FORMATION OF O,N-DISUBSTITUTED HYDROXYLAMINES AND KETOXIME ESTERS IN REACTIONS BETWEEN TRIAZENE 1-OXIDES AND BASES

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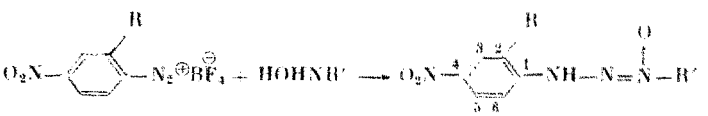
A new method has been put forward for the synthesis of O,N-disubstituted hydroxylamines and ketoxime esters that is based on the reaction of triazene 1-oxides containing strong electron-withdrawing substituents with bases.

Keywords: *O,N-disubstituted hydroxylamines, ketoximes, triazene 1-oxides, aryldiazonium tetrafluoroborates, bases.*

The reaction of triazene 1-oxides containing simple alkyl or aryl group substituents on the nitrogen atom of the triazene 1-oxide group with bases is known to result in the formation of salts of 1,3-disubstituted triazene 1-oxides [1]. It might be assumed that base treatment of triazene 1-oxides with electron-withdrawing substituents forming part of the molecule would also be accompanied by the formation of triazene oxide anions, which are promising synthons for the preparation of polyfunctional compounds of this series.

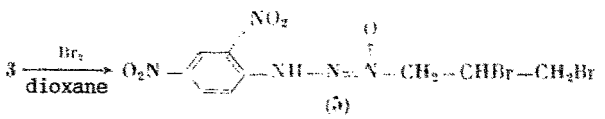
In order to synthesize these synthons, we have studied the behavior in basic media of 1-alkyl-3-aryltriazene 1-oxides (**1-5**) containing electron-withdrawing groups in the aromatic ring and/or at the α position of the alkyl section of the molecule. We have also studied compounds **6** and **7**, in which one of the nitrogen atoms of the triazene oxide sequence forms part of a phthalimide cyclic system.

3-Nitroaryl-1-alkyltriazene-1-oxides **1-4** were obtained by reaction of the corresponding aryldiazonium tetrafluoroborates with N-alkylhydroxylamines.



R=H, R′=C(CH$_3$)$_2$CN (1); R=NO$_2$, R′=CH$_3$ (2), CH$_2$CH=CH$_2$ (3), C(CH$_3$)$_2$CN (4).

The dibromo derivative **5** was synthesized by reaction of the alkyl-substituted triazene oxide **3** with bromine



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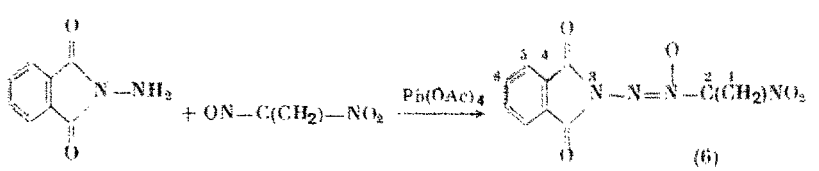
The 2-phthalimidodiazene 1-oxide **6** was synthesized in a similar manner to compound **7** according to the method in [2] by reaction of N-aminophthalimide with 2-nitro-2-nitrosopropane in the presence of Pb(OAc)$_4$).



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However, it transpired that, in contrast to the corresponding reactions of unfunctionalized triazene 1-oxides [1], the reactions of compounds **1-7** were not complete with the formation of triazene oxide anions but were accompanied by elimination of a nitrogen molecule and the formation of different classes of compounds whose structures were determined by the nature of the starting materials.

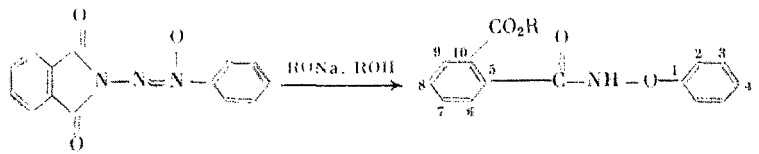
Thus, the products of the reaction between 1-alkyl-3-(2′,4′-dinitrophenyl)triazene 1-oxides **2, 3,** and **5** and KOH in an alcoholic medium are the previously unknown N-alkyl-O-(2′,4′-dinitrophenyl)hydroxylamines **8-10**.

