α-OXIDES IN REACTIONS WITH NH ACIDS OF THE HETEROCYCLIC SERIES

II.* ALKYLATION OF 3,5-DINITRO-1,2,4-TRIAZOLE WITH OLEFIN OXIDES

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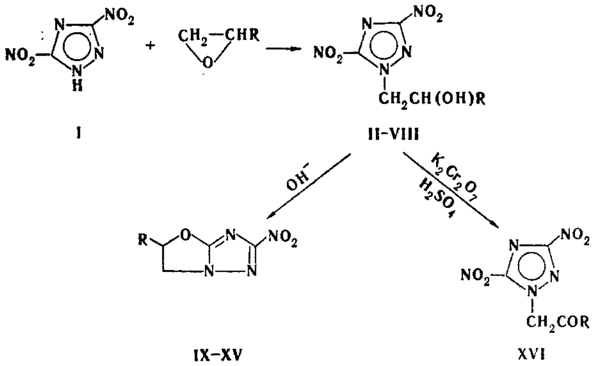
Alkylation of 3,5-dinitro-1,2,4-triazole with α-epoxides in aprotic media gave a number of 1-(2-hydroxyalkyl)-3,5-dinitro-1,2,4-triazoles, which readily undergo intramolecular cyclization with elimination of HNO_2 to give 5,6-dihydrooxazolo[3,2-b]-1,2,4-triazole derivatives.

As in the case of 3-nitro-5-bromo-1,2,4-triazole [1], the alkylation of 3,5-dinitro-1,2,4-triazole (I) with α-epoxides gives 1-(2-hydroxyalkyl)-3,5-dinitro-1,2,4-triazoles (II-VIII), which, in the presence of bases, undergo intramolecular cyclization with elimination of HNO_2 to give 5,6-dihydrooxazolo[3,2-b]-1,2,4-triazole derivatives (IX-XV).



II, IX R=H; III, X, XVI R=CH_3; IV, XI R=CH_2OCH_3; V, XII R=CH_2OH; VI, XIII R=CH_2Cl; VII, XIV R=CH_2ONO_2; VIII, XV R=$CH_2N(NO_2)CH_3$

The formation of secondary alcohols in the alkylation of 3,5-dinitro-1,2,4-triazole with unsymmetrical α-oxides is confirmed by oxidation of alcohol III to 1-(2-oxopropyl)-3,5-dinitro-1,2,4-triazole (XVI).

The signal of the methylene group bonded to the triazole substituent in the PMR spectrum of primary alcohol II lies at weaker field as compared with the signal of the methylene group attached to the hydroxyl group. The position of the signal of the methylene protons in the spectra of alcohols III-V is retained in the same region, and this constitutes evidence for attachment of the CH_2 group to the triazole ring, and, consequently, to the secondary character of the hydroxyl group. The presence of two nonequivalent methylene doublets in the spectrum of diol V attests to their nonequivalence and corresponds to a structure with a vicinal orientation of the hydroxyl groups.

In contrast to 3-nitro-5-bromo-1,2,4-triazole, alkylation with α-oxides of the considerably more acidic 3,5-dinitro-1,2,4-triazole (pK_a 3.05 [1] and −0.66 [2], respectively) is realized only in aprotic solvents (ether,

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*See [1] for communication I.

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acetone, and dioxane) during catalysis of undissociated NH acid I and therefore does not require an external catalyst. Reaction of the α-oxide principally with the alcohol solvent is observed when the reaction is carried out in aqueous alcohol media.

The isolation of 1-(2-hydroxyalkyl)-3,5-dinitro-1,2,4-triazoles from the reaction mixture is difficult because of their high solubilities in acidic media and the ease of their intramolecular cyclization during alkalization. In contrast to alcohols II-V, which could be isolated in pure form (Table 1), VI-VIII are unstable and undergo cyclization to give 5,6-dihydrooxazolo[3,2-b]-1,2,4-triazole derivatives even in the absence of bases and when they are stored or recrystallized. The reason for the increased tendency of these alcohols to undergo cyclization is the introduction of electron-acceptor groups into the substituent in the 1 position. The effect of the substituent is probably exerted on the ability of the alcohol to give the alkoxide anion necessary for attack at the C_5 atom of the triazole ring [3].

The considerably greater tendency of 1-(2-hydroxyalkyl)-3,5-dinitrotriazoles to undergo intramolecular cyclization as compared with their 5-bromo-substituted analogs is due to the greater mobility of the nitro group in the 5 position of the triazole ring as compared with halogen during nucleophilic substitution [4].

