronaph-**thalene from 1-Aminonaphtho[1,8-*de*]triazine

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Amination of naphtho[1,8-*de*]triazine with hydroxylamine-*O*-sulphonate afforded 1-amino-8-azido-1naphthalene and 1-aminonaphtho[1,8-*de*]triazine. Oxidation of the latter with lead tetra-acetate liberated nitrogen and gave 1,8-dehydronaphthalene which could be trapped by cycloaddition to dimethyl acetylenedicarboxylate or to *N*-phenylmaleimide.

WHILE 1,2-dehydrobenzene (I) has found wide synthetic application and its reactions have been studied in great detail, the known chemistry of the other dehydroaromatic intermediates is limited.<sup>2</sup> Our interest was with 1,8-de-hydronaphthalene (II) which should be more reactive than dehydrobenzene, but not so strained as to prohibit



completely its transient existence. Recently its stabilization by interaction of the two dehydro-orbitals has been calculated to be about one third of that determined for dehydrobenzene.<sup>3</sup>

We have previously obtained evidence for the generation of compound (II) in the pyrolysis of the sulphone

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<sup>1</sup> Part I, R. W. Hoffmann and W. Sieber, Annalen, 1967, 703, 96.

(III) at 230° by the formation of perylene (0.4%), and, in the presence of dimethyl acetylenedicarboxylate, by the formation of the adduct (IV) (0.15%).



Clearly, the inefficiency of this reaction made better sources for (II) desirable. In view of the elegant method of Campbell and Rees<sup>4</sup> for the generation of (I) by oxidation of 1-aminobenzotriazole we attempted an adaptation of this method for the generation of (II).

For this purpose the synthesis of 1-aminonaphtho-[1,8-de]triazine (VIII) was attempted by analogy with the preparation of 1-aminobenzotriazole by Trave and <sup>2</sup> R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,'

 <sup>2</sup> R. W. Hoffmann, Dehydrobenzene and Cycloalkynes, Verlag Chemie, Academic Press, Weinheim/New York, 1967.
 <sup>3</sup> R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499.

<sup>4</sup> C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 1964, 296.

Bianchetti.<sup>5</sup> 1-Amino-8-nitronaphthalene was diazotized and coupled with methyl cyanoacetate to give the ester (V) which, upon catalytic hydrogenation followed by diazotization, gave (VI). However, the amine (VIII)



was not generated by acid hydrolysis of (VI), agreement with the finding of Rees in and Storr<sup>6</sup> that (VIII) is decomposed by acid. We then studied the amination of naphtho[1,8-de]-triazine (VII) by hydroxylamine-O-sulphonate in the presence of sodium hydroxide: 12% of 1-amino-8-azidonaphthalene (IX) and 46% of the desired amine (VIII) were obtained. These products result from amination of the naphthotriazine (VII) in the 1- and 2- positions, the latter being followed by rearrangement to give the azide (IX).6

Oxidation of the amine (VIII) with lead tetra-acetate immediately liberated nitrogen. In the presence of dimethyl acetylenedicarboxylate the dehydrogenation gave dimethyl acenaphthene-1,2-dicarboxylate (IV) in 15% yield. It thus appears that (VIII) is dehydrogenated by lead tetra-acetate to the nitrene (X) followed immediately by fragmentation to two molecules of nitrogen and compound (II), which is then captured by dimethyl acetylenedicarboxylate.



Similarly, in the presence of N-phenylmaleimide, oxidation of the amine (VIII) resulted in an 8% yield of the adduct (XI). Oxidation of the amine (VIII) in the presence of maleic anhydride failed to give an adduct; instead perylene was isolated in 0.5% yield. Although perylene was obtained twice in this manner, its formation was not always reproducible. Therefore our previous statements<sup>1,2</sup> about the dimerization of (II)

formed from (VIII) to give perylene should be considered with reserve.

Provided that the nitrene (X) is the immediate precursor of (II), other routes to (X) should also generate (II). For this reason the synthesis of the toluene-psulphonate (XIII) was attempted. Reaction of the amine (VIII) with toluene-p-sulphonyl chloride under a variety of conditions led invariably to the bis-p-tolylsulphonyl product (XII) which, in turn, could be cleaved to (XIII) by the action of sodium methoxide. By treatment with sodium hydride (XIII) was cleanly converted into its sodium salt.



