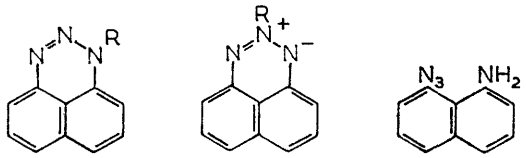
Reactive Intermediates. Part IV.[1] The Amination of Naphtho[1,8-*de*]-triazine

By **C. W. Rees** *† and **R. C. Storr**,† King's College, Strand, London W.C.2

Amination of naphtho[1,8-*de*]triazine with aqueous hydroxylamine-*O*-sulphonic acid gives 1-aminonaphtho-[1,8-*de*]triazine and 1-amino-8-azidonaphthalene. Amination with ethereal chloramine gives 1- and 2-amino-naphthotriazines and the latter was shown to rearrange to the amino-azide under the conditions of the hydroxylamine-*O*-sulphonic acid amination. Both 1- and 2-aminotriazines are rearranged smoothly by acid to the amino-azide. The stability of these triazines is compared with that of related triazoles, and mechanisms for their rearrangements are proposed.

SINCE oxidation of 1-aminobenzotriazole is a convenient route to benzyne,[2] similar oxidation of 1-aminonaphtho[1,8-*de*]triazine was expected to lead to the interesting '*meta*-aryne', 1,8-dehydronaphthalene.

1-Aminobenzotriazole is readily obtained, together with its isomer, 2-aminobenzotriazole, by direct amination of benzotriazole with hydroxylamine-*O*-sulphonic acid (HOS) in aqueous alkali;[2c] the direct amination thus parallels the essentially similar alkylation with dialkyl sulphate in alkaline solution. Since Perkins[3] has shown that similar alkylation of the triazine (Ia) gave both a red 1-alkyl (Ib) and a blue 2-alkyl derivative (IIa), direct amination was expected to give both 1- and 2-aminonaphthotriazines (Ic) and (IIb). However, treatment of (Ia) with HOS in alkali gave the red 1-amino-derivative (Ic) together with the colourless isomer 1-amino-8-azidonaphthalene (III) rather than the expected blue 2-aminotriazine (IIb). Spectral evidence supported structure (Ic); in particular the u.v. spectrum was very similar to those of triazines (Ib) and (Ia). Further support for structure (Ic) came from treatment with nitrous acid or diphenylnitrosamine, which gave naphtho[1,8-*de*]triazine, and oxidation, which gave 1,8-dehydronaphthalene. The amino-azide (III) formed an azo-dye on diazotisation and coupling with alkaline 2-naphthol, and was converted into 1,8-diaminonaphthalene on reduction. Spectral data fully supported the proposed structure.



(I) (II) (III)

a; R = H
b; R = alkyl
c; R = NH_2

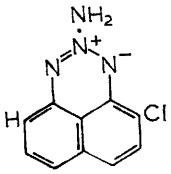
a; R = alkyl
b; R = NH_2

Since the 1-aminotriazine (Ic) is stable under the hot basic conditions of the HOS amination, the amino-azide (III) presumably arose by rearrangement of the initially formed 2-aminotriazine (IIb). Indeed milder conditions of amination with cold ethereal chloramine gave a slightly improved yield of the 1-amino-derivative together with small amounts of two blue compounds. Analyses and mass spectra indicated that these were 2-aminonaphtho[1,8-*de*]triazine (IIb) and a chloro-2-aminonaphthotriazine. The u.v. spectra of both blue compounds closely resembled those of the

† *Present address:* Department of Chemistry, The University, Leicester.

