1-Aryl-3-(carbamoylmethyl)triazenes: Synthesis, Spectroscopic Analysis and Cyclization to New 1,2,3-Benzotriazines

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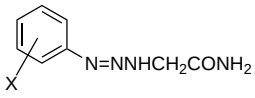
Reaction of a series of arene diazonium salts with glycinamide affords the N-coupling products the 1-aryl-3-(carbamoylmethyl)triazenes, $ArN{=}NNHCH_2CONH_2$ **3**, which have been characterized by ^1H and ^{13}C NMR spectroscopy. The reaction works well with electron withdrawing groups in the ortho- or para-position of the aryl moiety, but when the coupling reaction was attempted with a *p*-bromo-substituted diazonium salt, the reaction afforded the pentazadiene **8** and not the expected triazene. Triazenes with a reactive ester or cyano-substituent in the ortho-position of the benzene ring were found to undergo spontaneous cyclization to the respective 1,2,3-benzotriazine heterocycles **4a** and **5**. The 3-(carbamoylmethyl)-4-imino-1,2,3-benzotriazine (**5**) was characterized by further NMR experiments, ^{15}N NMR, and homonuclear correlated NMR spectra.

Introduction

1-Aryl-3-alkyltriazenes ($ArN{=}NNHR$) with appropriate substituents in the aryl and alkyl groups have been used as precursors for a variety of nitrogen-containing heterocycles.[1] For example, interaction of a reactive ortho-substituent in the aryl moiety with N-3 of the triazene affords derivatives of 1,2,3-benzotriazine.[2] On the other hand, if the alkyl group at N-3 has a reactive α-substituent, then interaction with N-1 of the triazene chain leads to 1,2,3-triazole derivatives. Thus, the 3-(cyanomethyl)triazenes **1** cyclize readily to give 1-aryl-5-amino-1,2,3−triazoles, which undergo facile Dimroth-type rearrangement to 5-(arylamino)-1,2,3-triazoles.[3] The analogous esters **2** undergo similar cyclization to afford 1-aryl-5-hydroxy-1,2,3-triazoles.[4] In this study, we set out to extend this approach to the amide-analogues **3** and we report the synthesis of a series of these 3-(carbamoylmethyl-)triazenes **3a**−**i**. We have also investigated the potential use of these triazenes as precursors of heterocyclic molecules.

$ArN{=}NNHCH_2X$
1 X = CN
2 X = CO_2Et



X
3a *p*-CO_2CH_3
b *p*-CN
c *p*-NO_2
d *p*-$COCH_3$
e *p*-Br
f *o*-NO_2
g *o*-CN
h *o*-CO_2CH_3
i *o*-$CO_2C_2H_5$

Experimental Section

All reagents were reagent grade materials purchased from the Aldrich Chemical Co. Ltd. and were used without further purification. Melting points were determined on a Reichert hot-stage microscope and are uncorrected. Infrared spectra were obtained using Nujol mulls. Chemical shifts were recorded in DMSO-d_6 unless otherwise noted and are relative to TMS.

^{15}N NMR spectra were recorded in DMSO solution at the Institute of Cancer Research, Sutton, U.K., at 25.36 MHz using a multinuclear 10 mm probe. Solutions were prepared by dissolving 1 mmol of each compound in dimethyl sulfoxide (2.4 mL) containing 30% (w/w) DMSO-d_6 with 30 mg of chromium acetylacetonate. A concentric capillary tube containing nitromethane was used as external reference. Spectra were recorded at 305 K.

1-Aryl-3-(carbamoylmethyl)triazenes (3). General Procedure The appropriate arylamine (0.01 mol) was dissolved, by heating if necessary, in 2 M hydrochloric acid (40 mL) and the solution cooled to 0 °C. The amine was then diazotised over 0.5 h. at 0 °C with sodium nitrite (0.011 mol) dissolved in a minimum volume of distilled water. If necessary, the diazonium salt solution was filtered before adding a solution of glycinamide hydrochloride (0.012 mol) in a minimum volume of distilled water. The reaction mixture was stirred for 1 h, whereupon the solution was clear. A ten-molar excess of sodium acetate trihydrate (30 g) dissolved in a minimum volume of distilled water was then added and the triazene precipitated over the course of the next 1 h. The product was then filtered, dried and recrystallized from an appropriate solvent to afford the following 1-aryl-3-(carbamoylmethyl-) triazenes [numbers in parentheses are those assigned to the minor tautomer in the tautomeric mixture]:

