Triazines and Related Products. Part IV.[1] Methylation of 3-Aryl-3,4-dihydro-4-imino-1,2,3-benzotriazines

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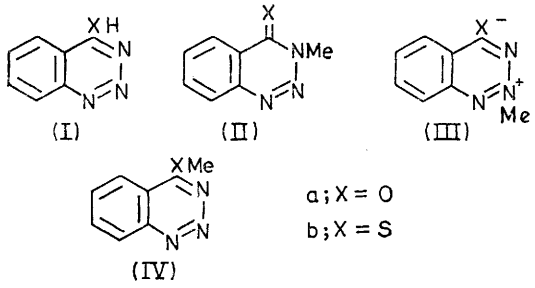
The title compounds undergo ring-opening in sodium ethoxide solution and subsequent treatment with methyl iodide affords mixtures of isomeric methylated *o*-cyanophenyltriazenes. The structures of the products have been elucidated by reduction to the component amines with stannous chloride in hydrochloric acid, and the applicability of this reagent in the study of other *o*-cyanophenyltriazenes has been explored. Catalytic hydrogenation of *o*-nitrophenyltriazenes yields benzotriazole as one of the products. Mechanisms for the ring-opening and reduction reactions have been proposed.

THE chemistry of derivatives of 1,2,3-benzotriazine is dominated by their ' masked diazonium ' character and the predisposition of the triazine ring to undergo heterolysis or homolysis at the N(2)–N(3) bond has been frequently exploited in synthetic studies.[2-4] However alkylation of the triazine ring has received only little interest.

Wagner and Gentzsch[5] methylated 4-hydroxy-1,2,3-benzotriazine (Ia) with dimethyl sulphate in sodium hydroxide and obtained the N(3)- and N(2)-alkylated products [(IIa) and (IIIa) respectively], whereas methylation of 4-mercapto-1,2,3-benzotriazine (Ib) afforded N(3)-, N(2)-, and *S*-methylated triazines [(IIb), (IIIb), and (IVb) respectively]. Similarly,

[1] Part III, H. N. E. Stevens and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1970, 765.
[2] ' The Chemistry of Heterocyclic Compounds,' Interscience, New York, 1956, vol. 10.
[3] M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1967, 1096.
[4] M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1968, 348.
[5] G. Wagner and H. Gentzsch, *Die Pharmazie*, 1968, **23**, 629.

salts of 4-hydroxy-1,2,3-benzotriazine (Ia) react with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide under various conditions to yield the acetylated N(3)-, N(2)-, and O-β-D-glucopyranosides.[6] Recent work on the



alkylation[7] and amination[8] of 1*H*-naphtho[1,8-*de*]triazine has demonstrated the formation of isomeric 1- and 2-alkyl (or amino)-naphthotriazines which are analogous to triazines of type (II) and (III).

Here we describe the methylation of the 4-imino-1,2,3-benzotriazines (V; R = H or Cl): in contrast to the aforementioned examples no alkylation on the *exo*- or *endo*-cyclic N atoms is observed.

as the methyltriazene (VIII; R = H) by its identity with the same triazene unambiguously prepared by interaction of diazotised anthranilonitrile and *N*-methylaniline; the triazene (VIII; R = H) prepared by this route also exhibited characteristic dimorphism. The isomeric methyltriazene m.p. 60—62° was accordingly assigned structure (IX; R = H); this was subsequently confirmed by reduction studies. Attempted synthesis of this triazene (IX; R = H) from diazotised aniline and *N*-methylanthranilonitrile yielded only tar: similarly interaction of aniline and *N*-methyl-*N*-nitrosoanthranilonitrile in acetic acid failed to realise the required methyltriazene.

Methylation of the chlorophenyltriazine (V; R = Cl) with methyl iodide in sodium ethoxide gave an analogous mixture of alkylated triazenes [(VIII) and (IX); R = Cl]. In contrast neither 3-phenyl- nor 3-*o*-nitrophenyl-1,2,3-benzotriazin-4(3*H*)-one are alkylated under these conditions.