Thermolysis of this salt at 160° liberated nitrogen, but gave neither (IV) nor (XI) in the presence of dimethyl acetylenedicarboxylate or N-phenylmaleimide. Photolysis 7 of the salt in dioxan-tetrachloroethylene liberated ca. one half of the nitrogen but no adduct between (II) and tetrachloroethylene could be isolated, perhaps because (II) reacted more readily with dioxan by hydrogen abstraction <sup>6</sup> to give naphthalene which was isolated in small yield. Photolysis of (VIII) in ether also gave some naphthalene, but presumably (II) is not involved here. The decomposition of 1,8-diazidonaphthalene made in 26% yield from 1,8-diaminonaphthalene, was also studied. Although its photolysis or thermolysis at 140° readily liberated nitrogen, no indication for the formation of (II) could be obtained by carrying out the thermolysis in the presence of dimethyl acetylenedicarboxylate or N-phenylmaleimide.

At this stage of our investigations we learned of similar results obtained by Rees and Storr<sup>8</sup> and, by mutual agreement, have discontinued our work on the generation of (II) from (VIII).

## EXPERIMENTAL

Methyl 8-Nitro-1-naphthylhydrazonocyanoacetate (V).-To 8-nitro-1-naphthylamine<sup>9</sup> (0.05 mole) in methanol (75 ml.) and conc. hydrochloric acid (16 ml.) a solution of sodium nitrite (0.06 mole) in water (10 ml.) was slowly added at 0° with stirring. A precooled solution of methyl cyanoacetate (0.05 mole) in methanol (25 ml.) was added and after stirring for 30 min. at 0° a solution of sodium acetate (30 g.) in water (125 ml.) was added. After 2 hr. the precipitate (m.p. 140-145°) was crystallised from benzene to give the ester (V), m.p. 158-160° (Found: C, 56.2; H, 3.4; N, C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub> requires C, 56·4; H, 3·4; N, 18·8%), **18·8**. i.r. (Nujol):  $\nu_{max.}$  2200, 1700, 1530, and 1330 cm.  $^{-1}.$ 

Methyl Naphtho[1,8-de]triazin-1-yliminocyanoacetate (VI). Compound (V) (5 mmole) in ethyl acetate (50 ml.) was hydrogenated over 5% palladium on carbon at  $0^{\circ}$  until the

<sup>7</sup> Cf. F. G. Willey, Angew. Chem., 1964, **76**, 144; Angew. Chem., Internat. Edn., 1964, **3**, 138. <sup>8</sup> C. W. Rees and R. C. Storr, Chem. Comm., 1965, 193.

- 9 H. H. Hodgson and J. Ratcliffe, J. Chem. Soc., 1949, 1314.

<sup>&</sup>lt;sup>5</sup> R. Trave and G. Bianchetti, Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., 1960, 28, 652.
<sup>6</sup> C. W. Rees and R. C. Storr, J. Chem. Soc. (C), 1969, 756.

uptake of hydrogen ceased. The solution was filtered and the solvent was evaporated off under reduced pressure; the yellow residue taken up in dioxan (10 ml.) and after addition of aqueous sodium nitrite (5 mmole) to the cooled solution, 15% aqueous hydrochloric acid (2.4 ml.) was added dropwise with stirring. Compound (VI), m.p. 134-137° (decomp.) (0.98 g., 70%) was precipitated by addition of water, and crystallised from dioxan to give violet crystals, m.p. 135° (decomp.) (Found: C, 60.2; H, 3.3; C<sub>14</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub> requires C, 60.2; H, 3.2%), i.r. (Nujol) vmax, 2200, 1700, 1580, 1530, 1400, 1320, 1270, 930, 830, and 720 cm.-1.

Amination of Naphtho[1,8-de]triazine (VII).-To a stirred suspension of naphtho[1,8-de]triazine 10 (6 mmole) in 2Naqueous sodium hydroxide (100 ml.) hydroxylamine-Osulphonic acid (10 g.) was added in small portions during 1.5 hr., the temperature being kept below 40°. After 15 min. the mixture was extracted with ether and the dried (MgSO<sub>4</sub>) extract was chromatographed on silica gel. Elution with benzene-chloroform (7:3) gave 1-amino-8-azido-naphthalene (IX) (0.13 g., 12%), m.p. 62-65°. A sample dissolved in ether, treated with Norite and precipitated with light petroleum gave needles, m.p. 81° (Found: C, 65·3; H, 4·5; N, 30·3.  $C_{10}H_8N_4$  requires C, 65·2; H, 4.4; N, 30.4%), i.r. (Nujol): v<sub>max.</sub> 3500, 2110, 1610, 1570, 1450, 820 and 760 cm.<sup>-1</sup>; the *picrate* (from ether) had m.p. 158-159° (Found: C, 46.8; H, 2.9; N, 23.5. C<sub>16</sub>H<sub>11</sub>N<sub>7</sub>O<sub>7</sub> requires C, 46.5; H, 2.7; N, 23.7%).