3-(Carbamoylmethyl)-1-[*p*-(methoxycarbonyl)phenyl]-triazene (3a): yield 99%; mp 174−177 °C (hexanes/ethyl acetate); $\nu_{max.}$ 3360 and 3250 (NH_2), 3180 and 3120 (NH), 1685 (C═O), 1660 (C═O), and 840 cm^{-1}; δ_H 3.81 (3H, s), 4.18 (4.31) (2H, s), 7.56 and 7.93 (2H), 8.16, 8.13, 7.80, 7.77 (8.09, 8.06, 7.49, 7.46) (4H, m), 11.42 (12.72); δ_C 46.25, 52.2, 154.2, 131.4, 122.3, 120.1 (151.0, 131.1, 119.4), 169.0 (166.0), 188.5; δ_N 70.50, 19.06, −126.42, −275.44. Anal. Calcd for $C_{10}H_{12}N_4O_3$: C, 50.85; H, 5.08; N, 23.73. Found: C, 51.76; H, 5.14; N, 21.40%.

3-(Carbamoylmethyl)-1-(*p*-cyanophenyl)triazene (3b): yield 75%; mp 155−156 °C (nitromethane); $\nu_{max.}$ 3380 and 3240 (NH_2), 3140 and 3120 (NH), 2180 (C≡N), 1655 (C═O), and 810 cm^{-1}; δ_H 4.11 (4.26) (2H, s), 7.26 and 7.29 (2H), 7.78, 7.75, 7.44, 7.41 (7.74, 7.70, 7.38) (4H, m), 11.59 (12.72 br); δ_C 46.4, 107.5, 153.9, 133.4, 121.1, 119.2, 169.7 (168.8). Anal.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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(4) Baines, K. M.; Vaughan, K.; Hooper, D. L.; Leveck, L. F. *Can. J. Chem.* **1983**, *61*, 1549.

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Calcd for $C_9H_9N_5O$: C, 53.20; H, 4.43; N, 34.48. Found: C, 53.16; H, 4.43; N, 33.62%.

3-(Carbamoylmethyl)-1-(*p*-nitrophenyl)triazene (3c): yield 78%; mp 146−148 °C (ethyl acetate); $\nu_{max.}$ 3370 and 3250 (NH_2), 3140 and 3100 (NH), 1650 (C═O), 1525 and 1310 (NO_2), and 830 cm^{-1}; δ_H 4.15 (4.30) (2H, s), 7.13 and 7.23 (2H), 8.21, 8.18, 7.50 and 7.47 (8.20, 8.17, 7.32, 7.29) (4H, m), 11.30 (12.40); δ_C 46.39, 120.8, 125.0, 125.9, 144.3 and 155.7, 169.5 (168.6); *m/z* 195 ($[M - N_2]^+$), 178 ($[O_2NC_6H_4N_3]^+$), 150 ($[O_2NC_6H_4N_2]^+$), 138 ($[O_2NC_6H_4NH_2]^+$), 122 ($[O_2NC_6H_4]^+$), 86 ($[NH_2COCH_2N_2]^+$), and 77 ($C_6H_5^+$). Anal. Calcd for $C_8H_9N_5O_3$: C, 43.04; H, 4.04; N, 31.39. Found: C, 43.05; H, 3.90; N, 30.43%.

3-(Carbamoylmethyl)-1-(*o*-nitrophenyl)triazene (3f): yield 51%; mp 67−73 °C (crude); $\nu_{max.}$ 3340 and 3280 (NH_2), 3160 (NH), 1650 (C═O), 1500 and 1325 (NO_2) and 770 cm^{-1}; δ_H 4.48 (2H, s), 6.21 and 6.46 (2H), 7.07−8.25 (4H, m) and 11.82; δ_C ($CDCl_3$) 63.4, 116.2, 121.8, 126.1, 132.6, 136.2, 138.0 and 170.7; m/z 150 ($[O_2NC_6H_4N_2]^+$), 138 ($[O_2NC_6H_4NH_2]^+$), 122 ($[O_2NC_6H_4]^+$), 86 ($[NH_2COCH_2N_2]^+$) and 77 ($C_6H_5^+$). Anal. Calcd for $C_8H_9N_5O_3$: C, 43.04; H, 4.04; N, 31.39. Found: C, 44.55; H, 4.12; N, 33.13%.

