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Synthesis of 3-Substituted 4-Imino-4,5-dihydro-1,2,3-triazole 1-Oxides and 4-Amino-1,2,3-triazole 1-Oxides

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A new synthesis of 4-imino-4,5-dihydro-1,2,3-triazole 1-oxides and 4-amino-1,2,3-triazole 1-oxides is proposed; the title compounds were prepared by intramolecular cyclization of 1-(1′-cyanoalkyl)-3-aryl(heteroaryl)triazene 1-oxides by treatment with a base.

1-Oxides of the 1,2,3-triazole series have a number of valuable properties (fluorescence,[1–3] insecticide[4,5] and fungicide[4] action) but they are highly inaccessible compounds. Previously described syntheses of 1,2,3-triazole 1-oxides[6–8] are of a limited scope and are characterized by low yields of the products.[9]

Herein, we report a new preparation of 1,2,3-triazole 1-oxides, based on the so far unknown cyclization reaction of 1-(1′-cyanoalkyl)-3-aryl(heteroaryl)triazene 1-oxides in basic media.

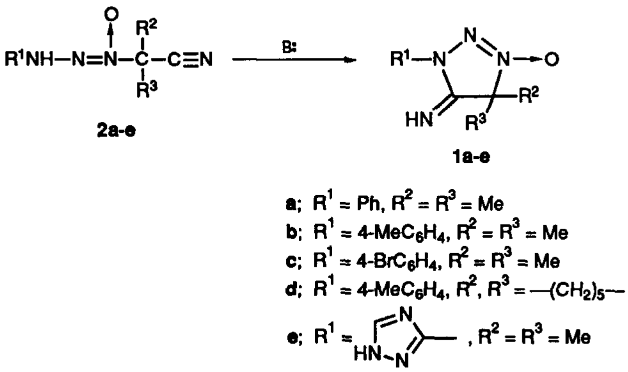
Hence, 1-(*t*-1′-cyanoalkyl)-3-aryl(heteroaryl)triazene 1-oxides give the corresponding 4-imino-4,5-dihydro-1,2,3-triazole 1-oxides **1a–e** in high yields on treatment with a base (Scheme 1, Table 1).

The reaction of 1-(1′-cyanoethyl)-3-aryl(heteroaryl)triazene 1-oxides bearing a hydrogen atom in an α-position to the triazene 1-oxide and cyano groups with a base does not, however, give the expected 4-imino-4,5-dihydro-1,2,3-triazole

