

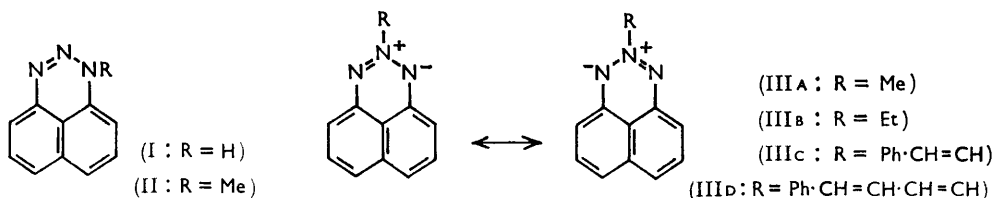
### 577. *The Nature of a Blue Triazine.*

By M. J. PERKINS.

A blue compound, first reported in 1909, is shown to be 2-methyl-2*H*-naphtho[1,8-*de*]triazine (IIIA), and thus to be the first member of a new class of heterocyclic compounds. Some simple reactions of this unusual tricyclic system are reported.

In a recent review<sup>1</sup> it was stated without comment that the red 1*H*-naphtho[1,8-*de*]triazine (I) gave, on base-catalysed methylation, a blue monomethyl derivative (II). In the original work by Sachs<sup>2</sup> neither analytical data nor physical characteristics were recorded for the blue product. Furthermore, Sachs suggested that the unexpected colour may have been due to the formation of an oxidation product.

Some confusion seems to have arisen concerning the compound of structure (II), which has been stated to give a blue product on oxidation<sup>3</sup> and to be prepared by diazotisation of 8-methylamino-1-naphthylamine.<sup>4</sup> The first of these statements appears to be a misinterpretation of Sachs's observations, and the origin of the second could not be located by the present author. 8-Methylamino-1-naphthylamine is apparently unknown.



It seemed possible that the profound change in electronic absorption on supposed methylation may have been due to the formation of 2-methyl-2*H*-naphtho[1,8-*de*]triazine (IIIA). This idea stemmed from analogy with the formation of nitromethane on methylation of the nitrite ion which is isoelectronic with the three-nitrogen system of the conjugate base of the triazine (I). Experimental evidence is now presented in support of the structure (IIIA) for the blue product, together with an outline of some of the reactions of this unusual triazine.

<sup>1</sup> Erickson, "Triazines, Tetrazines and Pentazines," Ed. Weissberger, Interscience, New York, 1956, p. 32.

<sup>2</sup> Sachs, *Annalen*, 1909, **365**, 53.

<sup>3</sup> Richmond, "Six-Membered Heterocyclic Nitrogen Compounds with three Condensed Rings," Ed. Weissberger, Interscience, New York, 1958, p. 544.

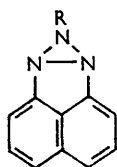
<sup>4</sup> Horwitz, "Heterocyclic Compounds," Vol. 7, Ed. Elderfield, Wiley, New York, 1961, p. 785.

After methylation of the triazine (I) with dimethyl sulphate and base, chromatography of the products gave two crystalline compounds, one blue and one red, each isolated in about 30% yield. The analysis of both compounds corresponded with that calculated for a monomethyl derivative of (I), and it was found that the red one showed an electronic absorption spectrum almost identical with that of compound (I). The infrared spectrum of the red product was likewise similar to that of compound (I), except that the strong N-H stretching absorption of the parent triazine was absent. On the basis of this evidence it is reasonable to assign structure (II) to this red product.

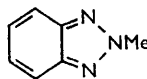
The infrared spectrum of the blue product was again somewhat similar to that of the parent triazine but with the N-H band absent, and absorptions in the visible and near ultraviolet were shifted to longer wavelengths. The assignment of structure (IIIA) to this compound rests largely on the facile hydrogenolysis of the triazine system. This results in the formation of 1,8-diaminonaphthalene and methylamine.

