# INTERACTION OF HETEROCYCLES AND NUCLEOPHILES

## III.* INTERCONVERSION OF THE METHINE SIGMA COMPLEXES DERIVED FROM 3,5-DINITROPYRIDINE AND METHOXIDE ION IN DIMETHYL SULPHOXIDE

By M. E. C. Biffin,† J. Miller,† A. G. Moritz,† and D. B. Paul†

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*Abstract*

The conversion of the methine complex (4; $R^1 = H$) into the more stable isomer (5; $R^1 = R^2 = H$) is reported.

### Introduction

Sigma complexes derived from nucleophiles and polynitroaromatic compounds, or their aza analogues, are of interest since they are relatively stable examples of the benzenide intermediates proposed for aromatic $S_N2$ reactions.[1] In the case of 2,4,6-trinitroanisole and related compounds, considerable attention has been focussed on the factors governing the conversion of methine adducts into their thermodynamically more stable acetal isomers.[2–5] In contrast, the interconversion of methine complexes has elicited no mention in the literature, although one such example is implied in the recent finding of Foreman and Foster[6] that 3,5-dinitrobenzonitrile forms the methine complexes (1) and (2) by reaction with the anion from diethyl ketone in dimethyl sulphoxide. It was recorded that the p.m.r. signals attributed to the former complex decayed with time in favour of those arising from the latter. We now report the ready conversion of a methine complex (4; $R^1 = H$) from 3,5-dinitropyridine (3; $R^1 = H$) into the more stable isomer (5; $R^1 = R^2 = H$) in DMSO. Some aspects of kinetic control in this reaction are discussed.

* Part II, *Aust. J. Chem.*, 1970, **23**, 957.

† Australian Defence Scientific Service, Department of Supply, Defence Standards Laboratories, P.O. Box 50, Ascot Vale, Vic. 3032.

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[3] Biffin, M. E. C., Miller, J., Moritz, A. G., and Paul, D. B., *Aust. J. Chem.*, 1969, **22**, 2561.

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[5] Crampton, M. R., and Gold, V., *J. chem. Soc.* (*B*), 1966, 893.

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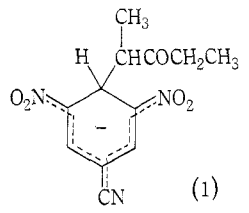
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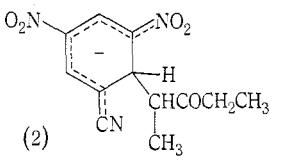
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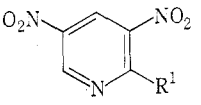
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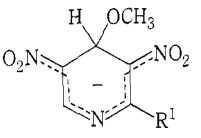
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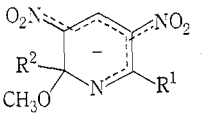
(5)

## Results and Discussion

Addition of sodium methoxide to a solution of 3,5-dinitropyridine in DMSO-$d_6$ caused the p.m.r. resonances from the substrate to disappear with the concurrent appearance of an $AX_2$ spectrum ($H_A$ 358·2, $H_X$ 500·5, $J$ 1·3$_2$ Hz). This spectrum, which is assigned to the C4 adduct (4; $R^1 = H$) decayed with time ($t_{0.5}$ 10 min) and was replaced by an AMX spectrum with signals at 514·9, 496·7, and 364·1 Hz. The latter spectrum persisted for several hours and is assigned to the C2 methine complex (5; $R^1 = R^2 = H$).

Table 1

P.M.R. spectral data in DMSO-$d_6$

Chemical shifts in Hz from internal tetramethylsilane at 60 MHz; coupling constants in Hz

| Formula | $R^1$ | $R^2$ | H2 | H4 | H6 | OMe | $J$ |
|---|---|---|---|---|---|---|---|
| (3) | H | — | 583·6 | 547·4 | (583·6) | — | 2·3$_4$ |
| (3) | D | — | 583·6 | 547·4 | (583·6) | — | 2·3$_4$ |
| (4) | H | — | 500·5 | 358·2 | (500·5) | 188 | 1·3$_2$ |
| (4) | D | — | 500·5 | 358·2 | — | 188 | 1·3$_2$ |
| (5) | H | H | 364·1 | 496·7 | 514·9 | 192[a] | [b] |
| (5) | D | H | — | 496·7 | 514·9 | 192[a] | 2·2$_7$ |
| (5) | H | D | 364·1 | 496·7 | — | 192[a] | 1·2$_3$ |

[a] Tentative assignment, this region obscured by the signal from sodium methoxide in DMSO-$d_6$.