(2, 3, 5) (8—10)

R=$^{7}CH_3$ (2, 8); $CH_2{}^{7}CH={}^{8}CH_2$ (3, 9);

$CH_2CHBrCH_2Br$ (5, 10).

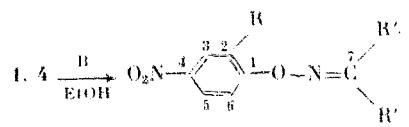
Reaction of 1-phenyl-2-phthalimidodiazene 1-oxide **7** with sodium alkoxides is accompanied by opening of the dioxopyrrolidine ring and the formation of N-benzoyl-O-phenylhydroxylamines (**11, 12**) in 91 and 52% yield, respectively. It should be pointed out that while the formation of compounds **8-10** occurs with retention of the bond between substituent R and the N^1 atom of the triazene group, the latter (R = Ph) migrates from the N^1 nitrogen atom to the oxygen atom of the N^1-O residue in the course of formation of products **11** and **12**



(7) (11, 12)

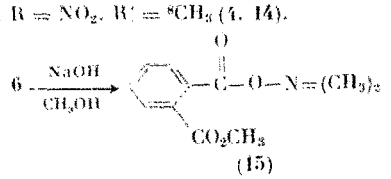
R = Me (11), Et (12).

A different reaction route occurs when 1-alkyl-3-substituted triazene oxides containing nitro and cyano groups at an α position relative to the oxidized nitrogen atom of the triazene sequence are involved in the process. Thus, the reaction of 1-(2′-cyanopropyl-2′)- and 1-(2′-nitropropyl-2′-propyl)-triazene 1-oxides **1, 4,** and **6** with alcoholic solutions of alkali metal hydroxides, in addition to loss of nitrogen, involves the elimination of nitrous acid or hydrocyanic acid residues and culminates in the formation of the corresponding ketoxime esters (**13-15**).



(13, 14)

R = H, R′ = CH_3 (1, 13); R = NO_2, R′ = $^{8}CH_3$ (4, 14).



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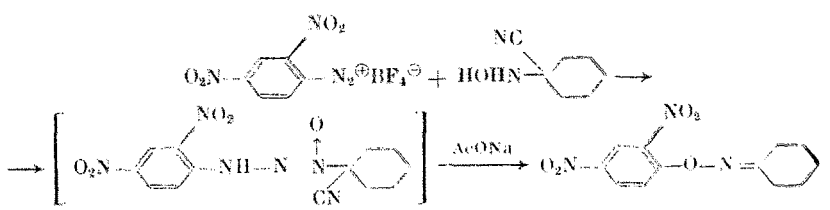
It is of interest that we isolated the oximino ester **16** in 18% yield directly from the reaction of 2,4-dinitrophenyldiazonium tetrafluoroborate with N-(1-cyanocyclohexyl-1)hydroxylamine, which is possibly due to fragmentation of the intermediate triazene 1-oxide (**17**) by the action of sodium acetate present in the system.



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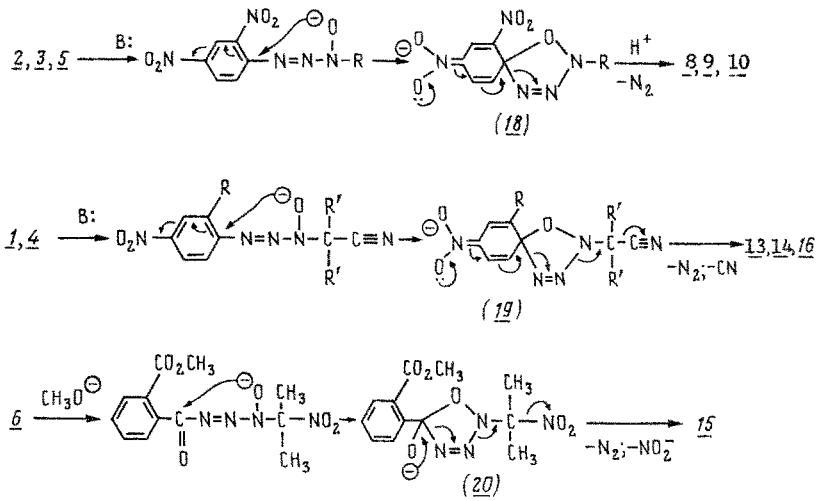
The structures of the freshly synthesized compounds **1-6, 8-11,** and **15** were established from the data of the IR, ^{1}H NMR, ^{13}C NMR, and mass spectra and the results of elemental analysis. The configuration of the substituents in the hydroxyl-