Ethylation of the triazine (I) also produced two compounds, red and blue, and the proton magnetic resonance spectra of these furnished support for analogous structural assignments. The methylene protons of the ethyl groups in these products appeared as relatively low-field quartets centred at  $\tau$  6.05 (red ethyl derivative), and  $\tau$  6.15 (blue ethyl derivative). More revealing, however, was the fact that the protons on the naphthalene ring of each compound absorbed in two regions, one at unusually high field ( $\tau \sim 3.8-4.2$ ). This high-field resonance corresponded in each case to the X part of an ABX spectrum, but for the red compound only one proton contributed to this, the remaining five aromatic protons appearing at lower field. For the blue compound, the corresponding distribution was 2 : 4, suggesting a higher degree of symmetry than in the red.

Structure (III) implies a planar molecule. The only evidence (apart from lack of precedent) contrary to the alternative formulation (IV), with a triaziridine ring, comes from observations of the reactivity of the blue compounds, and is wholly consistent with the charge separation represented in structure (III). For example, electrophilic substitution



(IV)



(V)

occurs very readily in the naphthalene nucleus, as evidenced by the formation of a tetrabromo-derivative of (IIIA). Compound (IIIA) is also soluble in cold concentrated sulphuric acid to give a water-soluble blue product, presumably a sulphonic acid. The methyl group of compound (IIIA) undergoes base-catalysed condensation with benzaldehyde to give a blue styryl derivative (IIIC) in which the visible absorption is moved to a higher wavelength than that of the methyl derivative (IIIA). The structure of the styryl derivative was established by elementary analysis, and by hydrogenation to 1,8-diaminonaphthalene and phenethylamine. The infrared spectrum shows absorptions characteristic of a 1,8-disubstituted naphthalene, of a monosubstituted benzene, and of a *trans*-1,2-disubstituted ethylene. Analogous condensation with cinnamaldehyde gives a green product in very poor yield which shows an infrared spectrum entirely consistent with its formulation as the all-*trans* isomer of 4-phenylbutadienyl derivative (IIID). However, satisfactory elementary analysis has not yet been carried out.

Insofar as the base-catalysed condensation of compound (IIIA) with benzaldehyde may be compared with the formation, from nitromethane, of  $\beta$ -nitrostyrene, the analogy between the two systems, mentioned above, is seen to be extended.

Comparison between the alkylation of the triazine (I) and that of diazoaminobenzene

and of benzotriazole is also interesting. Diazoaminobenzene appears to give only one product on alkylation, namely that in which the alkyl group is attached to one of the terminal nitrogen atoms. Methylation of benzotriazole, on the other hand, gives a mixture of 1- and 2-methylbenzotriazole, both of which seem to have fully developed aromatic character. (The quinonoid structure [V] appears to be a most unsatisfactory representation for 2-methylbenzotriazole<sup>5</sup>). Alkylation of 1*H*-naphtho[1,8-*de*]triazine provides a link between these two situations.

#### EXPERIMENTAL

Unless otherwise stated, melting points are corrected. Infrared spectra refer to Nujol mulls and ultraviolet and visible spectra to solutions in ethanol. The proton magnetic resonance spectra of the ethyl derivatives, discussed above, refer to solutions in carbon tetrachloride. These were recorded on a Perkin-Elmer 60 Mc. instrument.

1*H*-Naphtho[1,8-*de*]triazine (I).—This was prepared by diazotisation of 1,8-diaminonaphthalene in acetic acid, according to Waldmann and Back's procedure.<sup>6</sup> Some difficulty was experienced in purifying the product, probably because of the presence of polymeric substances. However, a purified specimen of triazine (red plates from acetic acid, m. p. *ca.* 230° decomp. Found: C, 70.6; H, 4.5. Calc. for C<sub>10</sub>H<sub>7</sub>N<sub>3</sub>: C, 71.0; H, 4.5%) had  $\lambda_{\text{max}}$  375 (N-H) 11.25, 12.28, and 13.23 (broad band)  $\mu$ , and 232.5, 338.5, and 452 m $\mu$  ( $\epsilon$  31,000, 10,000, and 750). The crude triazine gave satisfactory yields of alkylation products, and was therefore used in most alkylation experiments.

