# 5-(Arylamino)-1,2,3-triazoles and 5-Amino-1-aryl-1,2,3-triazoles from 3-(Cyanomethyl)triazenes

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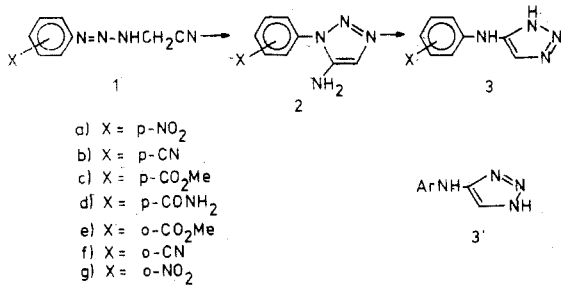
1-Aryl-3-(cyanomethyl)triazenes (1) cyclize in aprotic media, with Lewis base catalysis, to 5-amino-1-aryl-1,2,3-triazoles (2), whereas in protic media cyclization, followed by Dimroth rearrangement, affords the isomeric 5-(arylamino)-1,2,3-triazoles (3).

1,2,3-Triazoles with 4- or 5-amino substituents are available from a limited number of routes,[1,2] the classical methods being the displacement of halogen from 4- or 5-halo-1,2,3-triazoles by amines[3] and the reaction of aryl azides with acetonitriles.[4] Although triazenes are the recognized intermediates in the best-known route to 5-aminotriazoles, starting from an azide and an activated methylene compound,[2] the use of stable triazene precursors has not been fully explored. Smith et al.[5] observed the cyclization of the phenylcyanotriazene PhNHN=NCH(CN)Ph to 1,4-diphenyl-5-amino-1,2,3-triazole, and Potts and Husain obtained mesoionic 4-amino-1,2,3-triazolium chlorides from trisubstituted triazenes ($ArN{=}NN(CH_3)CH_2CN$).[6] We report here a convenient synthesis of 5-amino-1-aryl-1,2,3-triazoles (2) and 5-(arylamino)-1,2,3-triazoles (3) by unambiguous cyclization of the readily available 1-aryl-3-(cyanomethyl)triazenes (1). This method is particularly important for making 5-aminotriazoles which are unsubstituted at C-4 in the triazole ring.




Diazo coupling of aryl diazonium cations with $\alpha$-aminoacetonitrile in aqueous solution, neutralized with sodium acetate and buffered with a little acetic acid, readily affords the (cyanomethyl)triazenes 1.[7] The crude *p*-nitrophenyl- (**1a**), *p*-cyanophenyl- (**1b**), and [*p*-(methoxycarbonyl)phenyl]triazenes (**1c**) were usually of sufficient purity for immediate use in triazole synthesis; recrystallization of the triazenes from aprotic solvents, e.g., acetonitrile or benzene, did not show measurable cyclization, whereas recrystallization from ethanol did. Diazo coupling of $\alpha$-aminoacetonitrile with *p*-carbamoylbenzene diazonium salt did not proceed cleanly, and the crude triazene has resisted all attempts at purification. Nevertheless, a low yield of triazole was obtained by refluxing the crude triazene **1d** in ethanol (see below).

Conversion of the *p*-nitrophenyl- (**1a**) and (*p*-cyanophenyl)triazenes (**1b**) to the 5-(arylamino)-1,2,3-triazoles **3a** and **3b** was achieved cleanly by refluxing the triazene in absolute ethanol for 1–2 h; no trace of the isomeric triazoles **2a** and **2b** was evident in the NMR spectra of the crude products from these reactions. Recrystallization of the triazoles **3a** and **3b** from aqueous ethanol resulted in the formation of hydrated materials; the presence of water of hydration was evident from the elemental analysis and was confirmed by a band in the IR spectra at 3530 or 3580 $cm^{-1}$. This band was not present in the IR spectra of **3a** and **3b** after recrystallization from nitromethane; the absence of water of hydration in these samples was confirmed by elemental analysis. Likewise, the [[*p*-(methoxycarbonyl)phenyl]amino]triazole **3c** was obtained by refluxing the triazene **1c** in ethanol, but in this case an equilibrium mixture of the triazole isomers, **2c** $\rightleftharpoons$ **3c**, was formed, with **3c** predominant. Compound **3c** was obtained pure by recrystallization from aqueous ethanol and was not hydrated.

