Sulphonation of 3-Ethylidene-1-oxoisoindoline

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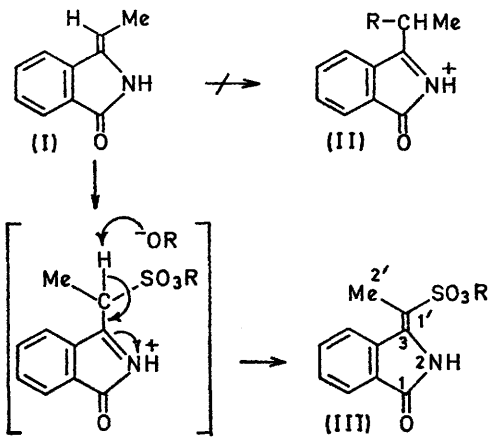
Summary An attempt to alkylate 3-ethylidene-1-oxoisoindoline with dimethyl sulphate gave unexpectedly 3-ethylidene-1′-methoxysulphonyl-1-oxoisoindoline (III; R = Me).

IN an attempt to prepare isoindol-1-ones or their cations [*e.g.* (II; R = H)] we measured the ^{1}H n.m.r. spectrum of 3-ethylidene-1-oxoisoindoline (I) in conc. sulphuric acid. The quartet at τ 3·65 (J 8Hz) slowly disappeared and the doublet at τ 8·23 (J 8 Hz) was replaced by a singlet at lower field (τ 7·73). Therefore, the species (II) was not formed and all attempts to isolate the new substance gave (I) in almost quantitative yield. We also heated (I) with dimethyl sulphate (30 mol.) at 190° for 10 min. in the hope of obtaining the methyl sulphate salt of (II; R = Me). The product that was isolated (55%) was not a salt. It had m.p. 131—132°, elemental analysis for $C_{11}H_{11}NO_4S$, M^+ 253, was soluble in organic solvents, and crystallised from benzene. The ^{1}H n.m.r. spectrum in $CDCl_3$ showed two methyl signals at τ 7·50 and 6·15 (singlets), four aromatic protons and a broad signal at τ 0·50 which disappeared on addition of D_2O. The i.r. spectrum (KBr disc) had intense peaks at ν 1320 (SO_2), 1725 (C=O), 1641 (C=C), and 3395 (sharp, NH) cm^{-1}. The data are consistent with the structure (III; R = Me), and the reaction is analogous to the formation of *C*-sulphonyl derivatives obtained by the reaction of enamines with sulphonyl halides.[1] The stereochemistry at the double bond was so chosen because it would allow for minimum steric hindrance during formation. The species obtained from (I) in conc. sulphuric acid was (III; R = H, or more probably with the C=O protonated) because all the chemical shifts were identical with those of the respective *C*-methyl and aromatic protons of (III; R = Me), which was recovered unchanged, in the same solvent. The u.v. spectrum of (I) in conc. sulphuric acid, after standing at 20° for 6 hr., was identical with that of (III; R = Me) in the same solvent (unaltered after 6 hr.). These findings must be kept in mind when alkylation of enamines with dimethyl sulphate is contemplated.



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[1] J. Szmuszkovicz, *Adv. Org. Chem.*, 1963, **4**, 68.