amine group of products **8-10** was demonstrated from the vicinal coupling constant $^3J_{^1H,^1H}$ = 5.0-8.7 Hz between the protons located on the nitrogen atom of the hydroxylamine residue and the α-carbon atom attached to it. The presence of a residue in compounds **11** and **12** was confirmed from the characteristic absorption frequencies of the C=O bond (1600-1630 cm^{-1}) and NH bond (3130-3140 cm^{-1}) in their IR spectra and the significant broadening of the signals in the ^{13}C NMR spectra of these compounds, recorded at room temperature. This type of broadening is typical of organic amides [3] and results from the hindered inherent rotation of the amide group about the C–N bond. By freezing a sample of **12** to −30°C it was possible to eliminates this hindered rotation and obtain a series of sharp ^{13}C signals corresponding to the more stable conformer. At the same time the chemical shift of the signal from the *i*-carbon atom of the monosubstituted aromatic ring was 166.3 ppm, which on taking into account the literature data of [4] and the ^{13}C NMR spectroscopic parameters of compounds **8** and **9** demonstrated that there is a C–O bond between the phenyl substituent and the oxygen atom of the hydroxylamine residue in products **11** and **12**.

Products **13, 14,** and **16** were identical to previously established compounds obtained by independent methods [5-7].

A possible scheme for the formation of O,N-disubstituted hydroxylamines and ketoxime esters in the reaction between triazene 1-oxides and bases, in our opinion, involves the conversion of the initially formed triazene 1-oxide salts to the cyclic intermediates **18-20**, which are stabilized through elimination of a nitrogen molecule and in the case of structures **19** and **20** by that of the suitably located NO_2 and CN groups.



The favorable effect of electron-withdrawing substituents on this reaction is accounted for in this scheme by an increase in electrophilicity of the α-carbon atom joined to the unoxidized nitrogen atom of the triazene 1-oxide group and the possibility of delocalization of negative charge from the triazene 1-oxide anion onto the oxygen atoms of the nitro group.

The formation of the O-arylhydroxylamines **11** and **12** from triazene 1-oxide **7** involves the migration of the unsubstituted benzene ring from the nitrogen atom to the oxygen atom of the N^1–O residue together with elimination of a nitrogen molecule. In this case, as for compounds **8-10** and **13-15**, the nitrogen molecule being eliminated is formed by the N^2 and N^3 atoms of the triazene sequence. This is supported by the complete retention of ^{15}N nitrogen in product **12** obtained from triazene 1-oxide **7** labeled with ^{15}N at the N^1 position.

EXPERIMENTAL

IR spectra were recorded on UR-20 and Specord M 80 instruments, NMR spectra were recorded on Bruker WM 250 (^1H — 250 MHz), Bruker AM-300 (^1H — 300 MHz, ^{13}C — 75.5 MHz, ^{14}N — 21.7 MHz) and Bruker AMX-400 (^1H — 400 MHz, ^{13}C — 100.6 MHz) spectrometers. The chemical shifts of the ^{13}C signals were measured relative to acetone-d_6 (δ 30.0 ppm) and those of ^{14}N were measured relative to nitromethane (external standard δ 0.0 ppm). The ratio of the signals of the protonated carbon atoms of the aromatic ring is determined using a two-dimensional CH correlation of the carbon atoms bonded to the nitro groups by comparison of the experimental values of δ with those calculated by an additive scheme [4]. Mass spectra were recorded on a Varian MAT CH-6 instrument with direct introduction of samples into the ion source, ionizing potential 70 eV, emission current 0.1 mA. TLC was conducted on Silpearl UV-250 silica gel.

The initial N-alkylhydroxylamines were obtained according to the methods in [8, 9]. Triazene 1-oxide **7** was synthesized according to the method in [2]. Compound **7** labeled with ^{15}N was obtained in a similar manner from ^{15}N-labeled nitrosobenzene.