Table 1 Yields and characteristic data for **1a**–**l**

Compound	M.p./°C	Yield (%)	IR ν/cm^{-1}	^{1}H NMR [$(CD_3)_2SO$] δ; (J/Hz)	MS m/z [I(%)]
1a	174–175	75	1465, 1500 [N(O)=N] 1670 (NH) 3260 (NH)	1.67 (s, 6H, CH_3) 7.18–7.58 (m, 5H, C_6H_5)	M$^+$ 204(18), 105(25), 77(100), 69(12), 57(2)
1b	163–164	83	1465, 1505 [N(O)=N] 1670 (NH) 3260 (NH)	1.71 (s, 6H, CH_3) 2.33 (s, 3H, CH_3Ar) 7.28 (d, 2H, m-H, C_6H_4, J 8.3) 7.89 (d, 2H, o-H, C_6H_4. J 8.3)	M$^+$ 218(52), 91(100), 69(74)
1c	148–151	65	1465, 1500 [N(O)=N] 1670 (NH) 3260 (NH)	1.62 (s, 3H, CH_3)^a 1.70 (s, 3H, CH_3) 7.23–8.03 (m, 4H, C_6H_4)	M$^+$ 284(28), 282(28), 185(13), 183(13), 157(47), 155(47), 76(15), 69(100), 57(8)
1d	132–134	50	1450, 1495 [N(O)=N] 1660 (NH) 2860 (CH) 2960 (CH) 3300 (NH)	1.40–2.10 (m, 6H, CH_2)^a 2.20 (s, sh., 7H, CH_2, CH_3) 7.13 (s, 4H, C_6H_4)	M$^+$ 258(28), 119(20), 91(100), 81(58)
1e	168–171	50	1465, 1480 [N(O)=N] 1670 (NH) 2600–3300 (CH, NH)	1.55 (s, 6H, CH_3) 8.53 (s, 1H, CH)	M$^+$ 195, 181, 69
1f	265–270	50	1465, 1515 [N(O)=N] 1660 (NH) 2600–3400 (CH, NH)	1.78 (d, 3H, CH_3, J 7) 5.80 (q, 1H, CH, J 7) 6.68 (s, 1H, NH) 8.28 (s, 1H, CH)	M$^+$ 181(56), 69(69), 68(38), 64(100)
1g	260–262	89	1460, 1490 [N(O)=N] 1650 (NH) 3260 (NH)	2.04 (s, 3H, CH_3) 5.99 (s, 2H, NH_2) 7.55 (s, 5H, C_6H_5)	M$^+$ 190(63), 77(100)
1h	235–237	70	1460, 1510 [N(O)=N] 1640 (NH) 2280 (NH)	1.96 (s, 3H, CH_3) 2.29 (s, 3H, CH_3Ar) 5.87 (s, 2H, NH_2) 7.37 (s, 4H, C_6H_4)	M$^+$ 204(100), 119(28), 91(60), 55(36)
1i	244–246	87	1450, 1490 [N(O)=N] 1650 (NH) 3335 (NH)	1.95 (s, 3H, CH_3) 5.97 (s, 2H, NH_2) 7.32–7.82 (m, 4H, C_6H_4)	M$^+$ 270(92), 268(92), 157(100), 155(100), 76(38), 55(77)
1j	293–295	70	1330 (NO_2) 1490 [N(O)=N] 1520 (NO_2) 1680 (NH) 3200 (NH)	2.06 (s, 3H, CH_3) 6.20 (s, 2H, NH_2) 7.87 (g, 2H, o-H, C_6H_4, J 9) 8.37 (d, 2H, m-H, C_6H_4, J 9)	M$^+$ 235(100), 122(14), 76(41), 54(35)
1k	264–266	75	1250 (C—O—C) 1450, 1495 [N(O)=N] 1650 (NH) 1730 (C=O) 3000–3430 (CH, NH)	–	M$^+$ 258(100), 242(18), 203(8), 145(88), 117(50), 89(54), 55(38)
1l	>300	–	1465, 1520 [N(O)=N] 1660 (NH) 2800–3400 (CH, NH)	2.04 (s, 3H, CH_3) 6.65 (s, 2H, NH_2) 8.73 (s, 1H, CH)	M$^+$ 181(77), 84(50), 69(100), 54(63)

^{a} Solvent used: CD_3COCD_3.



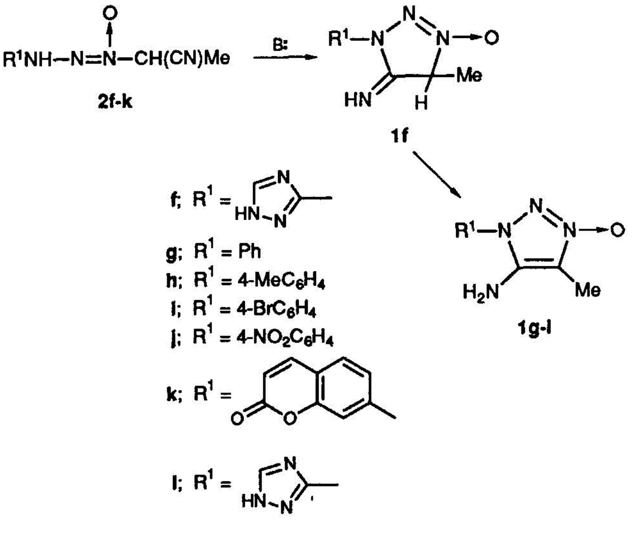
Scheme 1

1-oxides, but is accompanied by isomerization of the latter into 4-amino-1,2,3-triazole 1-oxides (Scheme 2, Table 1).

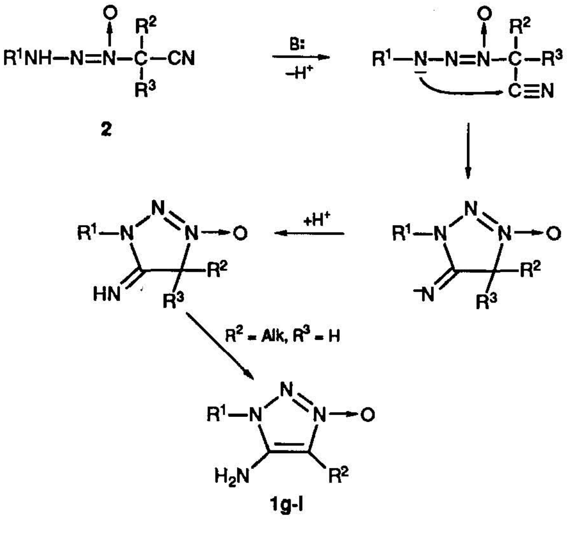
The initial cyclization product **1f** was isolated only in the case of 1-(1′-cyanoethyl)-3-(1′,2′,4′-triazol-3′-yl)triazene 1-oxide. Compound **1f** isomerizes to the thermodynamically more stable 4-amino-5-methyl-3-(1′,2′,4′-triazol-3′-yl)-1,2,3-triazole 1-oxide **1l** upon storage for a few weeks at room temperature.

