ARYL-NNO-AZOXY-α-NITROALKANES

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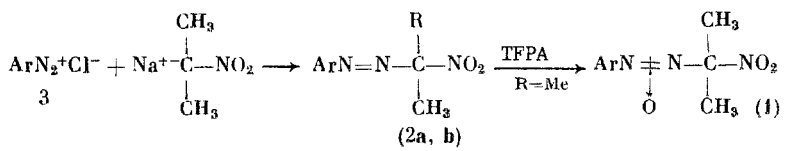
Two methods of synthesis of aryl-NNO-azoxy-α-nitroalkanes bearing either one or two reactive hydrogen atoms α to the azoxy and nitro groups are described. These methods involve protection of the latter by easily removable groupings, those used being acetoxy-methyl and acetal fragments. The regiochemical nature of the diazene oxide groupings in aryl-NNO-azoxy-α-nitroalkanes obtained by oxidation of the appropriate diazenes has been established by heteronuclear NMR and x-ray structural examination. Some of the chemical properties of these diazene oxides have been examined.

Keywords: *azoxynitroalkanes, regiochemistry, protective groups, x-ray structural examination.*

Among the numerous and varied α-substituted nitro compounds which have been reported, only one bears an arylazoxy group as an α-substituent (**1**) [1]. This was obtained by oxidation of the appropriate diazene with trifluoroperacetic acid (TFPA) (**2a**, R = Me), obtained by reaction of the 2-nitrophenyldiazonium salts (**3**) with 2-nitropropane.



Ar=*o*-$O_2NC_6H_4$.

Since the position of the N-oxide oxygen in the diazene oxide **1** has not been established, we have carried out an x-ray structural examination (see Fig. 1 and Tables 1 and 2). It was found that the N-oxide oxygen is bonded to the nitrogen attached to the alkyl portion of the molecule. The aryl and nitroalkyl substituents in **1** are trans to the azoxy fragment. Accordingly, the aryl radical and the N-oxide oxygen are situated on one side of the N=N bond, the internuclear distance between the N-oxide oxygen and the nitrogen of the aromatic nitro group being 0.33 Å less than the sum of the van der Waals radii, which presumably indicates electronic interaction between these atoms, which bear excess charges of opposite signs.

It was to be hoped that this reaction would prove quite general for the synthesis of aryl-NNO-azoxy-α-nitroalkanes, including those bearing additional functional groups in the α position of the nitroalkane radical, particularly since it has been reported in the patent literature [1] that this reaction is feasible with adducts of nitroethane in addition to those of secondary nitro compounds, although unfortunately no properties of the azo and azoxy products are reported.

However, we attempted to oxidize adducts **3** with salts of 1,1-dinitroethane **2b** [2] and nitroethane with TFPA, *meta*-chloroperbenzoic acid, or a mixture of 9% oleum and 96% H_2O_2, but these attempts failed, and depending on the oxidant used, either starting material was recovered or it underwent decomposition.

These findings can apparently be rationalized in terms of the low stability of the starting materials to acids, in conjunction with the reduced basicity of dinitroethane **2** and the reported [3] ease of isomerization of azo compounds derived from primary nitroalkanes (nitroethane in the present case) to the hydrazones. This supposition was confirmed by the spectral features of the adduct from nitroethane (IR spectra: 3325, 3280, 1615 cm^{-1}; PMR: singlet for Me, δ = 2.5 ppm), which conclusively prove the absence in these compounds of the grouping −N=N−CHMe.

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TABLE 1. Nonvalent Intramolecular Distances (r)

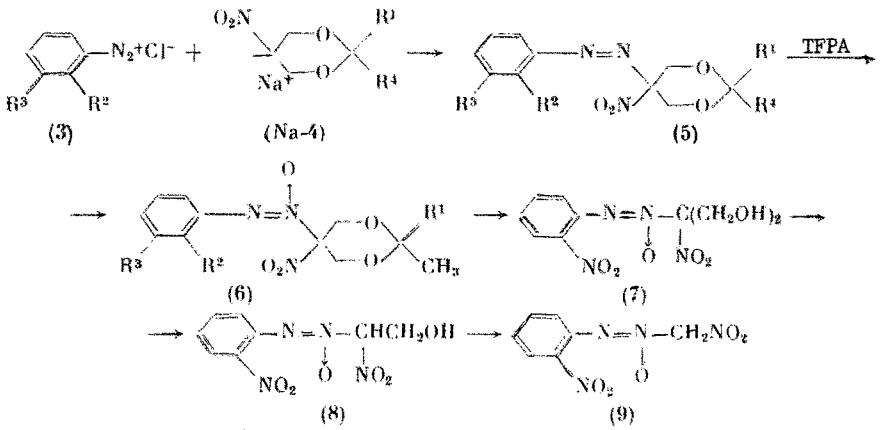
Interatomic distances	r, Å	ΣVR,* Å	A = Z−VR
$O^{21} \ldots C^{11}$	2.682	3.1	0.42
$O^{21} \ldots N^{3}$	2.667	2.9	0.33
$O^{21} \ldots C^{16}$	2.842	3.1	0.26
$C^{21} \ldots N^{31}$	2.755	2.9	0.15
$O^{21} \ldots O^{13}$	2.849	2.8	−0.05
$O^{21} \ldots C^{32}$	2.792	3.1	0.31
$N^{3} \ldots N^{1}$	3.038	3.0	−0.04
$N^{3} \ldots N^{2}$	3.045	3.0	−0.05
$O^{1(3)} \ldots N^{2}$	2.880	2.9	0.02
$O^{1(3)} \ldots C^{11}$	2.824	3.1	0.28
$O^{1(3)} \ldots N^{1}$	2.873	2.9	0.03
$O^{2(3)} \ldots C^{13}$	2.779	3.1	0.32
$O^{2(31)} \ldots N^{2}$	2.737	2.9	0.16
$O^{2(31)} \ldots C^{31}$	2.864	3.1	0.24
$O^{1(31)} \ldots C^{32}$	2.684	3.1	0.42

*ΣVR indicates the sum of the van der Waals radii (Pauling) of the corresponding atoms, $R_C = 1.70$, $R_O = 1.40$, $R_N = 1.50$ Å.