3-(4′-Nitrophenyl)-1-(2′-cyanopropyl-2′)triazene 1-Oxide (1). To 0.5 g (5 mmoles) of N-(2-cyanopropyl-2)-hydroxylamine and 1.70 g (15.5 mmoles) of $NaOAc \cdot 3H_2O$ in a mixture of 15 ml of water and 0.5 ml of acetic acid at 0°C and with stirring was added 1.20 g (5 mmoles) of 4-nitrophenyldiazonium tetrafluoroborate. The mixture was allowed to stand for 0.5 h. The precipitate that had formed was filtered off and washed with water and a 1:2 mixture of ether–hexane. Yield 0.92 g (74%) of compound **1**, mp 183-185°C. Found, %: C 48.12; H 4.65; N 28.40. $C_{10}H_{11}N_5O_3$. Calculated, %: C 48.19; H 4.42; N 28.11. IR spectrum (ν, cm^{-1}): 1340 (NO_2), 1490 [N(O)=N], 1520 (NO_2), 3220 (NH). PMR spectrum (DMSO-d_6, δ, ppm, J, Hz): 1.93 s (6H, CH_3), 7.45 d (2H, C_6H_4, J = 9), 8.18 d (2H, C_6H_4, J = 9). Mass spectrum, *m/z* (*I*, %): M^+ 249(53), 122(100), 75(24), 69(17). Compounds **2-4** were obtained in a similar manner.

1-Methyl-3-(2′,4′-dinitrophenyl)triazene 1-Oxide (2). Yield 96%, mp 195-196°C. Found, %: C 34.96; H 2.55; N 28.87. $C_7H_7N_5O_5$. Calculated, %: C 34.85; H 2.90; N 29.05. IR spectrum (ν, cm^{-1}): 1330 (NO_2), 1490 [N(O)=N], 1520 (NO_2), 3270 (NH). PMR spectrum (DMSO-d_6, δ, ppm, J, Hz): 4.10 s (3H, CH_3), 7.75 d (1H, H^6, C_6H_3, J = 9), 8.48 dd (1H, H^5, C_6H_3, ^1J = 9, ^2J = 2.5), 8.82 d (1H, H^3, C_6H_3, J = 2.5). Mass spectrum, *m/z* (*I*, %): M^+ 241(8), 195(25), 184(100), 168(20), 122(10), 75(45).

1-Allyl-3-(2′,4′-dinitrophenyl)triazene 1-Oxide (3). Yield 83%, mp 110-113°C. Found, %: C 40.11; H 3.62; N 26.43. $C_9H_9N_5O_5$. Calculated, %: C 40.45; H 3.37; N 26.22. IR spectrum (ν, cm^{-1}): 1310 (NO_2), 1460 [N(O)=N], 1500 (NO_2), 3230 (NH). PMR spectrum (acetone-d_6, δ, ppm, J, Hz): 4.91 d (2H, CH_2, J = 7); 5.25-5.70 m (2H, =CH_2), 5.87-6.55 m (1H, CH), 7.88 d (1H, H^6, C_6H_3, J = 9), 8.46 dd (1H, H^5, C_6H_3, ^1J = 9, ^2J = 2.5), 8.94 d (1H, H^3, C_6H_3, J = 2.5). Mass spectrum, *m/z* (*I*, %): M^+ 267(12), 195(61), 184(100), 168(28), 75(35), 56(31), 41(45).

3-(2′,4′-Dinitrophenyl)-1-(2′-cyanopropyl-2′)triazene 1-Oxide (4). Yield 53%, mp 137-140°C. Found, %: C 40.82; H 3.40; N 28.28. $C_{10}H_{10}N_6O_5$. Calculated, %: C 40.82; H 3.40; N 28.57. IR spectrum (ν, cm^{-1}): 1345 (NO_2), 1470 [N(O)=N], 1530 (NO_2), 3260 (NH). Mass spectrum, *m/z*: 294, 266, 195, 184, 168, 122, 75, 69.

1-(2′,3′-Dibromopropyl-1′)-3-(2′,4′-dinitrophenyl)triazene 1-Oxide (5). To 0.22 g (0.82 mmole) of compound **3** in 8 ml of dioxane at 0°C and with stirring was added dropwise 0.14 g (0.87 mmole) of Br_2, with the temperature gradually being increased to 45°C, and the mixture was kept at 45°C for 1.5 h. The solvent was removed, the residue was dissolved in 10 ml of CH_2Cl_2, and the resulting solution was poured into 50 ml of hexane. The precipitate which formed was filtered off. Yield 0.23 g (66%) of product **5**, mp 148-151°C. Found, %: C 25.16; H 2.54; Br 37.11; N 16.65. $C_9H_9Br_2N_5O_5$. Calculated, %: C 25.29; H 2.11; Br 37.47; N 16.39. IR spectrum (ν, cm^{-1}): 100 (NO_2), 1475 [N(O)=N], 1500 (NO_2), 3240 (NH). PMR spectrum (acetone-d_6, δ, ppm, J, Hz): 4.06-4.20 m (2H, CH_2–Br), 4.77-4.84 m (1H, CH), 4.97-5.08 m (2H, CH_2), 8.03 d (1H, H^6, C_6H_3, J = 9), 8.57 dd (1H, H^5, C_6H_3, ^1J = 9, ^2J = 2.5), 9.06 d (1H, H^3, C_6H_3, J = 2.5). Mass spectrum, *m/z* (*I*, %): M^+ 429(3), 427(3), 348(2), 346(2), 195(100), 168(12).

