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THE REACTIONS OF p-TOLUENESULPHONYL AZIDE WITH SUBSTITUTED INDOLES

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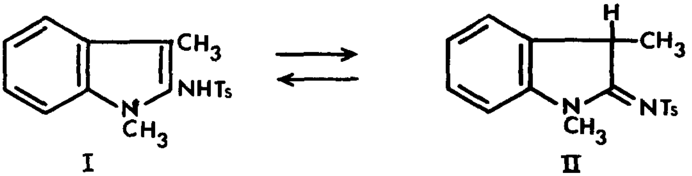
We have continued our study (1) of the reactions of azides by examining the products formed when substituted indoles are treated with p-toluenesulphonyl azide. 1,3-Dialkylindoles yield 2-sulphonamidoindoles (e.g., I). In chloroform the compounds exist in the imino form (II) and in DMSO as the amino form (I). In mixtures of the two solvents the n.m.r. spectra show the presence of both forms. 2,3-Dimethylindole forms the indolenine (IV) and 1,2,3-trimethylindole reacts with two moles of the azide giving (VI). This result suggests that the intermediate (III, R = CH_3) loses a proton to give (V) which adds a second molecule of tosyl azide and then eliminates diazomethane. This mechanism is supported by the observation that 1,3,3-trimethyl-2-methyleneindole reacts with arylsulphonyl azides forming diazomethane and a 2-arylsulphonylimino-1,3,3-trimethylindoline (2).

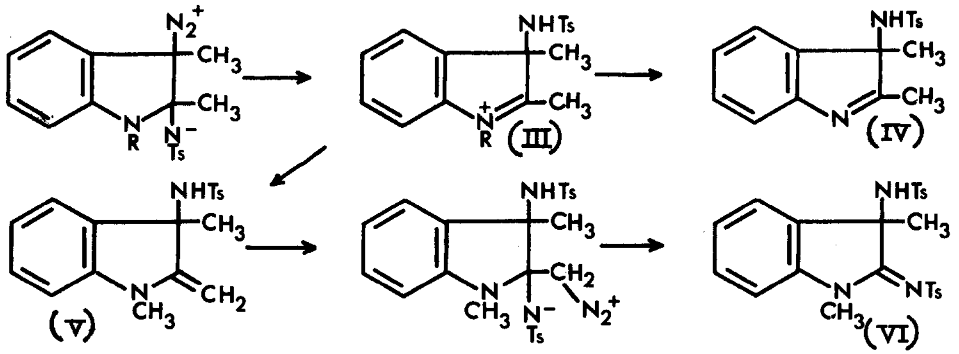


I II

(Ts= p-Me.C_6H_4.SO_2-)

From the reaction of tosyl azide and 9-methyltetrahydrocarbazole five compounds (VII, VIII, IX, X, XI) have been isolated. (VII) is an orange-coloured compound with an intense fluorescence in solution. Hydrolysis of (VII) yields (XII, R = CH_3) whose spectral properties, especially the intense fluorescence, are similar to those of the known (3) compound (XII, R = H). At its melting point (VII) rearranges to (VIII) which is identical with the material obtained by treating 1-amino-9-methyl-1,2,3,4-tetrahydrocarbazole (4) with p-toluenesulphonyl chloride in pyridine.

Refluxing both (IX) and (X) with aqueous alkali gave N-methyl-3,4-cyclopentenoquinolone (XIII,



R = CH_3) identical with the material obtained by methylating (XIII, R = H) (5) with dimethyl sulphate and sodium hydroxide. Attempts to convert (IX) into (X) by warming with aqueous alkali gave mixtures of products and starting material but (X) was formed from (IX) in good yield using 1,5-diazabicyclo[4.3.0.]non-5-ene. The ultraviolet spectrum of (X) was very similar to that of 2-benzenesulphonamidoquinoline which exists largely as the imino form in ethanolic solution (6).

The structure of (XI) has been determined by X-ray crystallography.

A plausible reaction scheme is indicated in the chart, the intermediate (XIV) reacting in two ways. It either undergoes a ring contraction to form (VII) or loses a proton to give (XV) (c.f. III→V). This enamine then adds a second molecule of tosyl azide and the adduct (XVI) undergoes a ring-enlargement (7) affording (IX) which eliminates p-toluenesulphonamide forming (X). Alternatively, (XV) is transformed into (VIII) by a 1,3-shift; the thermal transformation of (VII) into (VIII) probably occurs via (XV) (c.f. the formation of 1-hydroxy-1,2,3,4-tetrahydrocarbazole)(8). (XI) is formed from (VIII) by the addition of a second molecule of tosyl azide to give (XVII) followed by loss of nitrogen and ring-contraction. This suggestion is supported by the fact that heating pure (VIII) with p-chlorobenzenesulphonyl azide gave the compound (XI, CH_3 replaced by Cl). The presence of two different arylsulphonyl groups greatly assisted the interpretation of the mass spectrum of (XI).

For all the new compounds satisfactory elemental analyses were obtained, and the mass, I.R., U.V. and n.m.r. spectra support the assigned structures.