Analogous treatment of crude 1-(*p*-carbamoylphenyl)triazene (**1d**) in refluxing ethanol similarly gave an equilibrium mixture of triazoles, **2d** $\rightleftharpoons$ **3d**, but purification of this mixture gave only the 5-amino-1,2,3-triazole (**2d**), and the 5-(arylamino)triazole isomer **3d** has not been isolated in pure form. A more general approach to the 5-aminotriazoles **2** was found to be treatment of chloroform solutions of the triazenes **1** with suspended alumina for several days, in which case the 5-aminotriazoles were essentially free from 5-arylamino isomers. The 1-(*p*-nitrophenyl)- (**2a**), 1-(*p*-cyanophenyl)- (**2b**), and 1-[*p*-(methoxycarbonyl)phenyl]-5-amino-1,2,3-triazoles (**2c**) were all obtained in good yields by this method. An alternative method, which works well for the *p*-nitro- and (*p*-cyanophenyl)triazoles, is to recrystallize the triazene (**1a** or **1b**) from absolute ethanol; the short time of heating at the boiling point is sufficient to cause total cyclization without rearrangement. Conversion of the 5-amino-1-(*p*-cyanophenyl)triazole **2b** to the isomeric 5-[(*p*-cyanophenyl)amino]triazole **3b** was achieved by refluxing in ethanol for 1 h, demonstrating that the 5-aminotriazole **2** is an intermediate in the conversion **1** $\rightarrow$ **3** in hot ethanol. The cyclization **1** $\rightarrow$ **2** is rapid at the boiling point of ethanol, whereas the Dimroth rearrangement **2** $\rightarrow$ **3** is the slow step in the overall conversion.

The mechanism of the conversion **1** $\rightarrow$ **3** is illustrated in Scheme I. Triazenes of type **1** exist as mixtures of tautomers ($ArN{=}NNHCH_2CN \rightleftharpoons ArNHN{=}NCH_2CN$) in solution at ambient temperature.[8] The initial cyclization

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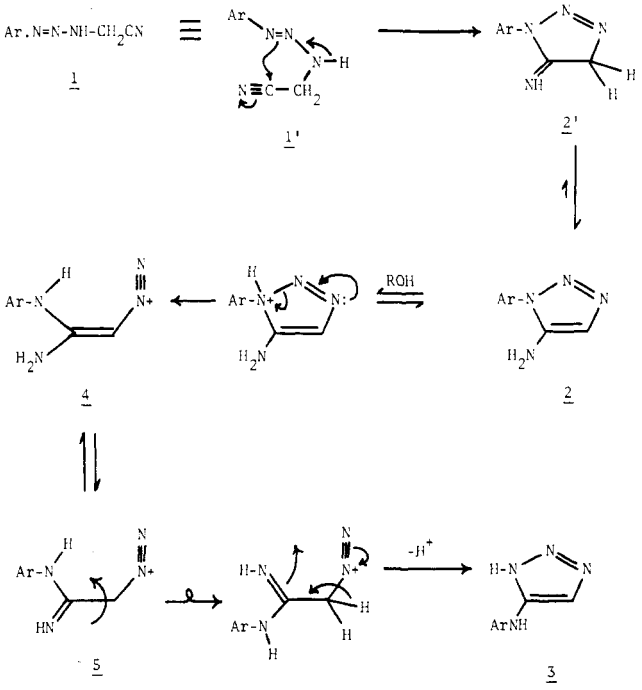
Scheme I



most likely proceeds from the anti isomer (1′) of the conjugated tautomer by intramolecular nucleophilic attack at the cyano group to give initially the 5-iminotriazole 2′, which immediately tautomerizes to the more stable, aromatic 5-aminotriazole 2. The Dimroth rearrangement of 2, which is catalyzed by protic solvents, probably involves protonation by solvent at the N-1 position and ring opening to the intermediate diazonium species 4, which must tautomerize to the imino diazonium species 5 to allow rotation around the C4–C5 bond. Recyclization of the diazonium group to the imino nitrogen, concomitant with proton loss from C4, affords the Dimroth isomer 3.