1-(2′-Nitropropyl-2′)-2-phthalimidodiazene 1-Oxide (6). This compound was obtained in a similar manner to the synthesis of oxide **7** by the method in [2], yield 69%, mp 92-94°C. Found, %: C 47.79; H 3.62; N 19.85. $C_{11}H_{10}N_4O_5$. Calculated, %: C 47.48; H 3.60; N 20.14. IR spectrum (ν, cm^{-1}): 1360 (NO_2), 1470 [N(O)=N], 1560 (NO_2), 1730 (C=O). NMR spectrum ($CDCl_3$, δ, ppm), ^1H: 2.29 s (6H, CH_3), 7.75-7.80 m (2H, C_6H_4); 7.83-7.92 m (2H, C_6H_4); ^{13}C: C^1 24.85, C^2 111.3, C^3 161.1, C^4 130.85, C^5 134.8, C^6 124.0; ^{14}N: −3.1 ($\Delta\nu_{1/2}$ = 112 Hz, NO_2), −39.15 ($\Delta\nu_{1/2}$ = 167 Hz, N → O). Mass spectrum, *m/z* (*I*, %): M^+ 278(2), 207(11), 147(82), 132(6), 107(55), 104(97), 77(100), 76(86), 44(24).

N-Methyl-O-(2,4-dinitrophenyl)hydroxylamine (8). To 0.2 g (0.83 mmole) of triazene oxide **2** in 10 ml of ethanol at 40°C and with stirring was added dropwise a solution of 0.05 g (0.89 mmole) of KOH in 3 ml of ethanol over a period of 0.5 h. The mixture was allowed to stand for 1.5 h, then diluted with water (150 ml), and extracted with ether (2 × 150 ml). The ether solution was dried with $MgSO_4$. After removal of the solvent by evaporation, product **8** was obtained, 0.16 g (90%), mp 66-69°C. Found, %: C 39.73; H 3.26; N 19.27. $C_7H_7N_3O_5$. Calculated, %: C 39.44; H 3.29; N 19.72. IR spectrum (ν, cm^{-1}): 1320 (NO_2), 1450, 1500 (NO_2), 3270 (NH). NMR spectrum ($CDCl_3$, δ, ppm, J, Hz): ^1H: 3.01 d (3H, CH_3, J = 6.8); 6.71 q (1H, NH, J = 6.8); 7.95 d (1H, H^6, C_6H_3, J = 9.4), 8.41 dd (1H, H^5, C_6H_3, ^1J = 9.4, ^2J = 2.6), 8.80 d (1H, H^3, C_6H_3, J = 2.6); ^{13}C: C^7 39.7, C^1 158.7, C^2 136.3, C^3 121.9, C^4 140.4, C^5 129.3, C^6 116.5. Mass spectrum, *m/z* (*I*, %): M^+ 213(83), 196(29), 184(100), 168(31). Compounds **9** and **10** were obtained in a similar manner.

N-Allyl-O-(2,4-dinitrophenyl)hydroxylamine (9). Yield 71%, mp 28-29°C. Found, %: C 45.56; H 3.92; N 17.46. $C_9H_9N_3O_5$. Calculated, %: C 45.19; H 3.77; N 17.57. IR spectrum (ν, cm^{-1}): 1345 (NO_2), 1480, 1530 (NO_2), 3300 (NH). NMR spectra ($CDCl_3$, δ, ppm, J, Hz): ^1H: 3.82 t (2H, CH_2, J = 9), 5.20-5.40 m (2H, =CH_2), 5.82-6.03 m (^1H, =CH), 6.72 t (1H, NH, J = 9), 7.98 d (1H, H^6, C_6H_3, J = 13.2), 8.38 dd (1H, H^5, C_6H_3, ^1J = 13.2, ^2J = 4.2), 8.74 d (1H, H^3,

