Formation of a Meisenheimer Salt from a Substituted Picramide and Potassium Methoxide in Methanol; the Isolation of a Neutral Meisenheimer Complex

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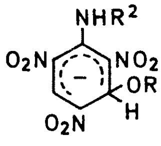
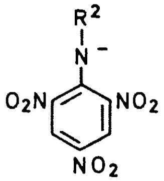
Summary The substituted picramide (III) gives the 1-σ (Meisenheimer) complex (IV) on treatment with KOMe in methanol; when an equivalent of HCl is added to (IV) the relatively stable neutral complex (V) is produced, which decomposes to (III) and methanol in polar solvents.

THE n.m.r. studies of Crampton and Gold[1] and Servis[2] have demonstrated that simple mono-substituted picramides give mixtures of the 3-σ complex (I) and the anion (II) on treatment with alkoxide ion. We now report that the substituted picramide (III) gives exclusively the 1-σ (Meisenheimer) complex (IV) on treatment with KOMe in methanol.

When a 10^{-3} M solution of (III) in methanol (λ_{max} 333, 400 nm) was treated with a molar equivalent of KOMe in methanol, a product with a visible spectrum typical of a Meisenheimer complex[3] (λ_{max} 420 nm, ϵ *ca.* $2 \cdot 8 \times 10^4$, 500 nm, ϵ *ca.* $1 \cdot 7 \times 10^4$) was formed. The product could be isolated as a brick-red solid in yields of *ca.* 80% by evaporating the reaction mixture to low bulk, adding cold ether, filtering off the resultant precipitate, and drying *in vacuo*. Support for the structure (IV) comes from elemental analysis;† i.r. (KBr disc): a series of strong overlapping bands between 1000 and 1230 cm^{-1} typical of Meisenheimer complexes,[4] strong band at 1685 (amide 1), and bands at 3520 and 3250 cm^{-1} (N–H); and n.m.r. spectrum [$(CD_3)_2SO$]: pair of doublets 8·57 and 8·46 (each 1H), doublet 4·08, (1H), multiplet 3·70 (1H), broad band 3·34 (4H), singlet 2·41 (3H), and a doublet 1·12 p.p.m. (3H). The band at 3·34 p.p.m. is attributed to the three methoxy-protons and a proton arising from a rapid base catalysed hydrogen–deuterium exchange of the amide-proton with the small quantity of D_2O/H_2O in the n.m.r. solvent. Support for this latter assignment comes from observations made on the n.m.r. spectrum of (III) in $(CD_3)_2SO$. When D_2O and a trace of piperidine are added to the n.m.r. tube, an absorption at 7·95 p.p.m. (1H, assigned to the amide N–H) rapidly decays and is replaced by an additional absorption at 3·28 p.p.m. (1H).



(I)



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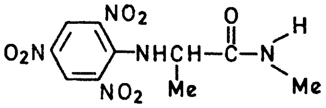
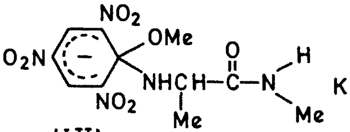


(III)



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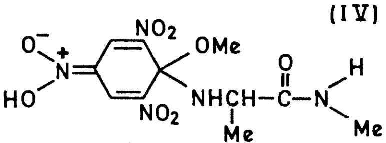
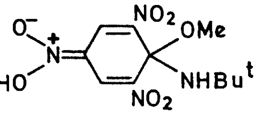
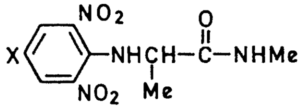


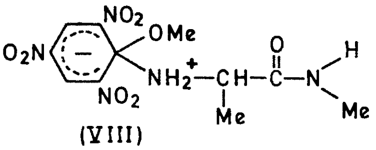
(V)



(VI)



(VII)



(VIII)

When a solution of (IV) in methanol (10^{-3}M) was treated with a molar equivalent of methanolic HCl, a new product with λ_{max} 394 and 500 nm was formed. This product decomposed in a first-order process ($k = 2{\cdot}65 \times 10^{-4}$ sec^{-1} at 25°) to yield (III). In another experiment, the product was isolated by low temperature evaporation of methanol solvent, dissolution of the red residue in acetone, filtration to remove potassium chloride, and evaporation of acetone at low temperature, followed by freeze-drying. The resultant red solid was homogeneous on t.l.c. when freshly prepared, but decomposed in polar solvents, and more slowly in the solid phase, to yield (III) and methanol only. Dissolution of this isolated product gave a u.v. visible spectrum identical with that of the *in situ* prepared compound with peaks at 395 and 500 nm.

We assign the structure (V),‡ a neutral Meisenheimer complex, to this compound on the grounds of: (i) correct elemental analysis, (ii) i.r. (KBr disc): a series of strong overlapping bands between 1000 and 1230, band at 1695, broad absorption 3500—3200 cm^{-1}; (iii) the H.M.O. calculations of Zollinger *et al.*[5] have shown that in 2,4,6-trinitro-Meisenheimer complexes the 4-nitro-substituent carries the bulk of the negative charge and, therefore, is the most likely site for protonation; and (iv) the nature of the decomposition products.

We were unable to obtain a satisfactory n.m.r. spectrum for (V) in $(CD_3)_2SO$ behause of its rapid decomposition in this solvent.

This appears to be only the second[6] report of the isolation of a neutral Meisenheimer complex; recently Clapp *et al.*[7] have also described spectroscopic evidence for the formation of (VI) in tetrahydrofuran solution.

We have also found that treatment of (III) with piperidine in methanol leads to (IV) (with piperidinium gegen-ion) and that (V) is produced on neutralisation of the reaction mixture with methanolic HCl. This unusual reaction, which occurs at a convenient rate at 25° and appears to be general for compounds of structure (VII) (where X is an electron-withdrawing group), will be the subject of a forthcoming publication.

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† Slightly low carbon analysis figures were obtained; these appear to be characteristic of isolated Meisenheimer complexes. See, for example, the work of Fendler *et al.* (refs. 8 and 9).

‡ A referee has suggested that the structure (VIII) is at least equally likely. We have considered this structure, but prefer (V) (see ref. 7).

[1] M. R. Crampton and V. Gold, *J. Chem. Soc.* (*B*), 1966, 893.
[2] K. L. Servis, *J. Amer. Chem. Soc.*, 1967, **89**, 1508.
[3] E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev.*, 1968, **22**, 123.
[4] L. K. Dyall, *J. Chem. Soc.*, 1960, 5160.
[5] P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, 1967, **50**, 548.
[6] M. J. Strauss and R. G. Johanson, *Chem. and Ind.*, 1969, 242.
[7] L. B. Clapp, H. Lacey, G. G. Beckwith, R. M. Srivastava, and N. Muhammad, *J. Org. Chem.*, 1968, **33**, 4262.
[8] J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, 1968, **33**, 977.
[9] J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, 1969, **34**, 689.

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