The unexpected appearance of these triazenes [(VIII) and (IX); R = H or Cl] can be explained by the observation that the 4-iminotriazines (V; R = H or Cl) undergo ring-fission in sodium ethoxide solution to form

TABLE 1

Spectroscopic properties * of alkylated *o*-cyanophenyltriazenes

Compound	U.v. and visible spectra [$\lambda_{max.}$ (nm); log ε in parentheses]				I.r. spectra $\nu_{max.}$ (cm.$^{-1}$)	N.m.r. spectra (τ values)
(VIII; R = H)	237 † (4·12)			350 (4·30)	2228 (CN)	6·29 (s, CH_3)
(VIII; R = Cl)	236 (4·14)			324 (4·22)	2228 (CN)	6·33 (s, CH_3)
(IX; R = H)			303 (3·97)	343 (4·17)	2211 (CN)	6·31 (s, CH_3)
(IX; R = Cl)	237 † (4·22)		302 (4·07)	343 (4·16)	2219 (CN)	6·26 (s, CH_3)
(XI; R = Me)	240 † (4·21)		310 † (4·06)	345 (4·24)	2212 (CN) 2223 (CN)	6·24 (s, CH_3)
(XI; R = Et)	240 † (4·20)		310 (4·04)	348 (4·20)	2212 (CN) 2222 (CN)	8·55 (t, CH_3) 5·55 (q, CH_2)
1,3-Di-*p*-cyanophenyl-1-Methyltriazene	239 (4·17)	249 (4·20)		363 (4·47)	2223 ‡ (CN)	6·30 (s, CH_3)

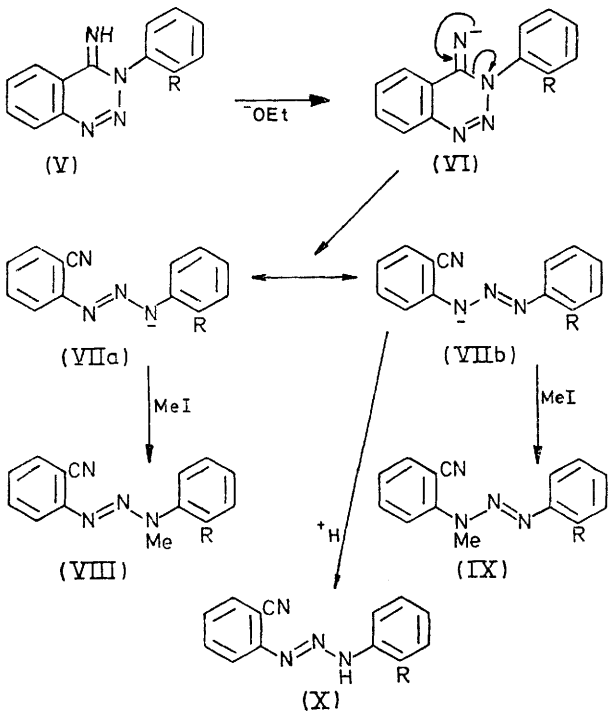
* U.v. and visible spectra were recorded on a Unicam SP 800 spectrometer (ethanol solutions). I.r. spectra were run (slow scan) on a Perkin-Elmer 257 instrument as KBr discs. N.m.r. spectra were recorded in $CDCl_3$ solutions ($SiMe_4$ as internal standard) on a Perkin-Elmer R 10 instrument. † Inflexion. ‡ Broad absorption.
s = Singlet. t = Triplet. q = Quartet.

The intense red colour which developed when the 4-iminobenzotriazine (V; R = H) was dissolved in sodium ethoxide solution was rapidly discharged when the solution was boiled with an excess of methyl iodide. Chromatographic fractionation of the product gave a pale yellow oil which appeared to be homogeneous (t.l.c.). However, the splitting of many of the absorptions in the i.r. spectrum of the oil, particularly in the cyano-region (absorptions at 2211 and 2228 cm^{-1}) indicated the presence of a mixture. Careful fractional crystallisation of the oil yielded two isomeric compounds, m.p. 83—84° (38%) and m.p. 60—62° (36%) with u.v., i.r., and n.m.r. spectra consistent with their formulation as methylated *o*-cyanophenyltriazenes (Table 1). Identification of the higher-melting isomer was complicated by its dimorphism (needle and prism forms), but it was characterised

