ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 1, pp. 87–99. © Pleiades Publishing, Inc., 2006.
Original Russian Text © R.A. Gazzaeva, A.N. Fedotov, E.V. Trofimova, O.A. Popova, S.S. Mochalov, N.S.Zefirov, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 1, pp. 94–106.

Synthesis of *o*-Nitrosoacylbenzenes from *o*-Nitrobenzyl Alcohols and Their Derivatives

R. A. Gazzaeva[1], A. N. Fedotov[2], E. V. Trofimova[2], O. A. Popova[1], S. S. Mochalov[2], and N. S. Zefirov[2]

[1] *Khetagurov North Osetian State University, Vladikavkaz, North Osetia, Russia*

[2] *Faculty of Chemistry, Lomonosov Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia*
e-mail: ssmoch@org.chem.msu.ru

Received November 12, 2004

Abstract—Nitration of substituted benzyl alcohols, as well as ethers and esters derived therefrom, with nitric acid in acetic anhydride was studied. The corresponding *o*-nitrobenzyl alcohols and their derivatives formed as the primary products are capable of being converted into *o*-nitrosoacylbenzenes by the action of acids.

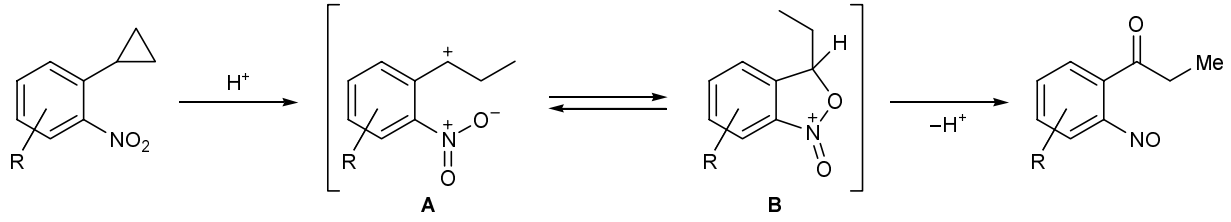
DOI: 10.1134/S1070428006010143

The presence in *o*-nitrosoacylbenzene molecules of spatially close nitroso and acyl groups capable of undergoing versatile transformations by the action of various reagents makes these compounds promising as synthons for preparation of difficultly accessible and practically important organic substances. For example, they can be converted into a variety of nitrogen- and oxygen-containing heterocyclic systems [1] whose synthesis by other methods is either difficult or impossible. On the other hand, extensive application of *o*-nitrosoacylbenzenes is limited because of the lack of general methods for their synthesis. Up to now, only one known procedure ensures preparation of a large number of *o*-nitrosoacybenzenes in high yields, namely acid-catalyzed rearrangement of *o*-nitrophenylcyclopropanes [2] (Scheme 1). This procedure is applicable to the synthesis of *o*-nitrosoacylbenzenes having various substituents in the benzene ring, but variations in the acyl group are in fact limited to propionyl fragment.

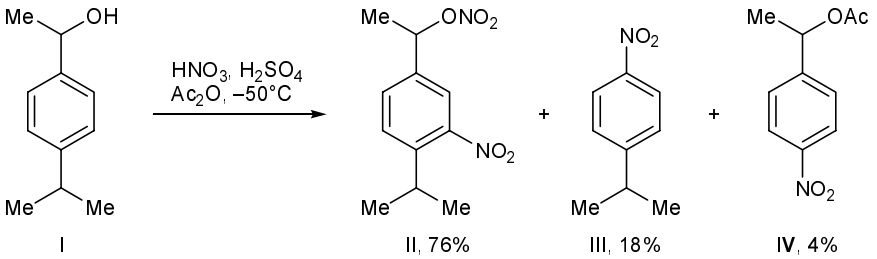
The key intermediates in the transformations of *o*-nitrophenylcyclopropanes into *o*-nitrosoacylbenzenes are benzyl type cations **A** and cyclic ions **B** derived therefrom via intramolecular stabilization involving the *ortho*-nitro group (Scheme 1). We presumed that analogous transformations into *o*-nitrosoacylbenzenes may be performed with aromatic nitro compounds having *ortho*-substituents capable of generating benzyl-like cations. Therefore, we tried to synthesize substituted *o*-nitrosoacylbenzenes from the corresponding *o*-nitrobenzyl alcohols and their ethers and esters.

It should be noted that only a few published data are available on *o*-nitrobenzyl alcohols. Their synthesis by nitration of 1-phenylalkanols was studied very poorly. Probably, Bak and Smallringe [3] were the only authors who showed that the reaction of unsubstituted benzyl alcohol with N_2O_5 in methylene chloride in the presence of a catalytic amount of tris(acetylacetonato)-iron(III) gives a mixture of *o*- and *p*-nitrobenzyl alcohols at a ratio of 1 : 2. Taking the above stated into account, the synthesis of *o*-nitrobenzyl alcohols and their ethers (esters) was a separate problem. Therefore, we examined the nitration of a series of substituted benzyl alcohols with nitric acid in acetic anhydride.

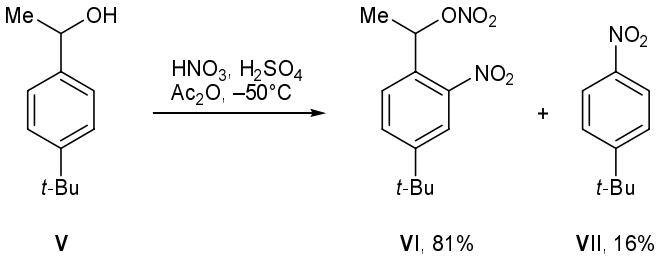
Scheme 1.



Scheme 2.



Scheme 3.

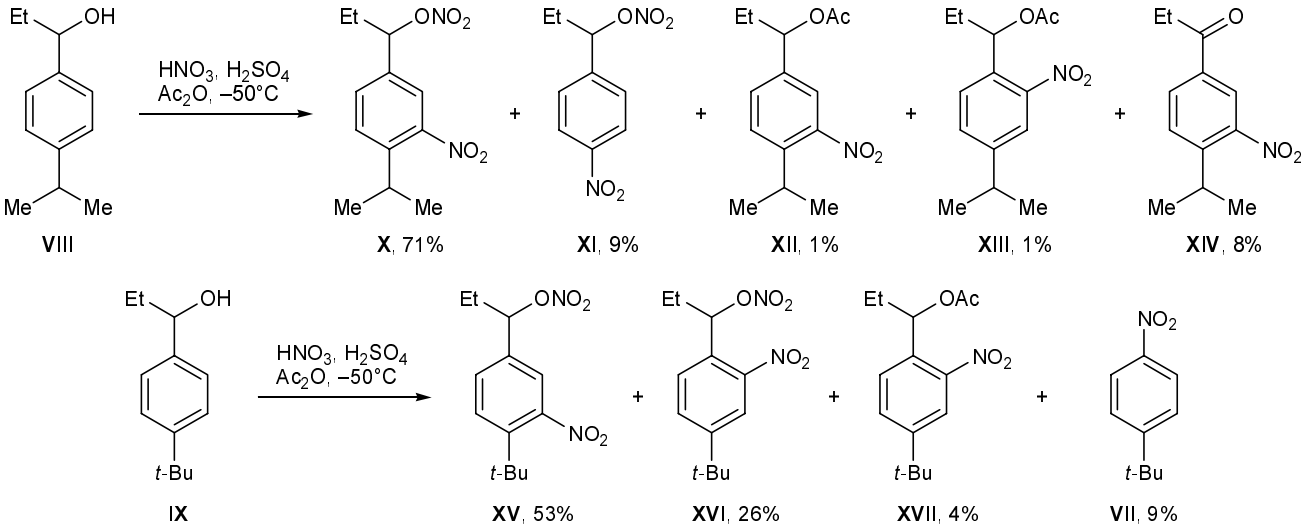


Insofar as hydroxymethyl group is generally believed [3, 4] to favor substitution at the *ortho* and *para* positions in reactions of aromatic compounds with electrophiles, we tried to enhance nitration at the *ortho* position via introduction of bulky substituents into the *para* position.

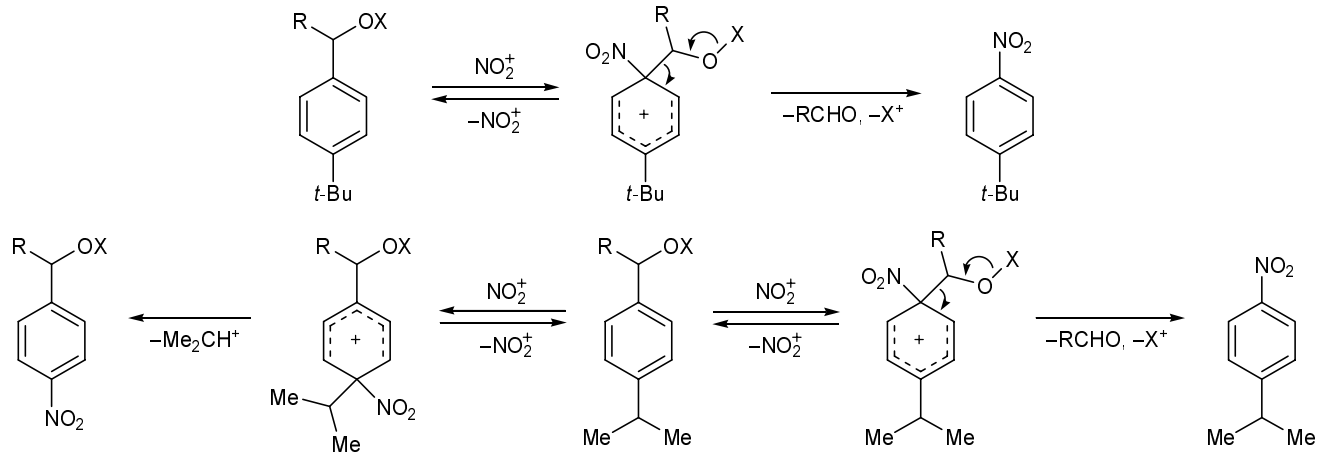
Substituted benzyl alcohols were nitrated with nitric acid in acetic anhydride in the presence of concentrated sulfuric acid under the conditions described previously for the nitration of 1-phenylethyl [5] and 1-phenylpropyl acetates [6]. The only difference was that the reactions were performed at –50°C rather than at 20°C. We found that even at such a low temperature all the examined benzyl alcohols underwent esterification and that the site of substitution in the aromatic ring was determined by the nature of the substituent at the benzylic carbon atom.

