hexane containing 10—25% of Et_2O). TLC was carried out on Silufol plates. The spots were visualized by spraying with concentrated H_2SO_4 and subsequent heating.

22,23,24,25,26,27-Hexanor-3α-hydroxy-17,14-*frido*-9β-lanosta-7,14,20-triene (3). A solution of 140 mg of hydroxy ketone **2** (m.p. 84—85 °C, prepared by the previously described method[8]) in MeOH (20 mL) was placed in a quartz cylindrical 30-cm cell (with an inner diameter of 20 mm and wall thickness of 2 mm) and heated to reflux in a water bath in order to remove dissolved oxygen from methanol. The cell was then cooled quickly to –20 °C, sealed with a polyethylene stopper, and irradiated (using no filter) with the full light of a DRSh-1000 high-pressure mercury vapor lamp, the cell being cooled with an air stream from a ventilator. After 10 h of irradiation methanol was removed, and the residue was chromatographed on SiO_2 (5 g). Elution with a 9 : 1 hexane—ether mixture yielded 30 mg of product **3** with m.p. 118—120 °C (from pentane) and $[\alpha]^{22}_{580}$ +133.8° (*c* 0.89; $CHCl_3$). UV (C_2H_5OH), λ_{max}/nm: 232 (ε 8800). IR (CCl_4), ν/cm^{-1}: 905, 1640, 3090 (–CH=CH_2), 3620 (OH). MS, *m/z* (I_{rel} (%)): 340 $[M]^+$ (100), 307 (26), 187 (26), 145 (28), 55 (90). High resolution MS, *m/z*: 340.27565; calculated for $C_{24}H_{36}O$: 340.27660. ^{13}C and ^1H NMR spectra are given in Table 1.

Elution with a 4 : 1 hexane—Et_2O mixture resulted in 80 mg of starting compound **2**, and the mixture of highly polar substances (30 mg) was eluted with Et_2O.

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Influence of *E*/*Z* isomerism of aldoximes on the direction of their alkylation with oxirane

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The reaction of *Z*-2-furaldoxime with oxirane afforded the *N*-alkylation product, *viz.*, α-2-furyl-*N*-(2-hydroxyethyl)nitron, in good yield. *E*-Benzaldoxime gave predominantly the *O*-alkylation product, while its *Z* isomer was converted into a mixture with the *N*-alkylation product slightly predominating.

Key words: oxirane, aldoximes, α-aryl-*N*-(2-hydroxyethyl)nitrons.

Oximes and oxiranes are attractive, simple, and readily available initial compounds for preparing α-aryl-*N*-(2-hydroxyethyl)nitrons. However, attempts to alkylate benzaldoxime[1,2] (m.p. 31—33 °C, which corresponds to the *E* isomer[3]) resulted in nitron in a yield of only 3—6%. In all cases, a product of *O*-alkylation of oxime or products of its subsequent oxidation were obtained as the major reaction products.[1] At the same time, in the case of alkylation of oximes with alkyl halides, the orientation of alkylation (*O*- or *N*-) depends directly on the *E* or *Z* configuration of the oxime used.[4] It was also reported[5] that the reaction of *Z*-benzaldoxime with 1,2-epoxybutane afforded *trans*-5-ethyl-2-phenyl-3-hydroxyoxazolidine in 70% yield. It is known[6] that 3-hydroxyoxazolidines can exist in tautomeric equilibrium with the open form of α-arylnitron. Based on the aforesaid, we suggested that the use of oximes with the *Z* configuration should shift the direction of the reaction

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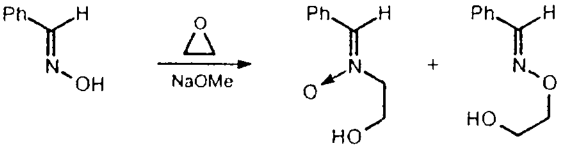
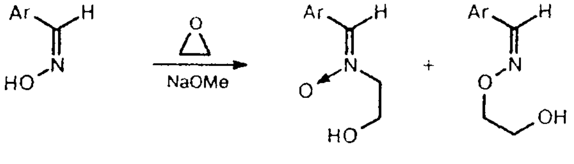
toward the predominant formation of *N*-alkylation products.

Actually, alkylation of *E*-benzaldoxime **1a** gave *N*- (**2b**) and *O*-alkylation (**3a**) products in a ratio of 1 : 5, while in the case of the *Z*-isomer **1b** the ratio was changed so that the content of *N*-alkylation product **2b** was increased (the ratio was 6 : 5). The reaction with *Z*-furaldoxime **1c** afforded predominantly arylnitron **2c** and the ratio of the *N*- (**2c**) and *O*-alkylation products (**3c**) was 10 : 1.