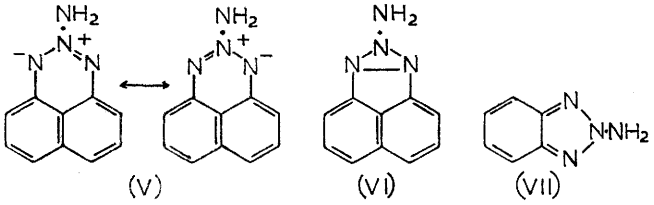
[1] Part III, C. D. Campbell and C. W. Rees, preceding paper.
[2] C. D. Campbell and C. W. Rees, (*a*) *Proc. Chem. Soc.*, 1964, 296; (*b*) *Chem. Comm.*, 1965, 192; (*c*) *J. Chem. Soc.* (*C*), 1969, 742.
[3] M. J. Perkins, *J. Chem. Soc.*, 1964, 3005.

blue 2-alkyltriazines.[3] N.m.r. spectroscopy indicated that the chloro-compound was 2-amino-4-chloronaphtho-[1,8-*de*]triazine (IV): only one of the high-field proton signals (quartets) characteristic of the 4-hydrogens of the 2-substituted triazine system (X part of an ABX system) was visible.



(IV)

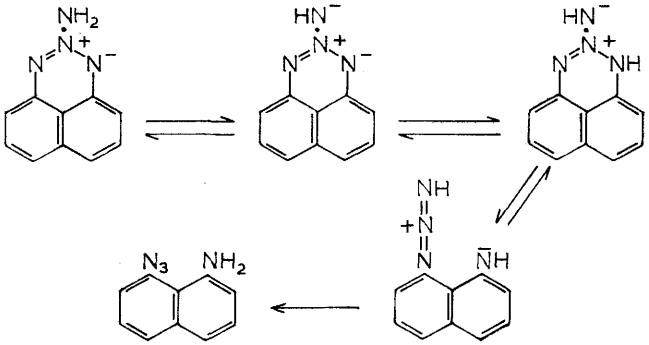
2-Aminonaphthotriazine (IIb) was shown to be the probable intermediate in the formation of 1-amino-8-azidonaphthalene in the HOS amination, since it readily rearranged to give the amino-azide (III) when treated with aqueous base under similar conditions. The base-catalysed rearrangement of (IIb) is presumably due to the greater acidity of the 2-amino-protons compared with those of the 1-amino-isomer, to be expected from a consideration of the electronic structure of the system. Polar contributions such as (V) must be important, since the only classical non-charged contribution would be the unlikely triaziridine[3] (VI); there are no quinonoid forms analogous to those of 2-aminobenzotriazole (VII). Significantly, 2-aminobenzotriazole does not rearrange under these conditions. Polar forms such as (V) would also explain the enhanced reactivity of the naphthalene nucleus towards electrophilic chlorination.



(V) (VI) (VII)

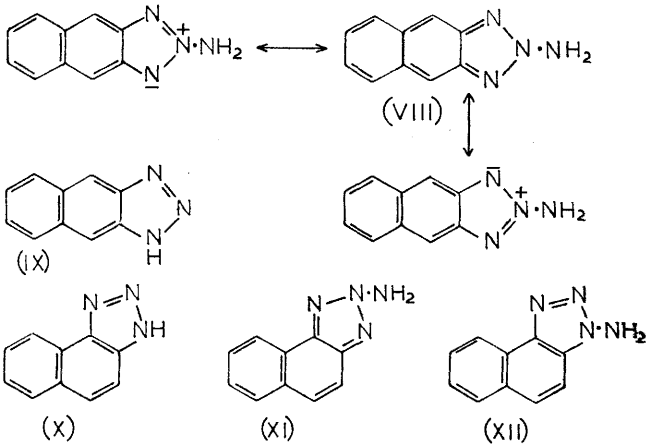
Perkins[3] has shown that the methyl group of 2-methylnaphthotriazine is more reactive than that in 1-methylnaphthotriazine, and that the former compound readily undergoes electrophilic substitution with bromine to form a tetrabromo-compound. In our case chloramine is presumably acting as the source of electrophilic chlorine. The higher proportion of initial 2-amination, based on the 1-amino-8-azidonaphthalene formed, in the aqueous HOS amination may be a solvent effect, the more polar solvent favouring the formation of the more polar species. The base-catalysed rearrangement of (V) can be formulated as shown (Scheme 1).