TABLE 2. Atom Coordinates in Cell Units ($\times 10^4$) and Anisotropic Thermal Parameters (A^2) as the B_{ij}* Coefficients

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N^{2}	52.2	640(4)	7438(2)	3.2(1)	2.8(2)	2.3(1)	−0.3(1)	0.6(1)	−0.0(1)
N^{3}	−404(3)	−3429(6)	8388(2)	4.8(2)	3.4(2)	3.9(2)	−0.1(1)	1.0(1)	0.5(2)
C^{16}	−908(3)	−1645(6)	8814(2)	2.7(2)	3.0(2)	2.7(2)	−0.5(2)	0.4(1)	−0.2(2)
C^{3}	358(3)	1580(6)	6631(2)	3.1(2)	2.8(2)	2.5(2)	0.4(2)	0.8(1)	−0.2(2)
N^{31}	744(3)	−427(6)	6175(2)	5.3(2)	4.5(2)	2.9(2)	0.7(2)	1.4(1)	−0.1(2)
C^{11}	−1227(3)	266(6)	8401(2)	2.3(1)	3.0(2)	2.4(2)	−0.4(2)	0.3(1)	−0.1(2)
O^{21}	902(2)	−248(4)	7888(1)	2.8(1)	6.1(2)	3.1(1)	0.7(1)	0.1(1)	1.3(1)
N^{1}	−1001(2)	917(4)	7586(2)	2.5(2)	3.0(2)	2.7(1)	−0.0(1)	0.6(1)	0.0(1)
C^{12}	−1831(3)	1789(6)	8803(2)	3.1(2)	3.5(2)	3.6(2)	−0.1(1)	0.9(1)	−0.7(2)
C^{23}	319(2)	−4604(4)	8793(2)	6.9(2)	4.4(2)	5.7(2)	2.1(1)	0.8(1)	1.6(1)
C^{14}	−1696(3)	−442(8)	10018(2)	3.6(2)	6.9(3)	2.5(2)	−1.4(2)	0.8(1)	−0.3(2)
C^{15}	−1133(3)	−2019(6)	9621(2)	3.3(2)	4.5(2)	2.6(1)	−0.7(2)	0.4(1)	0.7(2)
O^{13}	−771(2)	−3675(4)	7643(2)	7.3(2)	3.6(2)	3.8(1)	0.0(1)	0.8(1)	−0.7(1)
C^{13}	−2058(3)	1432(7)	9617(2)	3.8(2)	5.2(2)	3.6(2)	0.7(2)	1.4(1)	−1.3(2)
$O^{1(32)}$	1702(2)	−337(5)	5932(2)	6.3(2)	8.7(2)	8.5(2)	1.2(2)	4.0(1)	−2.2(2)
$O^{2(32)}$	38(3)	−1876(5)	6050(2)	9.7(2)	4.1(2)	6.4(2)	−1.5(2)	3.1(2)	−1.8(1)
C^{32}	1374(3)	3116(6)	6841(2)	4.5(2)	4.9(2)	4.6(2)	−1.2(2)	1.5(2)	−0.0(2)
C^{31}	−704(3)	2514(6)	6090(2)	4.1(2)	4.5(2)	3.0(1)	1.1(2)	0.8(1)	1.1(2)
$H^{11(2)}$	−2121	3222	8495						
$H^{1(12)}$	−2504	2598	9924						
$H^{1(14)}$	−1854	−667	10636						
$H^{1(15)}$	−878	−3473	9925						
$H^{1(31)}$	−354	2973	5572						
$H^{2(31)}$	−1029	3849	6352						
$H^{1(32)}$	1591	3680	6369						
$H^{2(33)}$	2045	2352	7086						
$H^{3(31)}$	−1417	1433	5990						
$H^{3(32)}$	1101	4313	7229						

*For hydrogen atoms with fixed coordinates, B was taken to be 5 $Å^2$.



$R^1 = H$, $R^4 = Me$ (4a); $R^1 = H$, $R^4 = Ph$ (4b); $R^1 = R^4 = H$ (4c);
$R^1 = R^4 = Me$ (4d); $R^1 = R^2 = H$, $R^3 = NO_2$, $R^4 = Me$ (5a);
$R^1 = R^4 = Me$, $R^2 = NO_2$, $R^3 = H$ (5b).

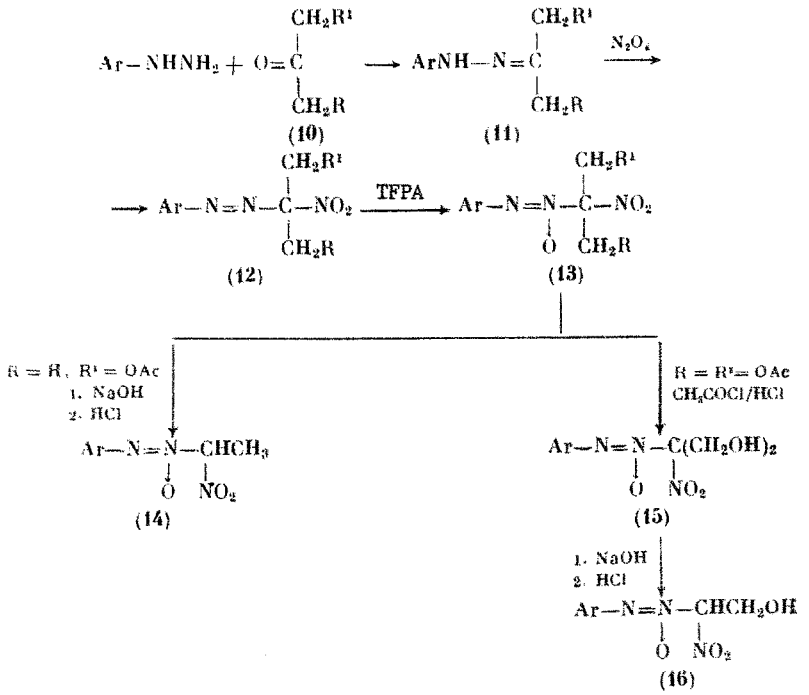
With these considerations in mind, we developed two routes to aryl-NNO-azoxy-α-nitroalkanes having in the alkyl radical either one or two hydrogen atoms in the α position to the nitro and azoxy groups, together with additional functional groups. The basic concept in these methods was protection of these reactive protons during the formation of the diazene oxide moiety. The key intermediates were nitroacetals and acetoxymethylated nitroalkanes.

