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NUCLEAR MAGNETIC RESONANCE STUDY OF MEISENHEIMER COMPOUNDS IN THE PYRIDINE SERIES

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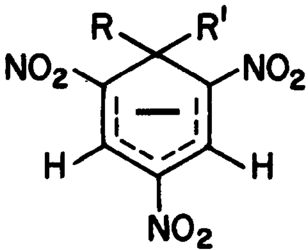
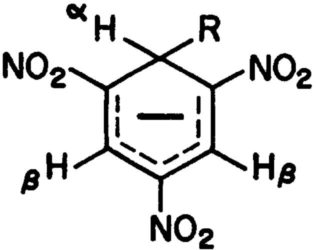
Very strong evidence in favour of the intermediate complex theory of nucleophilic aromatic substitution proposed by Bunnett (1) has been the characterisation of stable intermediates from certain highly activated substrates. Compounds of this type, eg. I (R = OCH_3) and II (R = $-OCH_3$, $-N(CH_2CH_3)_2$, $-CH_2COCH_3$) are usually known as Meisenheimer Compounds (2). Evidence is now presented from Nuclear Magnetic Resonance Spectroscopy for the existence of similar intermediates in the pyridine series.

Thus, the addition of sodium methoxide to a solution of 3,5-dinitropyridine in dimethylsulphoxide (DMSO) gives rise to a bright red coloured solution (λ_{max} = 487 mμ) and causes the disappearance of the 3,5-dinitropyridine resonances at 0.27 τ and 0.86 τ and the appearance of three new resonances of equal intensity at 1.38 τ, 1.70 τ and 3.92 τ ascribable to structure III (R = OCH_3). There is no evidence for the formation of the second isomer IV (R = OCH_3). The shift to higher fields has been found characteristic of the cyclopentadienate system in aromatic systems, and the resonance at 3.92 τ ascribed to the hydrogen atom on the SP^3 carbon atom is in agreement with those found for aromatic systems (table). Addition of excess diethylamine to this system gives rise to resonances ascribable to III (R = $N(CH_2CH_3)_2$). This compound is formally analogous to the proposed intermediate in the Chichibabin reaction (3).

Dilution of a solution of III (R = OCH_3) in DMSO with an equal volume of acetone yields a purple solution (λ_{max} = 519 mμ) and resonances ascribable to structure IV (R = CH_2COCH_3). There are also resonances corresponding to structure III (R = CH_2COCH_3) accounting for ~25% of the equilibrium mixture. The resonance ascribed to the hydrogen atom of the SP^3 carbon atom in structure III (R = CH_2COCH_3) consists of four lines of equal intensity, and not a triplet, giving further evidence of unsymmetrical substitution of the pyridine ring. Addition of acid in all cases regenerates 3,5-dinitropyridine.

Addition of sodium methoxide to a solution, 2-dimethylamino-3,5-dinitropyridine in DMSO gives a red colouration (λ_{max} = 448 mμ) and causes the disappearance of the aromatic resonances at 0.85 τ,


I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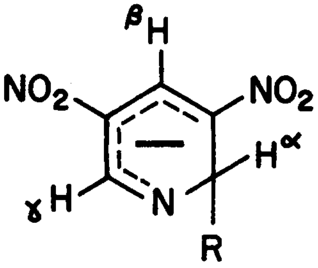
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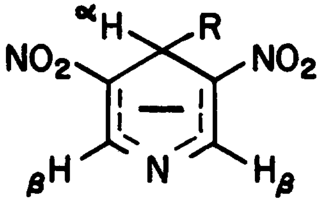
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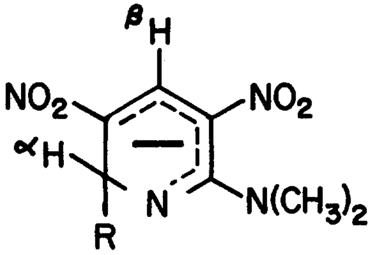
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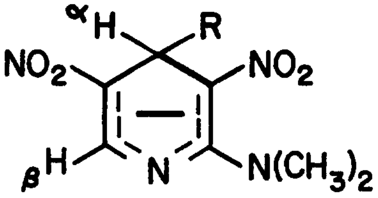
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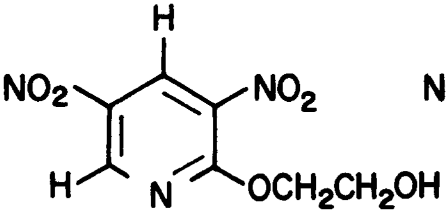
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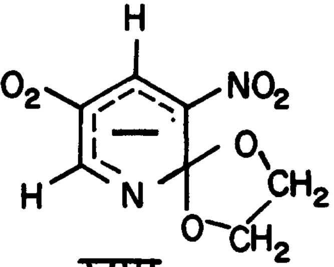
VIII

1.15 τ, and the appearance of two new resonances of equal intensity at 1.80 τ and 3.95 τ. The latter is characteristic of a proton attached to an SP^3 carbon atom in these systems, but it is not possible to deduce which of the two isomers V, VI (R = OCH_3) has been formed. Similarly, dilution of this solution with an equal volume of acetone gives two new resonances of equal intensity at 1.86 τ, 4.90 τ, (the latter of four lines of equal intensity showing unsymmetrical substitution of the ring) but it is not possible to distinguish between V and VI (R = CH_2COCH_3). Deuteration of this system has not been possible to date. In both cases, addition of acid regenerates the parent aromatic compound.

TABLE

Chemical Shift Data (τ values) and Intensities (in brackets) of

Pyridine Meisenheimer Compounds in DMSO

Structure	R	H_α	H_β	H_γ
II*	OCH_3	3.78 (1)	1.48 (2)	---
	$N(CH_2CH_3)_2$	4.33 (1)	1.53 (2)	---
	CH_2COCH_3	4.92 (1)	1.65 (2)	---
III	OCH_3	3.92 (1)	1.70 (1)	1.38 (1)
	$\acute{N}(CH_2CH_3)_2$	4.17 (1)	1.70 (1)	1.42 (1)
	CH_2COCH_3†	4.50 (1)	1.78 (1)	1.62 (1)
IV	CH_2COCH_3†	5.12 (1)	1.85 (2)	---

† 50% DMSO 50% acetone

* Reference 2 p. 77.

Addition of sodium methoxide to a solution of 2-(2'hydroxyethoxy)-3,5-dinitropyridine VII in DMSO gives a red colouration (λ_{max} = 462 mμ) and causes the disappearance of the NMR spectrum of the aromatic compound at .69 τ, .90 τ and the appearance of a tightly coupled AB system centered at 1.65 τ (rel. intensity 1) and a singlet (rel. intensity 2) at 5.88 τ corresponding to the ring and methylene protons of the spiro-compound VIII. 2-hydroxy-3,5-dinitropyridine absorbs at 1.2 τ in basic DMSO, so it would appear that no hydrolysis has taken place. Acidification of a solution of VIII regenerates the spectrum of VII.

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