

The Structure of the Product of a Janovsky Reaction: 1,3-Dinitrobenzene plus Alkali in Acetone Solution

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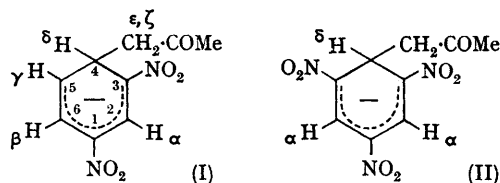
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On the basis of the electronic spectrum, Canback¹ suggested that the structure of the ion, which causes the purple coloration when strong alkali is added to an acetone solution of 1,3-dinitrobenzene, is (I). Although the structure of the corresponding trinitro-ion (II) has been established by n.m.r. spectroscopy,² there has been no conclusive argument in the case of the dinitro-compound, although the solid sodium salt shows the expected infrared spectrum.³ The n.m.r. spectrum has now been measured for a solution of (I) obtained by adding solid sodium methoxide to a solution of 1,3-dinitrobenzene in a 1:1 v/v mixture of dimethyl sulphoxide and acetone. The spectrum below τ 6 p.p.m. and the assignments are given in the Table.

protons in the acetyl side-chain must be non-equivalent. This is reflected in the quintuplet splitting of H δ (due to coupling with the two methylene protons and H γ). Confirmation of this assignment is obtained from the ion equivalent to (I) derived from perdeuterioacetone. The



TABLE

N.m.r. parameters for the sodium salt of (I) in 1:1 v/v dimethyl sulphoxide-acetone

Proton	Chemical shift (τ) (p.p.m.)	Multiplicity ^a of absorption	Spin-spin couplings ^a (c./sec.)
H α	1.6 δ	doublet	$J(\text{H}\alpha\text{-H}\beta) = 1.9$
H β	3.3 δ	quartet (double doublet)	$J(\text{H}\beta\text{-H}\alpha) = 1.9$; $J(\text{H}\beta\text{-H}\gamma) = 10.2$
H γ	4.6 δ	quartet (double doublet)	$J(\text{H}\gamma\text{-H}\beta) = 10.2$; $J(\text{H}\gamma\text{-H}\delta) = 5.0$
H δ	5.8 δ	quintuplet	$J(\text{H}\delta\text{-H}\gamma) = 5.0$; $J(\text{H}\delta\text{-H}\epsilon) \approx 5.0$; $J(\text{H}\delta\text{-H}\zeta) \approx 10.0$

^a weak coupling (H α -H δ) = 0.6 and (H β -H δ) = 1.0 c./sec. also occurs.

The non-equivalence of all four ring protons shows that if the nucleophilic attack is at an unsubstituted position, it must be at the 4(6) position. The assignments of H α and H δ are consistent with the absorptions of the corresponding protons in (II). An important consequence of structure (II) is that the asymmetry of the ring about C(4) makes this carbon atom "asymmetric", so that the methylene

n.m.r. spectrum below τ 6 p.p.m. of this ion is virtually identical with that of (I) except that H δ is now a doublet [split only by H γ , $J(\text{H}\delta\text{-H}\gamma) = 5.0$ c./sec.]. There is no evidence for the presence of any structural isomers of (I).

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