Triazine Intermediates in the Decomposition of 1-(*o*-Carbethoxyphenyl)-3-(*o*-cyanophenyl)-triazene in Aqueous Ethanol

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The thermal decomposition of 1-(*o*-carbethoxyphenyl)-3-(*o*-cyanophenyl)-triazene (**4**) in aqueous ethanol has been found to give 2-phenylquinazolin-4(3*H*)-one (**8**); the formation of triazine intermediates in the reaction has been established.

La décomposition thermique du (*o*-carbéthoxyphényl)-1 (*o*-cyanophényl)-3 triazène (**4**) dans l'éthanol aqueux conduit à la 3 *H*-phényl-2 quinazolinone-4 (**8**); la formation intermédiaire de triazine dans la réaction a été établie.

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In a previous report (1), the thermal decomposition of 1,2,3-benzotriazin-4(3*H*)-one (**1**) was found to give quinazolino[3,2-*c*][1,2,3]benzotriazin-8-one (**2**). An extensive study by Stevens and his co-workers (2–4) has shown that the imino-analogue of **2** is an intermediate in the conversion of 1,3-di-*o*-cyanophenyltriazene (**3**) to 4-amino-2-phenylquinazoline in aqueous ethanol. It was thus of interest to study the reactions of 1-(*o*-carbethoxyphenyl)-3-(*o*-cyanophenyl)-triazene (**4**), which, by analogy, would be expected to provide an alternative route to the triazinoquinazolone (**2**).

The coupling reaction of aromatic diazonium salts with primary aromatic amines is a general method of synthesis of diaryltriazenes (diazoamino compounds) (5), but the triazene **4** required for this study had not previously been reported. Diazotization of ethyl anthranilate, followed by coupling of the cold diazonium salt solution with anthranilonitrile, gave a 50% yield of 1-(*o*-carbethoxyphenyl)-3-(*o*-cyanophenyl)-triazene (**4**); the spectroscopic properties of this product are in accord with either of the tautomeric structures **4***a* ⇌ **4***b*.

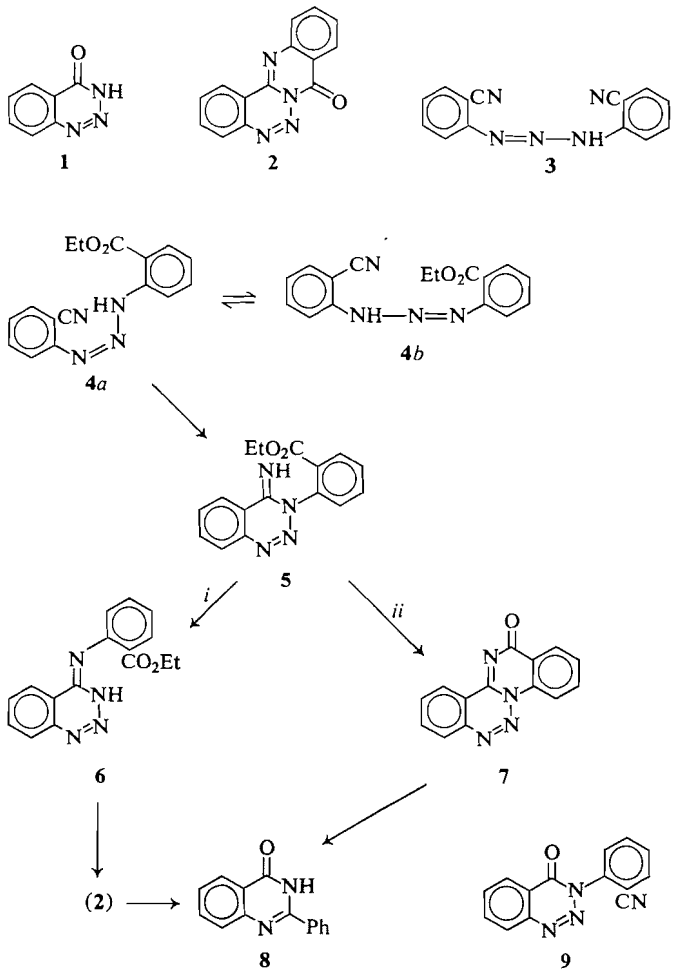
Prolonged refluxing (2–3 weeks) of the triazene **4** in 70% aqueous ethanol gave an 80% yield of 2-phenylquinazolin-4(3*H*)-one (**8**), which was identical with an authentic sample (6). Shorter reaction times in the same solvent medium gave mixtures of unchanged starting material (varying from 70% recovery after 2 h reflux to 10% after 100 h), the quinazolone **8**, and quinazolino[3,2-*c*][1,2,3]benzotriazin-8-one (**2**) (maximum yield 20% after 15 h reflux). The latter product, **2**, was identical with the product of thermolysis of 1,2,3-benzotriazin-4(3*H*)-one (**1**) (1). These results are summarized in Table 1.