A link between the ready rearrangement of 2-aminonaphthotriazine and the non-rearrangement of 2-aminobenzotriazole is provided by 2-aminonaphtho[2,3-*d*]-triazole (VIII). Thus amination of naphtho[2,3-*d*]triazole (IX) with HOS in aqueous alkali gave mainly the 1-amino-derivative but a small amount of 2-amino-3-azidonaphthalene was also formed, presumably arising by rearrangement of the expected 2-aminotriazole. In contrast, naphtho[1,2-*d*]triazole (X) was aminated normally, giving mainly 2- and 1-amino-derivatives (XI) and (XII), but t.l.c. indicated the presence of a third product, presumably 3-aminonaphtho[1,2-*d*]triazole. Barton,[4] in an independent study, confirmed that the major product was 1-aminonaphtho[1,2-*d*]triazole (XII) by an alternative unambiguous synthesis from 2-amino-1-nitronaphthalene. The structure of 2-aminonaphtho-[1,2-*d*]triazole was proved by its oxidation with lead



SCHEME 1

tetra-acetate to give *o*-cyanocinnamonitrile (*cf.* the formation of *cis,cis*-muconontrile from 2-aminobenzotriazole).[2c]



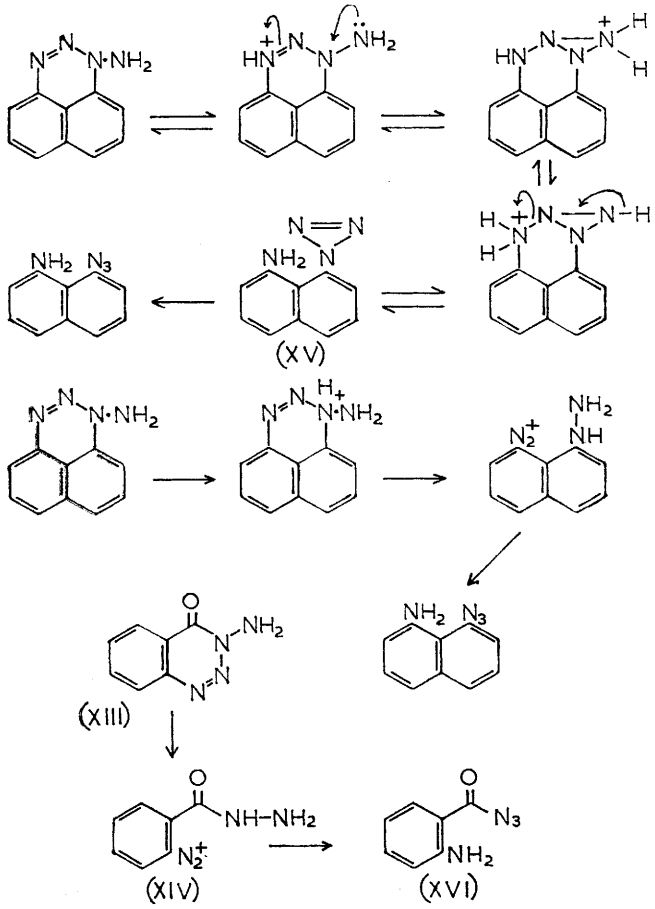
(VIII) (IX) (X) (XI) (XII)

The enhanced reactivity of 2-aminonaphtho[2,3-*d*]-triazole (VIII) can again be explained by a greater dipolar contribution to its structure than to those of the 2-substituted derivatives of benzotriazole and naphtho-[1,2-*d*]triazole.