A solution of KOH (0.01–2.5 mmol) in MeOH (1 ml) was added to a solution of the 1-(1′-cyanoalkyl)-3-aryl(heteroaryl)triazene 1-oxide (2.5 mmol) in MeOH (5 ml). For **1a**,**b**, **1e**–**i**, **1k** a catalytic amount was needed and for **1c**,**d**,**j** an equimolar quantity of the base was required. The mixture was stirred for 10–30 min and the products were filtered and washed with diethyl ether. Compound **1b** precipitates by dilution of the reaction mixture with water, **1j** by neutralization with acid. An

Mendeleev Commun., 1992, 2(4), 131–134



Scheme 2



Scheme 3

additional quantity of **1d** was obtained by TLC on silica gel. Yields and characteristics of **1a-l** are listed in Table 1. The molecular structure of **1a** (Fig. 1) was also proved by X-ray structural analysis.†

The probable reaction scheme occurs *via* deprotonation of the triazene-1-oxide fragment by treatment with base and subsequent nucleophilic attack on the electron-deficient C-atom of the cyano-group by the triazene-1-oxide anion (Scheme 3).

This assumption is confirmed by the suppression of the cyclization reaction of 1-(2′-cyanopropyl-2′)-3-aryltriazene 1-oxides with electron-deficient nitro groups in the aryl moiety, which diminishes the nucleophility of the triazene oxide group and directs the reaction towards the formation of a ketoxime ether.[10]

The starting compounds 1-(1′-cyanoalkyl)-3-aryl(heteroaryl)triazene 1-oxides **2a–k** were readily prepared by reaction of 2-cyano-2-hydroxyaminopropane[11] or 1-cyano-1-hydroxyaminoethane[11] with tetrafluoroborate salts of the corresponding aryl (heteroaryl) diazonium ion. The diazonium salt (5.0 mmol) was added to a stirred mixture of α-cyanoalkylhydroxy amine (5.0 mmol), NaOAc·$3H_2O$ (15.0 mmol) and AcOH (1–2%) (15 ml) at 0°C. The mixture was stirred for 30–60 min at this temperature, the products were filtered and washed with water and diethyl ether–hexane (1:2). Yields and characteristics of **2a–k** are presented in Table 2 on page 134.

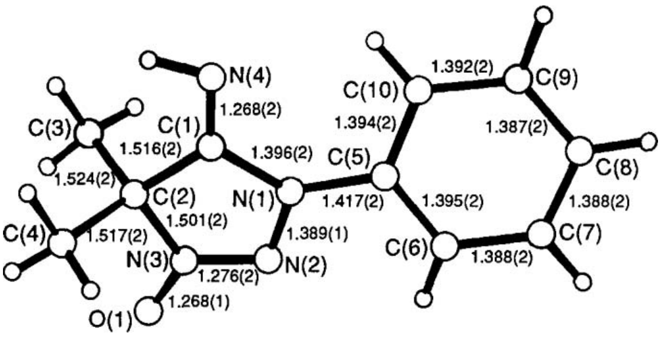


Fig. 1 Molecular structure of **1a**

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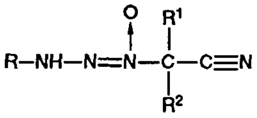
† *Crystal data* for **1a**: $C_{10}H_{12}N_4O$, $M = 204$, monoclinic, space group $P2_1/c$, $T = -150$ °C, $a = 9.592(5)$, $b = 9.926(4)$, $c = 11.347(5)$ Å, $\beta = 109.38(3)°$, $V = 1012(2)$ Å^3, $D_d = 1.331$ g cm^{-3}, $Z = 4$. Data were measured on a Siemens P3/PC diffractometer with Mo-Kα radiation ($\lambda = 0.71069$ Å, graphite monochromator) using $\theta/2\theta$ scan $\theta = 30°$. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares procedure. The hydrogen atoms were located in the difference Fourier map and refined isotropically. The final discrepancy factors are $R = 0.040$, $R_w = 0.041$ for 3138 independently observed reflections ($I > 2\sigma$). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1992, Issue No. 1.

