Synthesis of 3,3-disubstituted 1-(1*H*-tetrazol-5-ylmethoxy)triaz-1-ene 2-oxides

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3,3-Disubstituted 1-(tetrazol-5-ylmethoxy)triaz-1-ene 2-oxides were synthesized by heating the corresponding 1-cyanomethyl derivatives with sodium azide in DMF. The starting 1-cyanomethyl derivatives were prepared by either the reaction of chloroacetonitrile with the salts of 3,3-disubstituted 1-hydroxytriaz-1-ene 2-oxides or successive transformations of these salts to 1-methoxycarbonylmethyl and 1-carbamoylmethyl derivatives and further to 1-cyanomethyl derivatives.

Key words: 1-(tetrazol-5-ylmethoxy)triaz-1-ene 2-oxides, triaz-1-ene 2-oxides, 3,3-disubstituted 1-carbamoylmethoxytriaz-1-ene 2-oxides, alkylation, amidation, 1,3-dipolar cycloaddition.

During the last five decades, the search for new energetic substances, *i.e.*, potential powerful explosives, high performance components of rocket propellants, and powerful military gunpowders, is mainly focused on the organic *C*-(poly)nitro compounds, *N*-nitramines, and organic nitrates. The possibilities of these types of organic compounds have been largely exhausted. This forms the basis for the search for new energetic compounds in other classes of organic and inorganic compounds. The design of new energetic materials employing previously unused combinations of the well-known high-explosive groups is also rational.

1-Oxotriaz-1-ene 2-oxides are relatively new class of organic compounds. The first representatives of these compounds were described only in the late 1980s, but, in spite of this, hundreds of papers devoted to the synthesis and study of these compounds have been published to date. An interest in 1-oxytriaz-1-ene 2-oxides is due almost exclusively to the expected (and proved in many cases) pharmacological activities.[1,2] Besides, these compounds contain 1-oxytriaz-1-ene 2-oxide moiety, which similarly to *N*-nitramines (the representatives of the *N*-nitramine family, hexogen and octogen, are the most widely used common explosives) bears two oxygen atoms. It also should be emphasized that the calculated enthalpy of formation of the oxytriazene oxide moiety is higher than that of the *N*-nitramine group. Earlier, we have developed the synthetic approaches to 1-oxytriaz-1-ene 2-oxide derivatives bearing nitrate[3—5] and azide[6] groups. These compounds could be of interest as promising high energy substances. Recently, great interest has been directed to polynitrogen heterocycles characterized by enhanced enthalpy of formation, in particular, to the following tetrazole derivatives: *N*(1)-substituted tetrazoles,[7] 5-nitrotetrazoles,[8,9] 5-aminotetrazoles,[10] bitetrazoles,[11] 5,5′-azotetrazoles,[12] and tetrazoles bearing oxydiazene oxide moieties.[13] Energetic materials derived from tetrazoles have both covalent and salt structures; moreover, some of these materials show improved energetic properties. Thus, 5-hydrazinotetrazole nitrate has density of 1.834 g cm^{-3} and calculated detonation velocity of 9450 m s^{-1} being superior to octogen by this parameter.[12]

The aim of the present work is the synthesis and preliminary estimation of the properties of new type of energetic compounds, namely, tetrazoles bearing triazene oxide moieties.

One of the common methods for the synthesis of 5-substituted tetrazoles is the reaction between nitriles and sodium azide. To the best of our knowledge, 1-cyanomethoxy derivatives of triaz-1-ene 2-oxides have not been synthesized. We elaborated several procedures to 3,3-disubstituted 1-cyanomethoxytriaz-1-ene 2-oxides (Scheme 1).

We studied the reactions of the sodium salts of 3,3-disubstituted 1-hydroxytriaz-1-ene 2-oxides **1a—d** with chloroacetonitrile (Scheme 2). Salts **1a—d** are the ambidentate compounds and can be alkylated at two oxygen atoms. Alkylation at proximal oxygen atom provides poorly stable *N*-nitroso derivatives and alkylation at the distal oxygen gives the target oxytriazenes. Thus, the ambidentity of salts **1a—d** significantly affects the yields of the products. For instance, the reactions of compounds **1a—d** with chloroacetonitrile give the corresponding nitriles **2a—d** in 10—26% yields (see Scheme 2).