The isomerization of the 5-aminotriazoles 2 to the isomers 3 in protic media without the aid of a catalyst appears to be somewhat more facile than previously reported Dimroth rearrangements of 5-aminotriazoles which generally require basic catalysis in protic media.[2] For example, 1-benzyl-4-substituted-5-amino-1,2,3-triazoles are partially isomerized in hot basic solutions to equilibrium mixtures rich in 4-(benzylamino)-1,2,3-triazoles,[9] and 1,4-disubstituted 5-amino-1,2,3-triazoles are irreversibly isomerized to 4-phenyl-5-anilino-1,2,3-triazoles by refluxing in pyridine-type bases.[4] In the latter case, the effect of substituents in the aryl group parallels that observed in the present work: electron-withdrawing groups favor the isomerization to the 5-(arylamino)-1,2,3-triazole.

Structural assignments of triazoles 2 and 3 were made unequivocally on the basis of IR, UV, NMR, and mass spectral data. The UV spectra of the isomers are significantly different and characteristic of each. The 5-(arylamino)triazoles exhibit four absorption bands at 205, 218–230, 250–260, and 302–308 or 375 nm in ethanol, whereas the principal absorptions of the 5-amino-1-aryltriazoles are shifted to lower wavelengths at 205 and 246 or 277 nm (Table I). The IR spectra of these isomers are equally striking and are diagnostically different in the region of NH absorption. In general, the 5-aminotriazoles 2 show three NH stretching bands at 3410, 3320, and 3180–3240 $cm^{-1}$, whereas the NH bands of the 5-arylamino isomers 3 appear at 3360–3310, 3240–3180, and 3200–3100

Table I. UV Data of Representative 5-(Arylamino)- and 5-Amino-1-aryl-1,2,3-triazoles

| triazole (X) | $\lambda_{max}$, nm | $\epsilon$ |
|---|---|---|
| 3c ($MeO_2C$) | 308 | $2.11 \times 10^4$ |
| | 260 (sh) | $3.78 \times 10^3$ |
| | 225 | $5.13 \times 10^3$ |
| | 205 | $8.07 \times 10^3$ |
| 3b (CN) | 302 | $2.80 \times 10^4$ |
| | 260 (sh) | $7.23 \times 10^3$ |
| | 218 | $8.67 \times 10^3$ |
| | 204 | $1.39 \times 10^4$ |
| 3a ($NO_2$) | 375 | $1.63 \times 10^4$ |
| | 250 (sh) | $7.05 \times 10^3$ |
| | 230 | $9.62 \times 10^3$ |
| | 205 | $1.17 \times 10^4$ |
| 2b (CN) | 246 | $1.89 \times 10^4$ |
| | 205 | $1.82 \times 10^4$ |
| 2a ($NO_2$) | 277 | $8.17 \times 10^3$ |
| | 210 (sh) | $7.75 \times 10^3$ |
| | 205 | $8.00 \times 10^3$ |
| 3g (*o*-$NO_2$) | 410 | $4.23 \times 10^3$ |
| | 275 (sh) | $6.15 \times 10^3$ |
| | 236 | $1.33 \times 10^4$ |
| | 205 | $8.08 \times 10^3$ |

(w) $cm^{-1}$. In addition, the IR spectra of the 5-aminotriazoles 2 have a medium-intensity band at ca. 1645 $cm^{-1}$, presumably arising from C=C stretching in the triazole ring; this band is either very weak or not seen in the spectra of the 5-(arylamino)triazoles. As discussed previously, the presence of water of crystallization in some samples of the 5-(arylamino)triazoles 3a and 3b was diagnosed from the presence of a band in the IR above 3500 $cm^{-1}$ (See paragraph at the end of the paper about supplementary spectra.)

The triazoles are clearly distinguished by the $^1H$ NMR spectra in $Me_2SO$-$d_6$ solutions. The 5-aminotriazoles 2 are typified by a broad signal at $\delta$ 5.8–6.0 for the protons of the 5-$NH_2$ group and a sharp, one-proton signal at $\delta$ 7.0 assigned to the proton bound to C-4 of the triazole ring. The corresponding proton at C-4 of the 5-(arylamino)-triazoles 3 is shifted downfield at $\delta$ 7.56–7.57, within the doublets of the AA′BB′ pattern of the aryl group. The exocyclic NH proton of the 5-(arylamino)triazole is broad but quite distinct in the range $\delta$ 9.3–9.7, whereas the NH proton in the ring is observed downfield at $\delta$ 14.5–14.8; the latter signal is considerably broadened possibly because of the tautomerism in the triazole system (3 ⇄ 3′).