In the first instance, the method required the reaction of diazonium salts (such as **3**) with the sodium salts of 5-nitro-1,3-dioxanes (**4**), followed by oxidation of the resulting diazenes with TFPA to the arylazoxy derivatives, which were hydrolyzed to remove the acetal group, followed by stepwise removal of the hydroxymethyl groups.

For this method to be successful, it was necessary to observe several conditions. The aryl radical must bear a strongly electron-acceptor substituent in the *ortho* position, which facilitates both electronically and sterically the regioselective oxidation of the distal nitrogen of the diazene fragment. When only a *meta*-nitro group was present, determined by analysis of the ^1H and ^{14}N NMR spectrum of the oxidation product of TFPA — diazene **5a** approximately 1:2 mixture of the required distal diazene oxide **6** and its proximal (relative to the aromatic ring) regioisomer was formed in which the latter predominated. Further, the dioxane ring must possess a substituent in the 2 position (**4a, b**), since in its absence (**4c**) it was not found possible to selectively solvolyze the acetal fragment. When, however, two alkyl groups are present in the 2 position (**4d**) the substrate **5b** is unstable under the oxidation conditions. Introduction of methyl groups into positions 4 and 6 of the dioxane ring **4e** has no effect on the regiochemistry of the oxidation of the diazene grouping to the diazene **5c**, although it does inhibit further sovolysis of the acetal to the diazene oxide **6b**. The diazene **5d**, which meets all these conditions, on oxidation gives the azoxy derivative **6c**, the dioxane ring in which is cleaved smoothly on treatment of a solution of the diazene oxide **6c** with methanolic acetyl chloride, to give the diol **7**. Treatment of the latter with caustic alkali, followed by acidification, gave good yields of the compound from which one of the hydroxymethyl groups had been removed, this reaction proceeding so smoothly that if it is desired to work with the nitroalcohol (**8**) its precursor **7** may be used with equal success in basic media.

To remove the remaining hydroxymethyl group from the nitroalcohol **8**, another route is used, consisting in the chromic acid oxidation of this function to carboxyl, followed by spontaneous loss of carbon dioxide to give the aryl-NNO-azoxynitromethane (**9**).

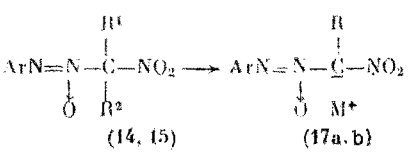
This method for the preparation of aryl-NNO-azoxy-α-nitroalkanes using an acetoxymethyl group for protection differs markedly from that described above. This is due to the fact that it is not possible to obtain diazenes (**12**) in this way, by reaction of diazonium salts with the β-nitroalkyl acetate (or 2-nitropropane-1,3-diol diacetate) in view of the instability of salts of these nitro compounds. The only step common to the two routes is oxidation of triazenes **12** to the diazene oxides **13**, although the overall sequence of the reactions will be seen from the following diagram (here and subsequently, Ar = 2,4-dinitrophenyl):



The presence of powerful electron acceptors in the ring is thus essential both for the regioselectivity of oxidation of the diazene grouping, and also for effecting the nitration stage of the hydrazines (**11**) with nitrogen tetraoxide, since otherwise concurrent nonselective nitration of the aromatic ring occurs to give a mixture of products [4].

The method used to remove the acetoxymethyl protecting groups from the diazene oxides **13** depends on their numbers. When one such group is present (**13a**, R = H), the object is attained by treatment with caustic alkali, which removes the acetyl group followed by desoxymethylation, both reactions proceeding smoothly in near-quantitative yields. In the case of the bis-analog (**13b**, R = $OCOCH_3$), this method is unsatisfactory, apparently as a result of the anion arising following removal of one acetoxymethyl group being stabilized by ejection of an acetate ion to give the highly reactive nitroolefin [ArN=N(O)C(NO_2)=CH_2], which undergoes further reactions. In the case of **13b**, therefore, the protection is removed stepwise, in acid solution (treatment of a methanol solution of **13b** with acetyl chloride) to remove the acetyl groups, the reaction stopping at the diol **15**, which like **7** on treatment with caustic alkali loses one hydroxymethyl group to give **16**. Attempts to effect a similar synthesis using the bromomethyl compounds **11a**, **12c**, and **13c** were unsuccessful as a result of the impossibility of removing the CH_2Br protecting group.

The arylazoxynitroalkanes obtained by the above methods were fully stable compounds with labile α protons (**13**, **9**, **14**, **16**), unlike the arylazonitro compounds, which isomerize to hydrazones, and display the chemical behavior expected for such nitro compounds. The presence of a reactive proton renders them (and their methylol precursors) convenient synthons for the preparation of a range of aryl-NNO-azoxy-α-nitroalkanes. In particular, they form stable salts with metals.

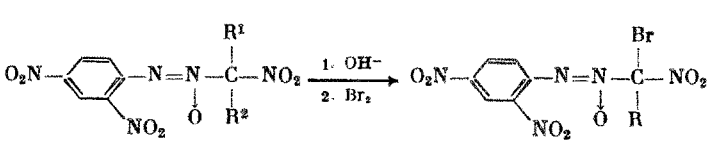


(**14**, **15**) (**17a**, **b**)

$R^1=R^2=CH_2OH$ (**15**); $R^1=H$, $R^2=CH_3$ (**14**); $R^1=H$, $R^2=CH_2OCOCH_3$ (**13**)

R=CH_2OH, M=Cs (**a**); R=CH_3, M=K (**b**)

These diazene oxides are smoothly halogenated in alkaline media to give α-halo or α,α-dihalo compounds depending on the structure of the starting material (**18**).