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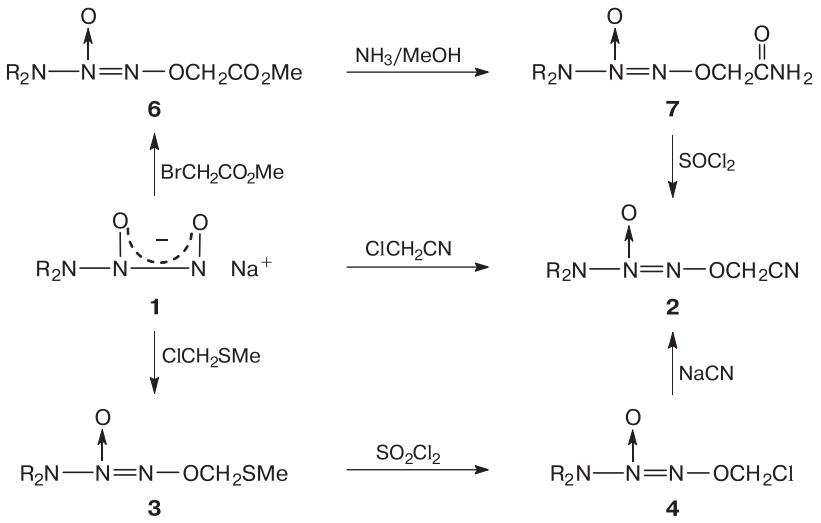
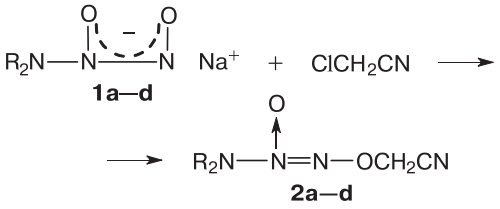
Scheme 1



Scheme 2



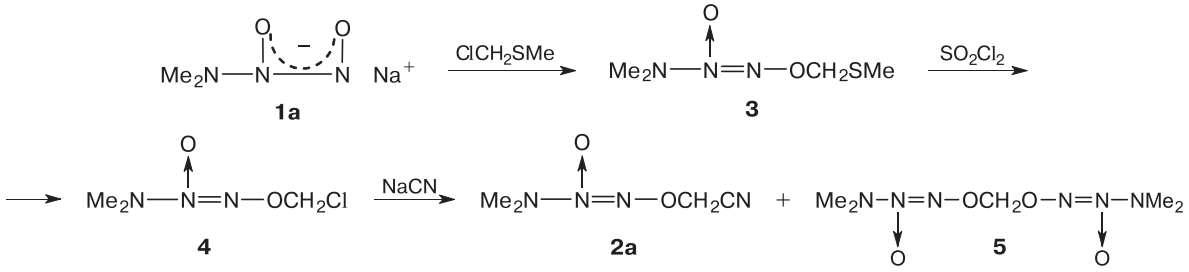
R = Me (**a**), Et (**b**); R + R = $(CH_2)_4$ (**c**), $CH_2CH_2OCH_2CH_2$ (**d**)

We studied the effects of the solvent nature, the reaction temperature, and the reaction time on the yields of products **2a**—**d**. Ethanol, acetonitrile, aqueous acetone, and DMSO were used as the solvents; salt **1a** was used as the model compound. It was found that in EtOH no reaction occured and no products were formed. In MeCN, the reaction is very slow and after 24 h from the reaction onset the yield of product **2a** was only ~3%. In aqueous acetone, the reaction was also slow and, moreover, some side reactions were found to proceed. The best results were achieved in DMSO at room temperature; however, even under these conditions the yields of product **2a** did not exceed 10%.