The nitration of 1-(4-isopropylphenyl)ethanol (**I**) led to formation of a mixture of products, the major of which was 1-(3-nitro-4-isopropylphenyl)ethyl nitrate (**II**) rather than the expected 2-nitro derivative (Scheme 2). Unlike alcohol **I**, 1-(4-*tert*-butylphenyl)-ethanol (**V**) under the same conditions was converted mainly into 1-(2-nitro-4-*tert*-butylphenyl)ethyl acetate (**VI**) (Scheme 3). Presumably, the observed difference in the orientation of nitro group in the nitration of alcohols **I** and **V** is determined by the nature of primary esterification product (nitrate in the case of

Scheme 4.



Scheme 5.



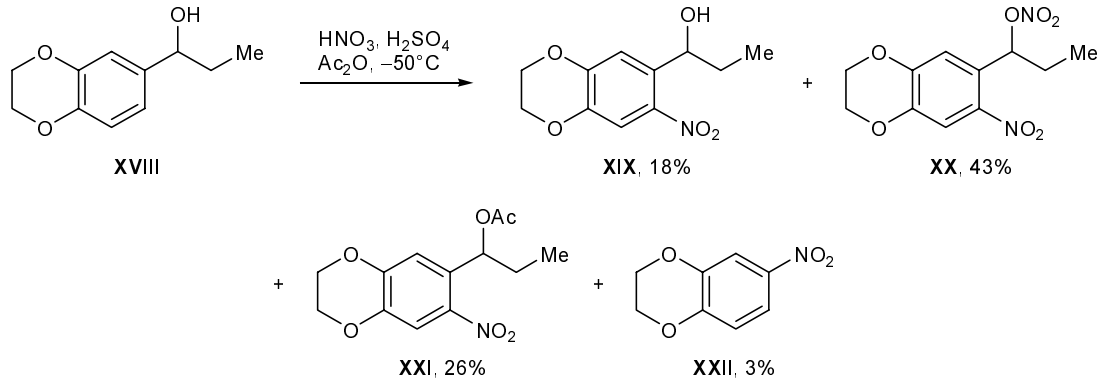
X = H, Ac, NO_2.

alcohol **I** and acetate in the reaction with **V**). The nitrate fragment guides the entering electrophile to the *meta* position, whereas the acetate moiety, to the *ortho* position. This assumption was confirmed by the results of nitration of 1-(4-isopropylphenyl)propan-1-ol (**VIII**) and 1-(4-*tert*-butylphenyl)propan-1-ol (**IX**) which are homologous to **I** and **V**, respectively. In both cases, the major nitration products were *meta*-nitro-substituted nitrates **X** and **XV** (Scheme 4), despite the fact that introduction of a nitro group to the *ortho* position with respect to the alkyl group is hindered for steric reasons. Nevertheless, 2-nitro-substituted nitrate **XVI** was obtained from *tert*-butyl derivative **IX**, though the overall *meta*/*ortho* isomer ratio (2:1) was in favor of the *meta*-nitro isomer.

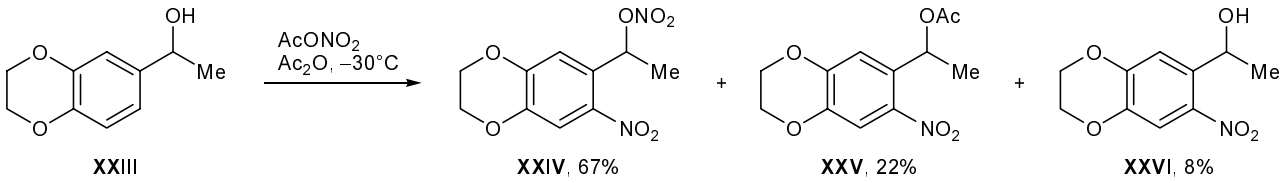
It should be emphasized that the nitration of alcohols **I**, **V**, **VIII**, and **IX**, apart from esterification and classical aromatic electrophilic substitution, was accompanied by nitrodealkylation. In the reactions with *tert*-butyl-substituted alcohols **V** and **IX** only the hydroxyalkyl (or acyloxyalkyl) group was replaced, while 4-isopropyl derivatives **I** and **VIII** gave rise to products of replacement of both hydroxy(acyloxy)alkyl and isopropyl groups (Scheme 5). Under analogous conditions, the nitration of 1-(3,4-ethylenedioxyphenyl)propan-1-ol (**XVIII**) was also accompanied by esterification, but the products were only 2-nitro-substituted derivatives, replacement of the oxypropyl fragment almost did not occur, and a small amount of unesterified nitro derivative was formed (Scheme 6).

Alcohol **XVIII** is more activated to electrophilic substitution, as compared to compounds **I**, **V**, **VIII**, and **IX**. The nitration of **XVIII** with acetyl nitrate in acetic anhydride in the absence of sulfuric acid gave rise to the same products, but one of these strongly prevailed (**XIX**, 4.7%; **XX**, 79%; **XXI**, 7%). Likewise, the nitration of 1-(3,4-ethylenedioxyphenyl)ethanol (**XXIII**) (which is homologous to **XVIII**) with acetyl nitrate afforded a mixture of *o*-nitro derivatives **XXIV** (67%), **XXV** (22%), and **XXVI** (8%) (Scheme 7). Raising the nitrating agent-to-substrate molar ratio to 6:1 in the reactions of alcohols **XVIII** and **XXIII** with

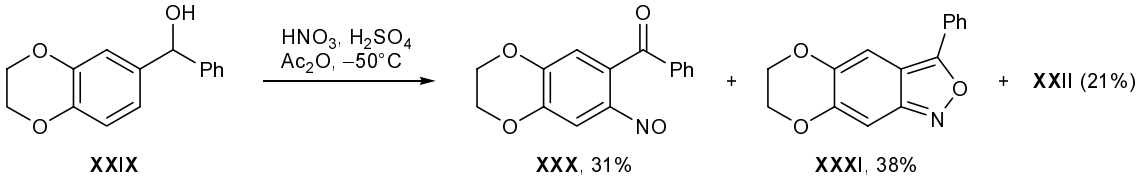
Scheme 6.



Scheme 7.



Scheme 8.



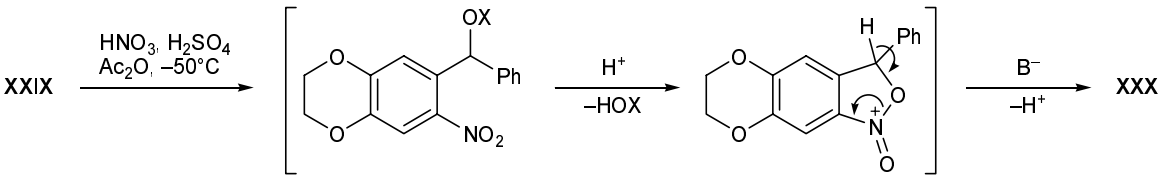
acetyl nitrate in acetic anhydride led to formation of only the corresponding 2-nitro- and 2,3-dinitro-substituted nitrates **XX**, **XXVII** and **XXIV**, **XXVIII**, respectively (see Experimental).

By nitration of 3,4-ethylenedioxyphenyl(phenyl)-methanol (**XXIX**) under the same conditions as in the reactions with alcohols **I**, **V**, **VIII**, **IX** we obtained 2-nitroso-4,5-ethylenedioxybenzophenone (**XXX**) and 5,6-ethylenedioxy-2,1-benzisoxazole (**XXXI**) instead of expected products of esterification and replacement at the aromatic ring. In addition, an appreciable amount of compound **XXII** was formed due to replacement of the hydroxybenzyl group in **XXIX** by nitro (Scheme 8).

The formation of nitroso derivative **XXX** and benzisoxazole **XXXI** in the nitration of alcohol **XXIX** is possible only when the primary esterification and electrophilic substitution products undergo acid-catalyzed rearrangement as shown in Scheme 9. These results indirectly support our assumption that *o*-nitrobenzyl alcohols and their esters are really capable of being converted into the corresponding *o*-nitrosoacylbenzenes. A relatively high yield of *ipso*-substitution product in the nitration with alcohol **XXIX** should be noted. Obviously, this reaction pathway is favored by elimination of benzaldehyde as departing group (Scheme 10).

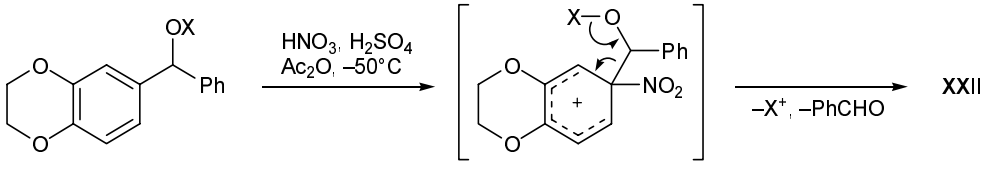
Thus the nitration of benzyl alcohols **I**, **V**, **VIII**, **IX**, **XVIII**, and **XXIII** gives rise to complex mixtures of products due to different orientations of the nitro group entering the benzene ring, different sites of *ipso* substitution, and formation of two types of esters, nitrates and acetates. Therefore, we made an attempt to enhance the reaction selectivity by excluding the latter pathway. For this purpose, we examined nitration of the corresponding benzyl acetates. No transesterification occurred in the reactions of benzyl acetates **XXXII**, **XXXIII**, and **XXXVI**–**XXXVIII** with nitric

Scheme 9.