the red triazene anions (VII; R = H or Cl) from which the free triazenes (X; R = H or Cl) can be recovered on acidification. 4-Anilino- and 4-*o*-chloroanilino-1,2,3-benzotriazine also isolated in these ethoxide decompositions are presumably formed by rearrangement of the 4-iminotriazines (V; R = H or Cl) respectively.[1] Interaction of the resonance-stabilised ambident anions [(VIIa) and (VIIb); R = H or Cl] with methyl iodide accounts for the formation of the alkylated triazene mixtures [(VIII) and (IX); R = H or Cl] according to Scheme 1: the alkylation of unsymmetrically substituted diaryltriazenes is well known to give mixtures.[9] Methylation of 1,3-di-*p*-cyanophenyltriazene under identical conditions yields the expected 1,3-di-*p*-cyanophenyl-1-methyltriazene (95%), but methylation or ethylation

[6] G. Wagner and H. Gentzsch, *Arch. Pharm.*, 1968, **12**, 923.
[7] M. J. Perkins, *J. Chem. Soc.*, 1964, 3005; P. Tavs, H. Sieper, and H. Beecken, *Annalen*, 1967, **704**, 150.
[8] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 756; R. W. Hoffmann, G. Guhn, M. Preiss, and B. Dittrich, *J. Chem. Soc.* (*C*), 1969, 769.
[9] T. W. Campbell and B. F. Day, *Chem. Rev.*, 1951, **48**, 299.

of 1,3-di-*o*-cyanophenyltriazene gives, in addition to 1,3-di-*o*-cyanophenyl-1-methyl-(or ethyl)triazene, small

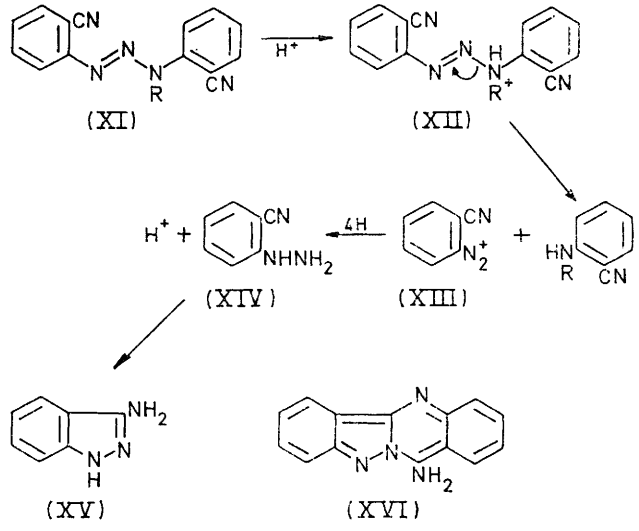


SCHEME 1

amounts of isomeric red compounds. The structure of these interesting compounds will form the subject of the succeeding paper in this series.

Reduction of diaryltriazenes to their component amines is a well-tried technique in structure determination.[9] In the *o*-cyanophenyltriazene series the cyano-group may subsequently participate in intramolecular cyclisation reactions. Thus, reduction of 1,3-di-*o*-cyanophenyltriazene (XI; R = H) with stannous chloride in hydrochloric acid produces 3-aminoindazole (XV) and anthranilonitrile.[3] Analogous reduction of the methyltriazene (VIII; R = H) gave only (t.l.c.) 3-aminoindazole and *N*-methylaniline: the isomer (IX; R = H) afforded *N*-methylanthranilonitrile as one of the products, thus confirming the previously assigned structures of these compounds.

The products formed from the reduction of related *o*-cyanophenyltriazenes are recorded in Table 2.



SCHEME 2

The appearance of these products is consistent with a reductive mechanism involving initial protonation of the triazene followed by fission to form a diazonium ion as illustrated in the reduction of 1,3-di-*o*-cyanophenyl-1-methyltriazene (XI; R = Me) (Scheme 2). Thus fission of the protonated triazene (XII; R = Me) yields *N*-methylanthranilonitrile and *o*-cyanobenzenediazonium chloride (XIII) which has been independently shown [10] to undergo reduction with stannous chloride to 3-aminoindazole (XV) through the intermediacy of *o*-cyanophenylhydrazine (XIV).