Low yields of the target products **2** prompted us to investigate other methods for their synthesis. Thus, salt **1a** was involved in the reaction with chloromethyl methyl sulfide to give 3,3-dimethyl-1-methylthiomethoxytriaz-1-ene 2-oxide (**3**) in 36% yield. Treatment of compound **3** with SO_2Cl_2 nearly quantitatively afforded 1-chloromethoxy-3,3-dimethyl-triaz-1-ene 2-oxide (**4**). The yield of the target nitrile **2a** in the reaction of chloride **4** with sodium cyanide was also low. This reaction also gives 1,1′-[methylenebis(oxy)]bis(3,3-dimethyltriaz-1-ene 2-oxide) (**5**) in low yield (11%) (Scheme 3). Similar transformations of chloromethyl derivatives of hydroxytriazene oxides were observed by us earlier.[14]

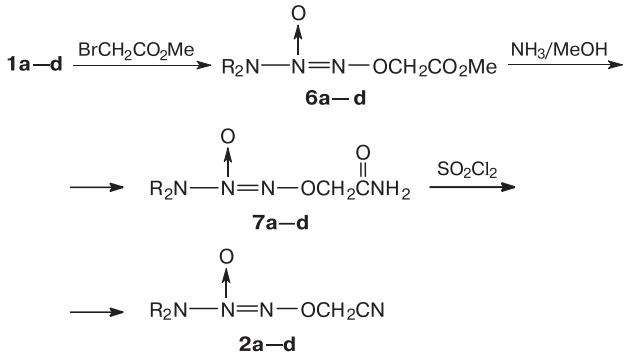
To elaborate the alternative approach to the key nitriles, we studied the reactions of salts **1a—d** with methyl bromoacetate. Hitherto unknown esters **6a—d** were isolated in 40—61% yields (Scheme 4). In this case, similarly to the reactions with chloroacetonitrile, the highest yields of the products were achieved in DMSO. Treatment of esters **6a—d** with methanolic ammonia gives the corresponding amides **7a—d** in the yields of 68—83%. Careful heating of amides **7a—d** in the thionyl chloride excess leads to the target 3,3-disubstituted 1-cyanomethoxytriaz-1-ene 2-ox-

Scheme 3



ides **2a—d** in ~70% yields (see Scheme 4). The overall yields of nitriles **2** obtained in the stepwise synthesis were 30—100% higher than those in one-step synthesis.

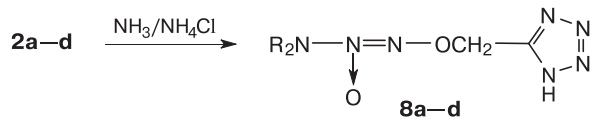
Scheme 4



R = Me (**a**), Et (**b**); R + R = $(CH_2)_4$ (**c**), $CH_2CH_2OCH_2CH_2$ (**d**)

The synthesized nitriles **2a—d** were involved in the 1,3-dipolar cycloaddition with sodium azide in the presence of ammonium chloride. The reaction was carried out in DMF at 60—70 °C to obtain tetrazoles **8a—d** in 20—70% yields (Scheme 5). The synthesized tetrazoles **8a—d** are colorless crystalline substances that melt at 75—240 °C. The structures of all newly synthesized compounds were confirmed by spectral data and elemental analysis.

Scheme 5



R = Me (**a**), Et (**b**); R + R = $(CH_2)_4$ (**c**), $CH_2CH_2OCH_2CH_2$ (**d**)

In summary, in the present work we succeeded to develop the synthesis of new energetic compounds, oxytriazene derivatives of tetrazoles, that contain an active oxygen and possess enhanced enthalpy of formation. These compounds can be of interest as both the promising energetic substances and the building blocks for the synthesis of new highly energetic materials. The intermediates synthesized in the study may be of interest as the nitric oxide donors capable of releasing NO under physiological conditions, *i.e.*, as the compounds showing important pharmacological activity.

Experimental

The reaction course was monitored by TLC on the precoated Silufol UV-254 plates. IR spectra were recorded on a Bruker-ALPHA FTIR spectrometer. NMR spectra were run on a Bruker-AM-300 instrument. High resolution electrospray ionization mass spectra were recorded with a Bruker micrOTOF II instrument. Sodium salts **1a—d**[14] and compounds **3** and **4**[15] were synthesized as earlier described.