The measurement of $^{13}C$ NMR spectra for these compounds confirmed the triazole structures proposed. The initially formed 5-aminotriazole 2a shows aromatic carbon signals at $\delta$ 117.6 (d), 125.0 (d), 141.0 (s), and 146.4 (s) and additionally at $\delta$ 123.7 (d) and 143.6 (s), with the latter peaks distinguished from those at $\delta$ 125.0 and 146.4 by their intensities. The rearranged triazole 3a was further characterized by measurement of the fully coupled spectrum: $\delta$ 113.9 (d, splitting 165.9 Hz, of t, 4.8 Hz), 125.9 (d, 167.8 Hz, of d, 4.7 Hz), 138.6 (t, 9.4 Hz, of t, 3.4 Hz), 149.5 (t, 8.9 Hz); the triazole ring carbons at $\delta$ 121.2 (d, 194.5 Hz) and 146.1 (d, 10.8 Hz). These splitting patterns are those expected from earlier work.[10]

Similarly for the 5-aminotriazole 2b, the proton-bearing carbon of the triazole ring is observed as a doublet (splitting 194 Hz) of triplets (splitting 3 Hz); the analogous proton of the isomer 3b is a simple doublet (splitting 194.4 Hz). A full account of the $^{13}C$ spectra of these triazoles will be reported elsewhere.

Mass spectra of triazoles of type 2 and 3 also serve to identify and distinguish the isomers. For example, the

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(10) M. Begtrup, *J. Chem. Soc., Perkin Trans. 2*, 736 (1976).

Table II. Physical Data of 5-(Arylamino)-1,2,3-triazoles (3)[a]

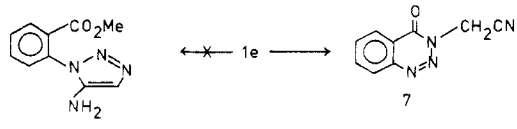
| compd (X) | yield, % | mp, °C | solvent | formula | IR, cm$^{-1}$ | NMR ($Me_2SO$), ppm AA'BB' | H(C-4) | HN$^1$ | *exo*-HN | X |
|---|---|---|---|---|---|---|---|---|---|---|
| **3a** (*p*-$NO_2$) | 99 | 212–213 | $CH_3NO_2$ | $C_8H_7N_5O_2$ | 3360, 3180, 3100 (w) | 8.07 (d), 7.30 (d, $J$ = 9 Hz) | 7.57 | 9.7 | 14.7 | |
| **3a** (*p*-$NO_2$, hydrate) | 97 | 212–214 | EtOH/$H_2O$ | $C_8H_7N_5O_2 \cdot H_2O$ | 3580, 3380, 3250, 3200 (w), 3160 (w) | | | | | |
| **3b** (*p*-CN) | 80 | 202–203 | $CH_3NO_2$ | $C_9H_7N_5$ | 3310, 3220, 3100 (w), 2225 | 7.65 (d), 7.37 (d, $J$ = 8 Hz) | 7.56 | 9.43 | 14.5 | |
| **3b** (*p*-CN, hemihydrate) | 85 | 202.5–204 | EtOH/$H_2O$ | $C_9H_7N_5 \cdot {}^1/_2H_2O$ | 3530, 3300, 3210, 3100, 2230 | | | | | |
| **3c** (*p*-$MeO_2C$) | 47 | 180–181.5 | EtOH/$H_2O$ | $C_{10}H_{10}N_4O_2$ | 3320, 3240, 3200, 1680 | 7.9 (d), 7.35 (d, $J$ = 9 Hz) | 7.57 | 9.33 | 14.5 | 3.82 (OMe) |
| **3g** (*o*-$NO_2$) | 70 | 201–204 | $CHCl_3$ | $C_8H_7N_5O_2$ | 3315, 3150, 3130 | 6.8–8.3 (m) | 7.9 | 9.7 | 14.8 | |

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for compounds **3a–c** and **3g**.

mass spectra of the *p*-nitrophenyl isomers **2a** and **3a** have molecular ions at 205 mass units; both mass spectra contain fragments at 177 (M – $N_2$, weak), 175 (M – NO, strong), 159 (M – $NO_2$, strong), 138 ($O_2NC_6H_4NH_2$), and 122 ($O_2NC_6H_4$) mass units. A distinguishing feature in the mass spectrum of **2a** is the strong fragment at $m/e$ 189, corresponding to loss of the primary amino group from the molecular ion; this fragment is not seen in the mass spectrum of **3a**.