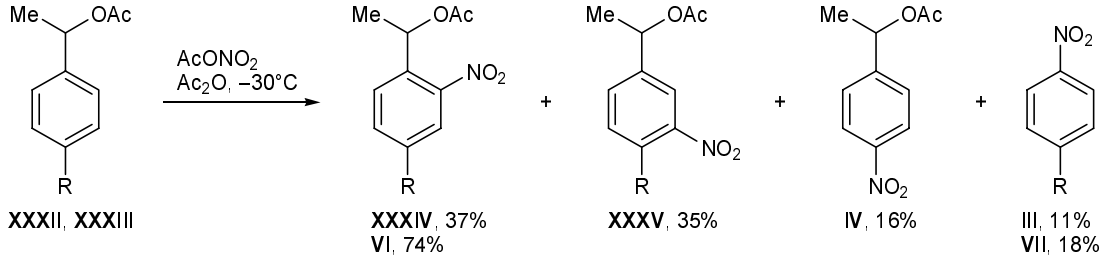
X = H, Ac, NO_2.

Scheme 10.

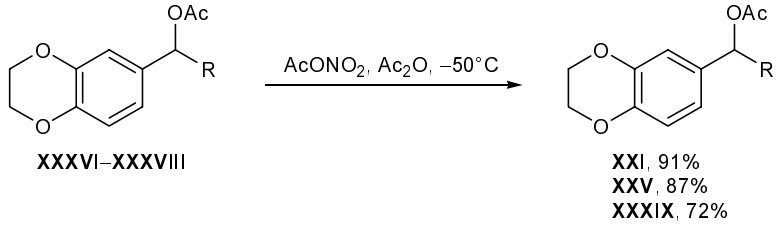


X = H, Ac, NO_2.

Scheme 11.



III, **XXXII**, **XXXIV**, **XXXV**, R = *i*-Pr; **VI**, **VII**, **XXXIII**, R = *t*-Bu.



XXV, **XXXVI**, R = Me; **XXI**, **XXXVII**, R = Et; **XXXVIII**, **XXXIX**, R = Ph.

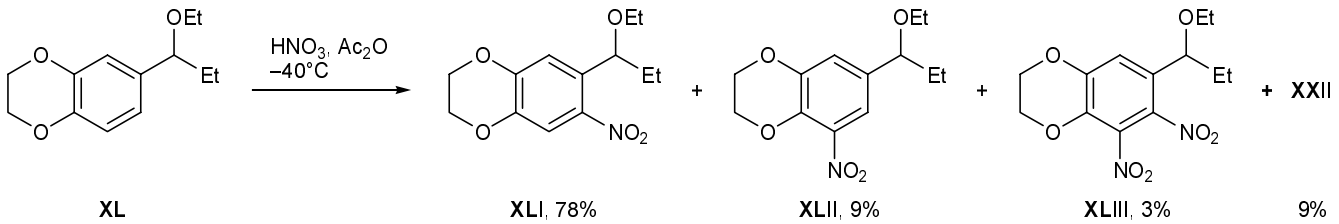
acid in acetic anhydride at –30 to –50°C: the products were the corresponding nitrobenzyl acetates, and in some cases, *ipso*-substitution products were isolated (Scheme 11).

The nitration of ethyl ether **XL** under analogous conditions was less selective. In this case, the major product was 1-ethoxy-1-(4,5-ethylenedioxy-2-nitrophenyl)propane (**XLI**, 78%), but isomeric *m*-nitro derivative **XLII** and dinitro compound **XLIII** were also formed. Moreover, even the ethoxypropyl group in initial ether **XL** was partially replaced to produce 9% of compound **XXII** (Scheme 12). Our results suggest that regioselective synthesis of 2-nitrobenzyl alcohols by the action of nitric acid in acetic anhydride is possible only with the use of preliminarily esterified benzyl alcohols (or the corresponding ethers).

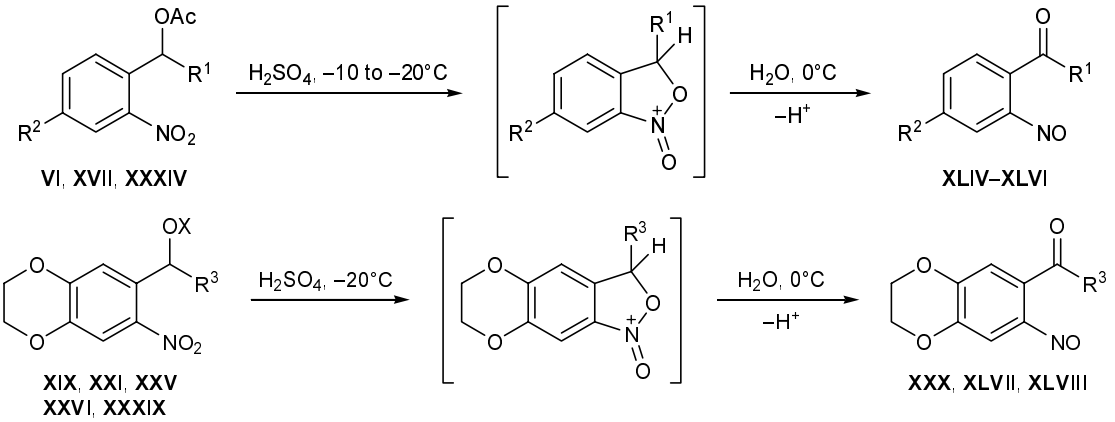
We also succeeded in demonstrating that 2-nitrobenzyl alcohols, as well as nitrates, acetates, or ethers derived therefrom, are capable of undergoing acid-catalyzed rearrangement into the corresponding *o*-nitrosoacylbenzenes (Schemes 13, 14). The rearrangement of *o*-nitrobenzyl alcohols, *o*-nitrobenzyl acetates, and *o*-nitrobenzyl ethers occurred without difficulties, whereas transformations of *o*-nitrobenzyl nitrates, at least of those derived from ethylenedioxybenzyl alcohols, under similar conditions were not selective. For example, 1-(4,5-ethylenedioxy-2-nitrophenyl)ethyl nitrate (**XXIV**) and 1-(4,5-ethylenedioxy-2-nitrophenyl)propyl nitrate (**XX**), apart from nitroso derivatives **XLVII** and **XLVIII**, afforded 1-(4,5-ethylenedioxy-3-nitro-2-nitrosophenyl)ethanone (**XLIX**) and 1-(4,5-ethylenedioxy-3-nitro-2-nitrosophenyl)propan-1-one (**L**), respectively, and the fraction of the latter was approximately twice as high as that of **XLVII** and **XLVIII** (Scheme 14).

The target *o*-nitrosoacylbenzenes were formed only at the stage of treatment of intermediate cyclic cations like **C** and **C'** (Scheme 14) with ice water. Presumably, in the transformations of nitrobenzyl nitrates **XX** and **XXIV**, the nitrating species is nitric acid liberated during the process via elimination of NO_3^- from the benzylic position by the action of sulfuric acid, and electrophilic nitration involves cyclic ions like **C**. Cationic intermediates **C'** thus formed are likely to be

Scheme 12.



Scheme 13.



XXXIV, **XLIV**, R^1 = Me, R^2 = *i*-Pr; **VI**, **XLV**, R^1 = Me, R^2 = *t*-Bu; **XVII**, **XLVI**, R^1 = Et, R^2 = *t*-Bu; **XXV**, **XXVI**, **XLVII**, R^3 = Me; **XIX**, **XXI**, **XLVIII**, R^3 = Et; **XXX**, **XXXIX**, R^3 = Ph; **XIX**, **XXVI**, X = H; **XXI**, **XXV**, **XXXIX**; X = Ac.

responsible for the formation of nitronitrosoacylbenzenes **XLIX** and **L**.

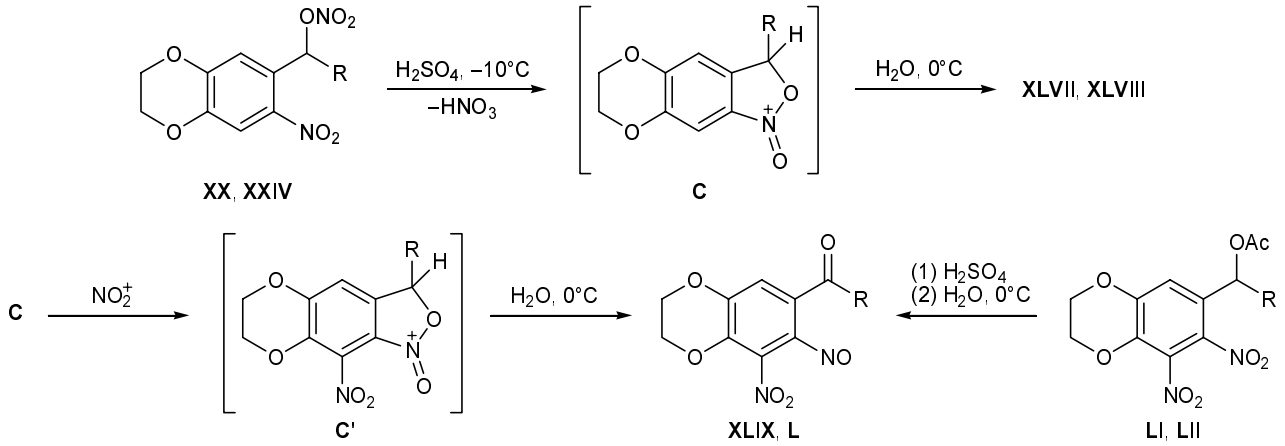
Compounds **XLIX** and **L** can be synthesized in quantitative yield by rearrangement of 1-(4,5-ethylenedioxy-2,3-dinitrophenyl)ethyl acetate (**LI**) and 1-(4,5-ethylenedioxy-2,3-dinitrophenyl)propyl acetate (**LII**), respectively, which were specially prepared by nitration of mononitro acetates **XXV** and **XXI** (see Experimental). By contrast, 1-(4,5-ethylenedioxy-2,3-dinitrophenyl)ethyl nitrate (**XXVIII**) failed to undergo rearrangement into nitroso compound **XLIX** even under more severe conditions. The latter fact indirectly supports our assumption that the rearrangement of mononitrobenzyl nitrates **XX** and **XXIV** involves formation of intermediate ions **C'** (Scheme 14) as a result of nitration of intermediates **C** with nitric acid liberated via denitration of the initial compounds.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker AW-300 (300 MHz) and Varian BXR-400 (400 MHz) instruments from solutions in $CDCl_3$ using tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on Finnigan SSQ-7000 GC–MS system (DB-1 30-m capillary column, carrier gas helium, oven temperature programming from 50 do 300°C at a rate of 10 deg/min). The reaction mixtures were separated by preparative thin-layer chromatography on alumina (activity grade II) and silica gel (40–100 μm); mixtures of diethyl ether, chloroform, and petroleum ether (40–70°C) at different ratios were used as eluent.

