Triazines and Related Products. Part III.[1] Synthesis and Rearrangement of 3,4-Dihydro-4-imino-1,2,3-benzotriazines

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A series of 3-substituted-3,4-dihydro-4-imino-1,2,3-benzotriazines (V) have been prepared by cyclization of the appropriate *o*-cyanophenyltriazenes (IV) in 70% aqueous ethanol or in ethanol containing 2% piperidine. Triazenes with powerful electron-withdrawing substituents cyclize directly to substituted 4-anilino-1,2,3-benzotriazines (VI). Rearrangement of 3-aryl-3,4-dihydro-4-imino-1,2,3-benzotriazines to the isomeric 4-anilino-1,2,3-benzotriazines has been effected in ethanol or in 2N-hydrochloric acid and is facilitated by electron-withdrawing substituents in the aryl nucleus. The contrasting stabilities of 3-benzyl- and 3-phenethyl-3,4-dihydro-4-imino-1,2,3-benzotriazine have been attributed to a steric affect.

PREVIOUS papers in this series [1,2] have described reactions of 1,3-di-*o*-cyanophenyltriazene which illustrate the utility of suitably substituted triazenes in the preparation of derivatives of 1,2,3-benzotriazine: the facility of these and other related cyclizations in the quinazoline series [3] may be attributed to a favourable orientation of substituents for intramolecular amine–nitrile addition. For example, 1-*o*-cyanophenyl-3-phenyltriazene is rapidly converted into 3,4-dihydro-4-imino-3-phenyl-1,2,3-benzotriazine in 70% aqueous ethanol,[4] whereas 1,3-di-*o*-cyanophenyltriazene undergoes analogous but more extensive cyclization, followed by reductive elimination of nitrogen to afford 4-amino-2-phenylquinazoline.[2,4]

Here, we describe the influence of substituents in determining the nature of the products formed in the cyclization of *o*-cyanophenyltriazenes.

As an introduction to this work the properties of the triazene esters (Ia—c) were re-examined. We have confirmed the observations of Mehner [5] that these triazenes crystallize unchanged from 95% ethanol, but cyclize to the benzotriazinones (IIIa—c) in ethanol containing substantial amounts of water.[6] The triazinones (IIIa—c) were also efficiently prepared from the esters (Ia—c) in 95% ethanol containing 2% piperidine. The triazenes (Ia—c) and all other diaryltriazenes described here are assigned the *trans*-configuration about the N:N bond because of the similarity of their u.v. and visible absorption spectra (Table 1) to those of *trans*-1,3-di-*p*-bromophenyltriazene.[7] Inspection of models confirms that only the *cis*-isomers (IIa—c) have a favourable juxtaposition of substituents for amine–ester interaction. Evidently cyclization to the benzotriazinones is preceeded by a *trans* ⟶ *cis* rearrangement [(I) ⟶ (II)].

The reactivity of the aforementioned triazene esters in the presence of water and base was paralleled in the *o*-cyanophenyltriazene series. When the triazenes (IV; R = Ph,[4] *o*-tolyl, or *o*-chlorophenyl) were boiled (10 hr.) in 95% ethanol and the course of the reaction was followed (t.l.c. and u.v./visible spectroscopy), mixtures containing the triazenes (IV), the corresponding 4-imino-1,2,3-benzotriazines (V), and the rearrangement products

[1] Part II, M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1968, 348.
[2] M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1967, 1096.
[3] A. Kreutzberger and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1969, 1282; M. F. G. Stevens and A. Kreutzberger, *Angew. Chem.*, 1969, **81**, 84; E. C. Taylor and R. V. Ravindranathan, *J. Org. Chem.*, 1962, **27**, 2622.
[4] M. W. Partridge and M. F. G. Stevens, *J. Chem. Soc.*, 1964, 3663.
[5] H. Mehner, *J. prakt. Chem.*, 1901, [2], **63**, 241.
[6] 'The Chemistry of Heterocyclic Compounds,' A. Weissberger, ed., Interscience, New York, 1956, vol. 10, p. 21.
[7] Yu. D. Kondrashev, *Kristallografiya*, 1961, **6**, 515.

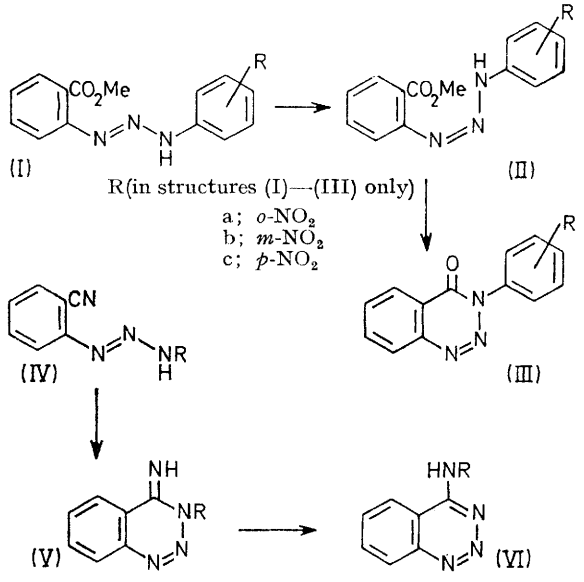
TABLE 1

U.v. and visible spectra [$\lambda_{max.}$ (nm.); log ε in parentheses] of triazenes (in ethanol)