Reactions of sodium salts 1a—d with chloroacetonitrile (general procedure). To a mixture of salt **1a—d** (8.0 mmol) and Na_2CO_3 (0.1 g, 1.0 mmol) in DMSO (15 mL), chloroacetonitrile (0.5 mL, 7.9 mmol) was added. The mixture was stirred at room temperature for 5 h, diluted with water, and extracted with diethyl ether (4×10 mL). The combined organic layers were washed with water, dried with Mg_2SO_4, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 1 : 1) afforded compounds **2a—d**.

1-Cyanomethoxy-3,3-dimethyltriaz-1-ene 2-oxide (2a). Yield 0.12 g (10%), oil. ^{1}H NMR ($CDCl_3$), δ: 3.06 (s, 6 H, NCH_3); 4.28 (s, 2 H, OCH_2CN). ^{13}C NMR ($CDCl_3$), δ: 42.045 (CH_3N); 57.358 (CH_2O); 114.713 (CN). ^{14}N NMR ($CDCl_3$), δ: −56.87. IR, ν/cm^{-1}: 2992, 2342, 1686, 1500, 1266, 1079, 1034, 945. MS (ESI), found: *m/z* 145.0717 $[M + H]^+$, 162.0985 $[M + NH_4]^+$, 167.0560 $[M + Na]^+$, 183.0276 $[M + K]^+$. $C_4H_8N_4O_2$. Calculated: 145.0720 [M + H], 162.0986 [M + NH_4], 167.0539 [M + Na], 183.0279 [M + K].

1-Cyanomethoxy-3,3-diethyltriaz-1-ene 2-oxide (2b). Yield 0.22 g (16%), oil. ^{1}H NMR ($CDCl_3$), δ: 1.13 (t, 6 H, 2 CH_3, J = 7.1 Hz); 3.28 (q, 4 H, 2 CH_2N, J = 7.1 Hz); 4.85 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 11.27 (CH_3); 47.65 (CH_2N); 57.40 (CH_2O); 114.56 (CN). ^{14}N NMR ($CDCl_3$), δ: −55.03. IR (neat), ν/cm^{-1}: 2983, 2941, 2211, 1519, 1499, 1453, 1383, 1242, 1080, 1026, 962, 928, 838, 683. MS (ESI), found: *m/z* 190.1290 $[M + NH_4]^+$, 195.0851 $[M + Na]^+$. $C_6H_{12}N_4O_2$. Calculated: 190.1299 [M + NH_4], 195.0852 [M + Na].

1-Cyanomethoxy-3-(pyrrolidin-1-yl)diaz-1-ene 2-oxide (2c). Yield 0.36 g (26%), colorless crystals, m.p. 75—77 °C (diethyl ether—hexane). ^{1}H NMR ($CDCl_3$), δ: 2.0 (m, 4 H, CH_2); 3.60 (m, 4 H, NCH_2); 4.75 (s, 2 H, OCH_2CN). ^{13}C NMR ($CDCl_3$), δ: 23.06 (CH_2C); 50.61 (CH_2N); 57.15 (CH_2O); 114.79 (CN). ^{14}N NMR ($CDCl_3$), δ: −50.32. IR, ν/cm^{-1}: 2995, 2957, 1480, 1272, 1029. MS (ESI), found: *m/z* 171.0878 $[M + H]^+$, 188.1145 $[M + NH_4]^+$, 193.0698 $[M + Na]^+$, 209.0437 $[M + K]^+$. $C_6H_{10}N_4O_2$. Calculated: 171.0877 [M + H], 188.1142 [M + NH_4], 193.0696 [M + Na], 209.0435 [M + K].

