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THE REACTION OF ANTI-METHYL-3-(1-METHYL-INDOLYL) KETOXIME WITH TOLUENE-p-SULPHONYL CHLORIDE

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Many cases of the reaction of toluene-p-sulphonyl chloride with oximes are recorded in the literature[2] and although, in some cases, the product is that expected from a Beckmann or Neber rearrangement, the oxime O-toluene-p-sulphonate is usually isolable.

In connection with an investigation of such compounds, anti-methyl-3-(1-methyl-indolyl) ketoxime[3] (I) was treated with toluene-p-sulphonyl chloride, in dry pyridine, at -5°. The resulting crystalline compound (IV), m.p. 112-113°, contained nitrogen and chlorine, but sulphur was absent. Elemental analysis and molecular weight determinations indicated the molecular formula to be $C_{11}H_{11}N_2Cl$.

The u.v., i.r., and n.m.r. spectra of compound (IV) were very similar to those exhibited by its precursor (I):

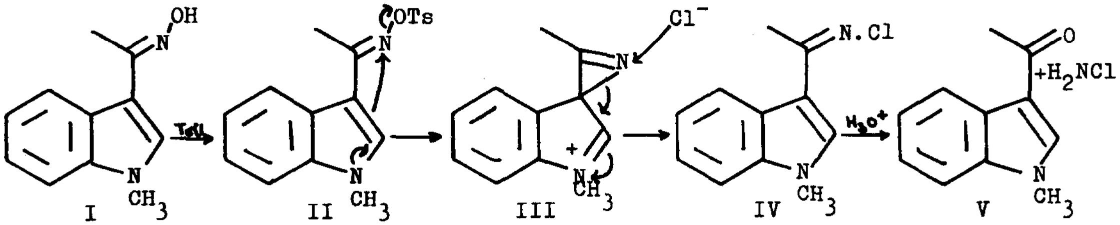
Compound (IV); $\nu_{max}^{CH_2Cl_2}$ 1600, δ_{CDCl_3} 8.47 (s), 7.32, 7.22 (m), 3.67 (s), 2.33 (s).

Ketoxime (I); $\nu_{max}^{CH_2Cl_2}$ 1550, δ_{CDCl_3} 8.08 (s), 7.14, 7.12 (m), 3.67 (s), 2.33 (s).

On heating with aqueous hydrochloric acid, (IV) yielded 1-methyl-3-(1-methyl-indolyl) ketone (V) and a gas, shown by chromatography to be oxygen, was evolved. It also liberated iodine from a potassium iodide solution in aqueous tetrahydrofuran, at room temperature.

The assigned structure (IV) explains the data presented.

$$H_2NCl + H_2O \rightarrow NH_3 + HOCl; \quad 2HOCl \rightarrow 2HCl + O_2.$$



As illustrated above, hydrolysis would yield the observed ketone (V) and chloramine, which itself hydrolyses to ammonia and hypochlorous acid. The latter would oxidise potassium iodide or, upon heating, yield oxygen gas.

Such behaviour has been noted for N-chloroketimines[4], which are, however, normally prepared by condensation of chloramine with ketones[5].

A possible mechanism for this unusual reaction is shown above.

The toluene-p-sulphonate ester (II) is presumed to be formed initially, followed by displacement of the toluene-p-sulphonate anion by the electrons of the hetero-ring, thus producing an azirine cation (III). This spiran intermediate is attacked by the most powerful nucleophile in the reaction medium, namely the chloride anion, to open the three membered ring and yield the N-chloroketimine (IV).

The fact that the isomeric anti-methyl-2-(1-methyl-indolyl) ketoxime[6] did NOT react in an analogous way supports the postulated mechanism, for in this case, an intermediate analogous to spiran (III) could not be formed. The Neber rearrangement is known to proceed through azirine intermediates[2].

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References and Notes

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