The formation of a small yield (2%) of the indazolo-

TABLE 2

Reduction of *o*-cyanophenyltriazenes with stannous chloride in hydrochloric acid

Compound [a]	Products [b]
(VIII; R = H)	3-Aminoindazole, *N*-methylaniline
(VIII; R = Cl)	3-Aminoindazole, *o*-chloro-*N*-methylaniline
(IX; R = H)	*N*-Methylanthranilonitrile
(IX; R = Cl)	*N*-Methylanthranilonitrile
(X; R = H) [c]	3-Aminoindazole, anthranilonitrile, aniline
(X; R = Cl) [d]	3-Aminoindazole, anthranilonitrile, *o*-chloroaniline
(X; R = Me) [d]	3-Aminoindazole, anthranilonitrile, *o*-toluidine
(X; R = NO_2) [d]	3-Aminoindazole, anthranilonitrile, *o*-phenylenediamine
1-*o*-Cyanophenyl-3-*m*-nitrophenyltriazene [d]	3-Aminoindazole, anthranilonitrile, *m*-phenylenediamine
1-*o*-Cyanophenyl-3-*p*-nitrophenyltriazene [d]	3-Aminoindazole, anthranilonitrile, *p*-phenylenediamine
(XI; R = H) [e]	3-Aminoindazole, anthranilonitrile
(XI; R = Me)	3-Aminoindazole, *N*-methylanthranilonitrile
(XI; R = Et)	3-Aminoindazole, *N*-ethylanthranilonitrile
	11-Aminoindazolo[3,2-*b*]quinazoline [e]

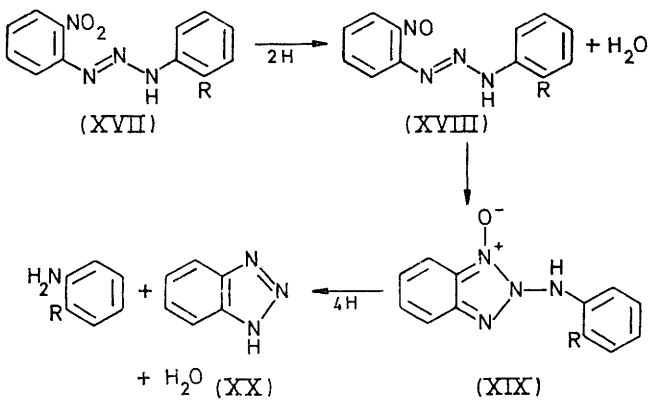
[a] Triazenes (25 mg) and stannous chloride dihydrate (50 mg) were shaken in 10N-hydrochloric acid (1 ml) for 2 h. [b] Products were liberated with 2N-sodium hydroxide solution (to pH 11) and extracted into ether. Samples were applied to thin-layer plates spread with either alumina or silica gel (0·25 mm), and developed with either benzene–acetone (7 : 3) or toluene–ethanol (8 : 2). [c] Ref. 12. [d] Ref. 1. [e] Ref. 3.

[10] F. C. Cooper, *J. Chem. Soc.*, 1958, 4212.

quinazoline (XVI) in addition to 3-aminoindazole and *N*-ethylanthranilonitrile in the reduction of the corresponding ethyltriazene (XI; R = Et) however remains unexplained. This tetracyclic compound has previously been prepared by reduction of 1,3-di-*o*-cyanophenyltriazene (XI; R = H) with stannous chloride in ethanol.[3] That the indazoloquinazoline does not derive by dealkylation of triazene (XI; R = Et) is implied since the dealkyltriazene (XI; R = H) affords only 3-aminoindazole and anthranilonitrile on reduction with stannous chloride in hydrochloric acid.[3] The possibility that the tetracyclic compound might derive by interaction of the 3-aminoindazole and *N*-ethylanthranilonitrile initially formed in the reduction was investigated, but no reaction occurs under the reduction conditions.

The double bond of triazenes (XI; R = H, Me, or Et) is inert to catalytic hydrogenation (PtO_2 at 25°). The nature of the reduction products from the *o*-cyanophenyltriazenes listed in Table 2 also excludes the interposition of triazane intermediates, *i.e.* R·NH·NH·NR^{1}R^2. For example reduction of the methyltriazene (XI; R = Me) gave no anthranilonitrile or *N*-*o*-cyanophenyl-*N*-methylhydrazine which might be expected to result from such a triazane intermediate. This *NN*-disubstituted hydrazine derivative, required as a reference sample in the t.l.c. studies, was readily prepared by zinc–acetic acid reduction of *N*-methyl-*N*-nitrosoanthranilonitrile. However unlike the de-methyl analogue *o*-cyanophenylhydrazine (XIV), it failed to cyclise (to 3-amino-1-methylindazole) under acid or alkaline conditions.