Compound					
1,3-Di-*p*-bromophenyltriazene	239 (4·21)		298 (3·99)	307 * (3·95)	362 (4·39)
1,3-Di-*p*-cyanophenyltriazene	242 * (4·18)	252 (4·23)	293 (3·76)	302 (3·80)	370 (4·50)
(Ia)					364 (4·27)
(Ib)	247 (4·12)				359 (4·35)
(Ic)					387 (4·41)
(IV; R = Ph) †	237 (4·08)		300 * (3·65)		368 (4·31)
(IV; R = *o*-Tolyl)	242 * (4·09)		300 * (3·81)		364 (4·25)
(IV; R = *o*-Chlorophenyl)	243 (4·11)		300 * (3·79)		361 (4·25)
(IV; R = *o*-Cyanophenyl)		251 (4·24)	300 * (3·92)	308 (3·94)	367 (4·30)
(IV; R = *m*-Cyanophenyl)		248 * (4·17)		316 (4·07)	362 (4·31)
(IV; R = *p*-Cyanophenyl)	238 (4·11)	255 (4·12)	294 * (3·78)	302 (3·83)	369 (4·44)
(IV; R = *o*-Nitrophenyl)	249 (4·12)	258 * (4·06)	280 (3·86)	333 (4·04)	392 (4·19)
(IV; R = *m*-Nitrophenyl)	246 (4·19)	259 * (4·06)			350 (4·27)
(IV; R = *p*-Nitrophenyl)	242 (4·10)	260 * (4·05)			388 (4·50)
(IV; R = Benzyl)	236 (4·13)		296 (4·15)		

* Inflection. † Ref. 4.

(VI) were obtained; the unchanged triazenes predominated. However, all the triazenes quantitatively cyclized (30 min.) to the 4-imino-1,2,3-benzotriazines (V; R = Ph,[4] *o*-tolyl or *o*-chlorophenyl) in boiling 70% aqueous



ethanol, but more slowly (*ca.* 10 hr.) in 95% ethanol containing 2% piperidine. The imine (V; R = *o*-tolyl) was also prepared (69%) by diazotization of *N*-*o*-tolyl-2-aminobenzamidine. The iminotriazines (V; R = *o*-tolyl or *o*-chlorophenyl) had similar spectroscopic properties to the 4-iminotriazine (V; R = Ph) the structure of which is established;[4] thus their u.v. spectra show characteristic double peaks in the ranges 260—270 and 305—320 nm. (Table 2) and their n.m.r. spectra show the aromatic protons split into two groups. The low-field 1H multiplet generally well separated from the other aromatic absorptions is assigned to the 5-H proton; similar separations have been reported in 4-cinnolones [8] and 4-quinazolones [9] but do not occur in 4-benzotriazinones (Table 3).

The rearrangement of the 4-iminobenzotriazine (V; R = Ph) to 4-anilino-1,2,3-benzotriazine (VI; R = Ph) in 2N-hydrochloric acid is now shown to be more extensive than previously thought,[4] since the imine also

TABLE 2

U.v. and visible spectra [$\lambda_{max.}$ (nm.); log ε in parentheses] of 1,2,3-benzotriazine derivatives (in ethanol)

Compound				
(V; R = Ph †)	260 (3·97)	268 (3·96)	307 (3·76)	318 (3·77)
(V; R = *o*-Tolyl)	260 (4·03)	268 (3·99)	305 (3·71)	317 (3·70)
(V; R = *o*-Chlorophenyl)	259 (4·05)	268 (4·02)	304 (3·70)	316 (3·68)
(V; R = *m*-Cyanophenyl)	259 (3·97)	267 (3·96)	307 (3·75)	317 (3·75)
(V; R = *m*-Nitrophenyl)	259 * (4·14)	270 * (4·08)	308 (3·77)	318 (3·77)
(V; R = Benzyl †)	261 (4·03)	269 (3·99)	307 (3·72)	318 (3·73)
4-Methylthiobenzotriazine			261 (3·65)	316 (3·92)
(VI; R = Ph†)			273 (3·76)	333 (4·00)
(VI; R = *o*-Tolyl)				317 (3·93)
(VI; R = *o*-Chlorophenyl)				315 (3·97)
(VI; R = *o*-Nitrophenyl)	237 * (4·25)		267 * (3·95)	313 (3·94)
(VI; R = *m*-Nitrophenyl)			267 * (4·09)	325 (4·15)
(VI; R = *p*-Nitrophenyl)				357 (4·15)
(VI; R = *m*-Cyanophenyl)			265 * (3·89)	329 (4·12)
(VI; R = *p*-Cyanophenyl)			267 * (4·06)	334 (4·27)
(VI; R = *o*-Aminophenyl)				307 (3·99)
(VI; R = *m*-Aminophenyl)				332 (3·93)
(VI; R = *p*-Aminophenyl)	243 (4·15)		292 (3·90)	350 (3·88)
(VI; R = Benzyl)			260 * (3·69)	317 (3·99)
(VI; R = Phenethyl)			260 * (3·70)	319 (3·98)

* Inflection. † Ref. 4.

quantitatively rearranged to the anilinotriazine in boiling 95% ethanol (120 hr.). Analogous Dimroth rearrangement of the chlorophenylimine (V; R = *o*-chlorophenyl) was complete in 30 hr. but the *o*-tolylimine (V; R = *o*-tolyl) gave an equilibrium mixture containing both isomers after 120 hr. The relative ease of rearrangement of the chloro-imine in ethanol was also evidenced in 2N-hydrochloric acid, conversion into the isomer (VI; R = *o*-chlorophenyl) being complete in 3 hr.; in contrast the *o*-tolyl-imine (V; R = *o*-tolyl) was in-

[8] A. W. Ellis and A. C. Lovesey, *J. Chem. Soc.* (*B*), 1968, 1393; J. M. Bruce, P. Knowles, and L. S. Besford, *J. Chem. Soc.*, 1964, 4044; J. M. Bruce and P. Knowles, *ibid.*, p. 4046.

