

# Reaction of 1,8-diazabicyclo[5.4.0]undec-8-ene with methyl 3,5-dinitrobenzoate and 1,3,5-trinitrobenzene

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## 1,8-Diazabicyclo[5.4.0]undec-8-ene (DBU) undergoes a double addition reaction with the title compounds forming crimson 2-aminoindole derivatives.

In the course of examining the complexation of 3,5-dinitrobenzoates of cholic acids with a variety of compounds it was observed that with DBU a red colour rapidly developed in  $\text{CHCl}_3$  and that, after some time, stable red compounds were formed. In order to determine whether these reactions were solely a function of the complexing ability of the cholic esters or due to the dinitrobenzoate function, methyl 3,5-dinitrobenzoate was treated in  $\text{CHCl}_3$  or EtOAc with DBU whereupon deep red solutions were formed with the colour intensity increasing for up to 2 d. Chromatography yielded starting material and two orange compounds. The less polar orange compound (19%) was shown by spectroscopy<sup>†</sup> to have structure **1**. The structure of the more polar product was assigned by spectroscopy.<sup>‡</sup> Assuming that DBU is also acting as a C-nucleophile in forming this product, structure **3** was assigned.

DBU reacts in a similar manner with 1,3,5-trinitrobenzene to give **2** (11%).<sup>§</sup>

A scheme to account for the formation of **1** and **3** is the initial reaction giving the Meisenheimer complexes **4** and **5** (the original red colour formed on mixing) from the ester and DBU acting as a C-nucleophile,<sup>¶</sup> followed by oxidation of the adducts to form the aryl compounds **6** and **7**; *ipso* displacement of the nitro group of **6** would then give the indole **1** whilst **7** cyclises to form the isoquinolone **3** (Scheme 1). There are a number of examples of DBU reacting as a C- and N-nucleophile,<sup>1</sup> but the order in which reaction occurs is not clear; in the current example DBU appears to be acting initially as a C-nucleophile.

1,3-Dimethylpiperidino-2-indole is reported<sup>2</sup> to absorb at  $\lambda_{\text{max}}/\text{nm}$  230 ( $\epsilon$  25 400), 290 (9300) and 296 (8950) thus the

introduction of the electron accepting  $\text{NO}_2$  and  $\text{CO}_2\text{Me}$  groups effects a large bathochromic shift of *ca.* 180 nm, presumably due to the donating power of both nitrogens of the enediamine system.

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## Footnotes

<sup>†</sup>  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_4$ ,  $\lambda_{\text{max}}/\text{nm}$  332 ( $\epsilon$  13 100) and 475 (5500);  $\nu_{\text{max}}/\text{cm}^{-1}$  1706;  $\delta_{\text{H}}$  8.41 (1 H, d, *J* 1.9), 7.81 (1 H, d, *J* 1.9), 3.85 (3 H, s) and  $7 \times$  (2 H, m) with the connectivities  $\delta_{\text{H}}$  4.08–2.10–3.38 and 3.48–1.95–1.91–2.78 (2D-COSY); in addition the signal at  $\delta_{\text{H}}$  4.08 showed an NOE to that at 7.81 (37%) and the 3.85 signal was enhanced by irradiation of these at 8.41 (15%) and 7.81 (9%).  $\delta_{\text{C}}$  166.95, 152.10, 135.33, 125.18, 119.85, 115.90, 111.16, 95.68, 54.01, 51.88, 48.99, 39.96, 28.42, 25.26, 24.51 and 21.80.

<sup>‡</sup>  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_4$ ;  $\lambda_{\text{max}}/\text{nm}$  462 (11 000);  $\nu_{\text{max}}/\text{cm}^{-1}$  1661;  $\delta_{\text{H}}$  9.17 (1 H, d, *J* 2.6), 8.65 (1 H, d, *J* 2.6), and  $7 \times$  (2 H, m) with the connectivities  $\delta$  4.16–2.10–3.38 and 3.62–1.94–1.75–2.28 (2D-COSY).

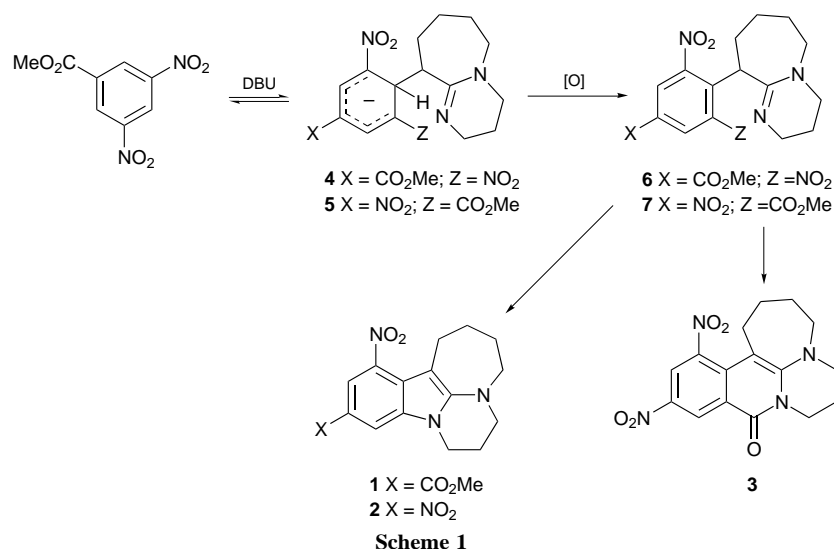
<sup>§</sup>  $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_4$ ,  $\lambda_{\text{max}}/\text{nm}$  340 (6000) and 470 (25 000);  $\delta_{\text{H}}$  8.62 (1 H, d, *J* 1.9), 7.92 (1 H, d, *J* 1.9) and  $7 \times$  (2 H, m) with the connectivities  $\delta_{\text{H}}$  4.10–2.36–3.44 and 3.59–2.04–1.95–2.78 (2D-COSY); irradiation of the signal at  $\delta_{\text{H}}$  4.10 generated an NOE at 7.92 (22%).

<sup>¶</sup> The exact nature of the nucleophile is not known and there are a number of possible formulations.

## References

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Scheme 1

