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CONDENSATION AND CYCLIZATION OF SOME POTENTIAL BIS-CARBANIONS WITH 1,3,5-TRINITROBENZENE

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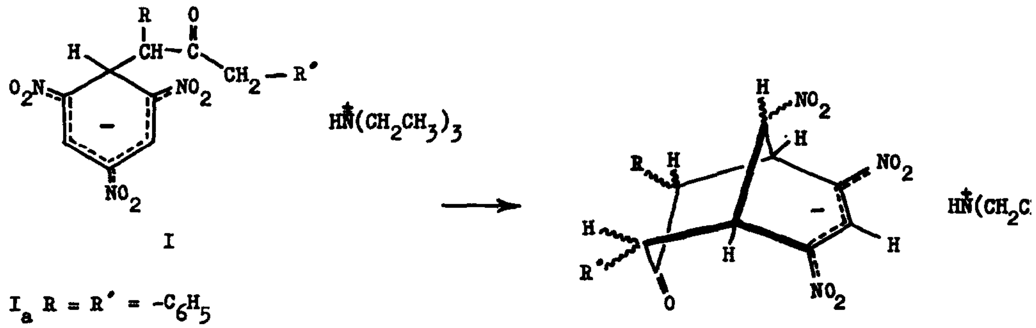
The condensation of carbanions with 1,3,5-trinitrobenzene has recently been of considerable interest and is the subject of a brief review (1). We wish to report here a novel intramolecular cyclization which occurs when two potential nucleophilic sites are present in the attacking carbanion.

When triethylamine is added to a saturated solution of 1,3,5-trinitrobenzene in dibenzylketone or acetylacetone an intensely coloured solution forms with a visible spectrum characteristic of Meisenheimer compounds such as I:[1]



I

II

I_a $R = R' = -C_6H_5$

I_b $R = CH_3-\overset{O}{\overset{\|}{C}}-$, $R' = -H$

II_a $R = R' = -C_6H_5$

II_b $R = CH_3-\overset{O}{\overset{\|}{C}}-$, $R' = -H$

Upon standing for 2 hours at room temperature a dark orange powder precipitates out when cold anhydrous ether is added to the reaction mixture. After recrystallization from ethanol, brilliant orange crystals are obtained which melt at 190°C (II_a) and 140° (II_b). The elemental analyses of the adducts are consistent with a structure containing one molecule each of 1,3,5-trinitrobenzene, ketone, and triethylamine. The visible spectra of II_a and II_b show a single absorption at $\sim$ 500 mμ characteristic of a dinitropropenide structure (2).

II may exist in a number of isomeric forms and the presence of isomers complicates the n.m.r. spectra of the crude adducts. A very poor yield (6%) of what appears to be a pure form of II_a is obtained upon recrystallisation of the crude material from ethanol. The n.m.r. spectrum of this product in DMSO D_6 shows a singlet at 8.6 p.p.m. (rel. area 1), a broad absorption at 7.3 p.p.m. (rel. area 10), a triplet at 6.0 p.p.m. (rel. area 1), and two separate multiplets at 4.4 and 4.7 p.p.m. (each with rel. area 2). The triplet and quartet of the triethylammonium cation are at 1.0 and 3.0 p.p.m. respectively.

Further discussion concerning the mechanism and scope of the reaction as well as further comments on structural isomerism involved will be published elsewhere.

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

[2] R. Foster and C.A. Fyfe, Tetrahedron, 21, 3363 (1965).