[9] Y. Hagiwara, M. Kurihara, and N. Yoda, *Tetrahedron*, 1969, **25**, 783.

completely rearranged even after 20 hr. in acid. Confirmation of the structures of the 4-anilinobenzotriazines (VI; R = Ph or *o*-chlorophenyl) was obtained by their formation from 4-methylthio-1,2,3-benzotriazine and the appropriate amines. They are assigned the 4-anilino-tautomeric form (VI) because of the close similarity between their u.v. spectra and that of 4-methylthio-1,2,3-benzotriazine (Table 2). The i.r. spectra of all the substituted 4-anilinobenzotriazines show a strong absorption at 1145 ± 10 cm.$^{-1}$ which is absent in the 3-aryl-3,4-dihydro-4-imino-isomers and represents a useful aid in identification (Table 4). Less helpful are the n.m.r. spectra of the 4-anilinobenzotriazines (Table 3) which show the characteristic low-field 1H multiplet assigned to the *peri*-proton (5-H), and previously experienced in the 3,4-dihydro-4-imino-series.

o-Cyanophenyltriazenes with strong electron-withdrawing substituents (IV; R = *o*-, *m*-, and *p*-nitrophenyl) cyclize directly in boiling 95% ethanol (both with and without 2% piperidine) to products identified as 4-nitroanilinotriazines (VI; R = *o*-, *m*- and *p*-nitrophenyl) by their characteristic spectroscopic properties. However the *m*-nitrophenyltriazene (IV; R = *m*-nitrophenyl) afforded the 4-imine (V; R = *m*-nitrophenyl) in boiling 70% aqueous ethanol, but the imine rearranged to the isomer (VI; R = *m*-nitrophenyl) on attempted crystallization from dimethylformamide, or in boiling 95% ethanol (3 hr.). The triazene (IV; R = *m*-nitrophenyl) also cyclized and rearranged to the triazine (VI; R = *m*-nitrophenyl) when melted. Cyclization and rearrangement of the nitrotriazenes (IV; R = *o*- and *p*-nitrophenyl) proceeded so rapidly in 70% aqueous ethanol that we were unable to isolate the intermediate 4-iminotriazines (V; R = *o*- and *p*-nitrophenyl).

Catalytic hydrogenation of the nitrotriazines (VI; R = *o*-, *m*-, and *p*-nitrophenyl) afforded the amines, the spectral properties and behaviour on melting of which were consistent with the formulation of these products as 4-aminoanilinobenzotriazines (VI; R = *o*-, *m*-, and *p*-aminophenyl).

The behaviour of cyano-substituted triazenes is comparable to that of the nitro-analogues, although decomposition of 1,3-di-*o*-cyanophenyltriazene (VII) is further complicated by the participation of both cyano-groups in the cyclization (see Scheme). Thus, the u.v. spectrum of the triazene (VII) in 95% ethanol underwent a smooth conversion (Figure 1) and at the end of the reaction the spectrum was almost identical to that of 4-amino-2-phenylquinazoline (XII), an observation that has been confirmed preparatively.[4] The disappearance of triazene (VII) was conveniently followed at 366 nm. a wavelength at which the quinazoline (XII) is transparent. The rectilinearity of log absorbance/time at

TABLE 3

N.m.r. spectra (τ values) of triazene and 1,2,3-benzotriazine derivatives excluding NH absorptions (peak multiplicity, and number of protons in parentheses).

Compound	Solvent	5H	Other aromatic absorptions	Other absorptions
(IV; R = Ph)	$CDCl_3$ *†		2·17—2·97 (m, 9)	
(IV; R = *o*-Tolyl)	$CDCl_3$		2·14—2·95 (m, 8)	CH_3, 7·59 (s, 3)
(IV; R = *o*-Chlorophenyl)	$CDCl_3$		2·13—2·94 (m, 8)	
(IV; R = *o*-Cyanophenyl)	$CDCl_3$		2·12—2·88 (m, 8)	
(IV; R = Benzyl)	$CDCl_3$		2·19—3·13 (m, 9)	CH_2, 5·18 (s, 2)
(V; R = Ph)	$CDCl_3$	1·67 (m, 1)	2·07—2·57 (m, 8)	
(V; R = *o*-Tolyl)	$CDCl_3$	1·64 (m, 1)	1·88—2·73 (m, 7)	CH_3, 7·80 (s, 3)
(V; R = *o*-Chlorophenyl)	$CDCl_3$	1·67 (m, 1)	1·87—2·50 (m, 7)	
(V; R = *m*-Cyanophenyl)	DMSO	1·65 (m, 1)	1·80—2·30 (m, 7)	
(V; R = Benzyl)	$CDCl_3$		2·00—2·80 (m, 9)	CH_2, 4·38 (s, 2)
3-Methyl-3,4-dihydro-4-oxobenzotriazine	$CDCl_3$		1·61—2·40 (m, 4)	CH_3, 5·94 (s, 3)
3-Ethyl-3,4-dihydro-4-oxobenzotriazine	$CDCl_3$		1·57—2·36 (m, 4)	CH_2, 5·45 (q, 2) CH_3, 8·48 (t, 3)
3-Phenyl-3,4-dihydro-4-oxobenzotriazine	$CDCl_3$		1·55—2·57 (m)	
4-Methylthiobenzotriazine	$CDCl_3$	1·65 (m, 1)	1·83—2·20 (m, 3)	CH_3, 7·18 (s, 3)
4-Mercaptobenzotriazine	DMSO	1·48 (m, 1)	1·75—2·20 (m, 3)	
(VI; R = Ph)	DMSO	1·35 (m, 1)	1·83—2·78 (m, 8)	
(VI; R = *o*-Tolyl)	$CDCl_3$		1·69—2·81 (m, 8)	CH_3, 7·70 (s, 3)
(VI; R = *o*-Chlorophenyl)	DMSO	1·47 (m, 1)	1·80—2·65 (m, 7)	
(VI; R = *o*-Nitrophenyl)	DMSO	1·51 (m, 1)	1·75—2·63 (m, 7)	
(VI; R = *p*-Cyanophenyl)	DMSO	1·36 (m, 1)	1·69—2·20 (m, 7)	
(VI; R = Benzyl)	DMSO	1·63 (m, 1)	1·85—2·25 (m, 3) 2·50—2·85 (m, 5)	CH_2, 5·07 (d, 2)
(VI; R = *o*-Aminophenyl)	DMSO	1·45 (m, 1)	1·83—2·25 (m, 3) 2·77—3·53 (m, 4)	
(VI; R = *m*-Aminophenyl)	DMSO	1·38 (m, 1)	1·84—2·10 (m, 3) 2·76—2·96 (m, 3) 3·41—3·60 (m, 1)	
(VI; R = *p*-Aminophenyl	DMSO	1·44 (m, 1)	1·86—2·20 (m, 3) 2·53 (d, 2) 3·29 (d, 2)	