1-Cyanomethoxy-3-(morpholin-4-yl)diaz-1-ene 2-oxide (2d). Yield 0.27 g (18%), oil. ^{1}H NMR ($CDCl_3$), δ: 3.40 (t, 4 H, NCH_2, J = 4.5 Hz); 3.75 (t, 4 H, OCH_2, J = 5.0 Hz); 4.78 (s, 2 H, OCH_2CN). ^{13}C NMR ($CDCl_3$), δ: 51.10 (CH_2N); 57.54 (CH_2CN); 65.38 (CH_2O); 114.68 (CN). ^{14}N NMR ($CDCl_3$), δ: −59.23. IR, ν/cm^{-1}: 2981, 2929, 2866, 1504, 1231, 1113, 1032, 929. MS (ESI), found: *m/z* 187.0819 $[M + H]^+$, 204.1086 $[M + NH_4]^+$, 209.0647 $[M + Na]^+$, 225.0385 $[M + K]^+$. $C_6H_{10}N_4O_3$. Calculated: 187.0826 [M + H], 204.1091 [M + NH_4], 209.0645 [M + Na], 225.0384 [M + K].

2,10-Dimethyl-5,7-dioxa-2,3,4,8,9,10-hexaazaundeca-3,8-diene 3,9-dioxide (5). To a solution of chloromethoxy derivative **4** (0.1 g, 0.65 mmol) in DMSO (3 mL), NaCN (0.03 g, 0.61 mmol) was added and the mixture was stirred at room temperature for 20 h. The mixture was diluted with water and extracted with diethyl ether (3×10 mL). The combined organic layers were washed with water, dried with Mg_2SO_4, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 1 : 1) afforded

0.01 g (14%) of compound **2a** and 0.01 g (11%) of compound **5**. Compound **2a** was identical to the sample described above; physicochemical properties of compound **5** were in agreement with those published earlier.[11]

Reactions of sodium salts 1a—d with methyl bromoacetate (general procedure). A stirred solution of sodium salt **1a—d** (10.0 mmol) in DMSO (30 mL), was treated dropwise with $BrCH_2CO_2Me$ (1.68 g, 11.0 mmol) at 10 °C. The mixture was kept at room temperature for 24 h, poured onto crushed ice (50 mL), and extracted with dichloromethane (4×25 mL). The combined organic layers were washed with water (3×10 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with dichloromethane, R_f 0.2—0.3) afforded compounds **6a—d**.

1-Methoxycarbonylmethoxy-3,3-dimethyltriaz-1-ene 2-oxide (6a). Yield 0.69 g (39%), oil. ^{1}H NMR ($CDCl_3$), δ: 3.00 (s, 6 H, 2 CH_3N); 3.76 (s, 3 H, CH_3O); 4.69 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 42.38 (CH_3N); 51.95 (CH_3O); 68.93 (CH_2O); 168.27 (CO). ^{14}N NMR ($CDCl_3$), δ: −52.9. IR (neat), ν/cm^{-1}: 2986, 2956, 1761, 1745, 1666, 1502, 1440, 1260, 1219, 1099, 1047, 952. MS (ESI), found: *m/z* 178.0829 $[M + H]^+$, 195.1095 $[M + NH_4]^+$, 200.0648 $[M + Na]^+$, 216.0386 $[M + K]^+$. $C_5H_{11}N_3O_4$. Calculated: 178.0822 [M + H], 195.1088 [M + NH_4], 200.0642 [M + Na], 216.0381 [M + K].

3,3-Diethyl-1-(methoxycarbonylmethoxy)triaz-1-ene 2-oxide (6b). Yield 0.92 g (45%), oil. ^{1}H NMR ($CDCl_3$), δ: 1.11 (t, 6 H, 2 CH_3, *J* = 7.0 Hz); 3.12 (q, 4 H, 2 CH_2N, *J* = 7.0 Hz); 3.77 (s, 3 H, CH_3O); 4.78 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 11.33 (CH_3); 48.63 (CH_3O); 52.38 (CH_2N); 69.04 (CH_2ON); 168.13 (CO). ^{14}N NMR ($CDCl_3$), δ: −60.20. IR (neat), ν/cm^{-1}: 2982, 2956, 1764, 1745, 1518, 1440, 1292, 1219, 1100, 1044, 971, 846, 709, 584. MS (ESI), found: *m/z* 206.1141 $[M + H]^+$, 223.1407 $[M + NH_4]^+$, 228.0962 $[M + Na]^+$, 244.0700 $[M + K]^+$. $C_7H_{15}N_3O_4$. Calculated: 206.1135 [M + H], 223.1401 [M + NH_4], 228.0955 [M + Na], 244.0694 [M + K].