Mild warming of 1-aminonaphtho[1,8-*de*]triazine (Ic) with dilute aqueous mineral acid caused rapid rearrangement to the amino-azide (III), almost quantitatively. 2-Aminonaphtho[1,8-*de*]triazine (IIb) was insoluble in aqueous acid but with warm ethanolic hydrogen chloride it also rearranged to give the azide (III), presumably by a mechanism similar to that proposed for its alkaline rearrangement. Acid-catalysed rearrangement of (Ic) could occur by either of the two

[4] J. W. Barton and S. A. Jones, *J. Chem. Soc.* (*C*), 1967, 1276.

mechanisms shown in Scheme 2. A mechanism of the latter type has been proposed for the acid-catalysed rearrangement of 3-amino-1,2,3-benzotriazin-4-one (XIII) to anthranilazide (XVI), where evidence for the intermediate diazonium compound (XIV) was obtained



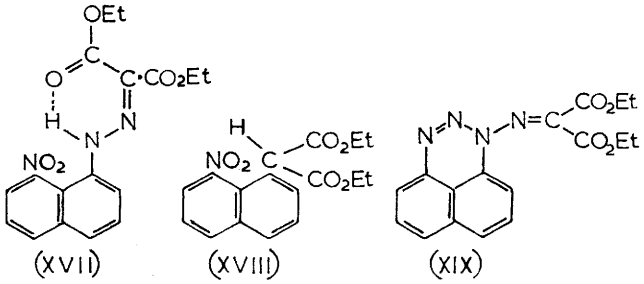
SCHEME 2

by the Bamberger–Goldberger test.[5] No similar evidence could be obtained in the case of (Ic). It is interesting to note that a cyclic structure [*cf.* (XV)] was initially proposed by Fischer [6] for the azide group. Similarly, aliphatic diazo-compounds were considered to have a cyclic structure, later replaced by a linear structure. However, diazirines are now known to be stable,[7] so that the intermediate (XV) could well exist.

Although the aminonaphthotriazines rearranged readily with acid, 1-aminobenzotriazole and 1-aminonaphtho[2,3-*d*]triazole did not rearrange even with hot concentrated hydrochloric acid. This agrees with the greater stability of the aromatic triazole systems compared with the triazine system, (*e.g.* [Ia] is known to act as a masked diazonium compound in strongly acid conditions [8]).

In view of the success of the modification [2c] of the method of Trave and Bianchetti [9] for the preparation of 1-aminobenzotriazole, a similar route was initially investigated for the preparation of 1-aminonaphtho[1,8-*de*]triazine from 1-amino-8-nitronaphthalene.

Diazotisation of 1-amino-8-nitronaphthalene and coupling with diethyl malonate gave the required diethyl mesoxalate 8-nitro-1-naphthylhydrazone (XVII) in poor yield (21%). However, appreciable amounts of 1-nitronaphthalene (17%) and diethyl 8-nitro-1-naphthylmalonate (XVIII) (8%) were also formed. The structures of compounds (XVII) and (XVIII) were



confirmed by i.r. and n.m.r. data. In particular the n.m.r. spectrum of (XVIII) showed a single-proton signal at τ 4·9 and two equivalent ethyl groups; the i.r. spectrum showed one carbonyl stretching frequency, at 1729 cm.$^{-1}$. N.m.r. of (XVII) indicated one proton at τ −2·75 and two non-equivalent ethyl groups, presumably owing to hydrogen-bonding of one of the carbonyls. The i.r. spectrum supported this, showing carbonyl absorptions at 1730 and 1680 cm.$^{-1}$.

In the case of *o*-nitroaniline no products analogous to nitronaphthalene and the ester (XVIII) were observed; however, the large steric *peri*-interaction in 8-nitronaphthalene-1-diazonium chloride might be expected to cause ready elimination of nitrogen.

The low yield and difficulty of isolation of (XVII) in the first stage of this route, together with the discovery of the instability to acid of the final product, 1-aminonaphtho[1,8-*de*]triazine, led us to abandon this approach, since the last stage would have involved hydrolysis of the triazine (XIX) with concentrated acid.