* $SiMe_4$ as internal standard. † Recorded on a Perkin-Elmer R 10 spectrometer.

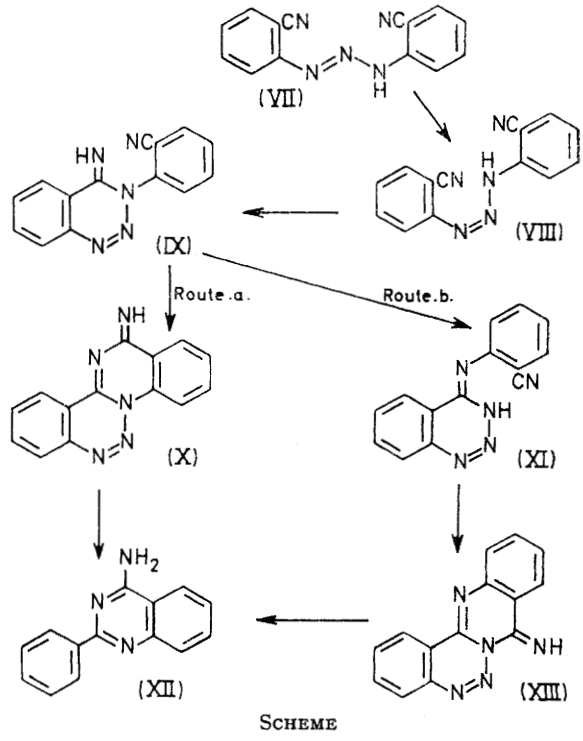
TABLE 4

Characteristic i.r.† absorption frequencies ($cm.^{-1}$) of triazene and 1,2,3-benzotriazine derivatives (KBr discs)

Compound	NH	CN	Other important absorptions
1,3-Di-*p*-cyanophenyltriazene	3232	2225	
(IV; R = Ph)	3210	2226	
(IV; R = *o*-Tolyl)	3250	2220	
(IV; R = *o*-Chlorophenyl)	3300	2223	
(IV; R = *o*-Cyanophenyl)	3215	2231	
(IV; R = *m*-Cyanophenyl)	3200	2233 *	
(IV; R = *p*-Cyanophenyl)	3270	2216 *	
(IV; R = *o*-Nitrophenyl)	3315	2230	
(IV; R = *m*-Nitrophenyl)	3285	2222	
(IV; R = *p*-Nitrophenyl)	3235	2230	
(IV; R = Benzyl)	3333	2216	
(Ia)	3220		1680 (CO)
(V; R = Ph)	3315		
(V; R = *o*-Tolyl)	3303		
(V; R = *o*-Chlorophenyl)	3295		
(V; R = *m*-Cyanophenyl)	3302	2229	
(V; R = *m*-Nitrophenyl)	3268		1527, 1348 (NO_2)
(V; R = Benzyl)	3282		
(VI; R = Ph)	3260		1149
(VI; R = *o*-Tolyl)	3200		1151
(VI; R = *o*-Chlorophenyl)	3399		1148
(VI; R = *m*-Cyanophenyl)	3260	2224	1147
(VI; R = *p*-Cyanophenyl)	3316	2220	1144
(VI; R = *o*-Nitrophenyl)	3290		1135
(VI; R = *m*-Nitrophenyl)	3263		1144
(VI; R = *p*-Nitrophenyl)	3339		1143
(VI; R = *o*-Aminophenyl)	3392		1147
	3190 *		
(VI; R = *m*-Aminophenyl)	3410		1145
	3310		
	3200		
(VI; R = *p*-Aminophenyl)	3411		1149
	3323		
	3210		
(VI; R = Benzyl)	3260		1154 *
(VI; R = Phenethyl)	3240		1165 *

* Denotes broad absorption. † Recorded on a Perkin-Elmer 257 Spectrophotometer (slow scan).

366 nm. confirmed a first-order disappearance of triazene with $t_{\frac{1}{2}}$ = 90 min. (at 38·2°). The presence of isosbestic points at 229 and 322 nm. indicated the absence of intermediates [(VIII)—(XI) and (XIII)] as absorbing species, and suggests that the rate-determining step is associated with the *trans* ⟶ *cis* [(VII) ⟶ (VIII)] rearrangement. Although decomposition of the triazene (VII) might logically be expected to proceed by route (a), we are unable to exclude route (b) because of the ready rearrangement of 4-iminobenzotriazines with electron-withdrawing substituents. For example, the *p*-cyanotriazene (IV; R = *p*-cyanophenyl) cyclized and rearranged directly to the *p*-cyanoanilinotriazine (VI; R = *p*-cyanophenyl) in either 70 or 95% aqueous ethanol. As with the corresponding *p*-nitrotriazene we were unable to isolate the intermediate 4-imine (V; R = *p*-cyanophenyl). When this reaction was studied spectroscopically there was a smooth transition (Figure 2) from the spectrum of triazene to triazine [(IV) ⟶ (VI); R = *p*-cyanophenyl]. In contrast to the behaviour of its *o*- and *p*-cyano-analogues the *m*-cyanophenyltriazene (IV; R = *m*-cyanophenyl) cyclized (Figure 3) both when melted or when heated in boiling 70% ethanol (30 min.) to yield the isolable 4-imine (V; R = *m*-cyanophenyl), which could be crystallized unchanged but rearranged to the isomer (VI; R = *m*-cyanophenyl) in boiling 95% ethanol (8 hr.) and in cold 2N-hydrochloric acid (3 hr.).