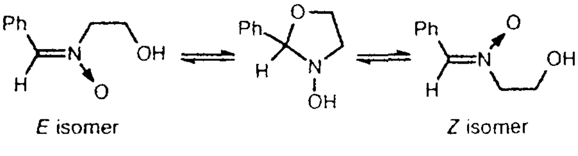
1a **2b** (1 : 5) **3a**



1b **2b** (6 : 5) **3b**
1c **2c** (10 : 1) **3c**

Ar = Ph (**b**), 2-furyl (**c**).

The reaction yielded *O*-alkylation products with retention of the configuration of the initial oxime, which is confirmed by the ^{1}H NMR spectral data. The chemical shift of the azomethine proton is 7.88 ppm (for **3b**) and 8.17 (for **3a**), which agrees with the published data.[4] In this connection, nitron with the *E*-configuration would be expected to form from *E*-benzaldoxime.[7] However, the spectral characteristics of the nitron isolated appeared to be identical with those of nitron **2b**. We believe that the thermodynamically less stable *E* isomer[8] was converted into the *Z* isomer through intermediate formation of oxazolidine due to the tautomeric equilibrium between the open form of α-arylnitron and the cyclic form of 3-hydroxyoxazolidine.[6]



Thus, the use of *Z*-aldoximes in the alkylation reaction with oxirane made it possible to obtain α-aryl-*N*-(2-hydroxyethyl)nitrons in good yields. It should be mentioned that the scope of this reaction is limited to the use of arenecarbaldoximes. Alkylation of ketoxime (2-acetylpyridine *Z*-oxime) did not proceed even at 25 °C. The use of acetone oxime resulted in the *O*-alkylation product, *viz*., 2-hydroxyethyl ether of acetone oxime **4**, in agreement with the data reported previously.[1]

Experimental

The IR spectra were recorded on Specord M-80 and UR-20 spectrometers in 1-mm thick KBr pellets (*C* 0.25%) and in CCl_4 solutions (*C* 5%). The UV spectra were obtained on a Specord UV- VIS spectrophotometer (EtOH). The ^{1}H NMR spectra were recorded on Bruker WP 200 and Bruker AC 200 spectrometers (200 MHz). The mass spectrum of compound **4** was measured on a Finnigan MAT8200 instrument (the temperature of vaporization was 230 °C, direct introduction of the sample).

Reactions of oximes with oxirane (general procedure). The reactions were carried out in methanol (30 mL) at −5 °C with the use of oxime (15 mmol), MeONa (15 mmol), and oxirane (1 mL). The duration of the reaction was 4 days. The reaction mixture was analyzed for the ratio of the *N*- and *O*-alkylation products based on integrated intensities of the signals of the azomethine protons in the ^{1}H NMR spectrum. The reaction mixture was concentrated, the residue was dissolved in water, the products were extracted with chloroform, the solution was dried with $MgSO_4$, and the solvent was distilled off. Before analyzing compound **2c**, the solid residue (1.8 g, the yield of the crude product was 80%) was twice recrystallized from ethyl acetate. In the case of compound **2b**, the oily residue was dissolved in diethyl ether (10 mL) and allowed to stand for 30 min after which the nitron precipitated (1.2 g, the yield of the crude product was 50%). Before analyzing, the product was twice recrystallized from a 2 : 1 hexane : ethyl acetate mixture. Compounds **3a** and **4** were isolated by column chromatography (SiO_2 100—140 mesh, $CHCl_3$) in 30 and 65% yields, respectively.

Compound 2b, m.p. 109—110 °C. Found (%): C, 65,13; H, 6.83; N, 8.57. $C_9H_{11}NO_2$. Calculated (%): C, 65.44; H, 6.71; N, 8.48. ^{1}H NMR (CD_3OD), δ: 4.06 (br.s, 4 H, 2 CH_2), 7.50 and 8.31 (both m, 3 H and 2 H, Ph), 7.84 (s, 1 H, $H_{azomethine}$). IR (in KBr pellets), ν/cm^{-1}: 3190 (O—H), 1605 (C=N). UV (EtOH), λ_{max}/nm (lg ε): 293 (4.36).

Compound 3a. Found (%): C, 64.70; H, 6.51; N, 9.17. $C_9H_{11}NO_2$. Calculated (%): C, 65.44; H, 6.71; N, 8.48. ^{1}H NMR (CD_3OD), δ: 3.84, 4.24 (both t, 2 H, 2 CH_2, *J* = 5 Hz), 7.39 and 7.59 (both m, 3 H and 2 H, Ph), 8.17 (s, 1 $H_{azomethine}$). IR (in a thin layer), ν/cm^{-1}: 3400 (O—H), 1595 (C=N). UV, (EtOH) λ_{max}/nm (lg ε): 262 (4.03).