EXPERIMENTAL

I.r. spectra of solids were measured for Nujol mulls and those of liquids for capillary films. U.v. spectra were measured for solutions in absolute ethanol. N.m.r. spectra were measured for carbon tetrachloride or deuteriochloroform solutions with tetramethylsilane as internal reference; except where noted the peaks were singlets and the peak areas corresponded to the number of protons assigned to them. In extractions with organic solvents, the organic layer was dried ($MgSO_4$) and evaporated under reduced pressure in a rotary evaporator.

Naphtho[1,8-de]*triazine.* (Ia)—The following method was found to be superior to that reported by Waldmann and Back.[10] 1,8-Diaminonaphthalene (40 g.) in ethanol and

[5] M. S. Gibson and M. Green, *Tetrahedron*, 1965, **21**, 2191.
[6] E. Fischer, *Annalen*, 1878, **190**, 67.
[7] E. Schmitz, *Angew. Chem. Internat. Edn.*, 1964, **3**, 333.
[8] L. F. Fieser and A. M. Seligman, *J. Amer. Chem. Soc.*, 1939, **61**, 136.
[9] R. Trave and G. Bianchetti, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1960, **28**, 652.
[10] H. Waldmann and S. Back, *Annalen*, 1940, **545**, 52.

glacial acetic acid was stirred at 0° while pentyl nitrite (27 g.) was added dropwise during several hours. The mixture was set aside overnight and the resulting precipitate was collected and washed thoroughly with ether to give crystalline naphtho[1,8-*de*]triazine (72%), m.p. *ca.* 230°, sufficiently pure for subsequent reactions. A pure sample, m.p. 235—237° (lit.,[3] 236—237°; lit.,[11] 260—263°) was obtained by elution with ethanol from basic alumina followed by crystallisation from ethanol.

Amination of Naphtho[1,8-de]*triazine* (Ia) *with Hydroxylamine-O-sulphonic Acid.*—Naphtho[1,8-*de*]triazine (0·06 mole) suspended in aqueous potassium hydroxide (0·24 mole in 200 ml.) was stirred at 70—80° while solid hydroxylamine-*O*-sulphonic acid [12] (0·06 mole) was added in small portions. More solid potassium hydroxide (0·12 mole) was then added, followed by more hydroxylamine-*O*-sulphonic acid (0·06 mole). The total addition was complete after about 3 hr. The mixture was cooled and filtered, and the residue was thoroughly washed with aqueous potassium hydroxide, then water, and finally extracted with ether until the extracts were almost colourless. The extracts were then dried and evaporated, and the residue was chromatographed on silica gel. Elution with 50% ether–light petroleum gave 1-*amino*-8-*azidonaphthalene* (III) (26%), needles, m.p. 79—80° (from light petroleum) (Found: C, 65·6; H, 4·4; N, 29·6. $C_{10}H_8N_4$ requires C, 65·2; H, 4·4; N, 30·4%), $\nu_{max.}$ 3500, 3380 (NH_2), and 2110 (N_3) cm.$^{-1}$, $\lambda_{max.}$ 232 (log ε 4·20), 252·5 (4·19), and 346 (3·94) mμ; τ 2·15—2·85 (m, 5H), 3·3 (q, 1H), and 4·6 (2H); *monoacetyl derivative*, needles, m.p. 147—148° (from ethanol) (Found: C, 64·2; H, 4·7; N, 24·3. $C_{12}H_{10}N_4O$ requires C, 63·7; H, 4·4; N, 24·8%). Elution with ether gave 1-*aminonaphtho*[1,8-de]*triazine* (37%), contaminated with a small amount of naphtho[1,8-*de*]-triazine. Further chromatography on basic alumina with ether as eluant gave pure 1-aminonaphtho[1,8-*de*]triazine, red needles, m.p. 154·5—155·5° (from ether or ethanol) (Found: C, 65·3; H, 4·3; N, 30·6. $C_{10}H_8N_4$ requires C, 65·2; H, 4·4; N, 30·4%), $\nu_{max.}$ 3415 and 3205 (NH_2) cm.$^{-1}$; $\lambda_{max.}$ 232·5 (log ε 4·42) and 339 (4·01) mμ; *benzylidene derivative*, red needles, m.p. 151—152° (from ethanol) (Found: C, 74·8; H, 4·6; N, 20·7. $C_{17}H_{12}N_4$ requires C, 75·0; H, 4·4; N, 20·6%).

