Preparation of σ-Complexes Analogous to Intermediates in Nucleophilic Aromatic Substitution Reactions

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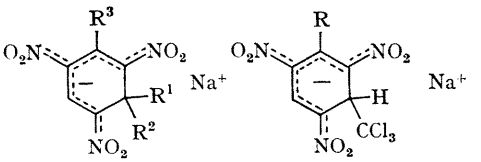
Summary Stable σ-complexes are formed by reaction of polynitro-compounds with haloforms or tetrachloromethane in the presence of base.

NUCLEOPHILIC aromatic substitution reactions proceeding by way of intermediate Meisenheimer complexes (I) are well known.[1] Stable σ-complexes are now reported (II) which are formed in reactions of polynitro-compounds with haloforms or CCl_4 in the presence of alkoxide ion or amines.

Thus, a 1·0M-solution of 1,3,5-trinitrobenzene in Me_2SO (2·5 ml.) and 5M-NaOMe in MeOH (0·5 ml) were kept for 10—20 min., and chloroform (3·6 ml.) was added. The mixture was kept at 40° for 5 hr., then diluted with water and ice, cooled, and filtered. The product (IIa) (red crystals) was unstable. The n.m.r. spectrum (in Me_2SO) showed signals at δ — 8·61 (doublet, *J* 1·5 Hz.), —6·35 (triplet, *J* 1·5 Hz.), of relative intensity 2 : 1.

When sodium methoxide was added to a solution of 1,3,5-trinitrobenzene in Me_2SO, the n.m.r. spectrum indicated the formation of a complex (I; $R^1 = H$, $R^2 = OMe$, $R^3 = H$). When chloroform was added to the solution, the signals corresponding to (I; $R^1 = H$, $R^2 = OMe$, $R^3 = H$) were replaced by those of (IIa).

Treatment of (IIa) with water or dilute acid (or merely leaving it exposed to the air) regenerated 1,3,5-trinitrobenzene. Addition of NaOMe to a solution of (IIa) in Me_2SO resulted in the formation of (I; $R^1 = H$, $R^2 = OMe$, $R^3 = H$), *i.e.*, complexes (I; $R^1 = H$, $R^2 = OMe$, $R^3 = H$) and (IIa) are in equilibrium.



(I) (II) a, R=H; b, R=OMe

2,4,6-Trinitroanisole, or the corresponding complex (I; $R^1 = R^2 = OMe$; $R^3 = H$), under similar conditions, gave complex (IIb), which showed n.m.r. signals at δ — 8·64 and —6·64 (doublets, *J* 1·7 Hz.), relative intensity 1 : 1.

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