1-(*p*-Acetylphenyl)-3-(carbamoylmethyl-)triazene (3d): yield 33%; mp 136−138 °C (chloroform); $\nu_{max.}$ 3350 and 3240 (NH_2), 3170 (NH), 1670 (C═O ketone), 1640 (C═O amide), and 825 cm^{-1}; δ_H 2.49 (3H, s), 4.10 (4.26) (2H, s), 7.22 and 7.09 (2H), 7.97, 7.94, 7.43 and 7.38 (8.13, 8.00, 7.80, 7.77) (4H), 10.95 (12.25); δ_C 26.6, 46.1, 112.6, 120.3, 129.7 and 154.1, 197.1 (190.38). Anal. Calcd for $C_{10}H_{12}N_4O_2$: C, 54.55; H, 5.45; N, 25.45. Found: C, 53.99; H, 5.30; N, 23.99%.

3-(Carbamoylmethyl)-1-(*o*-cyanophenyl)triazene (3g): yield 68%; mp 125−128 °C (crude); $\nu_{max.}$ 3420 and 3220 (NH_2), 3180 (NH), 2190 (C≡N), 1665, 1650 (C═O), and 740 cm^{-1}; when dissolved in chloroform or DMSO, the compound decomposed and a satisfactory NMR spectrum could not be obtained, although the ^1H NMR spectrum of the solution showed evidence for the formation of the cyclization product **5**.

3-(Carbamoylmethyl)-1-[*o*-(methoxycarbonyl)phenyl]-triazene (3h): yield 73%; mp 247−250 °C (crude); $\nu_{max.}$ 3390 and 3230 (NH_2), 3180 (NH), 1665 (C═O ester), 1630 (C═O amide), 740, and 690 cm^{-1}; δ_H 3.61 (3H, s), 5.44 (2H, s), 7.82 and 8.29 (2H, br s), 8.37−8.72 (4H, m).

3-(Carbamoylmethyl)-1-[*o*-(ethoxycarbonyl)phenyl]triazene (3i): yield 88%; mp 245 °C (crude); $\nu_{max.}$ 3365 and 3220 (NH_2), 3160 (NH), 1665 (C═O ester), 1645 (C═O amide), 740 and 685 cm^{-1}; δ_H 1.50 (3H, t), 4.73 (2H, q), 5.44 (2H, s), 7.83 and 8.31 (2H, br s), 8.37−8.72 (4H, m).

1,5-Bis(*p*-Bromophenyl)-3-(carbamoylmethyl)-1,4-pentazadiene [(p-BrPhN═N)$_2$NCH$_2$CONH$_2$] (8). *p*-Bromoaniline (0.01 mol) was dissolved in 2 M hydrochloric acid (40 mL), cooled to 0 °C, and diazotized over 30 min at 0 °C with sodium nitrite (0.011 mol) dissolved in a minimum volume of distilled water. The diazonium salt solution was treated with an aqueous solution of glycinamide hydrochloride (0.012 mol), and the reaction mixture was stirred for 1 h. The resulting clear solution was neutralized with a ten-fold excess of sodium acetate trihydrate (30 g) dissolved in a minimum volume of distilled water affording the 1,5-bis(*p*-bromophenyl)-3−(carbamoylmethyl)-1,4-pentazadiene (**8**), which precipitated from the solution over the course of stirring at 0 °C for 1 h. The product was filtered, dried, and recrystallized from ethyl acetate to afford the pure pentazadiene (**8**): yield 99%; mp 176−178 °C (from ethyl acetate); $\nu_{max.}$ 3370 and 3300 (NH_2), 1660 (C═O), and 815 cm^{-1}; δ_H 4.28 (2H, s), 8.58 (1H, br s) and 8.13 (1H, br s), 8.43, 8.46, 8.55, and 8.57 (8H); δ_C 44.3, 122.1, 123.9, 132.6, 146.8, and 165.7.