(**14**, **15**) (**18a**, **b**)

$R^1=H$, $R^2=CH_3$ (**14**); $R^1=R^2=CH_2OH$ (**15**). R=CH_3 (**a**), Br (**b**).

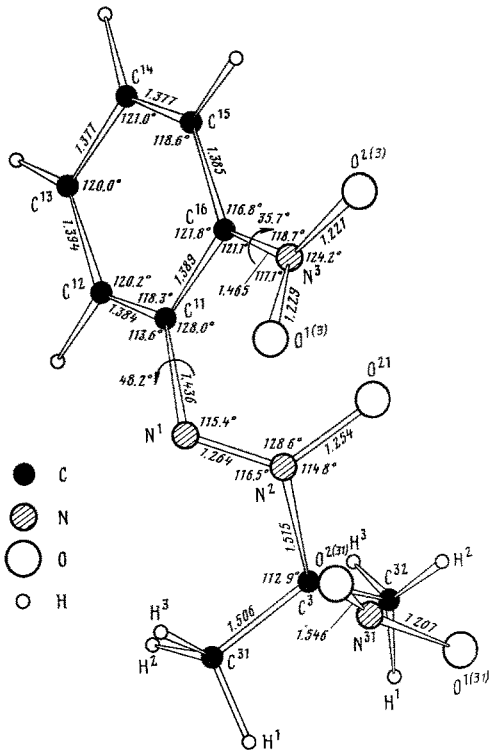
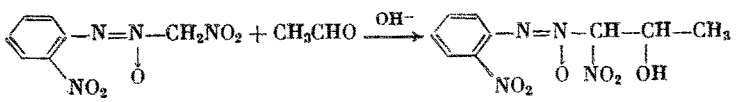


Fig. 1. Projection of the N-(1-methyl-1-nitroethyl)-N′-(2-nitrophenyl)diazene N-oxide onto the plane of the azoxy group. Angles, deg: $O^{1(31)}$-$N^{31}O^{2(31)}$ 125°C, $C^3N^{31}O^{2(31)}$ 117.4°C, $C^3N^{31}O^{1(31)}$ 117.5°C, $N^2C^3N^{31}$ 102.3°C, $N^2C^3C^{32}$ 108.2°C, $C^{31}C^3C^{32}$ 114.5°C, $N^{31}C^3C^{31}$ 107.0°C, $N^{31}C^3C^{32}$ 111.3°C; bond lengths, Å: C^3-C^{32} 1.501, $N^{31}-O^{2(31)}$ 1.207.

The compounds undergo the Henry reaction with aldehydes, which is characteristic of nitro compounds.



(9) (19)

The arylazoxynitroalkanes were all fully stable to heat. Liquids were stable on storage, and the solids even melted without decomposition.

The structures of the products were established by their elemental analyses and IR spectra (Table 3), ^1H NMR spectra (Tables 4 and 5), ^{13}C (Table 6), and ^{14}N and ^{15}N NMR spectra (including samples selectively enriched in the ^{15}N isotope, Table 7).

The location of the N-oxide oxygen was established (except for the x-ray examination of compound **1**) by heteronuclear NMR. Thus, the ^{13}C NMR spectrum of the diazepoxide **7** shows only two signals, broadened by $^{14}N-^{13}C$ interactions, for carbons bonded to oxidized nitrogen atoms (for the isomeric 2-(2-nitrophenyl-ONN-azoxy)-2-nitropropane-1,3-diol, three such broadened signals would be seen [5]). Selective suppression of the signal for the oxidized nitrogen of the diazepoxide residue at the ^{14}N frequency resulted in the appearance of a signal for the central carbon of the polynitroalkyl group. In addition, the ^{15}N NMR spectrum with selective transfer of polarization from the CH_2 protons to the ^{15}N nucleus resulted in the appearance of only two signals, namely at −8.1 (NO_2) and −52.8 ppm (=N → O), indicating removal of transfer of the CH_2 protons to three bonds of the oxidized nitrogens, which have similar $^3J_{^1H-^{15}N}$ values. In the ^{14}N NMR spectrum of compound **7**, the signals for the aromatic and aliphatic nitro groups overlap completely, so that the spectrum contains in all only two signals (at −10.9 and −53.9 ppm) with an integral intensity ratio of 2:1. Overall, these observations clearly indicate the existence of a single regioisomer of the diazene oxide **7**.