Further elution with chloroform-ether (1:1) gave 1-aminonaphtho[1,8-de]triazine (VIII) (0.50 g., 46%), m.p. 152-154°. A sample dissolved in ether, treated with Norite and precipitated with light petroleum gave red needles, m.p. 158° (Found: C, 65·1; H, 4·4; N, 30·6. C<sub>10</sub>H<sub>8</sub>N<sub>4</sub> requires C, 65.2; H, 4.4; N, 30.4%), i.r. (Nujol):  $\nu_{\rm max}$  3400, 3150, 1630, 1580, 1080, 830, 770, and 755 cm.<sup>-1</sup>, the picrate (from ether) gave black needles, m.p. 124° (Found: C, 46.9; H, 2.8; N, 23.5. C<sub>16</sub>H<sub>11</sub>N<sub>7</sub>O<sub>7</sub> requires C, 46.5; H, 2.7; N, 23.7%).

Dimethyl Acenaphthylene-1,2-dicarboxylate (IV).-To a solution of dimethyl acetylenedicarboxylate (15 mmole) and (VIII) (1.5 mmole) in anhydrous methylene chloride (6 ml.) a saturated solution of lead tetra-acetate (1.8 mmole) in methylene chloride was added with stirring. After the vigorous gas evolution had ceased, the mixture was evaporated and chromatographed on silica gel. Elution with chloroform--benzene (4:1) gave an oil which, upon trituration with a little ether or, better, by sublimation (150° 0.1 torr) gave the ester (IV), m.p. 92-96° (60 mg., 15%). Crystallisation from methanol gave orange needles, m.p. 103-103.5° (Found: C, 71.4; H, 4.7. C16H12O4 requires C, 71.6; H, 4.5%), i.r. (Nujol):  $v_{max}$  1720, 1630, 1530, 1350, 1280, 1230, 820, 760, and 720 cm<sup>-1</sup>, u.v. (EtOH),  $\lambda_{\rm max.}$  229 (e 2·1  $\times$  104), 334 nm. (1·2  $\times$  104).

Acenaphthene-1,2-dicarboxylic Acid N-Phenylimide (XI). -To N-phenylmaleimide (15 mmole) and (VIII) (1.5 mmole) dissolved in anhydrous methylene chloride (20 ml.), a saturated solution of lead tetra-acetate (1.8 mmole) in the same solvent was added with stirring. After gas evolution had ceased, the mixture was evaporated under reduced pressure and the residue was chromatographed on silica gel. Elution with benzene gave the imide (XI) (36 mg., 8%) as yellow crystals (from ethanol), m.p. 189-

<sup>10</sup> H. Waldmann and S. Back, Annalen, 1940, 545, 52.
<sup>11</sup> R. A. Friedel and M. Orchin, 'Ultraviolet Spectra of Aromatic Compounds,' John Wiley, New York, 1951, no. 563.

190° (Found: C, 80·1; H, 4·2; N, 4·5.  $C_{20}H_{13}O_2N$  requires C, 80.3; H, 4.4; N, 4.7%), i.r. (Nujol): v<sub>max</sub> 1700, 1200, 805, 770, 745, and 690 cm.<sup>-1</sup>.

Oxidation of the Amine (VIII) in the Presence of Maleic Anhydride.—To a solution of maleic anhydride (15 mmole) and (VIII) (1.5 mmole) in anhydrous acetonitrile (15 ml.) a saturated solution of lead tetra-acetate (1.8 mmole) in the same solvent was added with stirring. After gas evolution had ceased, the filtered solution was chromatographed on neutral alumina. Elution with carbon tetrachloride yielded fluorescent material which was purified by t.l.c. on silica gel, where it showed the same  $R_{\rm F}$  value as perylene. A u.v. spectrum of the purified sample showed the characteristic <sup>11</sup> absorptions of perylene at 363, 382, 407, and 434 nm., from which the yield was determined (0.5%).