[b] $J_{2,4}$ 1·2$_3$; $J_{2,6}$ 0·7$_0$; $J_{4,6}$ 2·2$_7$.

The spectra of the sigma complexes derived from 2-deutero-3,5-dinitropyridine (3; $R^1 = D$) also clearly demonstrated the methine-to-methine interconversion and enabled unambiguous assignments of chemical shifts and coupling constants to be made for the complexes (4; $R^1 = H$) and (5; $R^1 = R^2 = H$) (Table 1). The chemical

shifts of the C2 adduct are consistent with the unsubstantiated assignments suggested by Fyfe.[7] Failure to obtain a spectrum as soon as possible after mixing may account for the previous failure to observe signals arising from the C4 adduct.[7]

From a plot of the intensities of the methine proton signals from the two isomers with time $t$, extrapolated to $t = 0$, the difference in the activation energies for the formation of the deuterated complexes (4; $R^1 = D$) and (5; $R^1 = D, R^2 = H$) was shown to be $<0{\cdot}4$ kcal (cf.[8]). In such circumstances it is difficult to determine which isomer is kinetically preferred. Owing to the characteristics of the solvent employed it is not possible to carry out experiments at lower temperatures where definitive differences in complex concentrations would be more likely to be observed.

When sodium methoxide was added to a solution of 3,5-dinitropyridine in methanol-$d_4$, only signals from the C2 adduct were observed. Only one isomer, the kinetically controlled product, will be observed by p.m.r. under the conditions employed, if the activation energy difference for complex formation is in excess of *c.* $1{\cdot}3$ kcal mole$^{-1}$. Similarly, if the free energy difference between the complexes is greater than *c.* $1{\cdot}3$ kcal mole$^{-1}$, only the thermodynamically controlled product will be observed once equilibrium is established. Since only the C2 adduct was observed in methanol, it follows that either this complex is the kinetically and thermodynamically controlled product or that the C4 complex is kinetically preferred but interconverts into the C2 product too rapidly for observation. These arguments also apply to the formation of complexes from 2-methoxy-3,5-dinitropyridine and the 5-nitropyrimidines in DMSO, where we have only been able to detect one methine complex in each case.

The stability of the C2 adduct in DMSO is noteworthy in relation to that of the methine complexes from 2,4,6-trinitroanisole and 4-methoxy-3,5-dinitropyridine and attests to the destabilization of the latter by adverse differential steric and solvation effects.[3,4]

## Experimental

Instrumentation and reagents have been described elsewhere.[4]

3,5-Dinitropyridine was prepared from 2-hydrazino-3,5-dinitropyridine by oxidation with silver oxide.[9]

*2-Deutero-3,5-dinitropyridine*

A stirred suspension of 2-hydrazino-3,5-dinitropyridine ($1{\cdot}0$ g) in deuterium oxide (30 ml) was heated at 80° with red mercuric oxide ($8{\cdot}0$ g) for $2{\cdot}5$ hr. The mixture was filtered hot, and the residue washed with chloroform. The filtrate was extracted with chloroform ($3 \times 50$ ml) and the combined dried organic extracts were evaporated to give *2-deutero-3,5-dinitropyridine* ($0{\cdot}63$ g, 74%), m.p. 105° (light petroleum, b.p. 40–60°), *m/e* 170; perprotio impurity $<5\%$ as determined by n.m.r. and mass spectral measurement.

[7] Fyfe, C. A., *Tetrahedron Lett.*, 1968, 659.
[8] Eliel, E. L., "Stereochemistry of Carbon Compounds." (McGraw–Hill: New York 1962.)
[9] Plazek, E., *Recl Trav. chim. Pays-Bas*, 1953, **72**, 569.