3-(Carbamoylmethyl)-1,2,3-benzotriazin-4-one (4a). The crude triazene (**3h** or **3i**) was dissolved in a minimum volume of 95% ethanol with heating. The hot solution was filtered and the filtrate cooled slowly to afford the 3-(carbamoylmethyl)-1,2,3-benzotriazin-4-one (**4a**): yield 85%; mp 264−266 °C (ethanol); $\nu_{max.}$ 3370 and 3280 (NH_2), 1679 (C═O), 1678.5 (C═O), and 770 cm^{-1}; δ_H 4.98 (2H, s), 7.38 and 7.78 (2H, singlets) and 7.89−8.24 (4H, m); δ_C 51.7, 119.4, 124.5, 128.1, 133.0, 135.5, 143.8, 154.9, and 168.1; δ_N 33.13, −14.74, −151.29, and −274.60 (amide NH_2; inverted triplet with full NOE); M^+ 204 (12%), *m/z* 160 (100%) ($[M - CONH_2]^+$), 132 (57%) ($[N_2{\bullet}C_6H_4CO]^+$), 104 (40%) ($[C_6H_4N_2]^+$), and 77 (100%) ($[C_6H_5]^+$). Anal. Calcd for $C_9H_8N_4O_2$: C, 52.99; H, 3.95; N, 27.46. Found: C, 52.96; H, 4.00; N, 27.90%.

3-(Carbamoylmethyl)-4-imino-1,2,3-benzotriazine (5). The crude triazene (**3g**) was dissolved in a minimum volume of 95% ethanol at room temperature. The solution was left overnight, whereupon the 3-(carbamoylmethyl)-4-imino-1,2,3−benzotriazine (**5**) precipitated as long white needles together with a small amount of a purple byproduct. The crystals were washed with copious amounts of cold chloroform which removed the purple impurity to yield the pure iminotriazine **5**: yield 68%; mp >300 °C (ethanol); $\nu_{max.}$ 3330 and 3290 (NH_2), 3140 (NH), 1670 (C═O), 1615 (C═N), and 755 cm^{-1}; δ_H 4.88 (2H, s), 7.20 and 7.65 (2H, singlets), 7.69−8.31 (4H, m) and 8.70 (1H, s); δ_C 52.9, 118.2, 123.7, 127.8, 131.8, 133.2, 140.0, 149.4, and 168.7; δ_N 31.00, −29.01, −168.36, −177.08 (exocyclic imino *N*H; inverted broad doublet with full NOE), −275.05 (amide *N*H_2; inverted triplet with full NOE). M^+ 203 (10%), *m/z* 159 (100%) ($[M - CONH_2]^+$), 131 (8%) ($[N_2C_6H_4C{=}NH]^+$), 104 (60%) ($[C_6H_4N_2]^+$), and 77 (80%) ($[C_6H_5]^+$). Anal. Calcd for $C_9H_9N_5O$: C, 53.20; H, 4.43; N, 34.48. Found: C, 53.14; H, 4.71; N, 33.52%.

Results and Discussion

Synthesis. The coupling reaction of diazonium salts with glycinamide, $NH_2CH_2CONH_2$, affords moderate to good yields of the 3-(carbamoylmethyl)triazene (**3**), but there appears to be a requirement for the presence of a strongly electron-withdrawing substituent in the aryl moiety for triazene synthesis to succeed. Thus triazenes **3a-d** have been isolated and characterized, but the *p*-bromo-substituted analogue **3e** was not isolated. Attempts to synthesize **3e** resulted in the formation of the pentazadiene **8**, which presumably arises by formation of the triazene **3e** followed by further diazonium coupling at N-3 of the triazene. A similar requirement for the presence of electron-withdrawing substituents was reported in a study of the synthesis of simple 1-aryl-3-methyltriazenes, ArN═NNHCH$_3$.[5]

Purification of the triazenes **3a**−**d** required repeated recrystallization in order to obtain products with a sharp melting point for spectroscopic (IR and NMR) analysis, but analytical purity could not be achieved by recrystallization. Only compound **3b** gave reasonable elemental analysis. It is possible that the triazenes undergo decomposition in the hot solvent during recrystallization limiting the extent of purification possible. Thus we have relied on spectroscopic analysis to confirm the structural identity of the products, as well as direct and indirect chemical evidence.

