# STABLE σ ADDUCTS OF 4,6-DINITROTETRAZOLO[1,5-*a*]PYRIDINE WITH ALKOXIDE ANIONS

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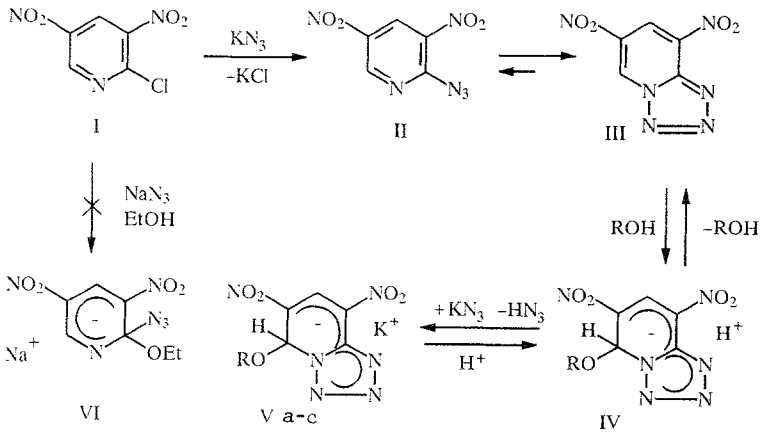
The σ complexing of 3,5-dinitropyridine and its derivatives has been studied rather thoroughly [1, 2]. However, no information regarding stable anionic σ complexes of tetrazolo[1,5-*a*]pyridines is available in the literature. Annelation of the tetrazole ring to a molecule, particularly to a pyridine molecule, should markedly increase the acceptor character of the system and the stability of the σ adducts. We have discovered the surprisingly smooth reaction of 2-chloro-3,5-dinitropyridine (I) with two equivalents of $KN_3$ in alcohol, which is accompanied by the formation of the potassium salts (Va-c) of the adducts and the liberation of one equivalent of $HN_3$:



V a R = Me, 96%; b R = Et, 85%; c R = $CHMe_2$, 79%

Lowe-Ma and coworkers [3] have reported carrying out a similar reaction (with $NaN_3$ in $C_2H_5OH$); however, incorrect structure VI was assigned to the reaction product. The PMR spectrum of V is identical to the spectrum described for VI. The IR spectra for these compounds are also similar; however, according to our data, the spectrum of a sample of Vb does not contain a band at 2110 $cm^{-1}$, which most likely belongs to traces of $NaN_3$ rather than to an azido group in the complex. The results of elementary analysis and the IR and PMR spectroscopic data prove structure V. The presence of an asymmetric center in the molecule at the $C_{(7)}$ atom is responsible for the nonequivalence of the geminal protons and methyl groups in complexes with ethoxide and isopropoxide anions. Treatment of adduct Va with trifluoroacetic acid leads to intermediate III, a solution of which in $CD_3OD$, according to the PMR data, contains acidic complex IV with alcohol. Potassium salt V of the adduct is isolated in the action of potassium salts (including $KN_3$) on complex IV, which confirms the proposed mechanism for the formation of the σ complexes.

The stability of the complexes is explained by the concerted participation in delocalization of the electron density of both the nitro groups and the tetrazole ring. Complexes Va-c are very stable during storage and decompose with sparking only at temperatures above 250°C.

**σ Adducts of 4,6-Dinitrotetrazolo[1,5-*a*]pyridine with Alkoxide Anions (General Method).** A 4.0-g sample of $KN_3$ was added to a solution of 5.0 g (0.0246 mole) of I in 50 ml of alcohol, and the mixture was stirred for 5 h. The precipitated orange crystalline complexes Va-c were removed by filtration, washed with water, and dried.

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**Adduct Va.** PMR spectrum ($d_6$-DMSO): 8.63 (1H, d, J = 0.7 Hz, 5-H); 7.21 (1H, d, J = 0.7 Hz, 7-H); 3.41 ppm (3H, s, $CH_3$). IR spectrum (mineral oil): 1578, 1575, 1548, 1261, 1170-1200, 1078 $cm^{-1}$.

**Adduct Vb.** PMR spectrum ($d_6$-acetone): 8.83 (1H, d, J = 0.7 Hz, 5-H); 7.14 (1H, d, J = 0.7 Hz, 7-H); 3.86 (2H, qq, $J_{AB}$ = 9 Hz, $\Delta\delta$ = 0.04, $CH_2$); 1.11 pm (3H, t, $CH_3$). IR spectrum: 1583, 1550, 1290, 1260, 1070 $cm^{-1}$.

**Adduct Vc.** PMR spectrum ($d_6$-DMSO): 8.70 (1H, s, 5-H); 7.20 (1H, s, 7-H); 1.03; 1.23 [6H, dd, $\Delta\delta$ = 0.2, $CH_3$ (A), $CH_3$ (B)]; 4.1-4.4 ppm (1H, m, $CHMe_2$). IR spectrum: 1590, 1545, 1283, 1250, 1162-1200, 1059 $cm^{-1}$.

PMR spectrum ($CD_3OD$) for a 5% solution of III: **III**: 9.43 (1H, d, J = 1.63 Hz, 5-H); 10.81 (1H, d, J = 1.63 Hz, 7-H); **II**: 9.15 (1H, d, J = 2.5 Hz, 4-H); 9.40 (1H, d, J = 2.5 Hz, 6-H); **IVa** (R = $CD_3$): 8.85 (1H, s, 5-H); 7.23 ppm (1H, s, 7-H). The ratio of III, II, and IVa was 2.5:1.0:7.0, respectively.

## REFERENCES


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