The quinazolone **8** may arise from the triazene **4** by either route *i* or *ii*, as shown in Scheme 1. Nucleophilic addition at the nitrile group in tautomer **4***a*, a characteristic reaction of *o*-cyanophenyltriazenes (2), would lead to the formation of the 3-aryl-4-iminobenzotriazine **5**, which could cyclize directly to the quinazolino-[1,2-*c*][1,2,3]benzotriazine (**7**; route *ii*). Alternatively, the intermediate ester **5** could undergo Dimroth rearrangement to the isomeric 4-aryliminotriazine **6**, followed by cyclization at the ortho-ester group to give the triazinoquinazolone (**2**; route *i*). A less likely source of the triazinoquinazolone **2** is the isomerization **7** → **2**. Reductive loss of nitrogen from either of the isomeric triazinoquinazolones, **2** or **7**, would then yield the observed product, 2-phenylquinazolin-4(3*H*)-one (**8**).

The available evidence almost overwhelmingly supports route *i* as the more likely mechanism. The triazinoquinazolone **2** is a minor product when the triazene **4** is refluxed in aqueous ethanol for short periods, and has been shown in a previous report (1) to undergo conversion to the quinazolone **8** after 15 h refluxing in aqueous ethanol. Stevens has shown (2*b*) that

TABLE I. Product distribution for the decomposition of the triazene **4** in refluxing aqueous ethanol

Reaction time	Yield (%)		
	Triazene (**4**) (recovered)	Quinazolino[3,2-*c*][1,2,3]-benzotriazin-8-one (**2**)	2-Phenylquinazolin-4(3*H*)-one (**8**)
2 h	70	12	—
15 h	32	20	6
100 h	10	—	20
3 weeks	—	—	81



SCHEME I

3-aryl-4-imino-1,2,3-benzotriazines undergo facile Dimroth rearrangement to the isomeric 4-arylimino-1,2,3-benzotriazines (such as **5** → **6**), and that the rearrangement is accelerated in triazines bearing electron-attracting substituents (*e.g.* **5**). It has also been established that the conversion of 1,3-di-*o*-cyanophenyltriazene (**3**) to 4-amino-2-phenylquinazoline (**4**) most likely proceeds in a manner analogous to route *i*.

The long reflux time required for complete

decomposition of the triazene **4** indicates an unusually low reactivity compared with compounds of similar structure. The cyclizations of *o*-cyanophenyltriazenes (2) and *o*-carbalkoxyphenyltriazenes (7) to the corresponding 1,2,3-benzotriazines require only 1–2 h reflux in 70% aqueous ethanol, and the conversion of the dinitrile **3** to 4-amino-2-phenylquinazoline is quantitative in 95% ethanol at 20° after 48 h (*3a*). These cyclizations cannot take place unless the triazene is in the less stable *cis*-configuration about the N=N bond, and in all reactions of this type there is probably a *trans* → *cis* isomerization prior to cyclization (*2b*). Inspection of models of the *cis*-configurations of triazenes **3** and **4** shows that, in the nitrile-ester (tautomer **4***a*), there is considerable steric interaction between the nitrile and ester groups, whereas in the dinitrile **3**, there is no interaction at all between the nitrile groups. Thus the low reactivity of the nitrile-ester **4** is probably a result of the instability of the *cis*-isomer due to steric factors. The models do not reveal any difference in the stability of the tautomers **4***a* and *b*, and thus do not explain why the expected product of cyclization of tautomer **4***b*, 3-(*o*-cyanophenyl)-1,2,3-benzotriazin-4-one (**9**), is not found in any of the reaction mixtures. The latter observation may be interpreted as a difference in reactivity of nitrile and carbethoxy groups towards nucleophilic addition of amino nitrogen.

Stevens (*3a*) found that decomposition of 1,3-di-*o*-cyanophenyltriazene (**3**) on alumina afforded quickly the imino-analogue of the triazinoquinazolone **7**, and by analogy alumina-catalyzed decomposition of the triazene **4** would be expected to give rise to **7**. However, the triazene **4** was found to decompose very slowly in the presence of alumina and a low yield of the triazinoquinazolone **2** was obtained. Evidently, if isomer **7** is formed in this reaction, it must isomerize readily to **2**.

Experimental

Melting points were obtained on a Fisher–Johns apparatus and are corrected. The i.r. spectra were recorded with liquid paraffin mulls on a Perkin–Elmer Infracord spectrophotometer, and the n.m.r. spectrum with a Varian A-60A spectrometer using tetramethylsilane as the internal standard. Mass spectral data were obtained with a Dupont–C.E.C. model 21-491 spectrometer. Merck grade alumina was obtained from Brinkmann Instruments (Canada) Limited.