In contrast to the inertness of triazenes (XI; R = H, Me, or Et) to catalytic hydrogenation, the *o*-nitrophenyltriazene (XVII; R = H) rapidly absorbed 3 mol equivalents of hydrogen. The only identifiable products



SCHEME 3

were benzotriazole (XX) and aniline. The observation that the reaction mixture shows a transient deep-green colour implies the intermediate formation of the *o*-nitrosophenyltriazene (XVIII; R = H). The cyclisation of *o*-nitrosoazo-compounds to benzotriazole 1-oxides (*cf.* XIX; R = H) is well documented,[11] and we propose that cyclisation and subsequent hydrogenation of the *o*-nitrosophenyltriazene (XVIII; R = H) proceeds as in Scheme 3. 1-*o*-Cyanophenyl-3-*o*-nitrophenyltriazene (XVII; R = CN) on hydrogenation analogously forms benzotriazole and anthranilonitrile.

EXPERIMENTAL

Light petroleum refers to the fraction b.p. 40—60°.

Methylation of 3,4-*Dihydro*-4-*imino*-3-*phenyl*-1,2,3-*benzotriazine* (V; R = H).—A deep-red solution was formed when the benzotriazine [12] (1·1 g) was added to a cold solution of sodium ethoxide prepared from sodium (0·15 g) and absolute ethanol (25 ml). After being boiled (1 h) with methyl iodide (2 ml) the resulting yellow solution was evaporated under reduced pressure. A solution of the residue in benzene (14 ml) and light petroleum (6 ml) was chromatographically fractionated on alumina (2 × 20-cm column) with benzene–light petroleum (1 : 1) as eluant. Evaporation of solvent from the pale yellow band gave an oil which when dissolved in hot, light petroleum (80 ml) deposited 1-*o*-*cyanophenyl*-3-*methyl*-3-*phenyltriazene* (0·45 g, 38%), m.p. 83—84° after further crystallisation from light petroleum (yellow needles or golden prisms) (Found: C, 71·2; H, 5·1; N, 23·7. $C_{14}H_{12}N_4$ requires C, 71·2; H, 5·2; N, 23·9%). The concentrated, chilled mother liquors slowly deposited 1-*o*-*cyanophenyl*-1-*methyl*-3-*phenyltriazene* (0·42 g, 36%) as yellow rosettes, m.p. 60—62° (from light petroleum) (Found: C, 71·0; H, 5·3; N, 23·5%).

Anthranilonitrile (2·36 g) in concentrated hydrochloric acid (30 ml) at 0° was diazotised with sodium nitrite (1·6 g) and the mixture was neutralised with an excess of sodium acetate. The red gum formed on the addition of *N*-methylaniline (2·14 g) rapidly solidified on being stirred at 0°. The product (80%) crystallised from light petroleum as either yellow needles or golden prisms, m.p. 83—84° and had an identical i.r. spectrum to the aforementioned 1-*o*-cyanophenyl-3-methyl-3-phenyltriazene. Attempted interaction of diazotised aniline with *N*-methylanthranilonitrile (1 mol) under the above conditions led to the formation of a dark intractable oil. A mixture of aniline and *N*-methyl-*N*-nitrosoanthranilonitrile (1 mol) in acetic acid at 25° for 3 days deposited a brown oil on dilution with water. Chromatographic fractionation failed to yield any identifiable products.

Methylation of 3-*o*-*Chlorophenyl*-3,4-*dihydro*-4-*imino*-1,2,3-*benzotriazine* (V; R = Cl).—Methylation of the chlorotriazine [1] with methyl iodide in sodium ethoxide according to the method described above furnished a pale yellow oil after chromatographic purification. Crystallisation of this from a mixture of light petroleum (25 ml) and benzene (2 ml.) gave 1-*o*-*chlorophenyl*-3-*o*-*cyanophenyl*-3-*methyltriazene* (0·38 g, 28%), m.p. 84—85° (pale yellow needles from light petroleum) (Found: C, 62·1; H, 4·1; N, 20·7. $C_{14}H_{11}ClN_4$ requires C, 62·0; H, 4·1; N, 20·7%). The chilled mother liquors slowly deposited 1-*o*-*chlorophenyl*-3-*o*-*cyanophenyl*-1-*methyltriazene* (0·40 g, 30%) as cream rosettes, m.p. 46—48° (from light petroleum) (Found: C, 61·8; H, 4·0; N, 20·5%).

