HETEROCYCLIC NITRO COMPOUNDS

V. 1-METHYL-3-NITRO-5-ALKOXY- AND -PHENOXY-1,2,4-TRIAZOLES*

L. I. Bagal, M. S. Pevzner,
V. Ya. Samarenko, and A. P. Egorov

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Reaction of 1-methyl-3,5-dinitro-1,2,4-triazole with alcohols or phenols in the presence of bases (tertiary amines) leads to replacement of the nitro group in the 5-position by an alkoxy or phenoxy group.

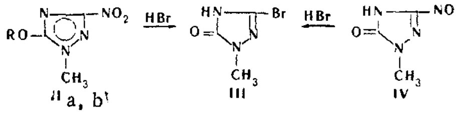
Methods for the preparation of ethers of 3(5)-hydroxy-1,2,4-triazoles have not been investigated to any extent up to the present time. The literature records only isolated instances of the synthesis of representative compounds of this type [2,3].

1,2,4-Triazoles derivatives containing both nitro and alkoxy or phenoxy groups have not been investigated.

In investigating nucleophilic substitution reactions of the nitro group in nitro derivatives of 1,2,4-triazole [4], we observed that reaction of 1-methyl-3,5-dinitro-1,2,4-triazole (I) with ammonia, methylamine, or diethylamine in alcoholic solution does not give the amino derivatives, but a compound identified as 1-methyl-3-nitro-5-ethoxy-1,2,4-triazole.

Further investigations led to the development of a convenient and fairly general method for the preparation of 1-methyl-3-nitro-5-alkoxy (phenoxy)-1,2,4-triazoles by the reaction of I with alcohols and phenols in the presence of tertiary amines (see Table 1). The use of tertiary amines (triethylamine) avoids the possible formation of amino derivatives as impurities.

Thin layer chromatography on alumina of the reaction products shows that, in all cases, a single isomer is formed. The structure of the compounds obtained was established by hydrolysis of the methoxy and ethoxy derivatives (IIa and IIb) with HBr which resulted in the simultaneous replacement of the second nitro group by bromine to give 1-methyl-3-bromo-1,2,4-triazole-5-one (III).



The triazolone III was also obtained from 1-methyl-3-nitro-1,2,4-triazole-5-one (IV) [4]. The phenoxy derivatives IId and IIe were very stable to acid hydrolysis, and remained unchanged even on heating for many hours. Alkaline hydrolysis resulted in decomposition, with the formation of ammonia, and no pure compound could be isolated.

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* For part IV, see [1].

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TABLE 1. 1-Methyl-3-nitro-5-alkoxy(phenoxy)-1,2,4-triazoles

Compound	R	mp, °C (solvent for recrystallization)	Molecular formula	Found				Calculated				IR spec., cm⁻¹ [5]		Yield, %
				C, %	H, %	N, %	*M*	C, %	H, %	N, %	*M*	ν_{NO_2}	ν_{C-O-C}	
IIa	CH_3	146 (ethanol	$C_4H_6N_4O_3$	30.47	4.18	35.59	154	30.35	154	35.45	158	1580; 1315	1240	71
IIб	C_2H_5	75 (ethanol	$C_5H_8N_4O_3$	34.50	4.44	32.80	169	34.90	4.66	32.55	172	1580; 1310	1230	60
IIв	*n*-C_3H_7	38 (petroleum ether)	$C_6H_{10}N_4O_3$	39.00	5.85	30.22	176	39.70	5.38	30.10	186	1580; 1315	1235	10
IIг	C_6H_5	124.5 (carbon tetrachloride-petroleum ether)	$C_9H_8N_4O_3$	49.10	3.60	25.48	218	49.10	3.64	25.44	220	1560; 1315		51
IIд	*m*-O_2N-C_6H_4	154.5 (dichloroethane-ether)	$C_9H_7N_5O_5$	41.50	3.06	26.58	260	40.75	2.64	26.42	265	1560; 1310 1515; 1360	1230	72
IIe	*p*-O_2N-C_6H_4	173 (dichloroethane-petroleum ether)	$C_9H_7N_5O_5$	40.72	2.93	26.38	—	40.75	2.64	26.42	265	1560; 1315 1525; 1360	1245	72

EXPERIMENTAL

1-Methyl-3-nitro-5-methoxy-1,2,4-triazole (IIa). To a solution of 2 g (11.5 mmole) of I [5] in 50 ml of methanol at 50° C was added 1.6 ml of triethylamine, and the mixture was heated at 60-70° C for 2 hr. The methanol was evaporated, and the residue was recrystallized from ethanol (6 ml per g).

1-Methyl-3-nitro-5-ethoxy-1,2,4-triazole (IIb) was obtained in a manner similar to IIa, in ethanolic solution.

1-Methyl-3-nitro-5-propoxy-1,2,4-triazole (IIc). A 6-g (35 mmole) quantity of I was dissolved in 130 ml of n-propanol at 85° C, and 4.8 ml of triethylamine was added. The mixture was heated for 3 hr at 95° C, the solvent was evaporated, and the residual oil was extracted with benzene. The benzene solution was washed with water and dried over calcium chloride, the solvent was removed at atmospheric pressure, and the residue was distilled in vacuo to give 0.6 g (10%) of a light-yellow oil, bp 130-133° C (0.5 mm), which crystallized on standing. After washing with petroleum ether, it had mp 38° C.

1-Methyl-3-nitro-5-phenoxy-1,2,4-triazole (IId). To a solution of 2 g (11.5 mmole) of I in a mixture of 15 ml of dioxane and 3 ml of water was added at room temperature a solution of 1.09 g (11 mmole) of phenol in 4 ml of dioxane. The mixture was heated for 3 hr at 65-70° C and kept for a day, the solvent was removed, and the residue was washed with water, dried, and recrystallized from a mixture of CCl_4 petroleum ether with the addition of alumina.

Nitrphenoxyderivatives IIe and IIf were obtained in a manner similar to IId, after heating for 4 hr at 80-85° C.

1-Methyl-3-bromo-1,2,4-triazole (III). A) A 0.75-g (4.8 mmole) quantity of IIa in a mixture of 8 ml of glacial acetic acid and 8 ml of 44% HBr was boiled for 3 hr at 110-115°C. The reaction mixture was cooled, poured into 40 ml of water, made basic to pH 8.5, and then extracted with 4 × 40 ml of chloroform to remove unreacted IIa. The aqueous solution was acidified with H_2SO_4 to pH 3.5-4, and extracted with 5 × 50 ml of chloroform. The extract was dried over calcium choride and the solvent was removed in vacuo to give 0.21 g (25%), mp 225° C (from dichloroethane). Found, %: C 20.20; H 1.80; Br 45.17; N 23.68. Mol wt 179. Calculated for $C_3H_4N_3OBr$, %: C 20.23; H 2.25; Br 44.92; N 23.60. Mol wt 178. IR spectrum, cm^{-1}: 1695 (C = O) and 700 (C–Br) [6].

Compound III was obtained in a similar manner from IIb, in 45% yield.

B) A 1-g (7 mmole) quantity of IV [4] was boiled in 11 ml of 44% HBr at 110-115° C for 4 hr. The mixture was cooled to 0° C, and the precipitate which separated was filtered off, washed with ice water, dried, and recrystallized from dichloroethane to give 0.25 g (20%) of product, mp 224.5-225.5° C, which was identical with the compound obtained by method A) (mp, IR spectrum, elementary composition).

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