 $1\-(NN-Di\-p\-toly|sulphony|amino)naphtho[1,8\-de]triazine$ (XII).—To a solution of toluene-p-sulphonyl chloride (0.01 mole) in anhydrous pyridine (10 ml.) was added dropwise with stirring a solution of (VIII) (5 mmole) in the same solvent (15 ml.). After stirring at 60° for 45 min. the mixture was poured on ice and acidified with 25% aqueous sulphuric acid. The precipitate was recrystallised from acetone (Norite) to give the product (1.1 g., 45%), m.p. 175-180°; crystallisation from acetonitrile gave brown crystals, m.p. 185° (decomp.) (Found: C, 58.6; H, 4.4; N, 11.1.  $C_{24}H_{20}N_4O_4S_2$  requires C, 58.5; H, 4.1; N, 11.4%) i.r. (Nujol):  $v_{\text{max}}$  1640, 1590, 1370 (disulphonimide <sup>12</sup>) 1180, 820, 760, 705, and 680 cm.<sup>-1</sup>.

1-(N-p-Tolylsulphonylamino)naphtho[1,8-de]triazine

(XIII).—To a solution of (XII) (1 mmole) in benzene (50 ml.) and methanol (50 ml.) methanolic sodium methoxide solution (1 mmole) was added dropwise with stirring. After 10 min. the solvent was removed and the residue was shaken for 30 min. with water (100 ml.). By neutralisation of the filtered solution with dilute sulphuric acid the product (XIII) (59%) was precipitated, m.p. 140-145°. Crystallisation from ethanol or from carbon tetrachloride gave brown crystals, m.p. 153—155° (decomp.) (Found:  $\breve{C}$ , 60.5; H, 4.0.  $C_{17}H_{14}N_4O_2S$  requires C, 60.3; H, 4.2%), i.r. (KBr): v<sub>max.</sub> 3260, 3180, 1630, 1580, 1340, 1160, 815, 760, 710, and 690 cm.<sup>-1</sup>.

Pyrolysis of the Sodium Salt of (XIII) .--- Sodium hydride (0.53 mmole) was added to a solution of (XIII) (0.53 mmole)in tetrahydrofuran (10 ml.). After the hydrogen evolution had stopped the solvent was removed at  $50^{\circ}/10^{-3}$  torr. Pyrolysis of this residue at  $160^\circ$  either neat or in the presence of a large excess of dimethyl acetylenedicarboxylate or of N-phenylmaleimide resulted in gas evolution. However, by t.l.c. on silica gel neither (IV) nor (XI) could be detected among the products.

Photolysis of the Sodium Salt of (XIII).-Sodium hydride (1.12 mmole) was added to a solution of (XIII) (1.12 mmole) in dioxan (85 ml., saturated with nitrogen). After the hydrogen evolution had stopped tetrachloroethylene (25 ml., saturated with nitrogen) was added and the solution was irradiated with a high-pressure mercury arc (S81 Quarzlampen GmbH, Hanau) in an irradiation apparatus 13 at 20°. The nitrogen evolution stopped after 46% had been liberated. After removal of the solvent naphthalene (9 mg., 4%) was isolated from the residue by sublimation at  $70^{\circ}/20$  torr.

Photolysis of (VIII).---A solution of (VIII) (1 mmole)

12 H. Dorn, G. Hilgetag, and A. Rieche, Angew. Chem., 1961, 73, 560.

<sup>13</sup> G. Wittig and H. F. Ebel, Annalen, 1961, 650, 20.

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in ether (100 ml.) was irradiated as above until the gas evolution stopped (60 min.). Chromatography of this solution on silica gel with carbon tetrachloride gave naph-thalene, m.p.  $76-79^{\circ}$ .

1,8-Diazidonaphthalene.—Finely ground sodium nitrite (14.5 mmole) was added in small portions with vigorous stirring to conc. sulphuric acid (8 ml.). The solution was cooled to  $0^{\circ}$  and then was added dropwise with vigorous stirring to a precooled solution of 1,8-diaminonaphthalene (6.33 mmole) in acetic acid. After 30 min. the mixture was poured on ice (10 g.) and water (20 ml.) followed by addition of urea (0.2 g.). After nitrogen evolution had ceased, a solution of sodium azide (12.3 mmole) in water (10 ml.) was added in small portions. The mixture was stirred for 30 min. at  $0^{\circ}$  and then adjusted to pH 5 by addition of aqueous sodium hydroxide. The resulting precipitate was washed with water and dried over potassium hydroxide. Sublim-

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