The transition of the 5-aminotriazole **2** to the 5-(arylamino)triazole **3** takes place slowly over a period of 1–2 weeks when solutions of **2** in $Me_2SO$-$d_6$ are kept at room temperature. The transition is readily observed by using the NMR spectrometer; the signals at ca. $\delta$ 6 and 7 of **2** disappear while those at $\delta$ 7.5 and 9.3–9.8 of **3** grow in; no intermediate species were evident from the NMR spectra. A more rapid transition, **2** → **3**, takes place when the 5-aminotriazoles are heated at the melting point; the reaction can be readily observed on the Koffler hot stage. The 5-aminotriazoles **2a–c** melt at lower temperatures than their isomers (**3a–c**), and almost immediately after melting they resolidify as long needles growing in the melt; the resolidified crytals remelt at the melting point of the corresponding 5-(arylamino)triazole. The thermal isomerization **2** → **3** occurs in the range 140–160 °C and appears to be a very clean reaction. The thermal isomerization was demonstrated on a micropreparative scale for the (*p*-cyanophenyl)triazole **2b**, which was converted in high yield to the isomer **3b**.

Whereas triazole synthesis of compound types **2** and **3** was straightforward with para-substituted phenyltriazenes, attempts to prepare some ortho-substituted analogues were less successful, and the reactions of ortho-substituted phenyltriazenes followed different routes. For example, the [*o*-(methoxycarbonyl)phenyl]triazene **1e** afforded the 3-(cyanomethyl)benzotriazinone **7**, rather than the triazole

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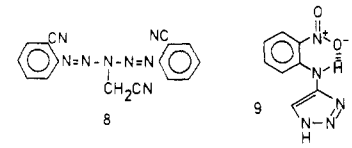
**6**, when cyclized by being refluxed in ethanol or in chloroform over alumina. Attempts to isolate the dinitrile **1f** by the addition of aminoacetonitrile to an aqueous solution of *o*-cyanobenzenediazonium chloride resulted in decomposition; when the product of the coupling was extracted immediately from the reaction mixture into methylene chloride and treated with alumina to encourage triazole formation, no cyclization products were evident. The only identifiable product of this reaction was the double diazo coupling product, the pentaazadiene **8**. Among ortho-

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substituted triazenes, only the (*o*-nitrophenyl)triazene **1g** undergoes cyclization to a triazole, and in this case only the rearranged triazole **3g** could be isolated, regardless of the reaction conditions. Triazene **1g** cyclized in chloroform over alumina much more readily than any other triazene in the series; reaction was complete after 12 h, and no trace of the isomeric triazole **2g** was evident in the reaction mixture. The apparent ease of the isomerization of **2g** to **3g** may be a consequence of the additional stability conferred on **3g** by intramolecular hydrogen bonding (e.g., **9**).

## Experimental Section

IR spectra were recorded as Nujol mulls with a Perkin-Elmer 299 spectrophotometer and UV–visible spectra were recorded in ethanol on a Varian Cary 219 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were obtained with a Varian CFT-20 spectrometer, and microanalyses were carried out by the Canadian Microanalytical Service. Melting points were recorded on a Koffler hot-stage melting point apparatus and are uncorrected.

**1-Aryl-3-(cyanomethyl)triazenes (1).** The (cyanomethyl)triazenes were prepared by our previously reported method:[7] the arylamine was diazotized in hydrochloric acid with sodium nitrite, and the diazonium salt solution was treated with an aqueous solution of aminoacetonitrile bisulfate, followed by an excess of sodium acetate. The precipitated triazene was removed by filtration, after further stirring in the cold for 30 min to 1 h, and could usually be recrystallized from aprotic solvents (e.g., hexane, benzene, or acetonitrile) without measurable cyclization to triazoles. These triazenes were as follows.