Attempted preparation of the former triazene from diazotised *o*-chloroaniline and *N*-methylanthranilonitrile, and

[11] Elderfield's 'Heterocyclic Compounds,' Wiley, New York, 1961, vol. VII, p. 397. See also H. Bauer, G. R. Bedford, and A. R. Katritzky, *J. Chem. Soc.*, 1964, 751.

[12] M. W. Partridge and M. F. G. Stevens, *J. Chem. Soc.*, 1964, 3663.

the latter triazene from diazotised anthranilonitrile and *o*-chloro-*N*-methylaniline were unsuccessful. Only intractable tars were formed.

Decomposition of 3-o-*Chlorophenyl*-3,4-*dihydro*-4-*imino*-1,2,3-*benzotriazine* (V; R = Cl) *in Sodium Ethoxide Solution*.—The chlorotriazine (1·2 g) gave a deep red solution when dissolved in sodium ethoxide solution [from sodium (0·15 g) in absolute ethanol (25 ml)]. After being boiled for 30 min the red solution was cooled, diluted with water (25 ml), and neutralised to pH 7 with 2N-hydrochloric acid. The mixture thus formed was rapidly extracted with benzene (4 × 25 ml). Evaporation of the solvent from the benzene solution and crystallisation of the residue from light petroleum afforded the rearrangement product 4-*o*-chloroanilino-1,2,3-benzotriazine (0·24 g), m.p. 168—169° (eff.) with an identical i.r. spectrum to an authentic sample.[1] The concentrated mother liquors deposited yellow crystals of 1-*o*-chlorophenyl-3-*o*-cyanophenyltriazene (0·45 g), m.p. 97—99° and identical to an authentic sample.[1]

Analogous decomposition of 3,4-dihydro-4-imino-3-phenyl-1,2,3-benzotriazine (V; R = H) gave a mixture of the rearrangement product 4-anilino-1,2,3-benzotriazine [1] and 1-*o*-cyanophenyl-3-phenyltriazene.[12]

Methylation of 1,3-*Di*-p-*cyanophenyltriazene*.—An orange solid was deposited when 1,3-di-*p*-cyanophenyltriazene [1] (2·47 g) was added to a cold sodium ethoxide solution [from sodium (0·28 g) and absolute ethanol (40 ml)]. This solid was transformed into yellow needles when the mixture was boiled with methyl iodide (4 ml) for 1 h. 1,3-*Di*-p-*cyanophenyl*-1-*methyltriazene* (2·43 g, 95%) was collected; it crystallised from ethanol as yellow needles, m.p. 199—200° (eff.) (Found: C, 68·8; H, 4·4; N, 26·8. $C_{15}H_{11}N_5$ requires C, 69·0; H, 4·2; N, 26·8%).

Methylation of 1,3-*Di*-o-*cyanophenyltriazene* (XI; R = H).—A solution of the triazene [13] (2·47 g) and sodium ethoxide (1·1 mol) in absolute ethanol (25 ml) was boiled with methyl iodide (4 ml) for 1½ h and the mixture was then evaporated to dryness under reduced pressure. The residue was dissolved in benzene and chromatographically fractionated on alumina. The mixed brown and red bands were eluted and the solvent was evaporated off. Trituration of the residue with 2N-hydrochloric acid afforded the acid-insoluble 1,3-*di*-o-*cyanophenyl*-1-*methyltriazene* (1·7 g, 65%), m.p. 136—138° (brown needles, from ethanol) (Found: C, 69·0; H, 4·4; N, 26·7. $C_{15}H_{11}N_5$ requires C, 69·0; H, 4·2; N, 26·8%). Basification (aqueous ammonia) of the acid-soluble material deposited a red solid (0·27 g, 10%), m.p. 181—182° (red needles, from benzene–light petroleum) [Found: C, 69·0; H, 3·8; N, 27·2; *M* (mass spec.) 261. $C_{15}H_{11}N_5$ requires *M*, 261].

