ZWITTER-IONIC C-σ-ADDUCTS BASED ON 4,6-DINITROTETRAZOLO[1,5-*a*]PYRIDINE

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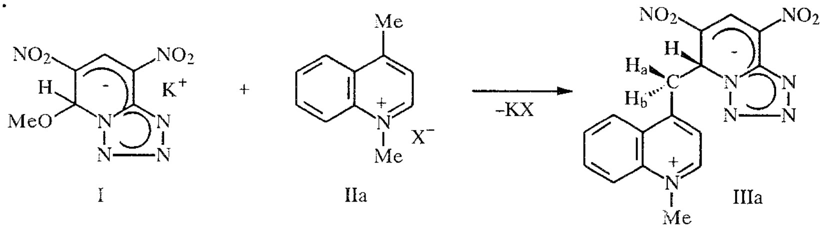
We have reported the isolation of stable σ adducts I with alcohols when the reaction of 2-chloro-3,5-dinitropyridine was carried out with two equivalents of KN_3 in alcohol [1]. We have discovered the formation of interesting compounds — zwitter-ionic σ complexes III — in the reaction of adduct I with an equivalent amount of 1-methyllepidinium salt IIa or similar compounds. At 120°C in DMF the reaction takes place in 10 min to give zwitter-ionic adduct IIIa, which is only slightly soluble in most solvents.



X = I⁻, ClO₄⁻

The reaction proceeds similarly with 1-ethyl-α- and 1-methyl-γ-picolinium salts (IIb and IIc) to give zwitter-ionic adducts IIIb and IIIc, respectively, as well as with other potential sources of anhydro bases.

The structures of the adducts were proved by the results of elementary analysis and IR and PMR spectroscopy. The characteristic location of the PMR signals of the protons of the $CH_3—N^+$ group, the shift of the 7-H signal to strong field, and the presence of an ABX system as a consequence of the nonequivalence of the geminal protons constitute evidence in favor of structure III.

Compounds IIIa-c were obtained as follows. A mixture of 0.01 mole of σ adduct I with 0.01 mole of quaternary salt IIa-c was heated in 10 ml of DMF at 120°C for 10 min. It was then cooled and treated with 5 ml of water, and IIIa-c were removed by filtration and washed with water and alcohol.

Compound IIIa ($C_{16}H_{13}N_7O_4$). This compound was obtained in 95% yield and had mp 246°C (dec.). PMR spectrum (d_6-DMSO): 8.55 (1H, s, 5-H); 6.61 (1H, q, J = 3.8, 6.2 Hz, 7-H); 4.11 (1H, dd, J = 3.8 and 17 Hz, H_a); 4.02 (1H, J = 6.2 and 17 Hz, H_b); 4.63 (3H, s, $N^+—CH_3$); 7.95-8.65 (4H, m, arom. H); 9.36 (1H, d, J = 5.9 Hz, H_α); 7.70 ppm (1H, d, J = 5.9 Hz, H_β). IR spectrum (here and subsequently, suspensions in mineral oil): 1599, 1544, 1539, 1452, 1340 cm^{-1}.

Compound IIIb ($C_{13}H_{13}N_7O_4$). This compound was obtained in 91% yield and had mp 244°C (dec.). PMR spectrum (d_6-DMSO): 8.66 (1H, s, 5-H); 6.63 (1H, q, J = 4.8 and 7.3 Hz, 7-H); 3.87 (1H, dd, J = 4.8 and 14 Hz, H_a); 3.83 (1H, dd, J = 7.3 and 14 Hz, H_b); 4.70 (2H, dq, $N—CH_2CH_3$); 1.47 (3H, t, CH_2CH_3); 9.11; 7.89; 8.12; 8.49 ppm (4H, m, H_{arom}). IR spectrum: 1622, 1573, 1548, 1375, 1341.

Compound IIIc ($C_{12}H_{11}N_7O_4$). This compound was obtained in 63% yield and had mp 250°C (dec.). PMR spectrum (d_6-DMSO): 8.57 (1H, s, 5-H); 6.56 (1H, t, J = 4.93 Hz, 7-H); 3.63 (2H, d, J = 4.93 Hz, CH_2); 4.28 (3H, s, $N^+—CH_3$); 8.83 (2H, d, J = 6.7 Hz, $2H_\alpha$); 7.67 ppm (2H, d, J = 6.7 Hz, $2H_\beta$). IR spectrum: 1635, 1566, 1543, 1430, 1402, 1340 cm^{-1}.

REFERENCES

1. I. E. Filatov, G. L. Rusinov, and O. N. Chupakhin, *Khim. Geterotsikl. Soedin.*, No. 8, 1145 (1992).

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