TABLE 3. Properties of Products Obtained

Compound	Yield, %	Mp, °C (solvent)	Found/calculated, %			IR spectrum (ν, cm^{-1})
			C	H	N	
2a	100	56–57 [a]	–	–	–	1560, 1535, 1450, 1390, 1355, 1320, 1200, 1155, 860, 820, 785, 755, 735, 705
2b	80	62.0–63.5 [b] (alcohol)	–	–	–	1590, 1580, 1535, 1450, 1440, 1390, 1360, 1345, 1330, 1185, 1130, 865, 840, 790, 780, 765
4a	100	Oil	–	–	–	–
4b	77	132–133 [d]	–	–	–	–
4c	–	Oil [d]	–	–	–	–
4d	79	118–121 [d]	–	–	–	–
4e	71	65–66 (50% alcohol)	–	–	–	–
5a	35	98.5–100.5 (hexane – $CHCl_3$, 3 : 1)	44.51 44.59	3.84 4.05	18.64 18.92	2880, 1540, 1380, 1170, 1120, 1090, 1050, 820, 770, 710
5b	83	87.5–89.5 (alcohol)	–	–	–	3010, 1570, 1535, 1450, 1395, 1385, 1355, 1305, 1270, 1200, 1150, 1100, 1060, 945, 830, 750
5c	67	105–106(alcohol)	47.71 48.15	4.52 4.94	17.39 17.28	2980, 2880, 1500, 1430, 1395, 1325, 1300, 1150, 1110, 1060, 960
5d	50	124–125 (hexane – $CHCl_3$, 4 : 1)	44.62 44.59	3.98 4.05	19.74 18.92	2880, 1540, 1380, 1170, 1120, 1070, 1040, 800, 780, 700
6a	75	Oil	–	–	–	2900, 1560, 1500, 1430, 1400, 1350, 1270, 1150, 1080, 1050, 860, 800, 770, 710
6b	68	91.5–94.5 (hexane)	46.09 45.88	4.50 4.71	16.30 16.47	2990, 2890, 1560, 1510, 1480, 1340, 1250, 1150, 1060
6c	70	90–92 (hexane – $CHCl_3$, 2 : 1)	42.32 42.31	3.95 3.85	17.91 17.95	2880, 1540, 1500, 1480, 1420, 1400, 1325, 1270, 1130, 1080, 1040, 845, 800, 770, 720
7	85	Oil	–	–	–	3350, 2900, 1550, 1500, 1480, 1320, 1140, 1100, 820, 730, 700
8	90	Oil	–	–	–	–
9	97	62–65 (alcohol)	–	–	–	3060, 2990, 1580, 1535, 1505, 1410, 1365, 1330, 1310, 880, 840, 790, 745, 710, 700
11a	100	123–125(alcohol)	–	–	–	3320, 3120, 3100, 1620, 1600, 1520, 1510, 1430, 1360, 1340, 1320, 1295, 1260, 1140, 1090
11b	100	114.5–115.5 (hexane – $CHCl_3$, 3 : 1)	–	–	–	3250, 3100, 1610, 1580, 1490, 1410, 1320, 1300, 1130, 1080
11c	70	104–109(alcohol)	–	–	–	3330, 3120, 3100, 1760, 1625, 1600, 1520, 1430, 1340, 1320, 1275, 1250, 1220, 1140, 1075
11d	65	86.5–88.0 (hexane – $CHCl_3$, 4 : 1)	44.09 44.07	3.92 3.95	15.87 15.82	3300, 3230, 3100, 2970, 2930, 2860, 1745, 1610, 1590, 1415, 1500, 1325, 1200, 1130, 1020
12a	84	Oil	–	–	–	3120, 1760, 1610, 1575, 1555, 1540, 1460, 1350, 1230, 1065, 920
12b	87	Oil	–	–	–	3100, 2960, 2880, 1750, 1605, 1570, 1540, 1450, 1345, 1220, 1060
12c	85	61.0–62.5 (hexane – $CHCl_3$, 4 : 1)	–	–	–	3120, 3040, 1610, 1585, 1540, 1450, 1345, 920, 860, 840, 750, 730

TABLE 3 (continued)

Compound	Yield, %	Mp, °C (solvent)	Found/Calculated, % C	H	N	IR spectrum (ν, cm^{-1})
13a	75	76.5–78.0 (hexane – CH_2Cl_2, 4 : 1)	36.75 36.97	3.03 3.08	19.46 19.61	3100, 2950, 2880, 1745, 1600, 1570, 1530, 1430, 1340, 1200, 1140, 1120, 1060, 800
13b	37	71.0–72.5 (methanol)	39.13 38.59	3.28 3.13	17.07 16.87	3100, 3020, 2960, 2920, 2880, 1755, 1600, 1580, 1530, 1500, 1445, 1370, 1345, 1215, 1050, 905, 830, 750, 735
13c	80	94–96 (alcohol – $CHCl_3$, 5 : 1)	28.50 28.60	2.09 2.12	18.12 18.52	3120, 3065, 3000, 1610, 1590, 1540, 1460, 1395, 1350, 1215, 1070, 925, 860, 840
14	86	Oil	–	–	–	3100, 3015, 2970, 1600, 1575, 1530, 1510, 1440, 1385, 1340, 1060, 830, 750, 730, 715
15	100	86.5–87.5 (hexane – $CHCl_3$, 3 : 2)	32.76 32.63	2.69 2.72	20.52 21.14	3300, 3100, 1600, 1580, 1520, 1495, 1450, 1340, 1245, 1070, 1030
16	79	Oil	–	–	–	3600–3300, 3100, 1600, 1575, 1525, 1345, 1060, 915, 825, 740, 720
18a	55	Oil	–	–	–	3100, 3015, 2970, 1600, 1575, 1530, 1510, 1440, 1385, 1340, 1060, 830, 750, 730, 715
18b	68	89–92	19.76 19.58	0.64 0.70	15.82 16.32	3100, 2590, 1485, 1330, 1060, 890, 845, 820, 790, 715
19	60	Oil	–	–	–	3600–3300, 3100, 1560, 1510, 1485, 1390, 1375, 1330, 1240, 1100

[a]Cf. [1]; 58.5-59.5.
[b]Cf. [2]; 52-54.
[c]Cf. [9] [sic].
[d]Cf. [7].
[e]Cf. [8] [sic].

EXPERIMENTAL

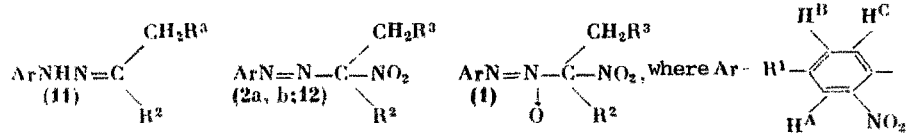
^{1}H NMR spectra were obtained on Tesla BS-467, Bruker WM-250, or Bruker AM-300 instruments, operating frequencies 60, 250, and 300 MHz, respectively, in solution in $CDCl_3$, $(CD_3)_2CO$, or $(CD_3)_2SO$, with the chemical shifts being measured relative to HMDS; the ^{13}C (75.5 MHz), ^{14}N (27.7 MHz), and ^{15}N (30.42 MHz) spectra being obtained on the Bruker AM-300 instrument. The ^{15}N NMR spectra were recorded using multi-impulse sequences of SPT and INEPT [6]. The chemical shifts for the ^{14}N and ^{15}N NMR spectra (δ, ppm from $MeNO_2$ as external standard) are given without correction for diamagnetic susceptibility. IR spectra were obtained on UR-20 on Specord IR instruments in KBr disks in the case of solids, or in the absence of a solvent in the case of liquids.