C_6H_3, J = 4.2); ^{13}C: C^7 55.2, C^8 131.5, C^9 120.3, C^1 159.1, C^2 136.0, C^3 121.7, C^4 140.2, C^5 129.2, C^6 117.0; ^{14}N: −17.7 ($\Delta\nu_{1/2}$ = 115 Hz, NO_2). Mass spectrum, *m/z* (*I*, %): M^+ 239(7), 184(72), 168(20), 73(13), 55(100), 41(33).

N-(2,3-Dibromopropyl-1)-O-(2,4-dinitrophenyl)hydroxylamine (10). Yield 89%, oil. Found, %: C 27.29; H 2.11; Br 40.26; N 10.64. $C_9H_9Br_2N_3O_5$. Calculated, %: C 27.07; H 2.25; Br 40.10; N 10.53. IR spectrum (ν, cm^{-1}): 1345 (NO_2), 1480, 1530 (NO_2), 3290 (NH). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 3.42-3.56 m (1H), 3.75-3.98 m (3H), 4.55-4.67 m (1H), 7.03 dd (1H, NH, ^1J = 8.7, ^2J = 5.0), 8.03 d (1H, H^6, C_6H_3, J = 10), 8.44 dd (1H, H^5, C_6H_3, ^1J = 10, ^2J = 3.0), 8.80 d (1H, H^3, C_6H_3, J = 3.0). Mass spectrum, *m/z*: M^+ 401, 399, 397, 184, 168, 136, 134.

N-(2-Methoxycarbonylbenzoyl)-O-phenylhydroxylamine (11). To 0.65 g (2.43 mmoles) of compound **7** in 15 ml of absolute MeOH at −10°C and with stirring was added dropwise a solution of 0.06 g (2.60 mmoles) of Na in 2 ml of absolute MeOH. The mixture was allowed to stand for 1 h, with the temperature gradually being increased to 20°C. The solution was neutralized and the product was isolated by means of TLC. Yield 0.60 g (91%) of compound **11**, mp 103-104°C. Found, %: C 66.00; H 5.49; N 5.00. $C_{15}H_{13}NO_4$. Calculated, %: C 66.42; H 5.17; N 4.80. IR spectrum (ν, cm^{-1}): 1270 (C−O−C), 1500, 1600 [(N)C=O], 1700 (C=O), 3130 (NH). PMR spectrum ($CDCl_3$, δ, ppm): 3.80 s (3H, CH_3), 7.00-8.00 m (9H, Ar). In the ^{13}C NMR spectrum there was a group of broad signals in the region 120-138 ppm due to the protonated carbon atoms of the aromatic rings and broad signals due to the carbonyl carbons and *ipso* carbons in the region 165-170 ppm. Mass spectrum, *m/z*: M^+ 271, 179, 163, 120, 104, 91.

N-(2-Ethoxycarbonylbenzoyl)-O-phenylhydroxylamine (12). This was obtained in a similar manner from triazene oxide **7**, with absolute EtOH as solvent, reaction time 2 h, temperature 40°C, yield 52%, mp 121-123°C. Found, %: C 66.73 H 5.28; N 4.84. $C_{16}H_{15}NO_4$. Calculated, %: C 67.37; H 5.26; N 4.91. IR spectrum (ν, cm^{-1}): 1280 (C−O−C), 1490, 1630 [(N)C=O], 1720 (C=O), 3140 (NH). NMR spectrum (acetone-d_6, δ, ppm, J, Hz, −30°C): ^1H: 1.08 t (3H, CH_3, J = 7.0), 4.13 q (2H, CH_2, J = 7.0), 7.15 t (1H, H^4, C_6H_5, J = 8.0), 7.38 br.t (2H, H^3, C_6H_5, J = 8.0), 7.46 d (1H, H^6, C_6H_4, J = 8.0), 7.53 t (1H, H^8, C_6H_4, J = 8.0), 7.66 br.t (1H, H^7, C_6H_4, J = 8.0), 7.81 br.d (2H, H^2, C_6H_5, J = 8.0), 7.96 d (1H, H^9, C_6H_4, J = 8.0); ^{13}C: CH_3 14.2, CH_2 61.9, C^2 120.5, C^4 125.6, C^6 128.2, C^3 129.2, C^8 129.6, C^9 130.1, C^7 133.4, C^5 and C^{10} 139.5 and 142.7, C^1 166.3; C=O 169.0 and 170.0. Mass spectrum, *m/z* (*I*, %): M^+ 285(1), 177(39), 149(100), 104(7), 91(39), 75(11). Compound **12** labeled with ^{15}N was obtained in a similar manner from ^{15}N-labeled compound **7**. Mass spectrum, *m/z* (*I*, %): M^+ 286(1), 177(50), 149(50), 104(7), 92(28), 76(11).

