A Novel Synthesis of 1,4-Dihydrocarbazole-1,4-dione

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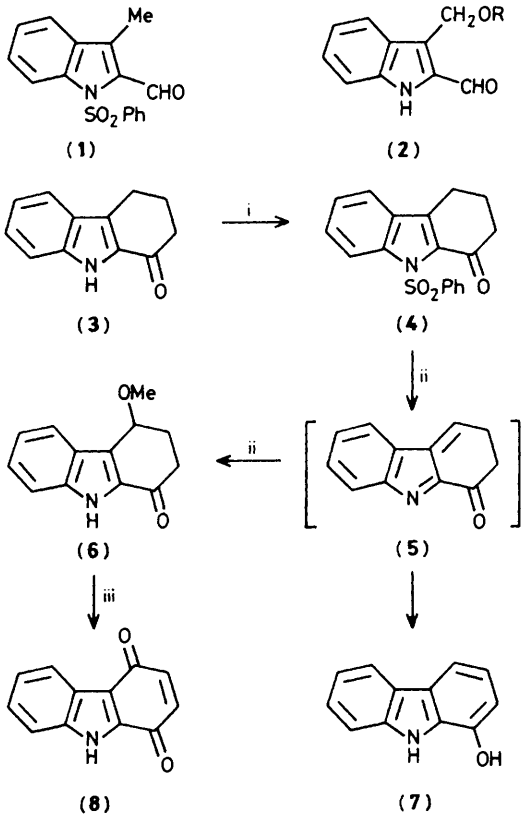
The direct introduction of a methoxy substituent into the 4-position of 9-phenylsulphonyl-1,2,3,4-tetrahydro-1-oxocarbazole provides a short synthetic route to 1,4-dihydrocarbazole-1,4-dione.

Current interest in the synthesis of carbazolequinones,[1] a sub-group of the wider class of carbazole alkaloids,[2] and our recent observations that the base-catalysed removal of the phenylsulphonyl protecting group during the preparation of 2-formyl-3-methylindole[3] resulted in the formation of the 3-alkoxymethyl-2-formyl derivative (**1**) → (**2**),[4] prompted an examination of a short synthetic route to 1,4-dihydrocarbazole-1,4-dione (**8**).

The key steps of the reaction sequence are the base-catalysed 1,4-elimination of benzenesulphinic acid from 9-phenylsulphonyl-1,2,3,4-tetrahydro-1-oxocarbazole (**4**) under the influence of an equivalent amount of methanolic



Reagents. i, $PhSO_2Cl$ in CH_2Cl_2, $Bu^n_4N^+HSO_4^-$, 50% aq. NaOH; ii, MeONa in MeOH under reflux; iii, $Ce(NH_4)_2(NO_3)_6$ in MeCN.

sodium methoxide, and the subsequent nucleophilic attack at the 4-position to give 4-methoxy-1,2,3,4-tetrahydro-1-oxocarbazole (**6**), m.p. 110 °C (76%).† The expected 1,2,3,4-tetrahydro-1-oxocarbazole (**3**) was also isolated in 23% yield. In contrast, however, when a large excess of sodium methoxide was used, in addition to the formation of (**6**) (56%), the only other product isolated in 24% yield was 1-hydroxycarbazole (**7**).[5]

The almost quantitative conversion of 9-phenylsulphonyl-1,2,3,4-tetrahydrocarbazole by methanolic sodium methoxide into 1,2,3,4-tetrahydrocarbazole suggests that the 1,4-elimination of the sulphinic acid is not concerted, but that the first step in the conversion of (**4**) into (**6**) is the removal of the proton from the 4-position, which is aided by the mesomeric effect of the 1-oxo group.[6] Subsequent expulsion of the phenylsulphonyl group leads to the intermediate (**5**), which can either undergo a nucleophilic addition reaction with the alcohol to produce (**6**) or, in the presence of an excess of base, undergo base-catalysed tautomerism to produce 1-hydroxycarbazole (**7**).

The observed inert character of the oxo compound (**6**) to aerial oxidation or to dehydrogenation over palladium on carbon and its relatively high stability in acidic media are compatible with the mechanism proposed for the formation of 1-hydroxycarbazole *via* (**5**), instead of by the direct oxidation of (**3**) or *via* (**6**). However, the conversion of (**6**) into 1,4-dihydrocarbazole-1,4-dione (**8**), m.p. 136 °C (76%), was readily effected by oxidation with cerium(IV) ammonium nitrate in acetonitrile and the quinone structure was established by full spectroscopic analysis‡ (*cf.* refs. 7 and 8). The observed rate of formation of (**8**) from (**6**) suggests that the reaction does not proceed *via* 1-hydroxycarbazole (**7**).

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References

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† The structures of all new compounds were fully established by elemental and spectroscopic analysis.

‡ $\nu_{max.}$ (Nujol) 3260, 1635, and 1610 cm^{-1}; $\lambda_{max.}$ (EtOH) 225 (log ε 5.27), 251sh (5.02), 256 (5.05), 267sh (4.86), 304 (4.13), and 399 nm (5.02); δ_H 6.72 (2H, s), 7.30—7.65 (4H, m) and 8.06—8.16 (1H, m); δ_C 114.5 (d), 116.5 (s), 122.6 (d), 124.4 (s), 124.6 (d), 127.0 (d), 135.9 (d), 136.3 (s), 138.5 (s), 139.5 (d), 180.6 (s), and 183.8 (s).