1-(4-Isopropylphenyl)ethanol (**I**), bp 141–142°C (24 mm), n_D^{20} = 1.5171 [7], 1-(4-*tert*-butylphenyl)-

Scheme 14.



XLIX, **LI**, R = Me; **L**, **LII**, R = Et.

ethanol (**V**), mp 66–68°C [8], 1-(4-isopropylphenyl)-propan-1-ol (**VIII**), bp 124–125°C (12 mm), n_D^{20} = 1.5116 [9], 1-(4-*tert*-butylphenyl)propan-1-ol (**IX**), bp 138–139°C (12 mm), n_D^{20} = 1.5025 [10], and 1-(3,4-ethylenedioxyphenyl)ethanol (**XXIII**), bp 156–157°C (2 mm) [11], were synthesized by reduction of the corresponding acylbenzenes with sodium tetrahydridoborate in ethanol. 1-(3,4-Ethylenedioxyphenyl)propan-1-ol (**XVIII**) and 3,4-ethylenedioxyphenyl(phenyl)-methanol (**XXIX**) were obtained in a similar way from 3,4-ethylenedioxypropiophenone and 3,4-ethylenedioxybenzophenone, respectively.

Compound **XVIII**. bp 188–190°C (16 mm). ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3), 1.68 m (1H) and 1.74 m (1H, C**H**$_2$CH$_3$), 2.11 br.s (1H, OH), 4.25 s (4H, OCH_2CH_2O), 4.48 t (1H, C**H**OH), 6.79 d.d (1H, H_{arom}, J_o = 8.4, J_m = 2.0 Hz), 6.82 d (1H, H_{arom}, J_o = 8.4 Hz), 6.85 d (1H, H_{arom}, J_m = 2.0 Hz). Found, %: C 67.71, 67.63; H 7.06, 7.04. $C_{11}H_{14}O_3$. Calculated, %: C 68.02; H 7.26.

Compound **XXIX**. Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 3.31 br.s (1H, OH), 4.09 s (4H, OCH_2CH_2O), 5.61 s (1H, CH), 6.75 m (2H, H_{arom}), 6.84 s (1H, H_{arom}), 7.17–7.33 m (5H, H_{arom}). Found, %: C 73.95, 74.07; N 5.65, 5.69. $C_{15}H_{14}O_3$. Calculated, %: C 74.36; H 5.82.

Acetylation of alcohols I, V, XVIII, XXIII, and XXIX) (*general procedure***).** Acetyl chloride, 0.1 mol, was added dropwise under vigorous stirring to a solution of 0.1 mol of alcohol **I**, **V**, **XVIII**, **XXIII**, or **XXIX** and 0.1 mol of *N*,*N*-dimethylaniline in 50 ml of anhydrous diethyl ether, maintaining the mixture evenly boiling. When the addition was complete, the mixture was heated for 2 h under reflux and was left to stand for 12 h. The ether solution was separated from the precipitate by decanting, the precipitate was washed with diethyl ether (2×40 ml), the solution was combined with the washings and washed with small portions of a 2 N sulfuric acid solution until the extract no longer turned turbid upon addition of alkali. The ether solution was dried over $MgSO_4$ and evaporated, and the residue was distilled under reduced pressure or purified by chromatography on aluminum oxide using diethyl ether–petroleum ether (1:3) as eluent.

1-(4-Isopropylphenyl)ethyl acetate (XXXII) was synthesized from 22 g (0.134 mol) of 1-(4-isopropylphenyl)ethanol (**I**). Yield 19.6 g (71%), bp 164–165°C (22 mm), n_D^{20} = 1.4988. ^{1}H NMR spectrum, δ, ppm: 1.26 d [6H, CH(C**H**$_3$)$_2$, J = 6.8 Hz], 1.53 d (3H, CHC**H**$_3$, J = 5.4 Hz), 2.04 s (3H, $COCH_3$), 2.89 sept [1H, C**H**(CH$_3$)$_2$], 5.87 q (1H, C**H**CH$_3$), 7.18 d (2H, H_{arom}, J_o = 8.8 Hz), 7.23 d (2H, H_{arom}, J_o = 8.8 Hz). Found, %: C 75.21, 75.33; H 8.52, 8.61. $C_{13}H_{18}O_2$. Calculated, %: C 75.69; H 8.79.

1-(4-*tert*-Butylphenyl)ethyl acetate (XXXIII) was synthesized from 26.7 g (0.15 mol) of 1-(4-*tert*-butylphenyl)ethanol (**V**). Yield 24.5 g (74%), bp 145–147°C (17 mm), n_D^{20} = 1.5010. ^{1}H NMR spectrum, δ, ppm: 1.31 s (9H, *t*-Bu), 1.54 d (3H, CHC**H**$_3$, J = 5.8 Hz), 2.06 s (3H, $COCH_3$), 5.81 q (1H, C**H**CH$_3$), 7.29 d (2H, H_{arom}, J_o = 8.2 Hz), 7.38 d (2H, H_{arom}, J_o = 8.2 Hz). Found, %: C 75.98, 76.01; H 8.98, 9.02. $C_{14}H_{20}O_2$. Calculated, %: C 76.32; H 9.15.

1-(3,4-Ethylenedioxyphenyl)ethyl acetate (XXXVI) was synthesized from 27 g (0.15 mol) of 1-(3,4-ethylenedioxyphenyl)ethanol (**XXIII**). Yield 23 g (69%), viscous oily substance, n_D^{20} = 1.5252. ^{1}H NMR spectrum, δ, ppm: 1.43 d (3H, CHC**H**$_3$, J = 6.4 Hz), 1.99 s (3H, $COCH_3$), 4.24 s (4H, OCH_2CH_2O), 5.18 q (1H, C**H**CH$_3$), 6.77–6.83 m (3H, H_{arom}). Found, %: C 64.36, 64.51; H 6.11, 6.19. $C_{12}H_{14}O_4$. Calculated, %: C 64.85; H 6.35.

1-(3,4-Ethylenedioxyphenyl)propyl acetate (XXXVII) was synthesized from 19.4 g (0.1 mol) of 1-(3,4-ethylenedioxyphenyl)propan-1-ol (**XVIII**). Yield 17.8 g (75%), viscous oily substance, n_D^{20} = 1.5224. ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, CHCH$_2$C**H**$_3$), 1.73 m (1H) and 1.91 m (1H each, CHC**H**$_2$CH$_3$), 2.11 s (3H, CH_3CO), 4.28 s (4H, OCH_2CH_2O), 5.57 m (1H, C**H**CH$_2$CH$_3$), 6.81 m (3H, H_{arom}). Found, %: C 65.87, 65.92; H 6.59, 6.61. $C_{13}H_{16}O_4$. Calculated, %: C 66.08; H 6.83.

3,4-Ethylenedioxyphenyl(phenyl)methyl acetate (XXXVIII) was synthesized from 24.2 g (0.1 mol) of 3,4-ethylenedioxyphenyl(phenyl)methanol (**XXIX**). Yield 21.6 g (76%), viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 2.1 s (3H, CH_3CO), 4.17 s (4H, OCH_2CH_2O), 6.62–6.68 m (3H, H_{arom}), 6.81 t (1H, CH), 7.19–7.35 m (5H, H_{arom}). Found, %: C 71.37, 71.48; H 5.41, 5.51. $C_{17}H_{16}O_4$. Calculated, %: C 71.81; H 5.67.

1-Ethoxy-1-(3,4-ethylenedioxyphenyl)propane (XXXIX) was isolated as by-product in the synthesis of compound **XVIII**. Yield 15%, bp 181–182°C (24 mm), n_D^{20} = 1.5188. ^{1}H NMR spectrum, δ, ppm: 0.82 t (3H, CH$_2$C**H**$_3$), 1.12 t (3H, OCH$_2$C**H**$_3$), 1.58 m and 1.75 m (1H each, C**H**$_2$CH$_3$), 3.24 m and 3.33 m (1H each, OC**H**$_2$CH$_3$), 3.96 t (1H, C**H**), 4.19 s (4H, OCH_2CH_2O), 6.71–6.81 m (3H, H_{arom}). Found, %:

C 69.88, 69.92; H 7.95, 8.01. $C_{13}H_{18}O_3$. Calculated, %: C 70.24; H 8.16.