X-ray crystal analysis was carried out on a Hilger automatic four-circle diffractometer using λ_{Mo} monochromatic radiation. The crystals of **1** were monoclinic, space group $P2_{1/n}$, a = 11.358(3), b = 6.228(3), c = 16.179(2) Å, β = 97.9(5)°, U = 1133.5(6) Å^3, Z = 4, ρ = 1.49 g/cm^3. There were 1983 reflections in all, of which 1136 (57.3%) had intensities $J > 3\sigma$ (obtained at 2θ = 60°). Structure calculations, refinement of positional and anisotropic thermal parameters, and geometric calculations were carried out using the EXTL and XTL suites of programs to a final R value of 0.052. Bond lengths and valence angles are shown in Fig. 1, and the intramolecular nonvalent distances in Table 1. Anisotropic thermal parameters and atom coordinates are shown in Table 2.

Column chromatography (CC) and TLC were carried out using Silpearl UV-254 (with a luminophore for TLC). Melting points were measured on a Kofler block. The IR spectral data, elemental analyses, and product yields are given in Table 3, and the ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectral data in Tables 4-7.

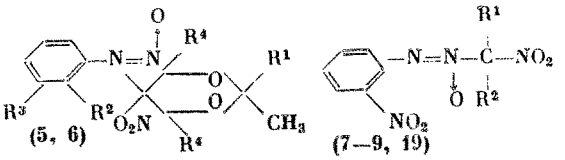
Preparation of 1,1-Dinitro-1-(2-nitrophenylazo)ethane (2b). A suspension of 3.45 g of 2-nitroaniline in 12.5 ml of concentrated HCl and 25 ml of water was diazotized at 0 to +2°C with a solution of 1.77 g of sodium nitrite in 10 ml of water, until a positive reaction was obtained with starch–iodine paper, followed by dropwise addition at the same temperature of a solution of 3 g of 1,1-dinitroethane in a mixture of 3.6 ml of 25% ammonia solution and 10 ml of water, basified with 25%

TABLE 4. ^{1}H NMR Data of **1** and **13-18** [solutions in $CHCl_3$, $CDCl_3$, CH_2Cl_2, $(CD_3)_2CO$, δ, ppm from HMDS, J, Hz)



Compound	R^1	R^2	R^3	C—CH_3	H_A	H_B	H_C	J_{AB}	J_{BC}	Others
1	NO_2	CH_3	H	2.20 s	8.92 m	8.57 m	7.85 m	–	–	–
2a	NO_2	CH_3	H	1.89 s	8.85 d	8.51 d.d	7.47 d	2.7	8.7	–
2b	H	NO_2	H	2.45 s	–	–	–	–	–	7.75m
11a	NO_2	CH_2Br	H	2.14s	8.92 d	8.20 d.d	7.83 d	2.7	10.0	4.13s
11b	NO_2	CH_2Br	Br	–	9.04 d	8.30 d.d	7.82 d	2.7	10.0	4.10s ; 4.22 s
11c	NO_2	CH_2OCOCH_3	H	2.04 s 2.08 s	8.94 d	8.19 d.d	7.78 d	2.7	10.0	2.08s /2.04 s; 4.72s
11d	NO_2	CH_2OCOCH_3	$OCOCH_3$	2.02 s 2.08 s	8.91 d	8.26 d.d	7.84 d	2.5	10.0	4.78 s; 4.84 s
12a	NO_2	CH_2OCOCH_3	H	1.90 s	8.92 d	8.65 d.d	7.58 d	2.7	9.3	2.02 s; 4.60 s
12b	NO_2	CH_2OCOCH_3	$OCOCH_3$	2.03 s (6H)	8.13 d	7.84 d.d	6.77 d	2.3	9.0	4.86 d.d (J=11.5)
12c	NO_2	CH_2Br	H	2.00 s	8.99 s	8.56 d	7.54 d	–	10.0	4.08 s
13a	NO_2	CH_2OCOCH_3	H	2.25 s	8.84 d	8.42 d.d	7.59 d	2.0	9.0	2.08 s; 4.96 s
13b	NO_2	CH_2OCOCH_3	$OCOCH_3$	2.1 s (6H)	8.84 d.d	8.54 d.d	7.63 d	1.95	7.8	5.05 s (4H)
13c	NO_2	CH_2Br	H	2.36 s	8.94 d	8.54 d.d	7.67 d	2.7	9.3	4.32 s
14	NO_2	H	H	2.20 (J=6.7)	8.86 d	8.56 d.d	7.65 d	2.0	8.7	6.52 q (J=6.7)
15	NO_2	CH_2OH	OH	–	8.79 a	8.56 d.d	7.78 d	2.0	9.3	4.55 s (4H); 4.92 s (2H)
16	NO_2	H	CH_2OH	–	8.73 d	8.51 d.d	7.71 d	2.5	8.7	6.75 t (J=6.4) 4.47 m
18a	NO_2	Br	H	2.82 s	8.94 d	8.55d.d	7.67 d	2.3	8.2	–
18b	NO_2	Br	CH_2R^3=Br	–	9.08 d	8.70d.d	7.81 d	2.7	9.3	–

