Tetrahedron Letters No.25, pp. 2021-2022, 1969. Pergamon Press. Printed in Great Britain.

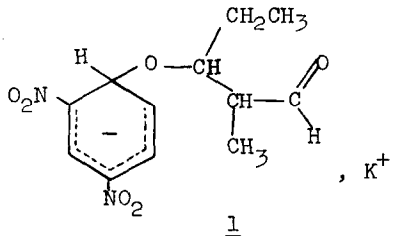
ISOLATION AND CHARACTERIZATION OF A PROPIONALDEHYDE sym-TRINITROBENZENE MEISENHEIMER COMPLEX

M. J. Strauss
Department of Chemistry, University of Vermont
Burlington, Vermont

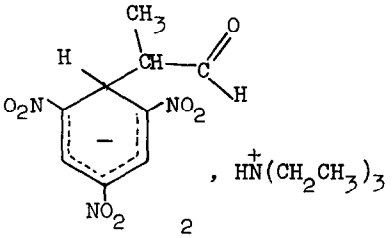
(Received in USA 21 February 1969; received in UK for publication 24 April 1969)

Although it is known that intense color develops upon addition of aldehydes to polynitrobenzenes in the presence of base (1,2,3), presumably resulting from Meisenheimer complex formation, there has been speculation about the exact structure of the species responsible (1,4). Gitis, Kaminskii, and Varlanova (3) report that with m-dinitrobenzene, potassium hydroxide, and propionaldehyde a preliminary aldol condensation occurs, followed by attack of aldolate anion on dinitrobenzene to give the Meisenheimer complex 1. They were unable to isolate this product however.

We wish to report here the isolation and structural characterization of the adduct 2 formed from propionaldehyde, sym-trinitrobenzene, and triethylamine.



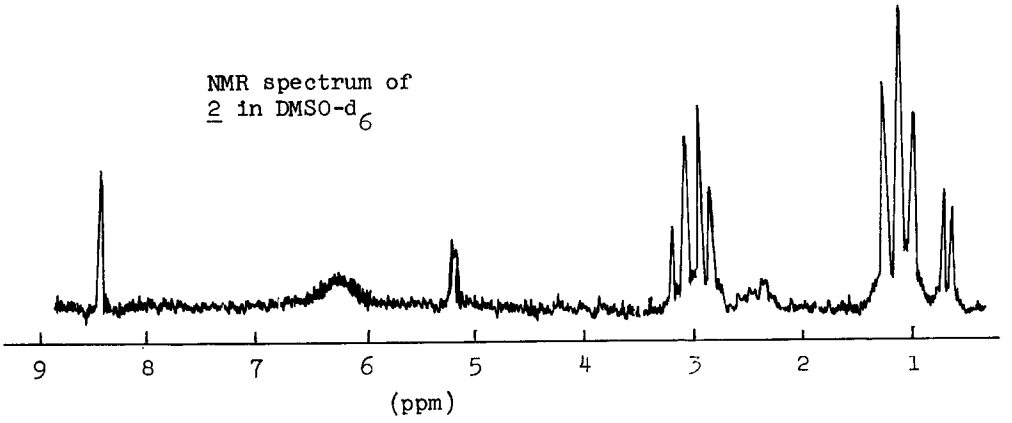
1



2

Addition of excess triethylamine to a saturated solution of sym-trinitrobenzene in propionaldehyde resulted in a dark purple solution, which after standing for

three minutes precipitated purple crystals. These were washed with anhydrous ether and dried at reduced pressure. Elemental analysis is indicative of a 1:1:1 adduct, Anal. Calcd. for $C_{15}H_{24}N_4O_7$: C, 48.38; H, 6.50; N, 15.05. Found: C, 48.42; H, 6.66; N, 14.93. The visible spectrum of the adduct in anhydrous methanol shows two absorptions at 470 and 566 mu characteristic of the cyclohexadienide system in Meisenheimer salts (4). The infrared spectrum shows a strong absorption at 1720 cm^{-1} (C=O). The nmr spectrum of the adduct in DMSO conclusively establishes the structure as 2.



The aldehydic proton (not shown above) appears as a singlet at δ9.7 (1H). The cyclohexadienide protons appear as a singlet at δ8.4 (2H). A broad absorption centered at δ6.2 (1H) results from the proton on triethylammonium cation. The sp^3-hybridized ring carbon appears as a doublet, δ5.2, J=2.5 cps, (1H). The quartet and triplet of triethylammonium cation appear centered at δ2.9 (6H) and δ1.2 (9H) respectively. The proton α to the carbonyl appears as an octet centered at δ2.3 (1H), coupled to the tetrahedral ring carbon (J=2.5 cps) and the α methyl group (J=7 cps). The absorption for this methyl appears as a doublet centered at δ0.8, J=7 cps (3H).

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