Nitration of benzyl alcohols I, V, VIII, IX, XVIII, and XXIX with nitric acid in acetic anhydride in the presence of sulfuric acid (*general procedure***).** A mixture of 12.6 ml (18.9 g) of HNO_3 (d = 1.5) and 21 ml (38.5 g) of H_2SO_4 (d = 1.84) was gradually added at –50°C to 140 ml of acetic anhydride. A solution of 0.1 mol of benzyl alcohol **I**, **V**, **VIII**, **IX**, **XVIII**, or **XXIX** in 20 ml of acetic anhydride was then added dropwise to the nitrating mixture, maintaining the temperature at –50°C. The mixture was stirred for 2 h at –50°C, poured into 750 ml of water, and extracted with chloroform. The extract was washed with a 2 N solution of sodium carbonate and water, dried over $MgSO_4$, and evaporated. The products were isolated by chromatography or recrystallization.

From 8.2 g (0.05 mol) of alcohol **I** we obtained 12.3 g of a mixture of products which were separated by column chromatography on silica gel (40–100 μm) using diethyl ether–hexane (1:3) as eluent to isolate 9.6 g (76%) of compound (**II**), 1.5 g (18%) of 1-isopropyl-4-nitrobenzene (**III**), and 0.41 g (4%) of nitro acetate (**IV**).

1-(4-Isopropyl-3-nitrophenyl)ethyl nitrate (II). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.28 d [6H, CH(C**H**$_3$)$_2$, J = 5.6 Hz], 1.66 d (3H, CH_3, J = 6.0 Hz), 3.39 sept [1H, C**H**(CH$_3$)$_2$], 5.96 q (1H, $CHONO_2$), 7.52 d (1H, 5-H, J_o = 8.0 Hz), 7.59 d.d (1H, 6-H, J_m = 2.0, J_o = 8.0 Hz), 7.73 d (1H, 2-H, J_m = 2.0 Hz). Found, %: C 51.51, 51.64; H 5.32, 5.41; N 10.75, 10.81. $C_{11}H_{14}N_2O_5$. Calculated, %: C 51.96; H 5.55; N 11.02;

1-Isopropyl-4-nitrobenzene (III). ^{1}H NMR spectrum, δ, ppm: 1.31 d [6H, CH(C**H**$_3$)$_2$, J = 6.4 Hz], 3.48 sept [1H, C**H**(CH$_3$)$_2$], 7.57 d (2H, J_o = 8.4 Hz), 8.26 d (2H, H$_{arom}$, J_o = 8.4 Hz). Mass spectrum, m/z (I_{rel}, %): 165 (41.8) $[M]^+$, 150 (100), 119 (18.9), 115 (6.3), 104 (35.4), 92 (36.1), 91 (55.7), 78 (25.3), 77 (36.7), 63 (12.0), 51 (20.5), 39 (17.7).

1-(4-Nitrophenyl)ethyl acetate (IV). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.56 d (3H, CHC**H**$_3$, J = 6.2 Hz), 2.12 s (3H, $COCH_3$), 5.92 q (1**H**, $CHCH_3$), 7.52 d (2H, H$_{arom}$, J_o = 8.8 Hz), 8.22 d (2H, H$_{arom}$, J_o = 8.8 Hz). Mass spectrum, m/z (I_{rel}, %): 209 (4.1) $[M]^+$, 167 (50.2), 150 (13.9), 119 (14.7), 103 (24.7), 91 (22.1), 77 (24.8), 63 (4.4), 51 (9.7), 43 (100). Found, %: C 56.98, 57.04; H 5.11, 5.12, N 6.32, 6.41. $C_{10}H_{11}NO_4$. Calculated, %: C 57.41; N 5.30; N 6.70.

The nitration of 8.9 g (0.05 mol) of alcohol **V**, followed by column chromatography on silica gel (40–100 μm, eluent hexane), afforded 1.61 g (18%) of initial alcohol **V**, 1.17 g (16%)* of 1-*tert*-butyl-4-nitrobenzene (**VII**) (identified by comparing with an authentic sample), and 8.79 g (81%)* of compound **VI.**

1-(4-*tert*-Butyl-2-nitrophenyl)ethyl acetate (VI). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.37 s (9H, *t*-Bu), 1.64 d (3H, CHC**H**$_3$, J 6.6 Hz), 2.08 s (3H, $COCH_3$), 6.32 q (1H, C**H**CH$_3$), 7.56 d (1H, 6-H, J_o = 8.2 Hz), 7.66 d.d (1H, 5-H, J_m = 1.6, J_o = 8.2 Hz), 7.94 d (1H, 3-H, J_m = 1.6 Hz). Found, %: C 62.99, 63.01; H 6.98, 7.02; N 4.97, 5.01. $C_{14}H_{19}NO_4$. Calculated, %: C 63.38; H 7.22; N 5.28.

The nitration of 17.8 g of alcohol **VIII**, followed by chromatographic separation in a column charged with silica gel (40–100 μm, eluent hexane), gave 19.2 g (71%) of compound **X**, 2.03 g (9%) of **XI**, and 1.77 g (8%) of **XIV**.

1-(4-Isopropyl-3-nitrophenyl)propyl nitrate (X). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.01 t (3H, CH_2C**H**$_3$), 1.31 d [6H, CH(C**H**$_3$)$_2$, J = 6.6 Hz], 1.88 m and 2.03 m (1H each, CHC**H**$_2$CH$_3$), 3.43 sept [1H, C**H**(CH$_3$)$_2$], 5.71 t (1H, $CHONO_2$), 7.52 d (1H, 5-H, J_o = 8.0 Hz), 7.55 d.d (1H, 6-H, J_m = 1.8, J_o = 8.0 Hz), 7.71 d (1H, 2-H, J_m = 1.8 Hz). Found, %: C 53.28, 53.41; H 5.86, 5.88; N 10.11, 10.17. $C_{12}H_{16}N_2O_5$. Calculated, %: C 53.72; H 6.01; N 10.44;

1-(4-Nitrophenyl)propyl nitrate (XI). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 0.99 t (3H, $CHCH_2C$**H**$_3$), 1.89 m and 2.03 m (1H each, CHC**H**$_2$CH$_3$), 5.78 t (1H, $CHONO_2$), 7.56 d (2H, H$_{arom}$, J_o = 8.4 Hz), 8.24 d (2H, H$_{arom}$, J_o = 8.4 Hz). Found, %: C 47.32, 47.36; H 4.21, 4.31; N 11.98, 12.17. $C_9H_{10}N_2O_5$. Calculated, %: C 47.79; H 4.46; N 12.39;

1-(4-Isopropyl-3-nitrophenyl)-1-propanone (XIV). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.25 t (3H, CH_2C**H**$_3$), 1.33 d [6H, CH(C**H**$_3$)$_2$, J = 6.4 Hz], 3.02 q (2H, C**H**$_2$CH$_3$), 3.45 sept [1H, C**H**(CH$_3$)$_2$], 7.61 d (1H, 5-H, J_o = 7.8 Hz), 8.12 d.d (1H, 6-H, J_m = 2.2, J_o = 7.8 Hz), 8.26 d (1H, 2-H, J_m = 2.2 Hz). Mass spectrum, m/z (I_{rel}, %): 221 (3.9) $[M]^+$, 204 (30.1), 192 (100), 175 (39.8), 160 (21.3), 147 (33.0), 131 (34.9), 115 (39.7), 103 (29.1), 91 (40.8), 77 (45.6), 57 (94.1).

The nitration of 9.6 g (0.05 mol) of alcohol **IX**, followed by separation of the product mixture by

* Calculated on the reacted alcohol **V**.

column chromatography on silica gel (40–100 μm) using diethyl ether–light petroleum ether (1:10) as eluent, gave 7.47 g (53%) of nitrate **XV**, 3.67 g (26%) of nitrate **XVI**, 0.81 g (9%) of 1-*tert*-butyl-4-nitrobenzene (**VII**) (identified by comparing with an authentic sample), and 0.54 g (4%) of acetate **XVII**.

1-(4-*tert*-Butyl-3-nitrophenyl)propyl nitrate (XV). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.01 t (3H, CH_2CH_3), 1.41 s (9H, *t*-Bu), 1.87 m and 2.02 m (1H each, $CHCH_2CH_3$), 5.68 t (1H, $CHCH_2CH_3$), 7.31 d (1H, H_{arom}, J_m = 2.0 Hz), 7.43 d.d (1H, H_{arom}, J_m = 2.0, J_o = 8.6 Hz), 7.59 d (1H, H_{arom}, J_o = 8.6 Hz). Found, %: C 54.98, 55.12; H 6.21, 6.26; N 9.47, 9.55. $C_{13}H_{18}N_2O_5$. Calculated, %: C 55.31; H 6.43; N 9.93;

1-(4-*tert*-Butyl-2-nitrophenyl)propyl nitrate (XVI). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.14 t (3H, CH_2CH_3), 1.37 s (9H, *t*-Bu), 1.97 m and 2.07 m (1H each, $CHCH_2CH_3$), 6.37 d.d (1H, $CHCH_2CH_3$, J_1 = 9.0, J_2 = 4.8 Hz), 7.55 d (1H, H_{arom}, J_o = 8.2 Hz), 7.70 d.d (1H, H_{arom}, J_m = 2.2, J_o = 8.2 Hz), 8.05 d (1H, H_{arom}, J_m = 2.2 Hz). Found, %: C 54.82, 55.01; H 6.19, 6.29; N 9.54, 9.59. $C_{13}H_{18}N_2O_5$. Calculated, %: C 55.31; H 6.43; N 9.93;

1-(4-*tert*-Butyl-2-nitrophenyl)propyl acetate (XVII). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.03 t (3H, CH_2CH_3), 1.32 s (9H, *t*-Bu), 1.86 m and 1.99 m (1H each, $CHCH_2CH_3$), 2.22 s (3H, CH_3CO), 6.15 d.d (1H, $CHCH_2CH_3$, J_1 = 7.6, J_2 = 4.0 Hz), 7.51 d (1H, H_{arom}, J_o = 8.2 Hz), 7.62 d.d (1H, H_{arom}, J_m = 1.8, J_o = 8.2 Hz), 7.95 d (1H, H_{arom}, J_m = 1.8 Hz). Found, %: C 64.02, 64.18; H 7.22, 7.31; N 4.78, 4.86. $C_{15}H_{21}NO_4$. Calculated, %: C 64.49; H 7.58; N 5.01.