Amination of Naphtho[1,8-de]*triazine* (Ia) *with Chloramine.*—Ethereal chloramine was prepared by a slight modification of the method of Theilacker and Wegner,[13] and was estimated iodometrically.

Naphtho[1,8-*de*]triazine (30 mmoles) and sodium hydride (34 mmoles) were heated under reflux overnight in dry ether. Chloramine in ether (430 ml. of 0·085M-solution; 36·5 mmoles) was then added to the cooled suspension, which was stirred overnight at 20°. The mixture was then filtered, evaporated, and chromatographed on silica gel. Elution with 20% ether–light petroleum gave 2-*amino*-4-*chloronaphtho*[1,8-de]*triazine* (IV) (0·7%), blue needles, m.p. 197—198° (from ether–light petroleum) (Found: C, 55·1; H, 3·1; N, 25·5. $C_{10}H_7ClN_4$ requires C, 54·9; H, 3·2; N, 25·6%), $\nu_{max.}$ 3360, 3180, and 3140 (NH_2) cm.$^{-1}$ $\lambda_{max.}$ 235·5 (log ε 4·50), 270 (3·85), and 350 (4·02) mμ; τ [$(CD_3)_2SO$] 2·71—3·16 (m, 4H) and 3·63 (q, 1H), *m/e* 220, 218, 191, 189 (Cl isotope pattern) 155, 127, and 126.

Elution with 30% ether–light petroleum gave 2-*aminonaphtho*[1,8-de]*triazine* (IIb) (1·8%), blue needles, m.p. 179—181° (from ether–light petroleum) (Found: C, 64·9; H, 4·6; N, 30·1. $C_{10}H_8N_4$ requires C, 65·2; H, 4·4, N, 30·4%), $\nu_{max.}$ 3300 and 3140 (NH_2) cm.$^{-1}$, $\lambda_{max.}$ 233·5 (log ε 4·50), 272 (3·85), 350 (4·06) mμ, *m/e* 184, 155, 140, and 127. Further elution with ether gave 1-aminonaphtho-[1,8-*de*]triazine (43%), contaminated with a little naphtho-[1,8-*de*]triazine.

Amination of Naphtho[2,3-d]*triazole* (IX).—Naphtho-[2,3-*d*]triazole was prepared by diazotisation of 2,3-diaminonaphthalene.[14] The product (20 mmoles) in potassium hydroxide solution [100 mmoles in water (100 ml.)] was stirred at 70° while solid hydroxylamine-*O*-sulphonic acid (40 mmoles) was added in small portions during 1·5 hr. The resulting cooled mixture was extracted with ether (10 × 100 ml.); the extracts were washed with aqueous potassium hydroxide and then water, dried, evaporated, and chromatographed on basic alumina. Elution with ether gave 2-*amino*-3-*azidonaphthalene* (2%), pale buff needles, m.p. 103—104° (from light petroleum) (Found: C, 65·3; H, 4·5; N, 30·5. $C_{10}H_8N_4$ requires C, 65·2; H, 4·4; N, 30·4%), $\nu_{max.}$ 3390, 3275, 3160 (NH_2), and 2093 (N_3) cm.$^{-1}$, $\lambda_{max.}$ 257 (log ε 4·46) and 355 (3·57) mμ, *m/e* 184, 158, 156, 155, 130, 129, 128, and 102. Elution with 5% methanol–ether gave 1-aminonaphtho[2,3-*d*]triazole (27%), plates m.p. 207—208° (from ethanol) (lit.,[4] 206—208°) (Found: C, 65·1; H, 4·4; N, 30·2%).

Naphtho[2,3-*d*]triazole was recovered on acidification of the basic aqueous mother liquors after the ether extraction.