TABLE 5. ^{1}H NMR Spectral Data



Compound	R¹	R²	R³	R⁴*	CH₃	CH₂O, —CHO, —O—CH—O	Ph
5a	H	H	NO_2	H	1.33d	5.00–4.15 m	8.51 s, 8.45–7.90 m, 7.80–7.40 m
5b	CH_3	NO_2	H	H	1.38 s 1.49 s	4.57 m	8.00–7.00 m
5c	H	NO_2	H	CH_3	1.28 d (J=5) 1.28 d (J=16)	4.54–5.48 m	8.29–7.38 m
5d	H	NO_2	H	H	1.26 d	4.93 t, 4.50 s	8.20–7.00 m
6a †	H	H	NO_2	H			
Distal					1.39 d (J=18)	5.31 m, 4.92 m	9.09 m, 8.58 m
Proximal					1.37 d (J=18)	4.77 m, 4.47 m	7.79 m, 9.03 m 8.35 m, 7.70 m
6b	H	NO_2	H	CH_3	1.41 m	5.35–4.45 m	8.22–7.13 m
6c	H	NO_2	H	H	1.37 d 1.39 d	5.20–3.73 m	8.16–7.00 m
7	CH_2OH	CH_2OH	–	–	–	5.19 s (1H) 4.63 s (2H)	8.07 m, 7.80 m 7.76–7.55 m
8	CH_2OH	H	–	–	–	6.83 t (1H) 4.55 d (2H) 4.37 s (1H)	8.1 m, 7.98 m 7.85–7.37 m
9	H	H	–	–	–	6.33 s (2H)	8.15–7.10 m
19	$CHCH_3$ OH	H	–	–	1.43 d (J=6)	6.25 m (J=2.5) 4.40–5.10 m (1H) 3.44 m (1H)	(5H) 7.30–8.13

*Substituents in the 4 and 6 positions of the 1,3-dioxane ring.

†Mixture of regioisomers (~ 1:2).

TABLE 6. ^{13}C NMR Spectral Data

Compound	Solvent	$CH_2/CH_2O(CH_2Br)$	CN_2	Ar
2d	$CDCl_3$	23.3	109.2	150.6(C^1), 122.8(C^2, C^6), 129.0(C^3, C^5), 132.0(C^4, ^1J=161.1, ^3J=7.2)
2a	$CDCl_3$	22.8	109.5 (^2J_m=4.6)	144.0(C^1, $^3J_{tr}$=6.5), 145.5(C^2, $^3J_{tr}$=7.4), 124.0(C^3), 131.2(C^4), 133.5(C^5), 118.4(C^6)
1	$CDCl_3$	24.3 ^1J=133.2 ^3J=2.8	112.4	137.0(C^1, $^3J_{tr}$=6.5) 142.2(C^2), 123.8(C^3), 128.7(C^4), 134.0(C^5), 124.6(C^6)
7	$(CD_3)_2CO$	61.4	114.5	137.0(C^1), 144.6(C^2), 134.9(C^3), 125.5(C^4), 125.1(C^5), 130.8(C^6)
13c	DMSO-d_6	21.6/31.0	127.0	138.6(C^1, $^3J_{tr}$=7.8), 142.5(C^2), 121.0(C^3), 147.4(C^4), 129.4(C^5), 125.4(C^6)
13d	DMSO-d_6	23.8	113.5	141.1(C^1, $^3J_{tr}$=7.8), 141.7(C^2), 120.5(C^3), 146.4(C^4), 129.0(C^5), 125.9(C^6)

TABLE 7. ^{15}N and ^{14}N NMR Spectral Data ($\delta^{15}N$, ±0.05 ppm from $MeNO_2$ as external standard)

Compound	Solvent	N^1	N^2	NO_2 aliphatic	NO_2 aromatic
2d [1]	$CDCl_3$	−25.3 and	−28.9 [2]	+11.0	–
2a	CCl_4	−26.4	−40.5	+9.9	−12.9
2a [3]	$CDCl_3$	−26.7	−40.6	+9.9	−13.0
1	$CDCl_3$	−48.9	−45.1	−0.3	−12.3
1	$CDCl_3$	−48.9	−45.1	4)	−12.4
	DMSO-d_6	−48.9	−44.2	+0.2	−11.4
13d	DMSO-d_6	−52.5	−41.2	−0.6	−16.8
					−17.4
6a [5,6]	$CDCl_3$	–	−47.5 (200) [7]	−12.08 (240) [7]	
		−63.4 (150) [7]			
7	$(CD_3)_2CO$	–	−52.8	−8.05	
				−10.9 [6] (164) [7]	
				−53.9 [6] (110) [7]	

[1]Synthesized from phenyldiazonium chloride and 2-nitropropane.

[2]Not assigned.

[3]Content of ^{15}N selectively increased to 12%, as described in [10].

[4]Not seen as a result of the low signal/noise ratio for the sample unenriched in ^{15}N. (Does not appear in the Russian original.)

[5]Mixture of distal and proximal regioisomers (~ 1:2).

[6]^{14}N NMR spectrum.

[7]Signal breadth and 1/2 height (Hz).

aqueous NaOH to pH 6, filtered, and the solid washed with water and recrystallized from alcohol. Compounds **2a** and **5** were obtained similarly.

Preparation of (5-nitro-1,3-dioxan-5-yl)methanols (4) was carried out from 2-nitropropane-1,2,3-triol (NPT) in the presence of BF_3 etherate with an excess of acetone, from NPT and benzaldehyde or paraldehyde in the presence of catalytic amounts of concentrated sulfuric acid [7], or by briefly boiling NPT with paraform in acetonitrile in the presence of BF_3 etherate. 2,4,6-Trimethyl-5-nitro-1,3-dioxane **4e** was obtained by boiling 3-nitropentane-2,4-diol with acetaldehyde or paraldehyde in benzene in the presence of catalytic amounts of concentrated sulfuric acid for 30 min.

Preparation of Sodium Salts of 5-Nitro-1,3-dioxanes (Na-4). To a solution of sodium ethoxide obtained by dissolving 2.4 g of metallic sodium in 55 ml of absolute alcohol, was added all at once a hot solution of **4d** in 65 ml of absolute alcohol. The solution was cooled to ~20°C, and the salt which separated was filtered off, washed on the filter with 150 ml of ether, and air-dried to give 18.94 g (98.5%) of Na-**4d**. The other Na-**4** were obtained similarly.