1-Methoxycarbonylmethoxy-3-(pyrrolidin-1-yl)diaz-1-ene 2-oxide (6c). Yield 1.24 g (61%), oil. ^{1}H NMR ($CDCl_3$), δ: 1.92 (m, 4 H, 2 CH_2, *J* = 3.6 Hz); 3.52 (t, 4 H, 2 CH_2N, *J* = 6.6 Hz); 3.75 (s, 3 H, CH_3O); 4.66 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 22.91 (CH_2); 50.80 (CH_3O); 52.10 (CH_2N); 68.98 (CH_2ON); 168.78 (CO). ^{14}N NMR ($CDCl_3$), δ: −53.46. IR (neat), ν/cm^{-1}: 2979, 2957, 2882, 1763, 1743, 1657, 1490, 1439, 1308, 1268, 1216, 1102, 1040, 958, 848, 705, 670, 586, 533. MS (ESI), found: *m/z* 204.0977 $[M + H]^+$, 221.1445 $[M + NH_4]^+$, 226.0800 $[M + Na]^+$, 242.0535 $[M + K]^+$. $C_7H_{13}N_3O_4$. Calculated: 204.0979 [M + H], 221.1244 [M + NH_4], 226.0798 [M + Na], 242.0538 [M + K].

1-Methoxycarbonylmethoxy-3-(morpholin-4-yl)diaz-1-ene 2-oxide (6d). Yield 1.12 g (51%), oil. ^{1}H NMR ($CDCl_3$), δ: 3.39 (t, 4 H, 2 CH_2N, *J* = 4.6 Hz); 3.74 (s, 3 H, CH_3O); 3.79 (t, 4 H, 2 CH_2O, *J* = 4.6 Hz); 4.70 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 51.49 (CH_3O); 52.20 (CH_2NCH_2); 65.56 (CH_2OCH_2); 69.18 (CH_2ON); 168.25 (CO). ^{14}N NMR ($CDCl_3$), δ: −55.18. IR (neat), ν/cm^{-1}: 2957, 2931, 2863, 1761, 1661, 1504, 1458, 1440, 1359, 1291, 1269, 1228, 1100, 1045, 957, 929, 874, 755, 710, 587, 561, 517. MS (ESI), found: *m/z* 220.0930 $[M + H]^+$, 237.1195 $[M + NH_4]^+$, 242.0752 $[M + Na]^+$, 258.0492 $[M + K]^+$. $C_7H_{13}N_3O_5$. Calculated: 220.0928 [M + H], 237.1193 [M + NH_4], 242.0747 [M + Na], 258.0487 [M + K].

Synthesis of amides 7a—d (general procedure). A solution of ester **6a—d** (5.0 mmol) in a saturated solution of ammonia in MeOH (20 ml) was kept at room temperature for 6 h and the volatiles were removed *in vacuo*. Crystallization of the residue from propan-2-ol—ethyl acetate afforded compounds **7a—d**.

1-Carbamoylmethoxy-3,3-dimethyltriaz-1-ene 2-oxide (7a). Yield 0.63 g (78%), colorless crystals, m.p. 123—124 °C. ^{1}H NMR (DMSO-d_6), δ: 2.93 (s, 6 H, 2 CH_3N); 4.49 (s, 2 H, CH_2); 7.30 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 42.10 (CH_3N); 70.75 (CH_2ON); 169.25 (CO). IR (KBr), ν/cm^{-1}: 3389, 3171, 2998, 1660, 1492, 1448, 1354, 1266, 1110, 1083, 1038, 950, 680, 540. Found (%): C, 29.64; H, 6.19; N, 34.33. $C_4H_{10}N_4O_3$. Calculated (%): C, 29.60; H, 6.22; N, 34.55.