Amination of Naphtho[1,2-d]*triazole* (X).—Naphtho-[1,2-*d*]triazole was prepared by diazotisation of 1,2-diaminonaphthalene.[15] The amination was carried out as described for naphtho[2,3-*d*]triazole, and the products were chromatographed on silica gel. Elution with 50% ether–light petroleum gave 2-aminonaphtho[1,2-*d*]triazole (3%), colourless needles, m.p. 165—166° (from ethanol) (lit.,[4] 166—167°) (Found: C, 65·0; H, 4·5; N, 30·3%).

Elution with ether gave 1-aminonaphtho[1,2-*d*]triazole (XII) (18%), colourless leaflets, m.p. 151—152° (from ethanol) (lit.,[4] 152—153°) (Found: C, 65·4; H, 4·5; N, 30·6%).

The chromatography fraction of 1-aminonaphtho-[1,2-*d*]triazole was shown (t.l.c.) to contain a trace of a third compound, which was removed by recrystallization.

Unchanged naphtho[1,2-*d*]triazole was recovered from the basic aqueous mother liquor by acidification.

Deamination of 1-*Aminonaphtho*[1,8-de]*triazine* (Ic).—1-Aminonaphtho[1,8-*de*]triazine (Ic) (1 mmole) and diphenylnitrosamine (1 mmole) were heated under reflux in dry benzene for 3 hr., then cooled. Naphtho[1,8-*de*]-triazine (71%), m.p. 225—230°, separated and was filtered off. The filtrate was evaporated and the residue was chromatographed on silica gel to give diphenylamine (85%), m.p. 50—51°, and a further fraction of naptho-[1,8-*de*]triazine (14%, total 85%).

Deamination of 2-*Aminonaphtho*[1,8-de]*triazine* (IIb).—A little 2-aminonaphtho[1,8-*de*]triazine (IIb) was similarly treated with diphenylnitrosamine. T.l.c. indicated diphenylamine and naphtho[1,8-*de*]triazine together with other unidentified products.

Treatment of 2-*Aminonaphtho*[1,8-de]*triazine* (IIb) *with Base.*—2-Aminonaphtho[1,8-*de*]triazine (IIb) (0·2 mmole)

[11] H. Sieper, *Chem. Ber.*, 1967, **100**, 1646.
[12] R. Gösl and A. Meuwsen, *Chem. Ber.*, 1959, **92**, 2521.
[13] W. Theilacker and E. Wegner, *Angew. Chem.*, 1960, **72**, 127.
[14] P. Friedlander and S. v. Zakrzewski, *Ber.*, 1894, **27**, 765.
[15] O. Diels, *Ber.*, 1921, **54**, 226.

was warmed with aqueous potassium hydroxide (2N) on a steam-bath for 5 min. The mixture was cooled and extracted with ether, and the extract was washed with water, dried, and finally adsorbed on to silica gel. Chromatography gave 1-amino-8-azidonaphthalene (66%), m.p. and mixed m.p. 78—80°.

Treatment of 1-*Aminonaphtho*[1,8-de]*triazine with Acid.*—1-Aminonaphtho[1,8-*de*]triazine was dissolved in aqueous sulphuric acid (2N) and warmed to 60° for several min. The solution was cooled, made alkaline, and extracted with ether. The extract was washed with water, dried, and adsorbed on to silica gel. Chromatography gave 1-amino-8-azidonaphthalene (88%), m.p. and mixed m.p. 78—79°, followed by a little tarry material.

Similar treatment of 1-aminonaphtho[1,8-*de*]triazine with hydrochloric acid (2N) gave 1-amino-8-azidonaphthalene (80%).

Treatment of 2-*Aminonaphtho*[1,8-de]*triazine* (IIb) *with Acid.*—2-Aminonaphtho[1,8-*de*]triazine (IIb) was insoluble in dilute aqueous acid and was unchanged by it. Mild warming of an ethanolic solution of (IIb) containing hydrogen chloride caused the blue colouration to fade. Careful neutralisation of the cooled solution with triethylamine, followed by t.l.c., indicated that all triazine (IIb) was converted into 1-amino-8-azidonaphthalene (III). A control experiment showed that the rearrangement was not base-catalysed by the triethylamine added.