**1-(*p*-Nitrophenyl)-3-(cyanomethyl)triazene (1a)**: yield 90%; mp 95–96 °C.

**1-(*p*-Cyanophenyl)-3-(cyanomethyl)triazene (1b)**: yield 77%; mp 198–201 °C (acetonitrile).

Table III. Physical Data of 5-Amino-1-aryl-1,2,3-triazoles (2)[a]

| compd (X) | method | yield, % | mp, °C | solvent | formula | IR, $cm^{-1}$ | NMR ($Me_2SO$), ppm: AA'BB' | H(C-4) | $NH_2$(5) | X |
|---|---|---|---|---|---|---|---|---|---|---|
| **2a** (*p*-$NO_2$) | B | 80 | 134 | $CHCl_3$ | $C_8H_7N_5O_2$ | 3410, 3320, 3240, 1640 | 7.7 (d), 8.4 (d, $J$ = 8 Hz) | 7.07 | 6.0 | |
| **2b** (*p*-CN) | A | 18 | 136 | EtOH | $C_9H_7N_5$ | 3410, 3320, 3200, 2240, 1645 | 8.05 (d), 7.8 (d, $J$ = 8 Hz) | 7.0 | 5.9 | |
| | B | 92 | 136 | $CHCl_3$ | | | | | | |
| **2c** (*p*-$MeO_2C$) | B | 36 | 145–149 | $CH_3CN$ | $C_{10}H_{10}N_4O_2$ | 3415, 3320, 3180, 1710, 1650 | 8.17 (d), 7.83 (d, $J$ = 9 Hz) | 7.0 | 5.87 | 3.93 (OMe) |
| **2d** (*p*-$H_2NCO$) | C | 30 | 231–233 | $H_2O$ | $C_9H_9N_5O$ | 3435, 3360, 3300, 3170, 1665, 1660 (sh) | 8.15 (d), 7.7 (d, $J$ = 8 Hz) | 7.0 | 5.8 | |

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for compounds **2a–d**.

**1-[*p*-(Methoxycarbonyl)phenyl]-3-(cyanomethyl)triazene (1c)**: yield 94%; mp 137.5–139 °C.

**1-(*p*-Carboxamidophenyl)-3-(cyanomethyl)triazene (1d)**: yield 44%; mp 143–145 °C.

**1-[*o*-(Methoxycarbonyl)phenyl]-3-(cyanomethyl)triazene (1e)**: yield 59%; mp 52–54 °C.

**1-(*o*-Nitrophenyl)-3-(cyanomethyl)triazene (1g)**: yield 27%; mp 85–87 °C.

**5-(Arylamino)-1,2,3-triazoles (3).** (i) The 1-aryl-3-(cyanomethyl)triazene (0.005 mol) was refluxed in absolute ethanol (50–100 mL) for 1–2 h. The solution was evaporated to dryness in vacuo and the residue purified to afford the 5-(arylamino)-triazole. The (*p*-nitrophenyl)- (**3a**) and (*p*-cyanophenyl)triazoles (**3b**) were recrystallized from nitromethane; attempted recrystallization of these triazoles from aqueous ethanol gave hydrated triazoles. The [*p*-(methoxycarbonyl)phenyl]triazole **3c** recrystallized from aqueous ethanol as the pure triazole. Physical data of these triazoles are given in Table II.

Treatment of the 1-(*p*-carbamoylphenyl)triazene (**1d**) in refluxing ethanol gave a mixture of triazoles, which was purified to give the 5-aminotriazole **2d** described below.

(ii) 5-Amino-1-(*p*-cyanophenyl)-1,2,3-triazole (**2b**, 100 mg) was refluxed in absolute ethanol (2.5 mL) for 1.0 h. Evaporation of the solution in vacuo afforded 5-[(*p*-cyanophenyl)amino]-1,2,3-triazole (**3b**, quantitative), which was identical (IR; mp and mmp 202–204 °C) with a sample prepared as in i above.

(iii) 5-Amino-1-(*p*-cyanophenyl)-1,2,3-triazole (**2b**, 50 mg) was heated dry in an oil bath at 175 °C for 0.5 h. The residue was identical (IR; mp 203–205 °C) with 5-[(*p*-cyanophenyl)amino]-1,2,3-triazole (**3b**), yield 40 mg (80%).

(iv) 1-(*o*-Nitrophenyl)-3-(cyanomethyl)triazene (**1g**, 100 mg) was dissolved in chloroform (10 mL), and basic alumina (1.0 g) was added. The mixture was stirred for 14 h at room temperature, whereupon the alumina was removed by filtration and washed well with aliquots of chloroform (approximately 150 mL total volume), and the combined chloroform washings were evaporated to afford 5-[(*o*-nitrophenyl)amino]-1,2,3-triazole (**3g**; see Table II).