Compound 2c, m.p. 118—119 °C. Found (%): C, 54.11; H, 5.88; N, 9.03. $C_7H_9NO_3$. Calculated (%): C, 54.18; H, 5.86; N, 9.03. ^{1}H NMR (CD_3OD), δ: 4.03 (s, 4 H, 2 CH_2), 6.69 and 7.74 (both m, 1 H and 2 H, 2-furyl), 7.79 (s, 1 $H_{azomethine}$). IR (in KBr pellets), ν/cm^{-1}: 3200 (O—H), 1610 (C=N). UV (EtOH), λ_{max}/nm (lg ε): 305 (4.31).

Compound 4: M$^+$ (high-resolution mass spectrum, found: *m/z* 117.07850), for $C_5H_{11}NO_2$, calculated: *m/z* 117.07898. ^{1}H NMR (CD_3OD), δ: 1.88 and 1.91 (both s, 3 H, 2 Me): 3.57, 4.08 (both t, 2 H, CH_2, *J* = 4 Hz). UV (EtOH), λ_{max}/nm (lg ε): 238 (2.9).

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Synthesis of 2-substituted 6,8-dinitro[1,2,4]triazolo[1,5-*a*]pyridines and the formation of the related zwitterionic σ-adducts

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A method for the synthesis of 2-substituted 6,8-dinitro[1,2,4]triazolo[1,5-*a*]pyridines is proposed. The method includes the reaction of 2-chloro-3,5-dinitropyridine with the corresponding 5-substituted tetrazoles. The resulting compounds react with anhydro bases of α- and γ-methylazinium salts to give zwitterionic σ-adducts.

Key words: 2-substituted 6,8-dinitro[1,2,4]triazolo[1,5-*a*]pyridines, 2-chloro-3,5-dinitropyridine, 5-substituted tetrazoles, anhydro bases, zwitterionic σ-adducts.

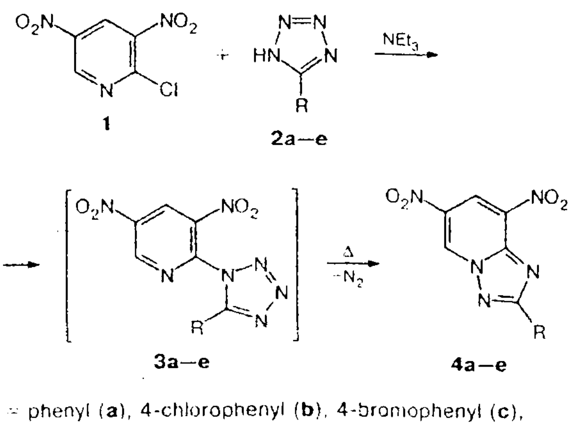
The addition products of nucleophilic agents to activated arenes (or hetarenes) (σ-adducts) are used as the starting compounds in some syntheses. However, they are mostly insufficiently stable, which precludes studies of these compounds. Earlier,[1] it was shown that introduction of nitro groups into the pyridine ring increases the rate of formation and stability of anionic σ-adducts. Stable zwitterionic σ-adducts were obtained by reaction of alkoxide-anionic σ-adducts of dinitrotetrazolo[1,5-*a*]pyridine with *N*-methylazinium salts as nucleophilic agents.[2] However, zwitterionic σ-adducts of azines are studied inadequately, and the influence of azoloannelation on their stability is still unclear.

The goal of this work is to synthesize the previously unknown 2-substituted 6,8-dinitro[1,2,4]triazolo[1,5-*a*]pyridines and their zwitterionic σ-adducts.

We could not obtain 2-hydrazino-3,5-dinitropyridine, a possible precursor of dinitrotriazolopyridine, because 2-chloro-3,5-dinitropyridine reacted with hydrazine vigorously to give a mixture of unidentified products.

For this reason, we developed a method for the synthesis of 2-substituted 6,8-dinitro[1,2,4]triazolo[1,5-*a*]pyridines (**4a—e**) that consists in the reaction of 2-chloro-3,5-dinitropyridine (**1**) with the corresponding 5-substituted tetrazoles **2a—e** in boiling acetonitrile in the presence of triethylamine (Scheme 1). Apparently, the formation of compounds **4a—e** proceeds *via* inter-

Scheme 1



R = phenyl (**a**), 4-chlorophenyl (**b**), 4-bromophenyl (**c**), 4-methoxyphenyl (**d**), 3,4-dimethoxyphenyl (**e**)

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