Reduction of 1-*Amino*-8-*azidonaphthalene* (III).—1-Amino-8-azidonaphthalene in aqueous hydrochloric acid (5N) was stirred for several hr. with granulated tin. The mixture was then made alkaline and extracted with ether. The extract was washed with water, dried, and evaporated to leave 1,8-diaminonaphthalene, (96%), as a coloured oil. Distillation gave a colourless solid m.p. and mixed m.p. 60°; trinitrobenzene addition compound, m.p. 223°.

Attempted Preparation of 1-*Aminonaphtho*[1,8-de]*triazine* (Ic) *from* 1-*Amino*-8-*nitronaphthalene.*—1-Amino-8-nitronaphthalene [16,17] (13·5 mmoles) and concentrated hydrochloric acid (4 ml.) were mixed to a paste, which was diluted with water (9 ml.). Sodium nitrite (15 mmoles) in water (2·5 ml.) was added below 5° to give a dark red solution, which was then added dropwise to a rapidly stirred suspension of diethyl malonate (13·5 mmoles) in water (10 ml.). The mixture was kept alkaline during this process by addition of sodium carbonate (4·5 g.). The products separated as an oily solid, which was extracted with chloroform. The chloroform extract was dried and evaporated on to silica gel for chromatography. Elution with 20% ether–light petroleum gave 1-nitronaphthalene (17%), yellow needles, m.p. 59° (from ethanol); picrate, m.p. 69—70°. Further elution gave *diethyl* 8-*nitro*-1-*naphthylmalonate* (XVIII) (8%), yellow crystals, m.p. 94—95° (from ethanol) (Found: C, 61·5; H, 5·1. $C_{17}H_{17}NO_6$ requires C, 61·6; H, 5·1%), $\nu_{max.}$ 1729 (ester C=O), 1513, and 1325 (NO_2) cm.$^{-1}$, $\lambda_{max.}$ 217 (log ε 4·63), 242 (4·06), and 335 (3·50) mμ, τ 1·1—2·43 (m, 6H), 4·9 (1H), 5·54 (q, 4H, *J* 7·8 c./sec.), and 8·67 (t, 6H, *J* 7·8 c./sec.).

Continued elution gave *diethyl mesoxalate* 8-*nitro*-1-*naphthylhydrazone* (XVII) (21%), pale orange crystals, m.p. 90—91° (from ethanol) (Found: C, 56·2; H, 5·1; N, 11·4. $C_{17}H_{17}N_3O_6$ requires C, 56·8; H, 4·7; N, 11·7%), $\nu_{max.}$ 1730 (ester C=O), 1680 (H-bonded C=O), 1525, and 1349 (NO_2) cm.$^{-1}$, $\lambda_{max.}$ 239 (log ε 4·32) and 351 (4·21) mμ, τ −2·75 (1H), 1·65—2·32 (m, 6H), 5·39 (q, 2H, *J* 7·8 c./sec.), 5·52 (q, 2H, *J* 7·8 c./sec.), 8·52 (t, 3H, *J* 7·8 c./sec.), and 8·57 (t, 3H, *J* 7·8 c./sec.).

Oxidation of 2-*Aminonaphtho*[1,2-d]*triazole* (XI).—2-Aminonaphtho[1,2-*d*]triazole (XI) (1 mmole) in methylene chloride was added dropwise to a stirred solution of lead tetra-acetate (1·5 mmole) in the same solvent. The solution was filtered, evaporated on to silica gel, and chromatographed. Elution with 30% ether–light petroleum gave *o*-cyano-*cis*-cinnamonitrile (58%), which was sublimed at 120°/2 mm. to give a colourless solid, m.p. and mixed m.p. 69—70° (lit.,[18] 70—70·5°).

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