The nitration of 4.85 g (0.025 mol) of alcohol **XVIII**, followed by chromatographic separation on aluminum oxide (activity grade II; diethyl ether–light petroleum ether, 1:3), gave 3.2 g (43.5%) of nitrate **XX**, 1.8 g (25.5%) of acetate **XXI**, 0.14 g (3%) of 1,2-ethylenedioxy-4-nitrobenzene (**XXII**), mp 120°C [16], and 1.1 g (18.5%) of nitro alcohol **XIX**.

1-(4,5-Ethylenedioxy-2-nitrophenyl)propyl nitrate (XX). mp 88–89°C. IR spectrum, ν, cm^{-1}: 1380, 1540 (NO_2); 1290, 1635 (ONO_2). ^{1}H NMR spectrum, δ, ppm: 1.11 t (3H, $CHCH_2CH_3$), 1.92 m and 2.06 m (1H each, $CHCH_2CH_3$), 4.40 m (4H, OCH_2CH_2O), 6.43 d.d (1H, $CHCH_2CH_3$), 7.03 s (1H, 6-H), 7.71 s (1H, 3-H). Found, %: C 46.76, 46.61; H 3.93, 4.01; N 9.63, 9.79. $C_{11}H_{12}N_2O_7$. Calculated, %: C 46.48; H 4.26; N 9.86;

1-(4,5-Ethylenedioxy-2-nitrophenyl)propyl acetate (XXI). mp 80–81°C. IR spectrum, ν, cm^{-1}: 1370, 1530 (NO_2); 1735 (CO). ^{1}H NMR spectrum, δ, ppm: 1.08 t (3H, $CHCH_2CH_3$), 1.92 m and 1.97 m (1H each, $CHCH_2CH_3$), 2.11 s (3H, CH_3CO), 4.30 m and 4.38 m (2H each, OCH_2CH_2O), 6.24 d.d (1H, $CHCH_2CH_3$), 7.01 s (1H, 6-H), 7.63 s (1H, 3-H). Found, %: C 55.67, 55.52; H 5.55, 5.61; N 4.71, 4.61. $C_{13}H_{15}NO_6$. Calculated, %: C 55.51; H 5.37; N 4.98;

1-(4,5-Ethylenedioxy-2-nitrophenyl)propanol (XIX). mp 156–157°C. IR spectrum, ν, cm^{-1}: 1380, 1532 (NO_2); 3260 (OH). ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, $CHCH_2CH_3$), 1.48 m and 1.66 m (1H each, $CHCH_2CH_3$), 4.32 m (4H, OCH_2CH_2O), 5.01 m (1H, $CHCH_2CH_3$), 5.14 br.s (1H, OH), 7.21 s (1H, 6-H), 7.48 s (1H, 3-H). Found, %: C 55.32, 55.41; H 5.31, 5.29; N 5.41, 5.65. $C_{11}H_{13}NO_5$. Calculated, %: C 55.22; H 5.47; N 5.85.

The nitration of 6.05 g (0.025 mol) of alcohol **XXIX**, followed by chromatographic separation on an Al_2O_3 plate (activity grade II; benzene), gave 0.95 g (21%) of 1,2-ethylenedioxy-4-nitrobenzene (**XXII**), mp 119°C [16], 2.1 g (31%) of compound **XXX**, and 2.4 g (38%) of benzisoxazole **XXXI**.

4,5-Ethylenedioxy-2-nitrosobenzophenone (XXX). Dark green crystals, mp 140–141°C. ^{1}H NMR spectrum, δ, ppm: 4.38 m (4H, OCH_2CH_2O), 7.02 s (1H, 3-H), 7.09 s (1H, 6-H), 7.41 t (2H, 3'-H, 5'-H), 7.54 t (1H, 4'-H), 7.78 d (2H, 2'-H, 6'-H). Found, %: C 66.49, 66.56; H 4.00, 4.03; N 4.94, 4.96. $C_{15}H_{11}NO_4$. Calculated, %: C 66.91; H 4.12; N 5.20;

5,6-Ethylenedioxy-3-phenyl-2,1-benzisoxazole (XXXI). mp 136–138°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 4.31 m (4H, OCH_2CH_2O), 6.95 s (1H, 7-H), 7.19 s (1H, 4-H), 7.42 t (1H, 4'-H), 7.51 t (2H, 3'-H, 5'-H), 7.91 d (2H, 2'-H, 6'-H). Found, %: C 71.21, 71.32; H 4.53, 4.41; N 5.31, 5.41. $C_{15}H_{11}NO_3$. Calculated, %: C 71.14; H 4.38; N 5.53.

Nitration of alcohols XVIII and XXIII, acetates XXXII, XXXIII, and XXXVI–XXXVIII, and ether XL with acetyl nitrate in acetic anhydride (*general procedure*). Nitric acid (*d* = 1.5), 5.5 ml, was added at –50°C to 60 ml of acetic anhydride, and the mixture was allowed to warm up to –10°C and was kept for 0.5 h at that temperature. The mixture was then cooled to –30°C, and a solution of 0.05 mol of the corre-

sponding alcohol or acetate in 10 ml of acetic anhydride was added. The mixture was stirred for 2 h at –30 to –10°C, poured into 400 ml of water, and extracted with diethyl ether. The extract was washed with water and a 2 N solution of Na_2CO_3, dried over $MgSO_4$, and evaporated, and the products were isolated by chromatography or recrystallization (see below).

The nitration of 3.9 g (0.02 mol) of alcohol **XVIII**, followed by column chromatography on Al_2O_3 (activity grade II; diethyl ether–hexane, 1:3), gave 4.5 g (79%) of compound **XX**, 0.4 g (7%) of **XXI**, and 0.22 g (4.7%) of **XIX**.

The nitration of 9 g (0.05 mol) of compound **XXIII**, followed by chromatography on Al_2O_3 (activity grade II; diethyl ether–petroleum ether, 1:3), gave 9 g (67%) of nitrate **XXIV**, 2.9 g (22%) of acetate **XXV**, and 0.9 g (8%) of nitroalcohol **XXVI**.

1-(4,5-Ethylenedioxy-2-nitrophenyl)ethyl nitrate (XXIV). mp 100–101°C (from ethanol). IR spectrum, ν, cm^{-1}: 1385, 1535 (NO_2); 1285, 1640 (ONO_2). ^1H NMR spectrum, δ, ppm: 1.70 d (3H, CH_3), 4.39 m (4H, OCH_2CH_2O), 6.61 q (1H, C**H**CH_3), 7.12 s (1H, 6-H), 7.72 s (1H, 3-H). Found, %: C 44.61, 44.69; H 3.51, 3.67; N 10.23, 10.35. $C_{10}H_{10}N_2O_7$. Calculated, %: C 44.45; H 3.73; N 10.37;

1-(4,5-Ethylenedioxy-2-nitrophenyl)ethyl acetate (XXV). mp 111–112°C (from ethanol). ^1H NMR spectrum, δ, ppm: 1.61 d (3H, CHC**H**$_3$), 2.10 s (3H, CH_3CO), 4.38 m (4H, OCH_2CH_2O), 6.39 q (1H, C**H**CH_3), 7.08 s (1H, 6-H), 7.65 s (1H, 3-H). Found, %: C 54.04, 54.13; H 4.91, 4.98; N 5.37, 5.51. $C_{12}H_{13}NO_6$. Calculated, %: C 53.93; H 4.90; N 5.24;

1-(4,5-Ethylenedioxy-2-nitrophenyl)ethanol (XXVI). mp 180–182°C (from ethanol). IR spectrum, ν, cm^{-1}: 1385, 1530 (NO_2); 3220 (OH). ^1H NMR spectrum, δ, ppm: 1.38 d (3H, CHC**H**$_3$), 3.2 br.s (1H, OH), 4.39 m (4H, OCH_2CH_2O), 4.75 q (1H, C**H**CH_3), 7.21 s (1H, 6-H), 7.51 s (1H, 3-H). Found, %: C 54.50, 54.56; H 4.71, 4.76; N 6.22, 6.37. $C_{10}H_{11}NO_5$. Calculated, %: C 53.33; N 4.92; N 6.22.

The nitration of 10.3 g (0.05 mol) of acetate **XXXII**, followed by chromatographic separation of the product mixture in a column charged with Al_2O_3 (activity grade II, diethyl ether–petroleum ether, 1:4.5), gave 4.64 g (37%) of acetate **XXXIV**, 4.39 g (35%) of acetate **XXXV**, 0.9 g (11%) of 1-isopropyl-4-nitrobenzene (**III**) (identified by the ^1H NMR data and comparison with an authentic sample), and 1.67 g (16%) of 1-(4-nitrophenyl)ethyl acetate (**IV**).