Methylation of 1*H*-Naphtho[1,8-*de*]triazine (I).—The triazine (5 g.) was stirred with a warm (*ca.* 50°) solution of sodium hydroxide (2 g.) in methanol (30 ml.), to give a deep red solution. To this solution, vigorously stirred, dimethyl sulphate (4.5 g.) was added dropwise, during 10 min. The reaction mixture was refluxed for a further 10 min., cooled, and shaken with a mixture of water (200 ml.) and benzene (200 ml.). The mixture was filtered, the benzene layer dried (MgSO<sub>4</sub>), and most of the solvent then removed under reduced pressure. The residue was chromatographed on basic alumina (Spence grade H) which was eluted with 1 : 1 benzene-light petroleum (b. p. 60—80°). The blue 2-methyl-2*H*-naphtho[1,8-*de*]triazine (IIIA) (1.7 g.) which was eluted first, crystallised from light petroleum (b. p. 80—100°) in glistening blue-black needles, m. p. 132° (Found: C, 72.2; H, 4.95; N, 23.1%; *M*, 175. C<sub>11</sub>H<sub>9</sub>N<sub>3</sub> requires C, 72.1; H, 4.95; N, 22.95%; *M*, 183),  $\lambda_{\text{max}}$  12.23, 13.10, 13.26  $\mu$ , and 231.5, 355, 559, 603, 655 m $\mu$  ( $\epsilon$  33,000, 12,900, 820, 820, and 570). The red 1-methyl-1*H*-naphtho[1,8-*de*]triazine (II) (2.0 g.) eluted next was crystallised from benzene-light petroleum (b. p. 60—80°) and then from carbon tetrachloride in red prisms, m. p. 91—92° (Found: C, 72.1; H, 4.9%),  $\lambda_{\text{max}}$  12.25, 13.10, 13.20  $\mu$ , and 231.5, 338, 451 m $\mu$  ( $\epsilon$  32,000, 10,200 and 950).

The blue product formed a 1,3,5-trinitrobenzene adduct (1 : 1), m. p. 154° (from ethanol) (Found: C, 51.1; H, 2.9. C<sub>17</sub>H<sub>12</sub>N<sub>6</sub>O<sub>6</sub> requires C, 51.5; H, 3.05%).

Ethylation of 1*H*-Naphtho[1,8-*de*]triazine (I).—A procedure similar to that described for methylation was adopted, and comparable yields of two products were obtained. The blue 2-ethyl-2*H*-naphtho[1,8-*de*]triazine (IIIB) had m. p. 84—85°, from light petroleum (b. p. 40—60°) (Found: C, 72.7; H, 5.6. C<sub>12</sub>H<sub>11</sub>N<sub>3</sub> requires C, 73.1; H, 5.6%). The 1 : 1 trinitrobenzene adduct had m. p. 108—109° (Found: C, 52.8; H, 3.4. C<sub>18</sub>H<sub>14</sub>N<sub>6</sub>O<sub>6</sub> requires C, 52.7; H, 3.4%). The red 1-ethyl-1*H*-naphtho[1,8-*de*]triazine had m. p. 73—74°, from ethanol (Found: C, 73.0; H, 6.1%).

Hydrogenation of 2-Methyl-2*H*-naphtho[1,8-*de*]triazine (IIIA).—The compound (0.536 g.) in ethanol was shaken with hydrogen at room temperature and atmospheric pressure, in the presence of 10% palladium on charcoal. Rapid absorption of 3 moles of hydrogen was accompanied by discharge of the blue colour of the solution. The solution was filtered, acidified with concentrated hydrochloric acid, and boiled to reduce the volume to about 10 ml. An excess of solid sodium hydroxide was then added and the solution boiled vigorously, the ethanol vapour being passed into a concentrated ethanolic solution of picric acid cooled in an ice-bath. About half the solution was distilled. Methylamine picrate (25%) (m. p. and mixed m. p.

<sup>5</sup> Boyer, "Heterocyclic Compounds," Vol. 7, Ed. Elderfield, Wiley, New York, 1961, p. 386.

<sup>6</sup> Waldmann and Back, *Annalen*, 1940, **545**, 52.