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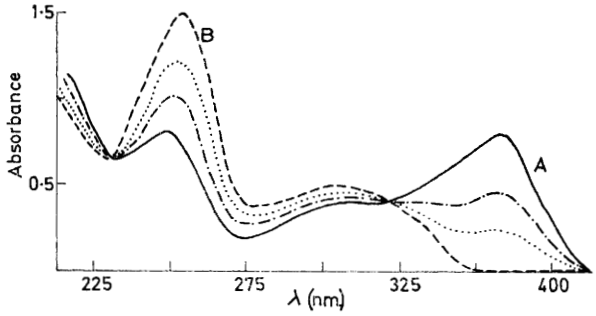


FIGURE 1 Decomposition of 1,3-di-*o*-cyanophenyltriazene (A) to 4-amino-2-phenylquinazoline (B) in 95% ethanol at 38·2°

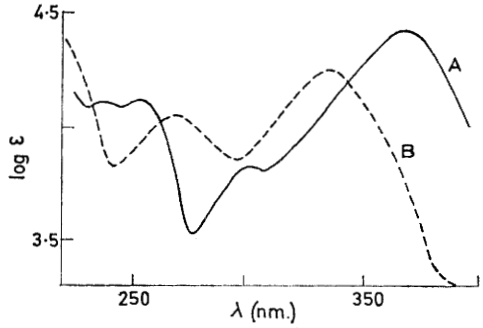


FIGURE 2 Absorption spectra of 1-*o*-cyanophenyl-3-*p*-cyanophenyltriazene (A) and 4-*p*-cyanoanilino-1,2,3-benzotriazine (B) in ethanol

Brown [10] has reviewed the influence of electron-withdrawing substituents on the rate of Dimroth rearrangements in related 1-substituted-1,2-dihydro-2-iminopyrimidines, and concludes that in certain instances their accelerating influences can be attributed

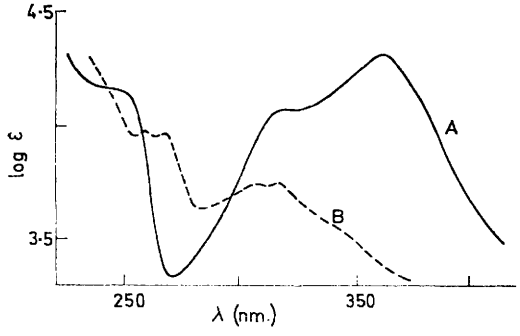
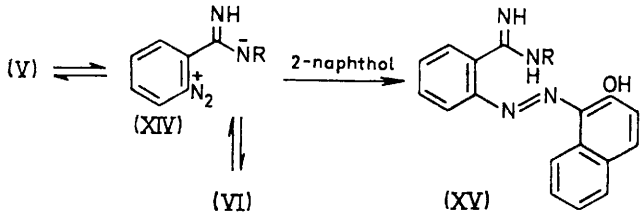


FIGURE 3 Absorption spectra of 1-*o*-cyanophenyl-3-*m*-cyanophenyltriazene (A) and 3-*m*-cyanophenyl-3,4-dihydro-4-imino-1,2,3-benzotriazine (B) in ethanol

purely to electronic effects.[11] Similar factors appear to operate in the rearrangement of 3-aryl-3,4-dihydro-4-imino-1,2,3-benzotriazines (V), and a series of triazines can be placed in order of increasing reactivity: R = *o*-tolyl < phenyl < *o*-chlorophenyl < *m*-cyanophenyl < *m*-nitrophenyl < *o*- and *p*-nitrophenyl. The probable interposition of a zwitterionic intermediate (XIV) in the rearrangement is indicated by the formation of an azonaphthol derivative (XV; R = Ph) when the 4-iminotriazine (V; R = Ph) is boiled with 2-naphthol in ethanol or butanol. The slow rearrangement of the



triazine (V; R = *o*-tolyl) and the rapid rearrangement of the nitro-analogues may reflect the degree of which the substituent stabilizes the proposed acyclic species (XIV). Accordingly, 4-iminotriazines (V) with electron-donating substituents [*cf.* (V; R = *o*-tolyl)] would be expected to rearrange only slowly (if at all) if electronic factors were solely responsible for reaction rate.

The factors influencing cyclization and rearrangement of 1-*o*-cyanophenyl-3-aralkyltriazenes are not clear. The benzyltriazene (IV; R = benzyl) cyclizes to the 4-imine (V; R = benzyl) in 70% aqueous ethanol,[4] and more efficiently in ethanol containing 2% piperidine. As expected, the imine is not rearranged in boiling ethanol (120 hr.) or in 2N-hydrochloric acid. However, the 4-benzylaminotriazine (VI; R = benzyl) prepared unambiguously from benzylamine and 4-methylthio-1,2,3-benzotriazine undergoes the reverse rearrangement to 4-imine (V; R = benzyl) in 2N-hydrochloric acid (10 days). Attempted synthesis of the phenethyltriazene (IV; R = phenethyl) from diazotized anthranilonitrile and phenethylamine surprisingly gave a poor yield of 4-phenethylamino-1,2,3-benzotriazine (VI; R = phenethyl) only. This phenethyltriazine resembled the benzyl analogue in being slowly converted (46 days) in acid into the isomer (V; R = phenethyl), but the imine reverted to the triazine (VI; R = phenethyl) when crystallized from ethanol. Electronic differences induced by benzyl and phenethyl substituents [*cf.* pK_a values [12] of benzylamine (9·34) and phenethylamine (9·83)] seem inadequate to account for the different stabilities of 3-benzyl-3,4-dihydro-4-imino-1,2,3-benzotriazine (V; R = benzyl) and its phenethyl homologue. Evidently, the more bulky phenethyl substituent is preferably accommodated on the exocyclic nitrogen. This may be attributed to a steric effect which discourages reversal of the initial equilibrium, imine ⇌ acyclic intermediate [(V) ⇌ (XIV)]. Significantly, 1-methyl-1,2-dihydro-2-iminopyrimidine undergoes rearrangement more slowly than its higher alkyl homologues.[10]