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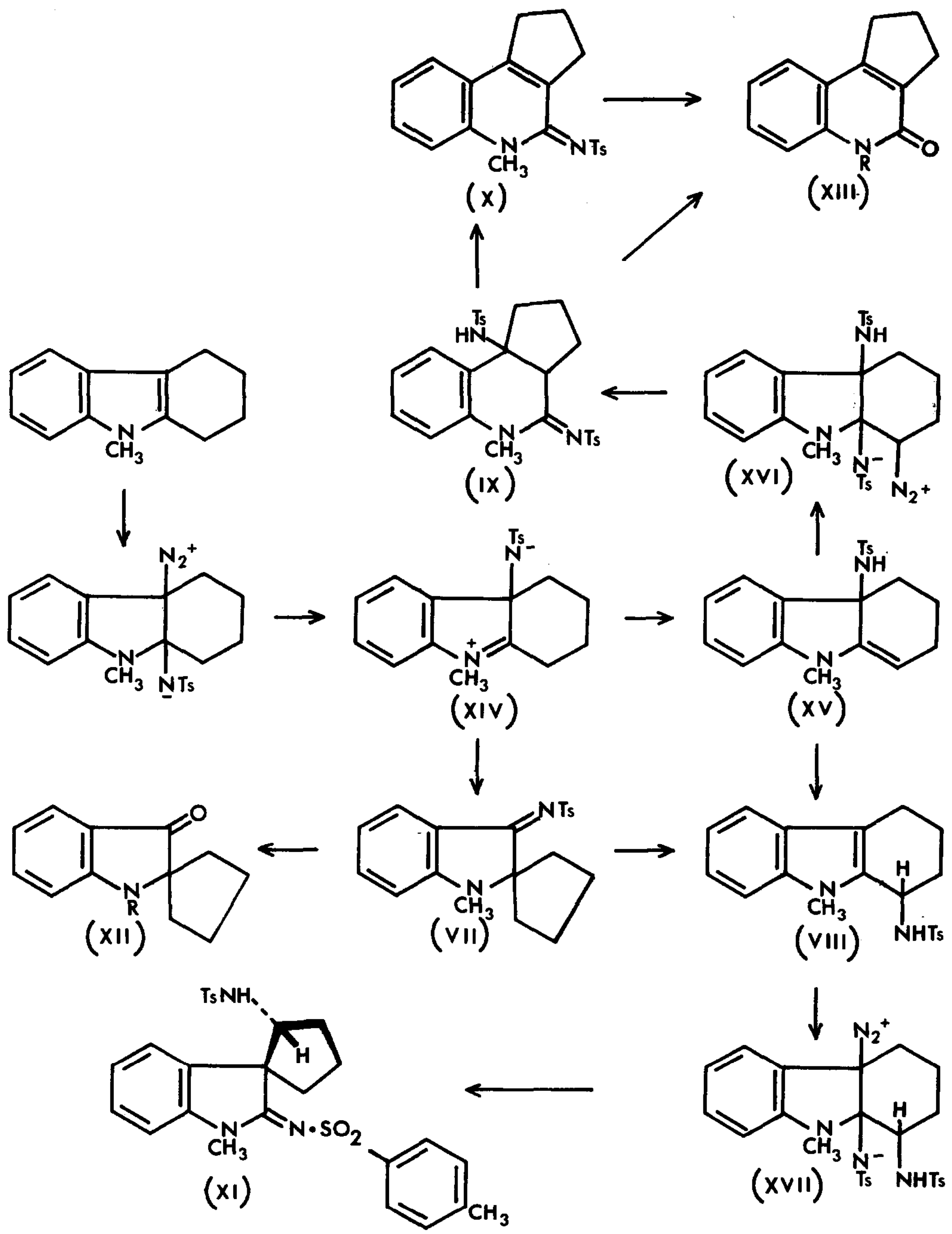
(X)
(XIII)
(IX)
(XVI)
(XIV)
(XV)
(XII)
(VII)
(VIII)
(XI)
(XVII)
NTs
O
R
TsHN
NH
Ts
N⁻
N₂⁺
NTs
CH₃
NHTs
TsNH
H
N·SO₂

(1) A. S. Bailey, M. C. Chum, and J. J. Wedgwood, *Tetrahedron Letters*, 5953 (1968); A. S. Bailey, W. A. Warr, G. B. Allison, and C. K. Prout, *J.Chem.Soc.* 956 (1970 C).

(2) M. Regitz and G. Himbert, *Annalen*, *734*, 70 (1970); we had independently carried out this reaction.

(3) S.G.P. Plant and M.L. Tomlinson, *J.Chem.Soc.*, 2127 (1950); B. Witkop, *J.Amer.Chem.Soc.*, *72*, 614 (1950).

(4) I. V. Shvedov, L. B. Altukhova, E. K. Komissarova, and A. N. Grinev, *Khim.Geterotsikl.Soedin. Akad.Nauk.Latv.SSR.*, 365 (1965); *Chem.Abs.*, *63*, 14800 (1965).

(5) B. K. Blount, W. H. Perkin, and S.G.P. Plant, *J.Chem.Soc.*, 1975 (1929).

(6) Yu. N. Sheinker, E. M. Peresleni, N. P. Zosimova, and Yu. I. Pomerantsev, *Russ.J.Phys.Chem. (Eng.Trans.)*, *33*, 306 (1959).

(7) J. E. McMurry, *J.Amer.Chem.Soc.*, *91*, 3676 (1969); R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Chem.Ber.*, *96*, 802 (1963).

(8) R.J.S. Beer, L. McGrath, and A. Robertson, *J.Chem.Soc.*, 2118 (1950).