1-(4-Isopropyl-2-nitrophenyl)ethyl acetate (XXXIV). Viscous oily substance. ^1H NMR spectrum, δ, ppm: 1.24 d [6H, (CH_3)$_2$CH], 1.59 d (3H, CHC**H**$_3$), 2.09 s (3H, CH_3CO), 2.98 sept [1H, (CH_3)$_2$C**H**], 6.29 m (1H, C**H**OAc), 7.48 d.d (1H, 5-H, J_m = 1.8, J_o = 8.6 Hz), 7.55 d (1H, 6-H, J_m = 1.8, J_o = 8.6 Hz), 7.77 d (1H, 3-H, J_m = 1.8 Hz). Found, %: C 61.88, 61.93; H 6.67, 6.74; N 5.17, 5.26. $C_{13}H_{17}NO_4$. Calculated, %: C 62.13; H 6.82; N 5.57;

1-(4-Isopropyl-3-nitrophenyl)ethyl acetate (XXXV). Viscous oily substance. ^1H NMR spectrum, δ, ppm: 1.32 d [6H, (CH_3)$_2$CH], 1.59 d (3H, CHC**H**$_3$), 2.11 s (3H, CH_3CO), 3.21 sept [1H, (CH_3)$_2$C**H**], 5.90 m (1H, C**H**CH_3), 7.52 d (1H, 5-H, J_o = 8.2 Hz), 7.58 d.d (1H, 6-H, J_m = 2.0, J_o = 8.2 Hz), 7.75 d (1H, 3-H, J_m = 2.0 Hz). Found, %: C 61.75, 61.83; H 6.63, 6.68; N 5.28, 5.34. $C_{13}H_{17}NO_4$. Calculated, %: C 62.13; H 6.82; N 5.57.

By nitration of 22 g (0.1 mol) of compound **XXXIII**, followed by column chromatography on Al_2O_3 (activity grade II; diethyl ether–hexane, 1:3), we obtained 19.6 g (74%) of 1-(4-*tert*-butyl-2-nitrophenyl)ethyl acetate (**VI**) and 3.2 g (18%) of 1-*tert*-butyl-4-nitrobenzene (**VII**).

The nitration of 5.6 g (0.025 mol) of acetate **XXXVI** with acetyl nitrate according to the general procedure, followed by recrystallization of the crude product from ethanol, gave 5.8 g (87%) of compound **XXV** with mp 111–112°C.

The nitration of 7.1 g (0.03 mol) of acetate **XXXVII** with acetyl nitrate according to the general procedure, followed by recrystallization of the crude product from ethanol, gave 7.7 g (91%) of compound **XXI** with mp 80–81°C.

The nitration of 5.7 g (0.02 mol) of acetate **XXXVIII** with acetyl nitrate, followed by column chromatography on Al_2O_3 (activity grade II; diethyl ether–hexane, 1:3), gave 4.7 g (72%) of acetate **XXXIX** and 0.65 g (18%) of 1,2-ethylenedioxy-4-nitrobenzene (**XXII**).

4,5-Ethylenedioxy-2-nitrophenyl(phenyl)methyl acetate (XXXIX). Viscous oily substance. ^1H NMR spectrum, δ, ppm: 2.14 s (3H, CH_3CO), 4.31 m (4H, OCH_2CH_2O), 7.14 s (1H, C**H**OAc), 7.22–7.38 m (5H, H_{arom}), 7.52 s (1H, 6-H), 7.68 s (1H, 3-H). Found, %: C 61.66, 61.81; H 4.22, 4.32; N 3.93, 4.01. $C_{17}H_{15}NO_6$. Calculated, %: C 62.00; H 4.59; N 4.25.

The nitration of 2.3 g (0.01 mol) of 1-ethoxy-1-(4,5-ethylenedioxy-2-nitrophenyl)propane (**XL**),

followed by thin-layer chromatography on an Al_2O_3 plate (activity grade II; diethyl ether–petroleum ether, 1:3), gave 2.1 g (78%) of compound **XLI**, 0.24 g (9%) of **XLII**, and 0.21 g of 1,2-ethylenedioxy-4-nitrobenzene (**XXII**) with an impurity of dinitro ether **XLIII**.

1-Ethoxy-1-(4,5-ethylenedioxy-2-nitrophenyl)-propane (XLI). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.06 t (3H, $CHCH_2C\mathbf{H}_3$), 1.23 t (3H, $OCH_2C\mathbf{H}_3$), 1.62 m and 1.68 m (1H each, $CHC\mathbf{H}_2CH_3$), 3.36 m (2H, $OC\mathbf{H}_2CH_3$), 4.34 m (4H, OCH_2CH_2O), 4.84 m (1H, $C\mathbf{H}CH_2CH_3$), 7.20 s (1H, 6-H), 7.61 s (1H, 3-H). Mass spectrum, *m*/*z* (I_{rel}, %): 267 (1.9) $[M]^+$, 238 (70.9), 210 (54.4), 206 (8.9), 192 (24.1), 178 (11.6), 162 (100), 149 (10.3), 134 (22.8), 121 (16.6), 107 (18.9), 91 (18.3), 79 (22.3), 69 (22.9), 51 (26.6). Found, %: C 58.01, 58.22; H 6.16, 6.24; N 4.89, 4.97. $C_{13}H_{17}NO_5$. Calculated, %: C 58.41; H 6.41; N 5.24;

1-Ethoxy-1-(4,5-ethylenedioxy-3-nitrophenyl)-propane (XLII). Viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, $CHCH_2C\mathbf{H}_3$), 1.22 t (3H, $OCH_2C\mathbf{H}_3$), 1.62 m and 1.80 m (1H each, $CHC\mathbf{H}_2CH_3$), 3.36 m (2H, $OC\mathbf{H}_2CH_3$), 4.24–4.42 m (5H, $C\mathbf{H}CH_2CH_3$, OCH_2CH_2O), 7.09 s (1H, 6-H, J_m = 2.2 Hz), 7.44 s (1H, 2-H, J_m = 2.2 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 267 (8.9) $[M]^+$, 238 (100), 222 (6.3), 210 (56.9), 194 (5.1), 164 (11.4), 136 (37.9), 107 (8.7), 91 (15.4), 80 (16.4), 79 (15.2), 65 (9.5), 51 (12.6).

1-Ethoxy-1-(4,5-ethylenedioxy-2,3-dinitrophenyl)propane (XLIII). Mass spectrum, *m*/*z* (I_{rel}, %): 312 (1.4) $[M]^+$, 283 (100), 255 (89.8), 237 (8.8), 221 (6.8), 207 (13.9), 178 (8.2), 161 (56.9), 151 (12.1), 133 (19.1), 107 (24.7), 91 (10.7), 77 (34.8), 65 (16.4), 59 (14.5), 53 (17.7), 43 (16.2).

Nitration of alcohols XVIII and XXIII and nitro acetates XXI and XXV with 6 equiv of nitric acid in acetic anhydride (*general procedure*). Nitric acid (d = 1.5), 12.5 ml, was added to 60 ml of acetic anhydride at –50°C, and a solution of 0.05 mol of alcohol **XVIII** or **XXIII** in 10 ml of acetic anhydride was then added at –50°C. The mixture was stirred for 1 h at –40 to –30°C and poured into 500 ml of warm water. The precipitate was filtered off, washed with water until neutral washings, and subjected to chromatography on a column charged with Al_2O_3 (activity grade II) using diethyl ether–chloroform–petroleum ether (1:1:3) as eluent.

From 9.7 g (0.05 mol) of alcohol **XVIII** we obtained 4.4 g (31%) of 1-(4,5-ethylenedioxy-2-nitrophenyl)propyl nitrate (**XX**) and 9.7 g (59%) of compound **XXVII**.

1-(4,5-Ethylenedioxy-2,3-dinitrophenyl)propyl nitrate (XXVII). mp 111–112°C. ^{1}H NMR spectrum, δ, ppm: 1.16 t (3H, $CH_2C\mathbf{H}_3$), 1.91 m and 2.11 m (1H each, $C\mathbf{H}_2CH_3$), 4.46 m (4H, OCH_2CH_2O), 6.41 m (1H, $CHONO_2$), 7.38 s (1H, 6-H). Found, %: C 39.69, 39.81; H 3.12, 3.18; N 12.38, 12.52. $C_{11}H_{11}N_3O_9$. Calculated, %: C 40.13; H 3.37; N 12.76.

From 9 g (0.05 mol) of alcohol **XXIII** we obtained 3.65 g (24%) of compound **XXIV** and 9.76 g (62%) of nitrate **XXVIII**.

1-(4,5-Ethylenedioxy-2,3-dinitrophenyl)ethyl nitrate (XXVIII). mp 124–125°C (from alcohol). IR spectrum, ν, cm^{-1}: 1382, 1540 (NO_2); 1280, 1650 (ONO_2). ^{1}H NMR spectrum, δ, ppm: 1.70 d (3H, $CHC\mathbf{H}_3$), 4.51 m (4H, OCH_2CH_2O), 6.19 m (1H, $CHONO_2$), 7.39 s (1H, 6-H). Found, %: C 38.34, 38.46; H 2.66, 2.74; N 13.10, 13.19. $C_{10}H_9N_3O_9$. Calculated, %: C 38.11; H 2.79; N 13.33.

1-(4,5-Ethylenedioxy-2,3-dinitrophenyl)propyl acetate (LII) was obtained by nitration of 2.8 g (0.01 mol) of acetate **XXI**, followed by recrystallization of the crude product from alcohol. Yield 2.6 g (81%), mp 106–107°C. ^{1}H NMR spectrum, δ, ppm: 1.07 t (3H, $CH_2C\mathbf{H}_3$), 1.89 m and 2.01 m (1H each, $C\mathbf{H}_2CH_3$), 2.12 s (3H, CH_3CO), 4.36 m (4H, OCH_2-CH_2O), 6.01 m (1H, $C\mathbf{H}OCOCH_3$), 7.21 s (1H, 3-H). Found, %: C 47.36, 47.55; H 4.11, 4.14; N 8.09, 8.21. $C_{13}H_{14}N_2O_8$. Calculated, %: C 47.85; H 4.32; N 8.59.