Ethylation of 1,3-*Di*-o-*cyanophenyltriazene* (XI; R = H).—Ethylation of the triazene with ethyl iodide in the manner described in the previous experiment yielded the acid-insoluble 1,3-*di*-o-*cyanophenyl*-1-*ethyltriazene* (45%), m.p. 97—98° (yellow rosettes, from *n*-hexane) (Found: C, 69·6; H, 4·9; N, 25·7. $C_{16}H_{13}N_5$ requires C, 69·8; H, 4·8; N, 25·4%), and an acid-soluble red solid (10%), m.p. 134—135° (red needles, from light petroleum) [Found: C, 69·9; H, 4·6; N, 25·8; *M* (mass spec.), 275. $C_{16}H_{13}N_5$ requires *M*, 275].

Reduction of 1-o-*cyanophenyl*-3-*methyl*-3-*phenyltriazene* (VIII; R = H).—The methyltriazene (0·5 g) was added to a solution of stannous chloride dihydrate (1·0 g) in concentrated hydrochloric acid (10 ml), and the mixture was stirred at room temperature (2 h). After basification (to pH 11) with 10N-sodium hydroxide–ice, the products were recovered into ether. Removal of ether and crystallisation of the residue from light petroleum gave 3-aminoindazole (0·22 g, m.p. 154—155°) identical to an authentic sample.[10] The evaporated mother liquor yielded *N*-methylaniline (0·15 g) with an i.r. spectrum identical to an authentic specimen. T.l.c. examination of the reaction mixture confirmed the absence of other products.

Reduction of 1-o-*cyanophenyl*-1-*methyl*-3-*phenyltriazene* (IX; R = H).—Reduction of the triazene (0·5 g) with stannous chloride (1·0 g) in concentrated hydrochloric acid (10 ml) gave a colourless solution which was basified to pH 11; the products were extracted into ether. Solvent was removed from the ether extract to afford *N*-methylanthranilonitrile (0·18 g), identical to a sample prepared by methylation of anthranilonitrile (see below).

Reduction of 1,3-*Di*-o-*cyanophenyl*-1-*methyltriazene* (XI; R = Me).—The triazene (1·0 g) was reduced with stannous chloride dihydrate (2·0 g) in concentrated hydrochloric acid (20 ml). Basification (to pH 11) gave products which were extracted into ether. Solvent was removed from the extract and the residue crystallised from benzene (10 ml) to give 3-aminoindazole [10] (0·46 g). *N*-Methylanthranilonitrile (0·40 g) was recovered from the benzene solution upon evaporation of the solvent. No other products were detected (t.l.c.).

Reduction of 1,3-*Di*-o-*cyanophenyl*-1-*ethyltriazene* (XI; R = Et).—Reduction of this triazene (1·0 g) in an analogous manner gave 3-aminoindazole (0·5 g), *N*-ethylanthranilonitrile (0·4 g), which was identical to a sample prepared by ethylation of anthranilonitrile (see below), and 11-aminoindazolo[3,2-*b*]quinazoline [3] (20 mg).

In Table 2 are recorded the products identified (t.l.c.) in the reductions with stannous chloride of related *o*-cyanophenyltriazenes.

N-*Methylanthranilonitrile*.—A mixture of anthranilonitrile (5·9 g) and methyl iodide (8·0 g) was heated in a sealed tube at 85° (18 h). The products were distributed between 1N-hydrochloric acid (50 ml) and ether (50 ml). Basification (aqueous ammonia) of the acid-soluble fraction gave a precipitate of *N*-methylanthranilonitrile (3·9 g, 59%), which crystallised from light petroleum as cream flakes, m.p. 69—70° (lit.,[14] m.p. 70°), and had $\nu_{max.}$ (KBr) 3392 (NH) and 2210 (CN) cm^{-1}. The acetyl-derivative of *N*-methylanthranilonitrile melted at 90—92° (lit.,[14] m.p. 92°). Unchanged anthranilonitrile (2·0 g) was recovered from the ether-soluble fraction.