The ortho-substituted 1-aryl-3-(carbamoylmethyl-)triazenes **3f**−**i** are inherently unstable. The *o*-cyano **3g**, *o*-methoxycarbonyl- **3h**, and *o*-ethoxycarbonyl- (**3i**) phenyltriazenes were isolable as crude products, which gave IR spectra consistent with the structures. The NMR spectra of the crude esters **3h** and **3i** confirmed the structural identity, but attempts to purify these ortho-substituted aryltriazenes by recrystallization resulted in cyclization to the corresponding 1,2,3-benzotriazine **4a** or **5**. The detailed characterization of these heterocyclic products is unequivocal evidence for the formation of the triazene precursors **3g**, **3h** and **3i** and indirectly confirms that the structures of the analogous triazenes **3a**−**d** are correct.

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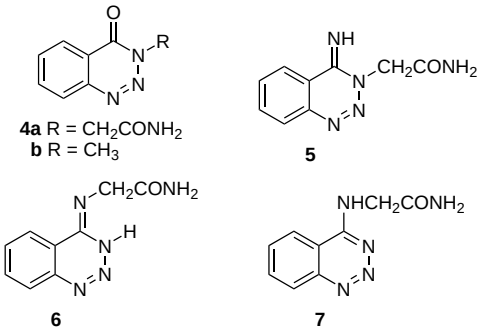

The (*o*-nitrophenyl)triazene **3f** was obtained from the reaction mixture in a very pure form, as evident in the NMR spectrum, but decomposed upon attempted recrystallization to afford *o*-nitroaniline. Yields of the ortho-substituted triazenes were, on average, lower than those of their para-substituted analogues perhaps as a result of their lesser stability. The instability of ortho-substituted 1-aryl-3-alkyltriazenes, particularly the *o*-nitro derivatives, has been noted before.[6]

Spectroscopic Analysis. All triazenes in the series **3a**−**i** show two NH stretching vibrations in the ranges 3220−3300 and 3340−3390 cm^{-1} deriving from the amide functional group, an amide carbonyl band in the range 1640−1660 cm^{-1} and aromatic out-of-plane bending vibrations at 810−850 cm^{-1} for para-substituents and at 740−770 cm^{-1} for ortho-substituted compounds. The triazene NH bands occur in the range 3120−3180 cm^{-1}; the para-substituted triazenes **3a**−**c** show two NH bands in this region arising from the tautomerism between the 1-aryl-3-alkyltriazene **9** and the 3-aryl-1-alkyltriazene **10**, which is consistent with previous studies of the IR spectra of monoalkyltriazenes.[7]

$$\underset{\mathbf{9}}{ArN{=}NNHCH_2CONH_2} \rightleftharpoons \underset{\mathbf{10}}{ArNHN{=}NCH_2CONH_2}$$

The tautomerism, **9** ⇌ **10**, is also evident in the NMR spectra of the para-substituted triazenes **3a**−**d**, recorded in DMSO-d_6, and gives rise to a doubling of the signals from all protons in the vicinity of the triazene moiety. Thus, the NH group of the major tautomer **9** gives rise to a signal in the range 10.95−11.59 ppm; the NH of the minor tautomer **10** occurs in the range 12.25−12.72 ppm. The methylene group gives rise to two sharp signals in the ranges 4.10−4.18 and 4.26−4.31 ppm, and the proton signals in the aromatic region are all doubled.

These observations are similar to those reported earlier in the NMR spectra of 1-aryl-3-methyltriazenes;[8,9] however, in the present study, we did not observe coupling between the NH and CH_2 groups in the more favorable tautomer **9**. Based on these previous reports, it is reasonable to assume that the NH and CH_2 resonances for the "unconjugated" triazene **10** are present at a lower field. Thus the relative amounts of each tautomer can be estimated from the relative intensities of the NMR signals to give the following results, expressed as the percentage of tautomer **9** present for each substituent: **3a**, *p*-CO_2Me, 63%; **3b**, *p*-CN, 55%; **3c**, *p*-NO_2, 47%; **3d**, *p*-$COCH_3$, 58%. These values are consistent with previous observations[8] that electron withdrawing substituents favor the presence of the unconjugated tautomer **10**.