EXPERIMENTAL

Light petroleum refers to the fraction b.p. 60—80°, and ethanol refers to 95% ethanol unless otherwise stated.

1-o-*Methoxycarbonylphenyl*-3-o-*nitrophenyltriazene* (Ia).—*o*-Nitroaniline was diazotized in concentrated hydrochloric acid and stirred with methyl anthranilate (1 mol.) in sodium acetate buffer (pH 7) at 0° for 2 hr. The *nitrophenyltriazene* (40%) crystallized from ethanol as yellow needles, m.p. 165—167° (Found: C, 55·8; H, 3·9; N, 18·7. $C_{14}H_{12}N_4O_4$ requires C, 56·0; H, 4·0; N, 18·7%). Similarly prepared were the corresponding *m*- and *p*-nitrophenyltriazenes.[5]

1,3-*Di*-p-*cyanophenyltriazene*.—Finely powered *p*-aminobenzonitrile (11·8 g.) suspended in 3N-hydrochloric acid (150 ml.) was treated at 0° with aqueous sodium nitrite (3·5 g. in 25 ml.), and stirred for 1 hr. Sodium acetate trihydrate (to pH 7) and ice–water (250 ml.) were added and the yellow paste was stirred at 0° for 2 hr. and then collected. Crystallization (ethanol) gave the *dicyanotriazene* (76%) as yellow needles, m.p. 234—235° (eff.) (Found: C, 68·4; H, 3·9; N, 28·4. $C_{14}H_9N_5$ requires C, 68·0; H, 3·7; N, 28·3%).

1-o-*Chlorophenyl*-3-o-*cyanophenyltriazene* (IV; R = *o*-chlorophenyl).—Diazotized anthranilonitrile (11·8 g.) was neutralized at 0° (sodium acetate) and coupled with *o*-chloroaniline (12·8 g.). The *chlorotriazene* (80%) solidified after 2 hr. and was collected and washed with water; it crystallized from light petroleum as orange rosettes, m.p. 97—99° (Found: C, 61·0; H, 3·5; N, 22·2. $C_{13}H_9ClN_4$ requires C, 60·8; H, 3·5; N, 21·8%).

In Table 5 are recorded analogous *o*-cyanophenyltriazenes similarly prepared.

N-o-*Tolyl*-2-*nitrobenzamidine*.—Interaction of *o*-toluidine toluene-*p*-sulphonate (6·0 g.) and 2-nitrobenzonitrile (3·0 g.) at 210° for 3½ hr., gave a black solid which was purified by

[10] D. J. Brown, 'Mechanisms of Molecular Migrations,' Thyagarajan, ed., vol. 1, John Wiley, 1968, p. 209.

[11] D. J. Brown and M. N. Paddon-Row, *J. Chem. Soc.* (*C*), 1967, 903.

[12] A. Albert and E. P. Serjeant, 'Ionisation Constants of Acids and Bases,' Methuen, London, 1962, p. 140.

repeated extraction into hot 2N-hydrochloric acid followed by basification (aqueous ammonia). The *nitroamidine* thus produced (2·0 g., 40%) was crystallized from benzene–light petroleum to give cream needles, m.p. 144—145° (Found: C, 66·0; H, 5·3; N, 16·6. $C_{14}H_{13}N_3O_2$ requires C, 65·9; H, 5·1; N, 16·5%).

Reduction of the nitroamidine with stannous chloride in concentrated hydrochloric acid afforded N-o-*tolyl*-2-*aminobenzamidine* (50%) as white needles (from light petroleum), m.p. 105—106° (Found: C, 74·4; H, 6·6; N, 19·0. $C_{14}H_{15}N_3$ requires C, 74·6; H, 6·7; N, 18·7%).

3,4-*Dihydro*-3-o-*nitrophenyl*-4-*oxo*-1,2,3-*benzotriazine* (IIIa).— 1-*o*-Methoxycarbonylphenyl-3-*o*-nitrophenyltriazene (1 g.) when boiled in ethanol (50 ml.) containing piperidine (1 ml.) deposited after 2 hr. the triazinone (84%), prepared from *o*-cyanophenyltriazenes in 70% aqueous ethanol.

4-o-*Chloroanilino*-1,2,3-*benzotriazine* (VI; R = o-*chlorophenyl*).—(i) The solution formed when 3-*o*-chlorophenyl-3,4-dihydro-4-imino-1,2,3-benzotriazine (0·5 g.) was boiled (30 hr.) in ethanol (10 ml.) was evaporated to dryness and the residue was triturated with water (5 ml.). The *chloroanilinotriazine* crystallized from benzene–light petroleum as yellow flakes (74%), m.p. 168—169° (eff.) (Found: C, 61·1; H, 3·7; N, 22·2. $C_{13}H_9ClN_4$ requires C, 60·8; H, 3·5; N, 21·8%).

(ii) The 4-iminotriazine (0·25 g.) in 2N-hydrochloric acid (10 ml.) was shaken at 25° for 3 hr. Basification (aqueous ammonia) deposited the same (i.r.) chloroanilinotriazine (92%) as in (i).

