Isolation and Structure of a Meisenheimer-type Compound from a Five-membered-ring Heteroaromatic Substrate

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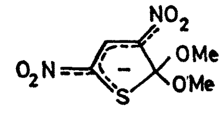
Summary The adduct formed between methoxide ion and 2-methoxy-3,5-dinitrothiophen is shown to have a Meisenheimer structure (II).

IN connection with our studies on reaction intermediates in nucleophilic heteroaromatic substitution, we report on the first Meisenheimer-type compound obtained from a five-membered-ring substrate, 2-methoxy-3,5-dinitrothiophen (I)

On addition of less than an equimolar amount of sodium methoxide to a 0·2M-solution of (I) in methanol, an intense purple colour develops immediately. A crystalline, purple 1:1 adduct (II), which gives a satisfactory elemental analysis, is obtained on removing the solvent at room temperature and washing with benzene. This compound decomposes easily in the presence of an excess of sodium methoxide in methanol solution.

The structure of compound (II) was proved by n.m.r., i.r., and visible spectral evidence. In $(CD_3)_2SO$ solution, the n.m.r. spectrum shows a low-field (τ 2·13) and a high-field (τ 6·72) singlet in the intensity ratio 1 : 6. Such peaks are assigned to an aromatic-like ring proton and to six equivalent methoxy-protons, and are consistent with a Meisenheimer structure as shown. In agreement with this, the i.r. spectrum of the solid displays strong absorptions between 1000 and 1250 cm.$^{-1}$, as observed with acetals[1] and with Meisenheimer compounds containing two geminal alkoxy-groups.[2] The electronic spectrum in methanol solution consists of two bands, whose λ_{max} values are 312 (ϵ 7·5 × 10^3) and 532 nm. (ϵ 2·3 × 10^4). The intensity of the latter band is of the same order of magnitude as the one generally displayed by Meisenheimer compounds in the same region.[3]



(II)

Information concerning the reaction

$$\text{(I)} + CH_3ONa \rightleftarrows \text{(II)}$$

in methanol solution at 20° has been obtained by standard spectral methods[3] at 532 nm. The equilibrium constant for the formation of (II) is so high that it cannot be precisely determined by these methods. It is greater than 2·5 × 10^5M^{-1}, *i.e.*, at least 15 times as great as that of the Meisenheimer compound derived from 2,4,6-trinitroanisole. In contrast, the rate constant for the formation reaction is *ca.* 20M^{-1}sec.$^{-1}$, and does not differ appreciably from that of the latter compound. Thus, the higher stability of compound (II) is possibly related to a relatively slow reverse reaction.

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[1] E. D. Bergman and S. Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.

[2] R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.* (*Australia*), 1966, **16**, 61.

[3] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1687.