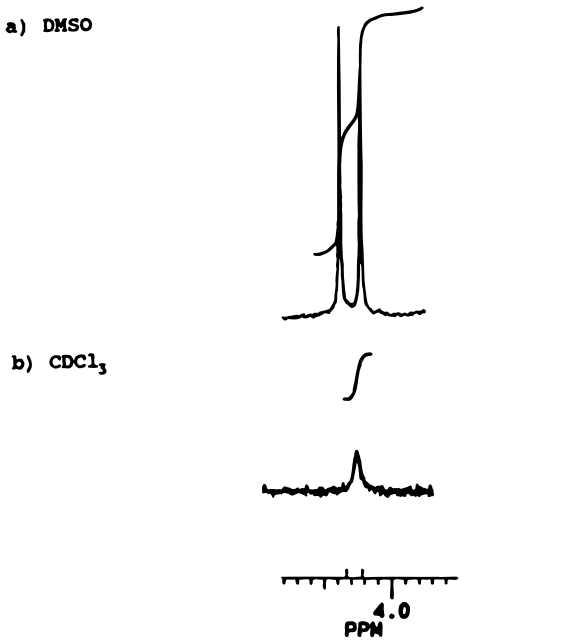

Figure 1. Comparison of the methylene signals in the ^1H NMR spectrum of the (*p*-nitrophenyl)triazene **3c** recorded in DMSO-d_6 (a) and $CDCl_3$ (b).

Previous work[9] on triazene tautomerism in DMSO solution has shown that this solvent slows the exchange rate of the NH proton through hydrogen bonding. Comparison of the NMR spectra of the (*p*-nitrophenyl)triazene **3c** in DMSO-d_6 and $CDCl_3$ provides another example of this effect. Figure 1 shows a comparison of the methylene signals in the two solvents; clearly, the faster exchange between the tautomeric forms in $CDCl_3$ results in a coalescence of the methylene signals. Coalescence of the methylene signals in the NMR spectrum of **3c** is also observed when the temperature of a solution of **3c** in DMSO-d_6 is raised to 60 °C. Figure 2 shows the change in the methylene region of the spectrum as the temperature is raised. This observation provides further verification of the presence of the tautomerism, **9** ⇌ **10**.

The 3-(carbamoylmethyl)triazenes **3a**−**d** were not sufficiently soluble in chloroform to permit ^{13}C NMR analysis, which instead was carried out using DMSO-d_6 as solvent. ^{13}C NMR signals were observed in the appropriate regions of the spectrum, but random pairing of signals due to the presence of the two tautomers complicated the interpretation and made unequivocal assignment of peaks difficult. Aromatic signals were observed between 112.6 and 155.7 ppm, while the methylene carbon signal was found between 46.1 and 46.4 ppm. The amide carbonyl carbon signal is found in the range 169.0−169.7 ppm.

The pentazadiene **8** is a nontautomerizable system and shows simple ^1H and ^{13}C NMR spectra that have been assigned unequivocally. The aromatic protons of **8** give rise to a clear AA'BB' pattern with J = 8.5 Hz. The methylene signal was found at 4.28 ppm, and two nonequivalent amide proton signals occur at 8.13 and 8.58 ppm. Furthermore, aromatic protons integrated to 8H, thus supporting the pentazadiene structure.

The (*o*-nitrophenyl)triazene **3f** gives rise to ^1H and ^{13}C NMR spectra of a single species in solution. By analogy