O-(4-Nitrophenyl)acetoxime (13). This was obtained in a similar manner to compound **8** from triazene oxide **1**, yield 50%, mp 101-103°C (cf. [5], mp 104-106°C). IR spectrum (ν, cm^{-1}): 1335 (NO_2), 1490, 1515 (NO_2). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 1.95 s (6H, CH_3), 7.12 d (2H, C_6H_4, J = 9), 8.08 d (2H, C_6H_4, J = 9). Mass spectrum, *m/z*: M^+ 194, 139, 123, 56.

O-(2,4-Dinitrophenyl)acetoxime (14). This was obtained in a similar manner from triazene 1-oxide **4**, yield 63%, mp 84-86°C (cf. [6], mp 86-87°C). IR spectrum (ν, cm^{-1}): 1340 (NO_2), 1475, 1525 (NO_2). NMR spectra ($CDCl_3$, δ, ppm, J, Hz): ^1H: 2.10 s (3H, CH_3), 2.18 s (3H, CH_3), 7.91 d (1H, H^6, C_6H_3, J = 9.4), 8.36 dd (1H, H^5, C_6H_3, ^1J = 9.4, ^2J = 2.7), 8.81 d (1H, H^3, C_6H_3, J = 2.7); ^{13}C: C^{8a} 17.3, C^{8b} 21.5, C^7 164.4, C^1 157.4, C^2 135.7, C^3 122.0, C^4 140.4, C^5 129.3, C^6 117.1; ^{14}N: −17.7 ($\Delta\nu_{1/2}$ = 137 Hz, NO_2).

O-(2-Methoxycarbonylbenzoyl)acetoxime (15). This was obtained in a similar manner to compound **11** from triazene oxide **6**, with reaction time 20 min, temperature −30°C, yield 15%, mp 80-82°C. Found, %: C 61.66; H 5.75; N 5.99. $C_{12}H_{13}NO_4$. Calculated, %: C 61.28; H 5.53; N 5.96. IR spectrum (ν, cm^{-1}): 1250 (C−O−C), 1490, 1720 (C−O−C=O), 1750 (N−C=O). PMR spectrum (acetone-d_6, δ, ppm): 2.01 s (3H, CH_3), 2.02 s (3H, CH_3), 3.83 s (3H, CH_3O), 7.67-7.83 m (4H, C_6H_4). Mass spectrum, *m/z*: 163, 135, 133, 104, 56.

O-(2,4-Dinitrophenyl)cyclohexanone Oxime (16). To 0.5 g (3.57 mmoles) of N-(1-cyanocyclohexyl-1)hydroxylamine and 0.75 g (5.51 mmoles) of $NaOAc \cdot 3H_2O$ in 20 ml of H_2O was added at 0°C and with stirring 1 g (3.55 mmoles) of 2,4-dinitrophenyldiazonium tetrafluoroborate. The mixture was allowed to stand for 25 min. The precipitate was filtered off and washed with ether. Product **16** was isolated from the filtrate by means of TLC, with yield 0.18 g (18%), mp 84-85°C (cf. [7], mp 85°C). IR spectrum (ν, cm^{-1}): 1340 (NO_2), 1470, 1535 (NO_2), 2870 (CH), 2945 (CH). PMR spectrum (acetone-d_6, δ, ppm, J, Hz): 1.68 br.s (6H, C_6H_{10}), 2.19-2.55 m (2H, C_6H_{10}), 2.55-2.85 m (2H, C_6H_{10}), 7.87 d (1H, H^6, C_6H_3, J = 9), 8.45 dd (1H, H^5, C_6H_3, ^1J = 9, ^2J = 2.5), 8.72 d (1H, H^3, C_6H_3, J = 2.5). Mass spectrum, *m/z*: M^+ 279, 184, 96, 69, 55.

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