214—215°, and infrared spectrum identical with that of an authentic specimen) soon separated from the distillate-picric acid solution. The alkaline residue was diluted with water, extracted with ether, and the ether solution dried and distilled. 1,8-Diaminonaphthalene (0.375 g., 81%) was obtained by distillation under reduced pressure, and identified by comparison with an authentic specimen (m. p. and mixed m. p. 60—62°, and identical infrared spectra).

Hydrogenation of the blue ethyl derivative (IIIB), followed by a similar working-up procedure, yielded ethylamine picrate and 1,8-diaminonaphthalene.

*Bromination of 2-Methyl-2H-naphtho[1,8-de]triazine (IIIA).*—A well-stirred solution of the blue compound (100 mg.) in acetic acid (5 ml.) was treated with bromine (*ca.* 0.6 g.) in acetic acid (2 ml.) at room temperature. The mixture was stirred for 10 min. and poured into water (20 ml.). The brown solid was digested thoroughly with boiling benzene; the resulting blue solution was filtered and the filtrate diluted with light petroleum (b. p. 80—100°). The solution was then concentrated and set aside to cool. The *tetrabromo-derivative* separated as a black crystalline powder with a metallic lustre, m. p. 212—213° (decomp.) (Found: C, 26.7; H, 1.4; N, 8.8.  $C_{11}H_5Br_4N_3$  requires C, 26.5; H, 1.0; N, 8.4%).

*Condensation of 2-Methyl-2H-naphtho[1,8-de]triazine (IIIA) with Aromatic Aldehydes.*—  
(a) *Benzaldehyde.* A solution of sodium ethoxide [from sodium (0.15 g.)] in ethanol (6 ml.) was added dropwise to a vigorously stirred boiling solution of the blue compound (230 mg.) in benzaldehyde (6 ml.) and ethanol (6 ml.). The mixture was refluxed gently with stirring for 1 hr., cooled, and distributed between benzene (100 ml.) and water (100 ml.). The mixture was filtered, and the benzene fraction was dried ( $MgSO_4$ ) and then most of the solvent was removed under reduced pressure. The residue was chromatographed on basic alumina, and a blue-green product (83 mg.) eluted with 1 : 2 benzene-light petroleum (b. p. 60—80°). This product had m. p. 168° after crystallisation from benzene-light petroleum (b. p. 80—100°) and was identified as 2- $\beta$ -styryl-2H-naphtho[1,8-de]triazine (IIIC) (Found: C, 79.8; H, 4.8.  $C_{18}H_{13}N_3$  requires C, 79.7; H, 4.8%),  $\lambda_{max.}$  10.52 (*trans*-CH:CH), 12.13, 13.05, 13.28 (doublet), 14.43  $\mu$  and 655  $m\mu$  ( $\epsilon$  800) (broad band). This was hydrogenated in ethanol over 10% palladium on charcoal, and the products were examined by paper chromatography. Three solvent systems were used, and the chromatograms were developed by spraying with ninhydrin reagent. By the use of authentic markers the chromatograms were shown to be consistent with the formation of 1,8-diaminonaphthalene and phenethylamine in the reaction.

(b) *Cinnamaldehyde.* This reaction was carried out by a procedure similar to the above, but only a very low yield (*ca.* 2%) of a black solid (m. p.  $\sim$ 165°) was obtained. This substance gave a green solution in a variety of organic solvents. Although the results of analysis were poor (Found: C, 82.5; H, 5.7.  $C_{20}H_{15}N_3$  requires C, 80.8; H, 5.1%), the infrared spectrum was consistent with the phenylbutadienyl structure (IIID). This spectrum included a strong absorption at 10.14  $\mu$  attributable to the all-*trans*-diene system.<sup>7</sup> The compound also had  $\lambda_{max.}$  12.20, 13.10, 13.45, 14.54  $\mu$  with counterparts in the spectrum of the styryl derivative, all of which are attributable to a monosubstituted benzene or a 1,8-disubstituted naphthalene.

I should like to thank Professor D. H. Hey, F.R.S., and Dr. C. W. Rees for their interest and encouragement.

DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF LONDON KING'S COLLEGE, LONDON W.C.2. [Received, October 23rd, 1963.]

<sup>7</sup> Lunde and Zechmeister, *Acta Chem. Scand.*, 1954, **8**, 1429.