1-(4,5-Ethylenedioxy-2,3-dinitrophenyl)ethyl acetate (LI) was obtained by nitration of 2.7 g (0.01 mol) of 1-(4,5-ethylenedioxy-2-nitrophenyl)ethyl acetate (**XXV**), followed by recrystallization of the crude product. Yield 2 g (74%), mp 132–133°C (from alcohol). ^{1}H NMR spectrum, δ, ppm: 1.58 d (3H, $CHC\mathbf{H}_3$), 2.01 s (3H, CH_3CO), 4.51 m (4H, OCH_2-CH_2O), 5.81 q (1H, $C\mathbf{H}OCOCH_3$), 7.39 s (1H, 3-H). Found, %: C 46.25, 46.38; H 3.94, 4.00; N 8.73, 8.81. $C_{12}H_{12}N_2O_8$. Calculated, %: C 46.15; H 3.87; N 8.97.

Transformation of *o*-nitrobenzyl alcohols XIX and XXIV, acetates VI, XVII, XXI, XXV, XXXIV, XXXIX, LI, and LII, nitrates XX and XXIV, and ether XLI into *o*-nitrosoacylbenzenes by the action of concentrated sulfuric acid (*general procedure*). Concentrated sulfuric acid was cooled to –20°C, and the corresponding *o*-nitrobenzyl derivative was added in portions under stirring, maintaining the temperature

at –20°C (the sulfuric acid–substrate ratio was 10:1 by weight). The mixture was stirred for 1 h at –20 to –10°C and poured into a tenfold amount (by weight) of a 1:1 ice–water mixture under vigorous stirring. The precipitate was filtered off, washed with water until neutral washings (pH = 7), and recrystallized from alcohol.

1-(4-*tert*-Butyl-2-nitrosophenyl)ethanone (XLV) was obtained from 10.6 g (0.04 mol) of 1-(4-*tert*-butyl-2-nitrophenyl)ethyl acetate (**VI**) and 57.5 ml of concentrated sulfuric acid (d = 1.84). Yield 7.3 g (89%), mp 141–142°C. ^{1}H NMR spectrum, δ, ppm: 1.38 s (9H, *t*-Bu), 2.66 s (3H, CH_3CO), 6.86 d (1H, 3-H, J_m = 1.2 Hz), 7.71 d (1H, 6-H, J_o = 6.8 Hz). Found, %: C 69.71, 69.88; H 7.16, 7.21; N 6.22, 6.38. $C_{12}H_{15}NO_2$. Calculated, %: C 70.22; H 7.37; N 6.82.

1-(4-*tert*-Butyl-2-nitrosophenyl)propan-1-one (XLVI) was obtained by the transformation of 1.4 g of 1-(4-*tert*-butyl-2-nitrophenyl)propyl acetate (**XII**). Yield 0.86 g (78%), mp 116–117°C [17].

1-(4,5-Ethylenedioxy-2-nitrosophenyl)ethanone (XLVII) was obtained from 2 g of 1-(4,5-ethylenedioxy-2-nitrophenyl)ethanol (**XXVI**). Yield 1.5 g (81%), mp 139–140°C (from alcohol). ^{1}H NMR spectrum, δ, ppm: 2.83 s (3H, CH_3CO), 4.34 m and 4.42 m (2H each, OCH_2CH_2O), 6.31 s (1H, 3-H), 7.29 s (1H, 6-H). Electron absorption spectrum: λ_{max} 748 nm (ε = 32). Found, %: C 57.48, 57.61; H 4.12, 4.19; N 6.22, 6.38. $C_{10}H_9NO_4$. Calculated, %: C 57.97; H 4.38; N 6.76. Likewise, compound **XLVII** was obtained from 5.34 g (0.02 mol) of 1-(4,5-ethylenedioxy-2-nitrophenyl)ethyl acetate (**XXV**). Yield 3.8 g (92%), mp 139°C.

1-(4,5-Ethylenedioxy-2-nitrosophenyl)propan-1-one (XLVIII) was obtained according to the general procedure from 2.4 g of 1-(4,5-ethylenedioxy-2-nitrophenyl)propanol (**XIX**), yield 1.95 g (87%), mp 119–120°C [15], as well as from 1.4 g (0.005 mol) of 1-(4,5-ethylenedioxy-2-nitrophenyl)propyl acetate (**XXI**), yield 0.95 g (86%), mp 120°C, and from 5.34 g (0.02 mol) of 1-ethoxy-1-(4,5-ethylenedioxy-2-nitrophenyl)propanol (**XLI**), yield 3.5 g (79%), mp 119–120°C [15].

1-(4-Isopropyl-2-nitrosophenyl)ethanone (XLIV) was obtained from 2.5 g (0.01 mol) of 1-(4-isopropyl-2-nitrophenyl)ethyl acetate (**XXXIV**). Recrystallization from alcohol gave 1.61 g (84%) of the product with mp 126–127°C. ^{1}H NMR spectrum, δ, ppm: 1.23 d [6H, $(CH_3)_2CH$], 3.01 sept [1H, $(CH_3)_2CH$], 6.72 d (1H, 3-H, J_m = 1.6 Hz), 7.65 d.d (1H, 5-H, J_m = 1.6, J_o = 7.6 Hz), 7.67 d (1H, 6-H, J_o = 7.6 Hz). Found, %: C 68.81, 68.88; H 6.58, 6.63; N 6.99, 7.08. $C_{11}H_{13}NO_2$. Calculated, %: C 69.09; H 6.85; N 7.32.

4,5-Ethylenedioxy-2-nitrosobenzophenone (XXX) was obtained from 3.3 g (0.01 mol) of 4,5-ethylenedioxy-2-nitrophenyl(phenyl)methanol (**XXXIX**). Yield 2.1 g (79%), mp 139–140°C.

The transformation of 1.42 g (5 mmol) of 1-(4,5-ethylenedioxy-2-nitrophenyl)propyl nitrate (**XX**), followed by chromatographic separation of the product mixture on silica gel plates (40–100 μm; diethyl ether–chloroform–petroleum ether, 1:1:3), gave 0.27 g (24%) of 1-(4,5-ethylenedioxy-2-nitrosophenyl)-propan-1-one (**XLVIII**), mp 119–120°C [15], and 0.63 g (47%) of 1-(4,5-ethylenedioxy-3-nitro-2-nitrosophenyl)propan-1-one (**L**), mp 113–114°C [15]. Compound **L** was also obtained by the transformation of 3.26 g (0.01 mol) of 1-(4,5-ethylenedioxy-2,3-dinitrophenyl)propyl acetate (**LII**). Yield 2.2 g (83%), mp 113°C.

The transformation of 2.7 g (0.01 mol) of 1-(4,5-ethylenedioxy-2-nitrophenyl)ethyl nitrate (**XXIV**), followed by chromatographic separation of the product mixture on silica gel plates (40–100 μm; diethyl ether–chloroform–petroleum ether, 1:1:3), gave 0.54 g (26%) of 1-(4,5-ethylenedioxy-2-nitrosophenyl)-ethanone (**XLVII**), mp 138–139°C, and 1.28 g (51%) of 1-(4,5-ethylenedioxy-3-nitro-2-nitrosophenyl)-ethanone (**XLIX**), mp 139–141°C (from alcohol).

Compound (**XLIX**) was also obtained by the rearrangement of 3.12 g (0.01 mol) of 1-(4,5-ethylenedioxy-2,3-dinitrophenyl)ethyl acetate (**LI**). Yield 2.2 g (87%), mp 139–140°C. ^{1}H NMR spectrum, δ, ppm: 2.51 s (3H, CH_3), 4.59 m (4H, OCH_2CH_2O), 7.46 s (1H, 6-H). Electron absorption spectrum: λ_{max} 752 nm (ε = 30). Found, %: C 48.02, 48.24; H 3.11, 3.16; N 10.91, 10.88. $C_{10}H_8N_2O_6$. Calculated, %: C 47.62; H 3.20; N 11.11.

REFERENCES

1. Mochalov, S.S. and Gazzaeva, R.A., *Khim. Geterotsikl. Soedin.*, 2003, p. 1123.
2. Shabarov, Yu.S., Mochalov, S.S., and Stepanova, I.P., *Dokl. Akad. Nauk SSSR*, 1969, vol. 189, p. 1028.
3. Bak, R.R. and Smallringe, A.S., *Tetrahedron Lett.*, 2001, vol. 42, p. 6747.
4. Reutov, O.A., Kurts, A.L., and Butin, K.P., *Organicheskaya khimiya* (Organic Chemistry), Moscow: Mosk. Gos. Univ., 1999, vol. 2, p. 415.

5. Ford-Moore and Rydon, H.N., *J. Chem. Soc*., 1946, no. 8, p. 679.
6. Chandhur, A.R. and Ghoch, T.N., *J. Indian Chem. Soc*., 1951, vol. 28, p. 563.
7. Dreyfus, P. and Notley, N.T., *J. Polym. Sci*., 1958, vol. 28, p. 611.
8. Mowry, D.T., Renoll, M., and Huber, W.F., *J. Am. Chem. Soc*., 1946, vol. 68, p. 1105.
9. Beets, M.G.J. and van Essen, H., *Recl. Trav. Chim. Pays–Bas*, 1951, vol. 70, p. 25.
10. Chen, F.E., Zhang, H., Yuan, W., and Zhang, W.W., *Synth. Commun*. 1991, vol. 21, p. 107.
11. Mochalov, S.S., Kosynkin, D.V., Yudin, I.D., Zavodskikh, K.A., Shabarov, Yu.S., and Zefirov, N.S., *Khim. Geterotsikl. Soedin*., 1994, no. 4, p. 472.
12. Heertjes, P.M. and Revallier, L.J., *Recl. Trav. Chim. Pays–Bas*, 1950, vol. 69, p. 262.
13. Shabarov, Yu.S., Mochalov, S.S., Fedotov, A.N., and Kalashnikov, V.V., *Khim. Geterotsikl. Soedin*., 1975, vol. 9, p. 1195.