1-(o-Carbethoxyphenyl)-3-(o-cyanophenyl)-triazene (4)

Ethyl anthranilate (3.3 g) was dissolved in concentrated hydrochloric acid (5.0 ml) and the solution diluted with water (100 ml), cooled to 0 °C, and diazotized to starch-iodide end-point with aqueous sodium nitrite (1.4 g in 10 ml). After the cold diazonium salt solution had been stirred for 15 min, a solution of *o*-aminobenzonitrile (2.1 g) in 2 *M* hydrochloric acid (20 ml) was added dropwise with constant agitation. The mixture was then made alkaline with an excess of sodium acetate, stirred for 2.0 h, and then filtered to yield the triazene **4** (2.4 g, 50%), m.p. 156–157 °C (yellow needles from ethanol), ν_{max} 3220 (NH), 2220 (C≡N), 1675 (C=O), and 1410 (N=N) cm^{-1}; δ ($CDCl_3$) 6.90–8.10 (8H, m, aromatic), 4.42 (2H, q, methylene), and 1.42 (3H, t, methyl) p.p.m.; *m/e* 294 (P, $C_{16}H_{14}N_4O_2$), 266 ($C_{16}H_{14}N_2O_2$).

Decomposition of the Triazene 4 in Aqueous Ethanol

General Procedure

1-(*o*-Carbethoxyphenyl)-3-(*o*-cyanophenyl)-triazene (**4**) (0.001 mol) was refluxed in 70% aqueous ethanol (50 ml) for times varying from 2 h to 3 weeks. Unreacted starting material was recovered from the cooled reaction mixture by filtration. Evaporation of the filtrate gave a yellow solid residue, which upon recrystallization from absolute ethanol afforded quinazolino[3,2-*c*][1,2,3]benzotriazin-8-one (**2**), m.p. and mixed m.p. 215–216 °C, ν_{max} 1720, 1660, and 1605 cm^{-1}, identical with an authentic sample (1).

Evaporation of the mother liquor from the recrystallization afforded 2-phenylquinazolin-4(3*H*)-one (**8**), m.p. 238–239 °C (needles, from ethanol), ν_{max} 1665 cm^{-1}, identical with an authentic sample (6). Table 1 shows the yields of these products obtained after different durations of refluxing.

Alumina-catalyzed Decomposition of the Triazene 4 in Anhydrous Benzene

Basic alumina (Merck, activity I, untreated) (3.0 g) was added to a solution of the triazene **4** (0.2 g) in anhydrous benzene (50 ml), and the suspension was stirred at room temperature for 42 h. The alumina was separated by filtration and washed with 10 × 20 ml aliquots of anhydrous benzene. The combined benzene filtrate and washings afforded, on evaporation, a yellow gummy solid, which, after repeated recrystallization from benzene/petroleum ether and subsequently from benzene, yielded the quinazolinobenzotriazinone **2** (8 mg, 5%), identical with a sample from the previous reaction. Evaporation of the combined mother liquors from the recrystallizations gave unreacted starting material (0.13 g, 65%).

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The Interception of *N*-Dibenzylaminonitrene Generated from *N*-Azido Dibenzylamine

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N-Dibenzylaminonitrene (**6**) has been shown to be generated from the decomposition of *N*-azido dibenzylamine (**9**) by its interception with 4-phenyl-1,2,4-triazoline-3,5-dione, as the azimine (**8**).

On a montré que le *N*-dibenzylaminonitrène (**6**) est issu de la décomposition de la *N*-azidodibenzylamine (**9**) par son interception avec la phényl-4 triazoline-1,2,4 dione-3,5, en tant qu'azimine (**8**).

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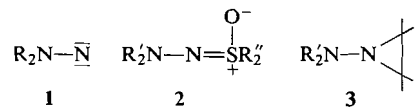
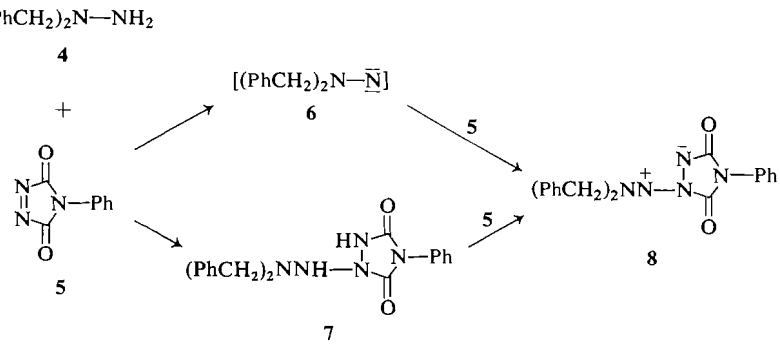
The concept of *N*-nitrenes (**1**) has gradually come of age (1) through a slow accumulation of results most conveniently rationalized via such intermediates, in particular, the formation of products resulting from nitrogen extrusion. Although the isolation of adducts such as **2** and **3** (2, 3) can be formally viewed as resulting from the trapping of *N*-nitrenes, it has not been established that such adducts did not arise from "prenitrene" precursors. Similarly, although the participation of **6** in the formation of **8**[2]



was suggested, it is also conceivable that **8** might have arisen via the oxidation of an initial tetrazane (**7**), without the intervention of **6** (4) (see eq. 1).

Earlier we had presented evidence for the

[1]



[1]Fellow of the Alfred P. Sloan Foundation. To whom inquiries should be addressed.

[2]In a recent private communication, Prof. Fahr has informed us that X-ray analysis of the adduct formed between 1,1-diphenylhydrazine and **5**, has confirmed the azimine structure.