Alkylation and Substitution Reactions of 2,4,6-Trinitroanisole. Isolation of a Reactive σ-Complex Intermediate

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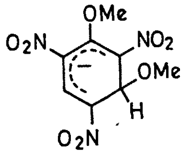
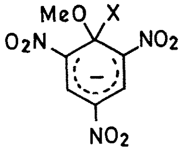
Summary A σ-complex has been isolated from the reaction of ethyl acetoacetate and 2,4,6-trinitroanisole in the presence of potassium t-butoxide, which, in the presence of acid decomposes to ethyl 2-picrylacetoacetate.

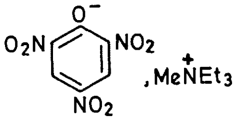
THE reaction of 2,4,6-trinitroanisole with potassium methoxide results in addition at C-3 of the aromatic compound to give the kinetically favoured σ-complex[1](I). This C-3 adduct is eventually converted into the more thermodynamically stable C-1 adduct (IIa).[1,2]



(I)



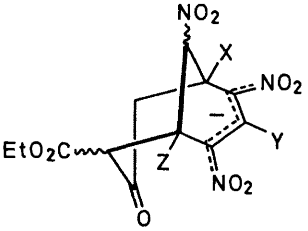
(IIa) X=OMe
(IIb) $X=\overset{+}{N}Et_3$
(IIc) $X=CH(Ac)CO_2Et$



(III)

It has been reported that 2,4,6-trinitroanisole reacts with triethylamine to yield the zwitterionic adduct (IIb).[3] The compound actually characterized was methyltriethylammonium picrate (III).[4] The report of an adduct between 2,4,6-trinitroanisole and acetone in the presence of triethylamine[5] is also incorrect, as the aromatic compound actually referred to was trinitrophenetole.[6] In fact, we have found that 2,4,6-trinitroanisole, acetone, and triethylamine yield (III) in quantitative yield. There has then been no report of a carbanion σ-complex with 2,4,6-trinitroanisole.

In connection with studies on the bicyclic adduct (IVa) which can be prepared from ethyl acetoacetate, *sym*-trinitrobenzene, and triethylamine[7] we attempted the preparation of (IVa), (IVb), and (IVc), or a mixture of these isomers by reaction of 2,4,6-trinitroanisole with ethyl acetoacetate. In order to prevent formation of trialkylammonium picrate, potassium t-butoxide was used to initiate the reaction. Stirring equivalent amounts of this base and 2,4,6-trinitroanisole in an excess of *ethyl acetoacetate*, diluted with anhydrous tetrahydrofuran, for 2 hr. at room temperature yielded a dark red precipitate. After washing with anhydrous ether and drying at reduced pressure, this material analysed correctly for the potassium salt of a 1:1 adduct of 2,4,6-trinitroanisole and ethyl acetoacetate. The n.m.r. spectrum $[(CD_3)_2SO, Me_4Si]$ is consistent with the C-1 adduct (IIc): δ 8·6 (s, 2H, ring-H), 3·4 (s, 3H, $C\mathit{H}_3O$-) and 2·2 (s, 3H $EtO_2C{\cdot}CH_2{\cdot}CO{\cdot}C\mathit{H}_3$); 3·8 (q, 2H, $CH_3C\mathit{H}_2{\cdot}O_2C{\cdot}CH_2Ac$), and 1·1 (t, 3H, $C\mathit{H}_3{\cdot}CH_2{\cdot}O_2C{\cdot}CH_2Ac$). The acidic exocyclic methine proton does not appear in the spectrum. This is a result of rapid exchange catalysed by trace amounts of base. Such behaviour has been observed in similar systems.[8]



(IVa) X=Y=Z=H
(IVb) X=OMe, Y=Z=H
(IVc) X=Y=H, Z=OMe
(IVd) Y=OMe, X=Z=H

Acidification of (IIc) with 0·1 N-H_2SO_4 results in a quantitative conversion into picryl ethylacetoacetate[9] (m.p. 96°) which was characterized by n.m.r., i.r., and elemental analysis.

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