Mendeleev Commun., 1992, 2(4), 131–134

Table 2 Yields and characteristic data for 1-(1′-cyanoalkyl)-3-aryl(heteroaryl)triazene 1-oxides **2a–k**


$$\mathrm{R{-}NH{-}N{=}\overset{\overset{O}{\uparrow}}{N}{-}\underset{R^2}{\overset{R^1}{C}}{-}C{\equiv}N}$$

Compound	M.p./°C	Yield (%)	IR ν/cm^{-1}	^{1}H NMR [(CD$_3$)$_2$CO] δ; (*J*/Hz)	MS *m*/*z* [*I*(%)]
2a	60–61	54	1480 [N(O)=N] 2260 (CN) 3260 (NH)	1.88 (s, 6H, CH$_3$) 7.18–7.42 (m, 5H, C$_6$H$_5$)	M$^+$ 204(15), 105(25), 69(11), 77(100)
2b	94–95	60	1470 [N(O)=N] 2260 (CN) 3210 (NH)	1.87 (s, 6H, CH$_3$) 2.20 (s, 3H, CH$_3$) 6.78 (s, 4H, C$_6$H$_4$)	M$^+$ 218, 119, 91, 77, 69, 57
2c	105–107	61	1450 [N(O)=N] 3235 (CN)	1.87 (s, 6H, CH$_3$) 7.10–7.65 (m, 4H, C$_6$H$_4$)	M$^+$ 284(15), 282(15), 185(25), 183(25), 157(65), 155(65), 77(20), 69(11), 57(100)
2d	125–127	66	1460 [N(O)=N] 2260 (CN) 2870, 2950 (CH) 3215 (NH)	1.35–2.07 (m, 6H, CH$_2$) 2.07–2.45 (m, 7H, CH$_2$, CH$_3$) 7.13 (s, 4H, C$_6$H$_4$) 2.18 (s, 3H, CH$_3$ Ar)	M$^+$ 258(9), 119(18) 91(100)
2e	144–146	61	1500 [N(O)=N] 2260 (CN) 2600–3300 (CH, NH)	1.85 (s, 6H, CH$_3$)[a] 8.22 (1H, CH)	M$^+$ 195(10), 96(100), 69(50), 68(40)
2f	124–126	51	1490 [N(O)=N] 2260 (CN) 2800–3300 (CH, NH)	1.69 (d, 3H, CH$_3$, *J* 7)[a] 5.73 (q, 1H, CH, *J* 7) 8.20 (s, 1H, CH)	M$^+$ 181, 96, 68, 54
2g	72–74	83	1480 [N(O)=N] 3320 (NH)	1.84 (d, 3H, CH$_3$, *J* 7) 5.57 (q, 1H, CH, *J* 7) 7.23–7.45 (m, 5H, C$_6$H$_5$)	M$^+$ 190(14), 105(36), 77(100)
2h	107–109	79	1470 [N(O)=N] 3205 (NH)	1.75 (d, 3H, CH$_3$, *J* 7) 2.20 (s, 3H, CH$_3$) 5.55 (q, 1H, CH, *J* 7) 7.19 (s, 4H, C$_6$H$_4$)	M$^+$ 204, 119, 107, 91
2i	117–118	82	1490 [N(O)=N] 3200 (NH)	1.84 (d, 3H, CH$_3$, *J* 7) 5.58 (q, 1H, CH, *J* 7) 7.13–8.00 (m, 4H, C$_6$H$_4$)	M$^+$ 270(17), 268(17), 185(55), 183(55), 174(22), 172(22), 157(100)
2j	155–156	81	1325, 1510 (NO$_2$) 1490 [N(O)=N] 3200 (NH)	1.82 (d, 3H, CH$_3$, *J* 7)[a] 5.60 (q, 1H, CH, *J* 7) 7.32–9.07 (m, 4H, C$_6$H$_4$)	M$^+$ 235(20), 150(46), 122(100), 75(37)
2k	172–174	58	1250 (C—O—C) 1490 [N(O)=N] 1725 (C=O) 2900–3200 (CH, NH)	1.79 (d, 3H, CH$_3$, *J* 7)[a] 5.83 (q, 1H, CH, *J* 7) 6.43 (d, 1H, H^1, *J* 10) 7.30–7.60 (m, 3H, H^3, H^4, H^5) 7.97 (d, 1H, H^2, *J* 10)	M$^+$ 258(100), 242(8), 203(8), 145(88), 117(50), 89(54)

[a] Solvent used: CD$_3$SOCD$_3$.