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On Attempted Diels-Alder Reaction of 1-Ethoxycarbonylindole-3-carboxaldehyde N,N-Dimethylhydrazone

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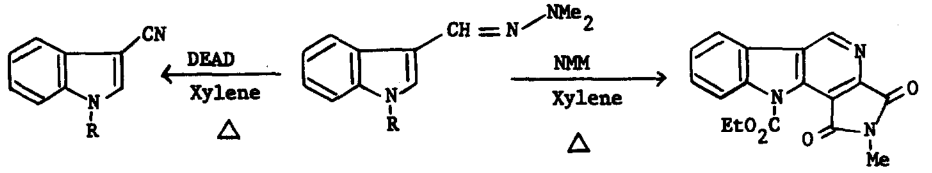
Abstract: The reaction of 1-ethoxycarbonylindole-3-carboxaldehyde N,N-dimethylhydrazone with five dienophiles has been studied, and the first use of this new azadiene in a Diels-Alder reaction with N-methylmaleimide has been achieved leading to a new synthesis of an [a]annellated γ-carboline.

The hetero Diels-Alder reaction of acyclic 1-aza-1,3-dienes is a well documented synthetic tool[1]. But the D.-A. reaction of azadienes having the C=C bond as a part of a (hetero) aromatic ring has been achieved only once using furfuraldoxime[2]. Three previous attempts to achieve such cyclisation of heteroaryl aldehyde N,N-dimethylhydrazones (NNDMH) as the azadienes have proved abortive[3-5]. The present report deals with the attempted D.-A. reaction of a new NNDMH, the title compound (1) with five dienophiles. The structures of all new compounds were determined by IR, PMR ($CDCl_3$) including homodecoupling experiments, CMR ($CDCl_3$) including selective ^{1}H-decoupled ^{13}C-NMR spectra and, in one case, EI-MS.

The new azadiene (1)[6] did not react with ethyl acrylate, maleic anhydride and naphthoquinone under a variety of conditions. With diethyl acetylenedicarboxylate (DEAD) under reflux in xylene, the product was identified as the 3-cyanoindole (2)[7]. It is likely to have been formed by a dienophile-catalysed 1,2-elimination at the hydrazone function of 1 which behaves as a three-centre ambident nucleophile[8]. Likewise, another NNDMH (3)[9] furnished, on similar treatment with DEAD, the 3-cyanoindole (4)[10].

With N-methylmaleimide (NMM) under reflux in xylene 1 yielded the fused γ-carboline (5)[11]. The elimination of dimethylamine and thermally induced dehydrogenation of the initially formed cycloadduct may lead to the formation of (5). The low yield of this product (30 %) is not unexpected from thermodynamic considerations and because of the known tendency of cyclic enamines to undergo decomposition.

This report thus records the first successful use of a hetaryl aldehyde NNDMH as the azadiene in a Diels-Alder reaction and a simple, hitherto unreported synthesis of an [a]annellated γ-carboline. Work is in progress to synthesise functionalised γ-carbolines using this successful cycloaddition with NMM.



2 : R=CO_2Et
4 : R=COPh

1 : R=CO_2Et
3 : R=COPh

5

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References and Notes

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6. M.p. 84°; IR: 1745 cm^{-1}; PMR: δ8.35 & 8.18, 1H, d each, J 7.5 Hz; 7.66 & 7.41, 1H, s each; 7.37 & 7.30, 1H, dt each, 7.5 & 1.2 Hz; 4.48, 2H, q & 1.47, 3H, t, 7.2 Hz; 2.98, 6H, s; CMR: δ150.9, 136.2, 128.1, 119.5 (all s), 127.6, 125.0, 123.7, 123.2, 122.6, 114.9 (all d), 63.1 (t), 42.8 (2x), 14.3 (both q).
7. M.p. 66°; IR: 2250, 1765, 1750 cm^{-1}; PMR: δ 8.21 & 7.72, 1H, d each, J 7.5 Hz; 8.14, 1H, s; 7.46 & 7.39, 1H, t each, 7.5 Hz; 4.56, 2H, q & 1.50, 3H, t, 7.2 Hz; CMR: 149.7, 134.5, 128.1, 113.7, 93.3 (all s), 132.8, 126.5, 124.6, 119.9, 115.7 (all d), 64.5 (t), 14.2 (q); MS: m/z 215 (M+H ; 45%), 142 (100), 115 (20), 88 (9).
8. B.S.-Poncin, A.M. H.-Frisque and L. Ghosez, Tetrahedron Lett., 23, 3261 (1982).
9. A.M. Echavarren, J. Org. Chem., 55, 4255 (1990); we prepared it from indole-3-carbaldehyde by treatment with N,N-dimethylhydrazine followed by benzoylation (PhCOCl, Et_3N, Δ).
10. M.p. 108-110°; IR: 2200, 1710 cm^{-1}; PMR: δ8.35, 1H, dd, J 1.5 & 7.2 Hz; 7.85, 1H, s; 7.8-7.73, 3H, m; 7.7, 1H, tt, 7.5 & 1.2 Hz; 7.58, 2H, t, 7.5 Hz; 7.51 & 7.46, 1H, dt each, 7.2 & 1.5 Hz; CMR: δ167.8, 135.3, 132.9, 128.3, 113.6, 93.6 (all s), 134.3, 133.1, 129.4 (2x), 129.1 (2x), 126.8, 125.3, 119.8, 116.6 (all d).
11. M.p. 178-181°; IR: 1750, 1715 cm^{-1}; PMR: δ 9.48, 1H, s; 8.13 & 8.21, 1H, d each, J 7.5 Hz; 7.65 & 7.50, 1H, t each, 7.5 Hz; 4.63, 2H, q & 1.42, 3H, t, 7.2 Hz; 3.27, 3H, s; CMR: δ166.5, 165.0, 150.7, 149.4, 140.6, 137.6, 126.1, 122.1, 113.9 (all s), 146.6, 130.0, 124.7, 120.8, 115.1 (all d), 65.0 (t), 24.2 & 14.0 (both q).

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