1-Carbamoylmethoxy-3,3-diethyltriaz-1-ene 2-oxide (7b). Yield 0.65 g (68%), colorless crystals, m.p. 87—88 °C. ^{1}H NMR (DMSO-d_6), δ: 0.97 (t, 6 H, 2 CH_3, *J* = 7.0 Hz); 3.06 (q, 4 H, 2 CH_2N, *J* = 7.0 Hz); 4.55 (s, 2 H, CH_2); 7.27 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 11.23 (CH_3); 47.56 (CH_2N); 70.65 (CH_2ON); 168.98 (CO). Found (%): C, 38.32; H, 7.42; N, 29.62. $C_6H_{14}N_4O_3$. Calculated (%): C, 37.89; H, 7.42; N, 29.46.

1-Carbamoylmethoxy-3-(pyrrolidin-1-yl)diaz-1-ene 2-oxide (7c). Yield 0.78 g (83%), colorless crystals, m.p. 126—128 °C. ^{1}H NMR (DMSO-d_6), δ: 1.85 (t, 4 H, 2 CH_2, *J* = 6.5 Hz); 3.43 (t, 4 H, 2 CH_2N, *J* = 6.3 Hz); 4.44 (s, 2 H, CH_2O); 7.29 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 22.35 (2 CH_2); 50.56 (2 CH_2N); 70.63 (CH_2ON); 169.46 (CO). ^{14}N NMR (DMSO-d_6), δ: −53.25. IR (KBr), ν/cm^{-1}: 3400, 3175, 2984, 1665, 1492, 1477, 1345, 1267, 1085, 1031, 960, 672, 551, 544. Found (%): C, 38.35; H, 6.49; N, 29.79. $C_6H_{12}N_4O_3$. Calculated (%): C, 38.30; H, 6.43; N, 29.77.

1-Carbamoylmethoxy-3-(morpholin-4-yl)diaz-1-ene 2-oxide (7d). Yield 0.85 g (83%), colorless crystals, m.p. 103—105 °C. ^{1}H NMR (DMSO-d_6), δ: 3.29 (t, 4 H, 2 CH_2, *J* = 4.45 Hz); 3.70 (t, 4 H, 2 CH_2N, *J* = 4.45 Hz); 4.50 (s, 2 H, CH_2O); 7.29 (s, 2 H, NH_2). ^{13}C NMR (DMSO-d_6), δ: 51.08 (CH_2NCH_2); 64.93 (CH_2OCH_2); 70.63 (CH_2ON); 169.13 (CO). ^{14}N NMR (DMSO-d_6), δ: −54.79. IR (KBr), ν/cm^{-1}: 3419, 3323, 3206, 2870, 1707, 1685, 1613, 1489, 1428, 1307, 1269, 1231, 1111, 1093, 1046, 958, 876, 600, 556, 504. Found (%): C, 35.31; H, 5.93; N, 27.38. $C_6H_{12}N_4O_4$. Calculated (%): C, 35.29; H, 5.92; N, 27.44.

Reactions of amides 7a—d with thionyl chloride (general procedure). A mixture of amide **7a—d** (5.0 mmol) and $SOCl_2$ (5 mL) was heated at 60—70 °C for 3 h. The volatiles were removed *in vacuo*. Purification of the residue by preparative TLC (development with CH_2Cl_2) afforded nitriles **2a—d** identical to the samples described above. The yields were as follows: **2a**, 0.42 g (72%); **2b**, 0.6 g (70%); **2c**, 0.59 g (70%); **2d**, 0.67 g (72%).

Synthesis of tetrazoles 8a—d (general procedure). To a solution of nitrile **2a—d** (0.7 mmol) in DMF (5 mL), NaN_3 (0.14 g, 2.1 mmol) and NH_4Cl (0.05 g, 0.9 mmol) were added and the mixture was stirred at 60—70 °C for 12 h. Removal of the volatiles *in vacuo* and purification of the residue by preparative TLC afforded compounds **8a—d**.