N-*Methyl*-N-*nitrosoanthranilonitrile*.—Addition of a solution of sodium nitrite (1·4 g) in water (5 ml) to an ice-cold solution of *N*-methylanthranilonitrile (2·6 g) in 2N-hydrochloric acid (10 ml) deposited the *nitroso-compound* (2·7 g, 85%), which crystallised from benzene–light petroleum as cream needles, m.p. 52—53°; and $\nu_{max.}$ (KBr) 2218 (CN). and 1445 cm^{-1} (NO) (Found: C, 59·8; H, 4·5; N, 26·1. $C_8H_7N_3O$ requires C, 59·6; H, 4·4; N, 26·1%).

N-o-*Cyanophenyl*-N-*methylhydrazine*.—The aforementioned nitroso-compound (1·7 g) in acetic acid (10 ml) was added during 15 min to a suspension of zinc dust (4·0 g) in water (10 ml) at 20—25°. The mixture was stirred at 25° for 1½ h, warmed to 80°, and filtered. The insoluble zinc residues were washed with 2N-hydrochloric acid (25 ml) and the combined filtrates were basified with aqueous sodium hydroxide–ice. Evaporation of the solvent from a

[13] J. Pinnow and C. Sämann, *Chem. Ber.*, 1896, **29**, 623.
[14] P. Grammaticakis, *Bull. Soc. chim. France*, 1953, 207.

chloroform extract of the mixture yielded the *hydrazine* (1·3 g), $\nu_{max.}$ (film) 3415, 3340, 3200 (NH), and 2202 (CN) cm^{-1}, as a brown oil which was not further purified. Its *o-nitrobenzylidene-derivative* (from the hydrazine and *o*-nitrobenzaldehyde, in ethanol) had m.p. 140—141° (yellow plates, from ethanol) (Found: C, 64·2; H, 4·4; N, 20·1. $C_{15}H_{12}N_4O_2$ requires C, 64·3; H, 4·3; N, 20·0%).

Reduction of the nitroso-compound with stannous chloride in concentrated hydrochloric acid gave *N*-methylanthranilonitrile (75%).

N-*o*-Cyanophenyl-N-methylhydrazine was unaffected when heated for prolonged periods in ethanol, ethanol containing 2% piperidine, or in 0·5N-hydrochloric acid and starting material was recovered.

N-*Ethylanthranilonitrile*.—Interaction of anthranilonitrile (5·9 g) and ethyl iodide (8·6 g) at 80° for 17 h, gave N-*ethylanthranilonitrile* (6·5 g, 89%) which crystallised from aqueous ethanol as white needles, m.p. 30—31° (Found: C, 73·7; H, 6·5; N, 18·8. $C_9H_{10}N_2$ requires C, 73·9; H, 6·9; N, 19·2%); $\nu_{max.}$ (film) 3280 (NH) and 2210 cm^{-1} (CN).

[15] E. Bamberger, *Chem. Ber.*, 1895, **28**, 225.
[16] ' Practical Heterocyclic Chemistry,' A. O. Fitton and R. K. Smalley, Academic Press, London, 1968, p. 47.

Its *acetyl-derivative*, m.p. 67—68° (plates, from ether–light petroleum); $\nu_{max.}$ (film) 2228 (CN) and 1660 cm^{-1} (CO) (Found: C, 70·0; H, 6·3; N, 14·5. $C_{11}H_{12}N_2O$ requires C, 70·2; H, 6·4; N, 14·9%).

Hydrogenation of 1-o-*Nitrophenyl-3-phenyltriazene* (XVII; R = H).—A solution of the nitrotriazene [15] (1·0 g) in ethanol (30 ml) containing platinum oxide (25 mg) rapidly absorbed 3 mol equiv. of hydrogen. The solution was filtered, solvent was removed and the residue was steam-distilled. The nonvolatile residue (0·35 g.) was identical to an authentic sample of benzotriazole.[16] The steam-volatile fraction was identified as aniline by conversion to its azonaphthol derivative.

Analogous hydrogenation of 1-*o*-cyanophenyl-3-*o*-nitrophenyltriazene (XVII; R = CN) afforded benzotriazole and anthranilonitrile.

The triazenes (XI; R = H, Me, or Et) were inert to catalytic hydrogenation at atmospheric pressure.

We gratefully acknowledge the award of a research scholarship (to H. N. E. S.) from the directors of Allen and Hanburys Ltd.

[0/070 *Received, January* 15*th*, 1970]