TABLE 5

o-Cyanophenyltriazenes (IV)

Compound (IV) R =	Yield (%)	M.p.	Formula	% Found (required) C	H	N
Ph	67 [a]	107—108°				
o-*Tolyl*	50 [b,c]	84—85	$C_{14}H_{12}N_4$	71·3 (71·2)	5·3 (5·1)	23·8 (23·7)
Benzyl	94 [c]	82—83 (eff.)	$C_{14}H_{12}N_4$	71·4 (71·2)	5·0 (5·1)	23·6 (23·7)
o-*Nitrophenyl*	95 [d]	173—176 (eff.)	$C_{13}H_9N_5O_2$	58·3 (58·4)	3·4 (3·4)	26·1 (26·2)
m-*Nitrophenyl*	91 [e]	185 (resol.)	$C_{13}H_9N_5O_2$	58·0 (58·4)	3·5 (3·4)	26·3 (26·2)
p-*Nitrophenyl*	88 [e]	240—241 (eff.)	$C_{13}H_9N_5O_2$	58·1 (58·4)	3·6 (3·4)	26·2 (26·2)
o-Cyanophenyl	95 [f]	131—133 (eff.)	—	—	—	—
m-*Cyanophenyl*	88 [e]	150 (resol.)	$C_{14}H_9N_5$	67·9 (68·0)	3·9 (3·7)	28·2 (28·3)
p-*Cyanophenyl*	63 [e]	179—180 (eff.)	$C_{14}H_9N_5$	67·8 (68·0)	3·9 (3·7)	28·1 (28·3)

[a] Ref. 4. [b] Also formed as a by-product 4-*amino*-2′-*cyano*-3-*methylazobenzene* (17%), m.p. 153—155° (red needles, from ethanol) (Found: C, 70·9; H, 5·1; N, 23·9. $C_{14}H_{12}N_4$ requires C, 71·2; H, 5·1; N, 23·7%). Reduction of this azobenzene with stannous chloride in ethanol (see ref. 4) gave 3-*amino*-2-(4-*amino*-3-*methylphenyl*)*indazole* (21%), m.p. 144—145° (Found: C, 70·4; H, 6·1. $C_{14}H_{14}N_4$ requires C, 70·6; H, 5·9%). [c] From light petroleum. [d] From ethanol. [e] From benzene. [f] J. Pinnow and C. Sämann, *Chem. Ber.*, 1896, **29**, 623.

TABLE 6

3,4-Dihydro-4-imino-3-substituted 1,2,3-benzotriazines (V)

Compound (V) R =	Yield (%)	M.p.	Formula	% Found (required) C	H	N
Ph	80 [a]	112—114°				
o-*Tolyl*	54 [b,c]	100—101	$C_{14}H_{12}N_4$	71·0 (71·2)	5·3 (5·1)	23·6 (23·7)
Benzyl	95 [a,d]	119—120				
m-*Nitrophenyl*	90 [e]	230—231 [f] (eff.)	$C_{13}H_9N_5O_2$	58·7 (58·4)	3·2 (3·4)	25·9 (26·2)
m-*Cyanophenyl*	96 [e,g]	224—226 [f] (eff.)	$C_{14}H_9N_5$	68·4 (68·0)	3·9 (3·7)	28·1 (28·3)

[a] Ref. 4. [b] Also prepared (69%) by diazotisation of N-*o*-tolyl-2-aminobenzamidine in 1N-hydrochloric acid with sodium nitrite (1 mol.) followed by basification (aqueous ammonia). [c] From light petroleum. [d] Also prepared (100%) by rearrangement of 4-benzylamino-1,2,3-benzotriazine in cold 2N-hydrochloric acid (10 days) followed by basification (aqueous ammonia). [e] From ethanol. [f] M.p. variable, dependent on heating rate. [g] Also prepared (100%) by heating 1-*o*-cyanophenyl-3-*m*-cyanophenyltriazene at 150° for 10 min.

m.p. 187—189°. Analogous cyclization of the corresponding *m*- and *p*-nitrophenyltriazenes afforded the *m*-nitrophenyltriazinone (90%), m.p. 240—242° (eff.) and the *p*-nitrophenyltriazinone (92%), m.p. 254—255° (eff.) [lit.,[5] m.p. 238° (eff.) and 252—254° (eff.) respectively].

3-o-*Chlorophenyl*-3,4-*dihydro*-4-*imino*-1,2,3-*benzotriazine* (V; R = o-*chlorophenyl*).—A solution of 1-*o*-chlorophenyl-3-*o*-cyanophenyltriazene (1 g.) in 70% aqueous ethanol (60 ml.) was boiled for 30 min.; evaporation of the solvent, and crystallization of the residue from acetone gave the *chlorobenzotriazine* (0·75 g.) as ochre rosettes, m.p. 137—138° (Found: C, 61·0; H, 3·7; N, 22·2. $C_{13}H_9ClN_4$ requires C, 60·8; H, 3·5; N, 21·8%). The same chlorotriazine (86%) was produced when the triazene was boiled (2 hr.) in ethanol containing 2% of piperidine.

In Table 6 are listed 4-iminobenzotriazines similarly

(iii) Interaction of 4-methylthio-1,2,3-benzotriazine [13] (0·4 g.) and *o*-chloroaniline (0·3 g.) in boiling ethanol (10 ml.) for 66 hr. led to a slow evolution of methanethiol. Evaporation of solvent and crystallization of the resultant residue from benzene–light petroleum gave the same chlorotriazine (50%) as in (i) above.

In Table 7 are listed substituted 4-aminobenzotriazines prepared by similar routes.