3,3-Dimethyl-1-(1*H*-tetrazol-5-ylmethoxy)triaz-1-ene 2-oxide (8a). Acetonitrile was used as an eluent. Yield 0.038 g (29%). M.p. 114—117 °C. ^{1}H NMR (DMSO-d_6), δ: 2.90 (s, 6 H, CH_3); 5.22 (s, 2 H, OCH_2). ^{13}C NMR (DMSO-d_6), δ: 42.28 (CH_3N); 66.69 (CH_2O); 156.44 (NCN). ^{14}N NMR (DMSO-d_6), δ: −54.47. IR, ν/cm^{-1}: 3447, 1468, 1065, 1021. MS (ESI), found: *m/z* 188.0885 $[M + H]^+$, 210.0704 $[M + Na]^+$. $C_4H_9N_7O_2$. Calculated: 188.0890 [M + H], 210.0710 [M + Na].

3,3-Diethyl-1-(1*H*-tetrazol-5-ylmethoxy)triaz-1-ene 2-oxide (8b). Diethyl ether was used as an eluent. Yield 0.03 g (20%).

M.p. 72—75 °C. ^{1}H NMR (DMSO-d_6), δ: 0.93 (t, 6 H, CH_3, J = 7.0 Hz); 3.07 (q, 4 H, NCH_2, J = 7.0 Hz); 5.49 (s, 2 H, OCH_2). ^{13}C NMR ($CDCl_3$), δ: 11.25 (CH_3C); 47.64 (CH_2N); 64.72 (CH_2O); 153.74 (NCN). ^{14}N NMR ($CDCl_3$), δ: −57.95. IR, ν/cm^{-1}: 2924, 1448, 1232, 1078, 1019. MS (ESI), found: m/z 216.1207 $[M + H]^+$, 233.1469 $[M + NH_4]^+$, 238.1026 $[M + Na]^+$, 254.0765 $[M + K]^+$. $C_6H_{13}N_7O_2$. Calculated: 216.1203 [M + H], 233.1469 [M + NH_4], 238.1023 [M + Na], 254.0762 [M + K].

3-(Pyrrolidin-1-yl)-1-(1*H*-tetrazol-5-ylmethoxy)diaz-1-ene 2-oxide (8c). Ethanol was used as an eluent. Yield 0.1 g (67%). M.p. 124—126 °C. ^{1}H NMR (DMSO-d_6), δ: 1.84 (s, 4 H, CH_2); 3.39 (s, 4 H, NCH_2); 5.16 (s, 2 H, OCH_2). ^{13}C NMR (DMSO-d_6), δ: 22.23 (CH_2C); 50.67 (CH_2N); 66.39 (CH_2O); 156.62 (NCN). ^{14}N NMR ($CDCl_3$), δ: −54.45. IR, ν/cm^{-1}: 3393, 1473, 1282, 1085, 1025. MS (ESI), found: m/z 214.1043 $[M + H]^+$, 231.1309 $[M + NH_4]^+$, 236.0863 $[M + Na]^+$, 252.0606 $[M + K]^+$. $C_6H_{11}N_7O_2$. Calculated: 214.1047 [M + H], 231.1312 [M + NH_4], 236.0866 [M + Na], 252.0606 [M + K].

3-(Morpholin-4-yl)-1-(1*H*-tetrazol-5-ylmethoxy)diaz-1-ene 2-oxide (8d). Ethanol was used as an eluent. Yield 0.11 g (69%). M.p. 242—244 °C (EtOH). ^{1}H NMR (DMSO-d_6), δ: 3.28 (t, 4 H, NCH_2, J = 4.5 Hz); 3.72 (t, 4 H, OCH_2, J = 5.0 Hz); 5.25 (s, 2 H, OCH_2). ^{13}C NMR (DMSO-d_6), δ: 51.24 (CH_2N); 64.99 (CH_2CN); 66.95 (CH_2O), 156.45 (NCN). ^{14}N NMR ($CDCl_3$), δ: −57.28. IR, ν/cm^{-1}: 3392, 1483, 1241, 1108, 1013. MS (ESI), found: m/z 252.0819 $[M + Na]^+$, 274.0637 $[M + 2 Na]^+$. $C_6H_{11}N_7O_3$. Calculated: 252.0816 [M + Na], 274.0635 [M + 2 Na].

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