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(8) Vaughan, K. *J. Chem. Soc., Perkin Trans. 2* **1977**, 17.
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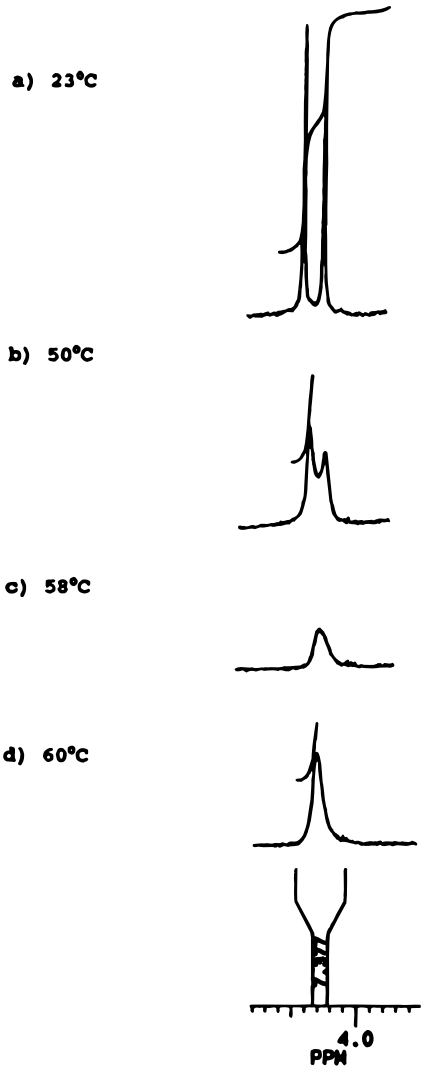
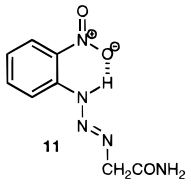


Figure 2. Coalescence of methylene signals in the ^{1}H NMR spectrum of the (*p*-nitrophenyl)triazene **3c** in DMSO-d_6 during a variable temperature NMR experiment showing the presence of two tautomeric forms.

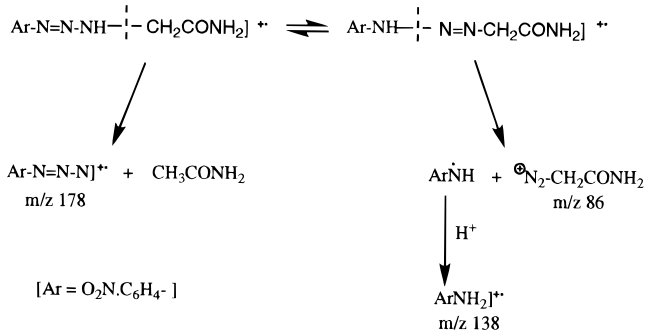
with other ortho-substituted monoalkyltriazenes,[8] it is likely that the single species of **3f** is the intramolecularly hydrogen-bonded nonconjugated tautomer **11**. The ^{1}H



NMR spectrum of **3f** shows an aromatic multiplet between 7.07 and 8.25 ppm with J = 7.9 Hz, a single methylene signal at 4.48 ppm, amide NH signals at 6.21 and 6.46 ppm, and a single triazene NH signal at 11.82 ppm. The ^{13}C NMR spectrum of **3f** showed signals in all appropriate regions; aromatic carbons were assigned unequivocally using additivity rules.[10]

Mass spectral analysis was performed on two representative compounds of this series, namely the *p*-nitro- (**3c**) and *o*-nitro- (**3f**) phenyltriazenes. Neither spectrum

Scheme 1



showed the presence of a molecular ion, but the fragments observed can be correlated well with the fragmentation pathways shown in Scheme 1. Fragments are observed from both tautomers; the conjugated tautomer splits apart at the N3−αC bond to give the fragment at *m*/*z* 178, whereas the unconjugated tautomer fragments at the N2−N3 bond to give the fragment *m*/*z* 86 and the neutral arylamino radical which is observed as the protonated fragment at *m*/*z* 138.

Cyclization to 1,2,3-Benzotriazines. Attempts to purify either the [*o*-(methoxycarbonyl)- (**3h**) or the [*o*-(ethoxycarbonyl)phenyl]triazenes (**3i**) results in cyclization to 3-(carbamoylmethyl)-1,2,3-benzotriazin-4-one (**4a**). The cyclization is nearly quantitative and the product crystallizes in an analytically pure state from the cold solution. The IR spectrum of **4a** shows two amide NH stretching bands at 3280 and 3370 cm^{-1}, whereas the carbonyl absorption bands are not resolved using double beam instrumentation. Using diffuse-reflectance FTIR, the carbonyl bands are resolved and observed at 1678.5 and 1679 cm^{-1}.