Preparation of 2-Methyl-5-nitro-5-(2-nitrophenylazoxy)-1,3-dioxanes (6). To an emulsion of 6.0 ml of 88% H_2O_2 in 300 ml of dry dichloromethane at 5-10°C was added dropwise 31 ml of trifluoroacetic anhydride, followed at 10-15°C by a solution of 4.7 g the diazene **5d** ($R^1 = R^3 = H$, $R^2 = NO_2$, $R^3 = Me$) in 30 ml of dry dichloromethane. The mixture was boiled under reflux for 3 h, poured onto ice, and washed cautiously with saturated $NaHCO_3$ solution to give 4.13 g of crystalline **6c**, which was further purified by crystallization. The remaining diazene oxides **6** were obtained similarly, as were **13a, b** and the diazene oxide **13c** obtained from α-bromoacetone.

Preparation of 2-Nitro-2-(2-nitrophenyl-NNO-azoxy)propane-1,3-diol (7). To a solution of 4.13 g of dioxane **6c** in 300 ml of methanol was added dropwise 20 ml of acetyl chloride. The mixture was boiled under reflux for 10 h, evaporated, applied to a column of silica gel 40/100, height 4-5 cm on a glass filter, washed with benzene to remove 0.6 g of unreacted **6c**, followed by ethyl acetate to give 3.22 g of product **7**. The diazene oxide **15** was obtained similarly, into which the precursor **13b** was converted completely on treatment with acetyl chloride and methanol.

Preparation of 2-Nitro-2-(2-nitrophenyl-NNO-azoxy)ethanol (8). A solution of 0.78 g of the diol **7** in the minimum amount of methanol or acetone was added to ~ 150 ml of water, a concentrated aqueous solution of 2 g of KOH added dropwise, acidified with 50% sulfuric acid, and this procedure repeated twice more, followed by extraction with ether to give 0.63 g of nearly pure **8** as an oil which was free from contamination with the starting material **7**.

Preparation of Nitro-(2-nitrophenyl-NNO-azoxy)methane (9). To a solution of 0.28 g of **8** in 2 ml of ether or dichloromethane was added a solution of 0.56 g of sodium dichromate in 0.6 ml of water, followed by the dropwise addition with stirring and cooling of 0.55 ml of concentrated sulfuric acid in 0.33 ml of water. After 5 h at ~20°C, extraction with ether or dichloromethane gave 0.24 g of **9** as a yellow oil which decomposed on attempting TLC on silica gel.

Preparation of Mono- and Dibromoacetone 2,4-Dinitrophenylhydrazones (11a, b). A solution of 3 g of 2,4-dinitrophenylhydrazine and 3 g of α,α-dibromoacetone was boiled in ethyl acetate for 30 min, then the mixture was evaporated to give 6 g of **11b**. Compound **11a** was obtained similarly.

Preparation of α,α-Diacetoxyacetone 2,4-Dinitrophenylhydrazone (11d). A mixture of 2.7 g of **11b**, 1.5 g of fused potassium acetate, and 0.22 g of 18-crown-6 was boiled for 2 h in chloroform, then stirred for ~18 h at ~20°C, filtered, the filtrate evaporated, the residue extracted with ether until it was no longer decolorized, then subjected to CC under pressure (eluent benzene–ethyl acetate 4:1 by volume) to give 1.56 g of **11d**. Similarly, from the monobromide **11a** there was obtained the acetoxyhydrazone **1c**.

Preparation of 1,3-Diacetoxy-2-nitro-(2,4-dinitrophenylazo)propane (12b, R = $OCOCH_3$). To a solution of 3.4 g of the hydrazone **11d** (3.4 g) in 20 ml of dry dichloromethane was added dropwise at 10-15°C a solution of 4.2 g of N_2O_4 in 20 ml of dichloromethane, and the mixture stirred for 30 min at ~20°C. It was then washed with 10% aqueous sodium carbonate, and the organic layer dried over $MgSO_4$. Removal of the solvent followed by CC gave 3.32 g of dark red oil (**12b**). Obtained similarly was **12a** (R = H), and the diazene from the bromoacetone **12c**.

Preparation of 1-Nitro-(2,4-dinitrophenyl-NNO-azoxy)ethane (14) from Its Potassium Salt (16a, M = K). To a solution of 0.3 g of **13a** (R = H) in 3 ml of methanol was added dropwise at −15 to 10°C with stirring a solution of 0.1 g of KOH in 2 ml of methanol. The resulting suspension of the salt **16a** which separated was stirred for a further 10-15 min without further cooling, then poured into three times its volume of water, and acidified at ~0°C with 5% aqueous sulfuric acid to pH 3-4, then extracted with ethyl acetate or dichloromethane to give **14** as a yellow oil which crystallized.

Preparation of 2-Nitro-(2,4-dinitrophenyl-NNO-azoxy)ethanol (16) and Its Cesium Salt (17b). A solution of 0.2 g of **15** in 2 ml of alcohol at ~0°C was treated dropwise with a solution of 0.09 g of CsOH in 1 ml of ethanol, and the mixture filtered to give 0.11 g of the dark red salt **17b**, which on treatment with dry hydrogen chloride gave 0.06 g of **16** as a yellow oil, which decomposed slowly on storage at ~20°C.

Preparation of α-Halodi Derivatives of Nitro-(nitrophenyl-NNO-azoxy)methane (18). An aqueous-ethereal emulsion of the compounds **9, 14, 7,** or **15** was treated with excess caustic alkali or sodium carbonate; then an excess of halogen was added, and the product (**18a** or **18b**) extracted with ether.

Preparation of 2-Nitro-(2-nitrophenyl-NNO-azoxy)propan-2-ol (19). To a solution of 0.54 g of **9** in a mixture of 4 ml of alcohol and 4 ml of ether was added at 0-5°C 0.2 ml of acetaldehyde, followed by slow dropwise addition of a solution of 0.10 g of NaOH in 0.20 ml of water. After stirring for a further 1 h at ~20°C the mixture was decomposed by adding ~20 ml of water, acidified with an equimolar amount of acetic acid, and the product **19** (0.39 g) isolated by TLC after extraction with ether.

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