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THE REACTION OF 2-CARBETHOXY-1-METHYLINDOLE WITH TOLUENE-p-SULPHONYL AZIDE

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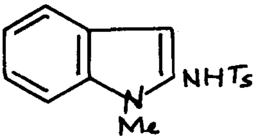
As part of our work[1,2,3] on the reactions of organic azides with indoles we examined the reaction of tosyl azide with 1-methylindole.[4] The major product of this reaction is the 2-substituted compound (I), and the isomeric compound 1-methyl-3-p-tolylsulphonylaminoindole (II) is formed in small quantity; the following synthesis makes compound (II) readily available and gives further support to the proposed structure.

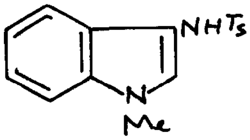
Warming 2-carbethoxy-1-methylindole with tosyl azide in pyridine solution affords a compound to which we assign structure (III, R = Et). The structure is supported by analytical and spectroscopic data. Alkaline hydrolysis of (III, R = Et) yields (III, R = H) and the latter, on decarboxylation gives compound (II).

An unexpected feature of the n.m.r. spectrum ($CDCl_3$) of (III, R = Et) is that the signal associated with C(4)H appears at very low field ($\tau = 1.82$). This effect is not observed in the spectra of (II), of (IV), and of 2-carbethoxy-1-methylindole; nor is it observed in the spectrum of (III, R = Et) when the spectrum is recorded in $(CD_3)_2SO$. The m.p. of (IV) is 12° higher than that of (III, R = Et) and (III, R = Et) and (IV) have identical R_f values.

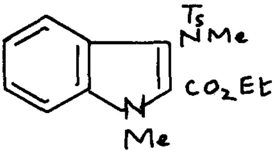
These facts point to a strong intramolecular hydrogen bond between the NH and CO_2Et groups of compound (III, R = Et) in the solid state and in solution in $CDCl_3$, this bond being disrupted in $(CD_3)_2SO$ solution. This would constrain the $ArSO_2$ group to the conformation indicated in the formula, placing



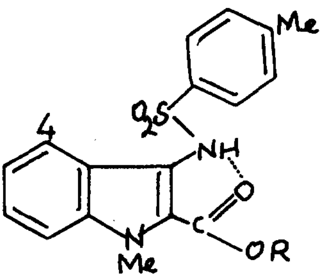
(I)



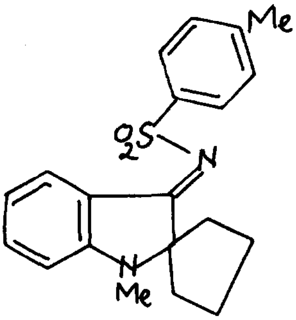
(II)



(IV)



(III)



(V)

the SO_2 group near to C(4)H and causing this proton to be deshielded with respect to the other aromatic protons. In the n.m.r. spectrum of (V)[2] the signal of C(4)H also appears at very low field (τ = 1.46).

(1) A. S. Bailey and J. J. Merer, J.Chem.Soc., 1345 (1966 C).

(2) A. S. Bailey, R. Scattergood, and (Mrs) W. A. Warr, J.Chem.Soc., 2479 (1971 C).

(3) A. S. Bailey and (Mrs) W. A. Warr, G. B. Allison and C. K. Prout, J.Chem.Soc., 956 (1970 C); A. S. Bailey, R. Scattergood, and (Mrs) W. A. Warr, J.Chem.Soc., 3769 (1971 C); A. S. Bailey, A. J. Holton, and J. F. Seager, J.C.S., 1003 (1972 Perkin I).

(4) A. S. Bailey, A. J. Buckley, (Mrs) W. A. Warr, and (Mrs) J. J. Wedgwood, J.C.S., in press (1972 Perkin I).

All compounds described here have given analytical and spectroscopic data in agreement with the proposed structures.