The ^{1}H NMR spectrum of **4a** clearly shows the absence of the NH proton and of the *O*-alkyl group due to the elimination of ROH during the cyclization. The ^{13}C NMR spectrum of **4a** is assigned by comparison with the 3-methyl analogue **4b**, which was synthesized by the known[11] cyclization of 1-[*o*-(methoxycarbonyl)phenyl]-3-methyltriazene. The ^{13}C NMR spectrum of **4b** has a single carbonyl at 155.0 ppm; the analogous signal in the spectrum of **4a** is at 154.9 ppm, leading to the assignment of the amide carbonyl carbon of **4a** at 168.1 ppm. This observation correlates with the assignment of the signal at 168.7 ppm to the amide carbonyl of compound **5**, the cyclization product obtained from the *o*-(cyanophenyl)-triazene **3g**. Thus the imino carbon at the C4 of the triazine ring of **5** must be assigned to the signal at 149.4 ppm.

Cyclization of the crude *o*-(cyanophenyl)triazene **3g** takes place when the triazene is dissolved in ethanol at room temperature and left overnight; the benzotriazine **5** crystallizes from the solution. 4-Imino-1,2,3-benzotriazines are known to undergo Dimroth rearrangement,[12] which in the case of **5** would lead to the isomer **6**, or its aromatized tautomer **7**. All the spectroscopic evidence of this product points to structure **5** and eliminates structures **6** and **7**.

The most important evidence for structure **5** is found in the nitrogen-15 NMR spectrum compared to the ^{15}N

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(11) LeBlanc, R. J.; Vaughan, K. *Can. J. Chem.* **1972**, *50*, 2544.

(12) Stevens, H. N. E.; Stevens, M. F. G. *J. Chem. Soc.*, Sect. *C (Organic)* **1970**, 765.

spectrum of related imidazotetrazines[13] and 1,2,3-benzotriazines.[14] The ^{15}N signals from the nitrogen atoms at N1, N2, and N3 in **5** are very close in chemical shift to the signals from N1, N2, and N3 in the analogous triazinone **4a**. Significantly, the nitrogen atom at N3 in **5** is not directly bonded to a hydrogen, since there is no inversion of the signal under full NOE, thus ruling out structure **6**. A signal at −177.08 ppm in the ^{15}N spectrum of **5**, assigned to the exocyclic nitrogen at C4, does undergo inversion with full NOE, and the chemical shift of this nitrogen suggests sp^2 hybridization, as in **5**, rather than the sp^3 hybridization of the exocyclic nitrogen at C4 in structure **7**. Thus structure **5** is well supported by the ^{15}N NMR evidence.

Further evidence to eliminate assignment of structure **7** for this product was obtained from ^1H NMR experiments. Structure **7** contains the -$NHCH_2$- moiety, and coupling between the exchangeable NH and the CH_2 should be evident at low temperature. Variable temperature ^1H NMR to −70 °C showed no coupling between the NH and CH_2 signals. This was further investigated by conducting the more sensitive 2-dimensional (2-D) NMR technique, homonuclear correlated (HOMCOR) NMR spectroscopy. If the NH−CH_2 coupling were present, it would be indicated by a cross peak between the NH and CH_2 group. The absence of a cross peak in the area expected provides further evidence to dismiss structure **7** and to support the assignment of structure **5** to the product of decomposition of the triazene **3g**.

By analogy with the extensive work of Stevens and coworkers on the synthesis and rearrangement of 4-imino-1,2,3-benzotriazines,[12] it should be feasible to prepare the 4-(alkylamino)-1,2,3-benzotriazine (**7**) by Dimroth rearrangement of **5**. However, all of our efforts to effect the rearrangement of **5**, e.g., by refluxing in ethanol or by catalysis with alumina, failed to produce any recognizable product.

The mass spectra of the 1,2,3-benzotriazines **4a** and **5** were obtained and molecular ions were clearly visible at the expected values.

Conclusions

In conclusion, we have established that the triazenes in the series **3a**−**d** and **f**−**i** can be synthesized by diazonium coupling with glycinamide, and we have characterized the products by all available methods. Triazenes with reactive ortho-substituents in the aryl moiety have been found to undergo spontaneous cyclization to the 1,2,3-benzotriazines **4a** and **5**, which have been fully characterized. We have investigated the potential of these triazenes **3** to cyclize by interaction of the N1-nitrogen atom with the carbonyl group of the carbamoyl moiety, which should afford the 1,2,3-triazole system, but so far without success.

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