TABLE 1. 1-(2-Hydroxyalkyl)-3,5-dinitro-1,2,4-triazoles

Compound	R	mp, °C (crystallization solvent)	Empirical formula	Found, %			Calculated, %			IR spectra, ν, cm^{-1}			PMR spectra,* δ, ppm (J, Hz)				Yield, %
				C	H	N	C	H	N	ν_{NO_2}	ν_{OH}	ν_{ring}	CH_2	CHO	CH_2O	R	
II	H	57—58 (dichloroethane—chloroform, 1 : 2)	$C_4H_5N_5O_5$	24,1	2,2	34,6	23,6	2,4	34,5	1580 1320	1060 3200—3600	1515, 1440 1370, 1140	5,23 t (6)	—	4,30 t (6)	—	36
III	CH_3	101—102 (chloroform)	$C_5H_7N_5O_5$	28,2	3,2	32,7	27,7	3,2	32,3	1580 1320	1080 3200—3600	1515, 1430 1380, 1140	4,65 d (7)	4,10 m	—	1,65 d (7)	71
IV	CH_2OCH_3	69—70 (carbon tetrachloride)	$C_6H_9N_5O_6$	29,0	3.7	28,3	29.1	3,6	28.3	1580 1320	1080 3200—3600	1515, 1430 1365, 1130	5,10 d (6)	4,50 m	3,65 (6)	3,40 s	77
V	CH_2OH	104—105 (dichloroethane—chloroform, 2 : 1)	$C_5H_7N_5O_6$	26.2	2,8	30,1	25,8	3,0	30,0	1580 1320	1050, 1100 3200—3600	1515, 1430 1365, 1140	5,20 d (6)	4,50 m	3,90 d (6)	—	45

*The PMR spectra of II and V were obtained from nitrobenzene solutions, and the PMR spectra of III and V were obtained from dimethyl sulfoxide solutions; s is singlet, d is doublet, t is triplet, and m is multiplet.

EXPERIMENTAL METHOD

The PMR spectra were recorded with an R-12 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of films of the compounds were obtained with a UR-20 spectrometer.

1-(2-Hydroxyalkyl)-3,5-dinitro-1,2,4-triazoles (II-VIII). A 5.7-g (0.035 mole) sample of the sodium salt of triazole I was dissolved in 54 ml of 3% hydrochloric acid, and the solution was extracted with diethyl ether (four 25-ml portions). The extract was dried with anhydrous magnesium sulfate, 0.07 mole of the epoxide* was added to it with cooling, and the mixture was kept in a sealed vessel for 2-3 days. The ether was then removed, and the residue was extracted repeatedly with boiling dichloroethane to give II-V (Table 1), or the alcohol, without isolation, was treated with alkali.

1-(2-Oxopropyl)-3,5-dinitro-1,2,4-triazole (XVI). A solution of 2 g of alcohol III in 6 ml of concentrated sulfuric acid was added to a heated (to 60°) mixture of 4 ml of concentrated sulfuric acid, 20 ml of water, and 1.9 g (0.0065 mole) of potassium dichromate, and the mixture was held at this temperature for 30 min. It was then cooled and extracted with ethyl acetate. The extract was dried with calcined magnesium sulfate, and the solvent was removed in vacuo to give a product with mp 136-137° [from dichloroethane—chloroform (1 : 2)] in 91% yield. IR spectrum: 1320, 1580 (NO_2), 1140, 1350, 1450, 1525 (ring), 1180, and 1730 (CO) cm^{-1}. Found: C 27.6; H 2.2; N 33.0%. $C_5H_5N_5O_5$. Calculated: C 27.9; H 2.3 N 32.6%.

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*3-(N-Nitro-N-methyl)-1,2-epoxypropane was synthesized by the method in [5].

2-Nitro-5,6-dihydrooxazolo[3,2-b]-1,2,4-triazoles (IX-XV). The crude alcohol (II-VII) was dissolved in 40 ml of water, and the solution was made alkaline to pH 8 with 0.1 N sodium hydroxide solution. The resulting precipitate was removed by filtration, washed with water, and crystallized. The yields were 70-85% (based on triazole I). Compounds IX-XIV were identical to the compounds described in [1]. 2-Nitro-5-(N-nitro-N-methylaminomethyl)-5,6-dihydrooxazolo[3,2-b]-1,2,4-triazole (XV) had mp 171-171.5° (from dichloroethane). IR spectrum: 1360, 1560 ($C-NO_2$); 1280, 1525 ($N-NO_2$); 1130, 1430, 1525 (triazole ring); 1600 cm^{-1} (oxazole ring). Found: C 29.5; H 2.0; N 34.2%. $C_6H_8N_6O_5$. Calculated: C 29.5; H 3.3; N 34.4%.

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