4-o-*Aminoanilino*-1,2,3-*benzotriazine* (VI; R = o-*aminophenyl*).—Hydrogenation of 4-*o*-nitroanilino-1,2,3-benzotriazine over Adams catalyst in ethanol at 45° yielded the *aminotriazine* (50%), m.p. 194—195° (eff.) as buff microprisms (from ethanol) (Found: C, 66·0; H, 4·7; N, 29·2. $C_{13}H_{11}N_5$ requires C, 65·8; H, 4·7; N, 29·5%).

[13] G. Wagner and H. Gentzsch, *Pharmazie*, 1968, **23**, 629.

4-m-*Aminoanilino*-1,2,3-*benzotriazine* (VI; R = m-*aminophenyl*).—Catalytic hydrogenation of the *m*-nitrotriazine gave the m-*aminotriazine* (81%), m.p. 206—207° (eff.) as brown prisms (from ethanol) (Found: C, 65·7; H, 5·1; N, 29·4%). 4-p-*Aminoanilino*-1,2,3-*benzotriazine* (VI; R = *P-aminophenyl*) analogously prepared (60%) had m.p. 216—218° (eff.) (Found: C, 66·2; H, 5·1; N, 29·5%).

TABLE 7

Substituted 4-amino-1,2,3-benzotriazines (VI)

Compound (VI) R =	Yield (%) by route (i)	(ii)	(iii)	M.p.	Formula	% Found (required) C	H	N
Ph	95 [a]	100 [b]	50	200—201° (eff.)				
o-*Tolyl*		33 [c,d]		163—164 (eff.)	$C_{14}H_{12}N_4$	71·4 (71·2)	5·3 (5·1)	24·0 (23·7)
Benzyl			48 [c]	207—209 (eff.)	$C_{14}H_{12}N_4$	70·8 (71·2)	5·2 (5·1)	24·1 (23·7)
m-*Cyanophenyl*	98 [e]	100 [g,h]		242—243 (eff.)	$C_{14}H_9N_5$	68·2 (68·0)	3·9 (3·7)	28·0 (28·3)
p-*Cyanophenyl*	95 [h,i]			229—230 (eff.)	$C_{14}H_9N_5$	67·8 (68·0)	3·3 (3·7)	28·5 (28·3)
o-*Nitrophenyl*	95 [j,k]			207—209 (eff.)	$C_{13}H_9N_5O_2$	58·0 (58·4)	3·7 (3·4)	26·2 (26·2)
m-*Nitrophenyl*	89 [h,l]			244—245 (eff.)	$C_{13}H_9N_5O_2$	58·7 (58·4)	3·5 (3·4)	26·2 (26·2)
p-*Nitrophenyl*	98 [m,n]			237—238 (eff.)	$C_{13}H_9N_5O_2$	58·8 (58·4)	3·6 (3·4)	25·8 (26·2)

[a] In 120 hr. [b] Ref. 4. [c] In 20 hr. [d] From benzene–light petroleum. [e] In 8 hr. [f] From ethanol. [g] In 3 hr. [h] From butanol. [i] Obtained directly from triazene (IV; R = *p*-cyanophenyl) in boiling 70% ethanol (10 hr.). [j] From triazene (IV; R = *o*-nitrophenyl) in boiling ethanol (120 hr.). [k] From benzene. [l] From the 4-iminotriazine (V; R = *m*-nitrophenyl) in ethanol (3 hr.), or directly from the triazene (IV; R = *m*-nitrophenyl) on melting (at 185°) or in boiling ethanol (120 hr.). [m] From triazene (IV; R = *p*-nitrophenyl) in boiling ethanol (10 hr.). [n] From aqueous dimethylformamide.

4-*Phenethylamino*-1,2,3-*benzotriazine* (VI; R = *phenethyl*).—(i) Anthranilonitrile (11·8 g.), diazotized at 0° in concentrated hydrochloric acid was coupled with phenethylamine (12·1 g.) at 0° in the presence of an excess of sodium acetate. The brown resin was stirred at 0° for 4 hr. and was then collected and crystallized from 50% aqueous ethanol to afford the *phenethyltriazine* (7·3 g., 29%), as plates, m.p. 202—204° (eff.) (Found: C, 71·8; H, 5·8; N, 22·7. $C_{15}H_{14}N_4$ requires C, 72·0; H, 5·6; N, 22·4%).

(ii) Interaction of phenethylamine (1·82 g.) and 4-methylthio-1,2,3-benzotriazine (2·68 g.) in boiling ethanol (10 ml.) precipitated (after 5 hr.) the same (i.r.) phenethyltriazine (65%), m.p. and mixed m.p. 202—204° (eff.).

Rearrangement of 4-*phenethylamino*-1,2,3-*benzotriazine* (VI; R = *phenethyl*).—A suspension of the phenethylaminotriazine (0·1 g.) in 2N-hydrochloric acid (10 ml.) was shaken at 25° for 46 days. Basification with aqueous ammonia deposited a cream solid which was deduced to be 3,4-*dihydro*-4-*imino*-3-*phenethyl*-1,2,3-*benzotriazine* (V; R = phenethyl) on the evidence of its u.v. spectrum (in ethanol) which showed peaks at 260, 269, 306 and 318 nm. (*cf.* benzyl analogue, Table 2). Crystallization of this 4-imine from ethanol led to rearrangement and recovery of 4-phenethylamino-1,2,3-benzotriazine (75 mg.).

o-(2-*Hydroxy*-1-*naphthylazo*)-N-*phenylbenzamidine* (XV; R = Ph).—2-Naphthol (0·22 g.) and 3,4-dihydro-4-imino-3-phenyl-1,2,3-benzotriazine (0·33 g.) were boiled in butanol (5 ml.) for 6 hr. The *naphthylazo-derivative* (0·12 g., 22%) which was deposited after 2 days crystallized from ethanol as red needles, m.p. 242—243° (Found: C, 75·5; H, 4·9; N, 15·0. $C_{23}H_{18}N_4O$ requires C, 75·4; H, 5·0; N, 15·3%).

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