**5-Amino-1-aryl-1,2,3-triazoles (2). Method A.** The 1-aryl-3-(cyanomethyl)triazene (1.5 g) was dissolved in the minimum volume of hot ethanol (25 mL), and the solution was allowed to cool to room temperature. The crystalline material was separated to afford the 5-aminotriazole (see Table III).

**Method B.** The 1-aryl-3-(cyanomethyl)triazene (250 mg) was dissolved in the minimum volume of chloroform (250–500 mL), and basic alumina (2.5 g) was added. The suspension was stirred for 7 days at room temperature. The mixture was filtered to remove alumina and the filtrate evaporated to dryness in vacuo. The residue was the 5-aminotriazole (see Table III).

**Method C.** 1-(*p*-Carbamoylphenyl)-3-(cyanomethyl)-1,2,3-triazene (**1d**, 2.1 g) was refluxed in absolute ethanol (150 mL) for 1.0 h. Evaporation of the solution to dryness in vacuo and recrystallization of the residue from water afforded 5-amino-1-(*p*-carbamoylphenyl)-1,2,3-triazole (**2d**, 0.64 g; see Table III).

**3-(Cyanomethyl)-1,2,3-benzotriazin-4-one (7).** (i) 1-[*o*-(Methoxycarbonyl)phenyl]-3-(cyanomethyl)-1,2,3-triazene (**1e**, 0.5 g) was dissolved in chloroform (50 mL), and basic alumina (5 g) was added to the solution. The suspension was stirred at room temperature for 10 days. The alumina was removed by filtration and washed with chloroform, and the combined filtrate and washings were evaporated to afford 3-(cyanomethyl)-1,2,3-benzotriazin-4-one (**7**): 0.31 g (74%); mp 109–111 °C (white needles from aqueous ethanol); $\nu_{max}$ 1690 $cm^{-1}$; $^1H$ NMR $\delta$ 5.33 (s, 2 H, $CH_2$), 7.8–8.5 (m, 4 H, aromatic). Anal. Calcd for $C_9H_6N_4O$: C, 58.06; H, 3.25; N, 30.09. Found: C, 57.85; H, 2.90; N, 30.02.

(ii) The triazene **1e** (0.5 g) was refluxed in absolute ethanol (10 mL) for 1 h. Evaporation of the solution afforded the triazinone **7** (crude yield quantitative), which was recrystallized from aqueous ethanol, with charcoal, and was identical with a sample prepared as in i above.

**3-(Cyanomethyl)-1,5-bis(*o*-cyanophenyl)pentaza-1,4-diene (8).** *o*-Aminobenzonitrile (4.28 g) was diazotized in concentrated hydrochloric acid (10 mL), diluted with water (90 mL), and kept at 0 °C with sodium nitrite (2.65 g) for 5 h. The diazonium salt solution was treated with aminoacetonitrile bisulfate (7.1 g) under an atmosphere of nitrogen and the mixture stirred for 0.5 h, followed by the addition of sodium acetate hydrate (60 g). After 10 min, the precipitated product was extracted into methylene chloride (~200 mL). The methylene chloride layer was washed with water, dried over $MgSO_4$, and filtered. The filtrate was poured onto basic alumina (50 g) and the suspension stirred for 3 days. The alumina was removed by filtration and the filtrate evaporated to dryness under vacuum with moderate heating. Recrystallization of the residue from ethanol/dimethyl sulfoxide gave the pentazadiene **8**: 0.71 g (12%); mp 148.5–150 °C (golden needles); $\nu_{max}$ 2235 $cm^{-1}$; $^1H$ NMR $\delta$ 5.63 (s, 2 H, $CH_2$), 7.6–8.2 (m, 8 H, aromatic); mass spectrum, $m/e$ 286 (P – $N_2$), 258 (P – $2N_2$). Anal. Calcd for $C_{16}H_{10}N_8$: C, 61.15; H, 3.18; N, 35.67. Found: C, 61.52; H, 3.15; N, 35.66.

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**Supplementary Material Available:** Full UV spectra and the N–H vibration region of the IR spectra of the *p*-cyanophenyltriazoles **2b** and **3b** (2 pages). Ordering information is given on any current masthead page.