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A NEW SYNTHESIS OF N-ARYLSULPHONYLPYRROLES

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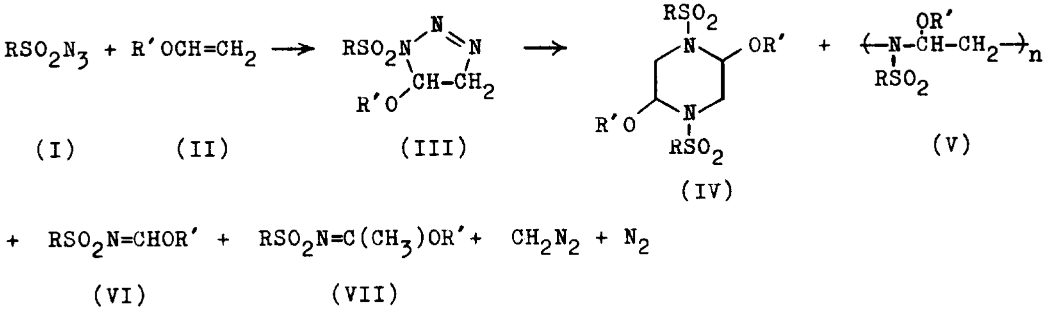
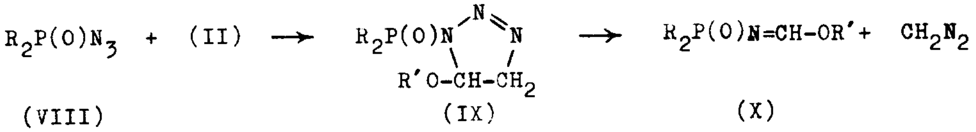
1,3-Dipolar cycloaddition of benzenesulphonyl azide (Ia) to alkyl vinyl ethers (II) (ca. 1:2 molar ratio) is reported to give, after decomposition of the triazoline intermediate (III), a piperazine derivative (IV), a polymer (V), some imidoesters (VI & VII), diazomethane and nitrogen.[1]



a) R = C_6H_5 ; b) R = p-$CH_3C_6H_4$; c) R′= n-C_4H_9 ; d) R′= i-C_4H_9 .

(Scheme 1)

N-Phosphorylated imidoformates (X), which are formed by an analogous process, are obtained in good yields from the reaction of organic phosphorus azides (VIII) and alkyl vinyl ethers.[2] Here a large excess of the ether (II) is employed and the reaction is conducted at the boiling temperature of the vinyl ether. In view of the relative sensitivity of arylsulphonyl azides to changes in reaction conditions, and for the purpose of comparison between the



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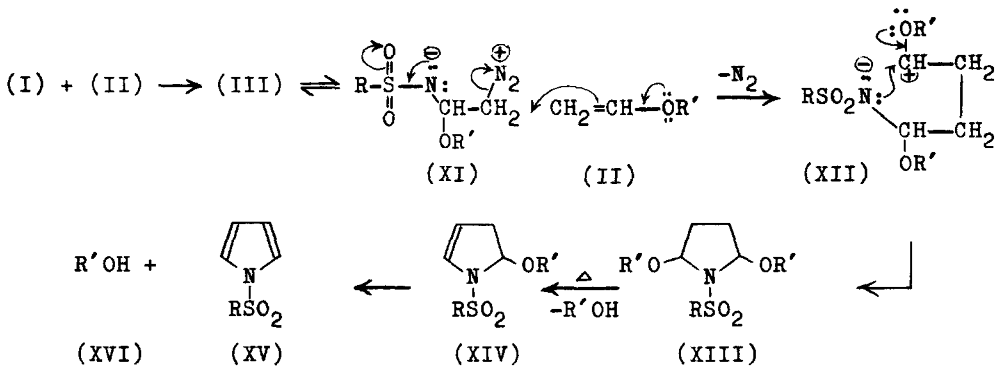
behaviour of the two azides (I & VIII), the reactions of benzenesulphonyl, and of tosyl azides with alkyl vinyl ethers (IIc or d) were investigated. It was found that when the azide (I) was flooded with the vinyl ether (1:20 molar proportion) a mild exothermic reaction ensued with a moderate evolution of gas. The mixture developed a yellow tint as the reaction approached completion (ca. 96 hrs.). The excess of the vinyl ether and other volatile matter were removed by distillation leaving an oily residue. Purification of this oil could not be achieved, because it was too unstable to be distilled and it could not be induced to crystallise. Preliminary examination of the IR and NMR spectra of this crude oil suggested that it probably consisted of a mixture of (XIII) and (XIV) (see Scheme 2). The oil was dissolved in diethyl ether (containing a few drops of conc. HCl) and was refluxed for two hours. This effected the conversion of the oil to the pyrrole derivative (XV) and the alcohol (XVI). The ether solution was washed with an aqueous solution of $NaHCO_3$ and dried. Removal of the solvent left a viscous liquid which upon distillation (reduced pressure) afforded the alcohol (XVI), and the solid (XV) remained as the residue. The former and the latter compounds were obtained in 2:1 molar proportions respectively. The alcohol (XVI) was characterised by IR and GLC. Compounds (XVa & b) were purified by crystallisation (Methanol) and were characterised by elemental and spectral analyses and by mixed melting points with authentic samples. Thus, N-(benzenesulphonyl)pyrrole (XVa, $C_{10}H_9NO_2S$) was obtained in 69% yield; m.p. 87-88°. NMR:(CCl_4,τ) 2.14 & 2.42 (m, Ph); two triplets at 2.87 & 3.74 (J=3 cps)(AA′BB′-system, pyrrole protons).[3] IR:(Nujol) strong bands at 1350 (asym.), 1180 (sym. vib. SO_2); 755, 730, 680 cm^{-1} (Ph).

N-(p-toluenesulphonyl)pyrrole (XVb, $C_{11}H_{11}NO_2S$) was obtained in 58% yield; m.p. 104-105°. NMR:($CDCl_3$,τ) two doublets at 2.24 & 2.70 (J=8)(AA′BB′-system, p-disubstituted benzene);[3] two triplets at 2.80 & 3.69 (J=3 cps)(AA′BB′-system, N-substituted pyrrole);[3] and a sharp singlet at 8.39 (CH_3). IR: (Nujol) 1350 (asym.), 1175 (sym. vib. SO_2); 758, 704, 670 cm^{-1} (Ph). Both compounds (XVa & b) gave correct analyses.

Authentic samples of N-(benzenesulphonyl)pyrrole and N-(p-toluenesulphonyl)pyrrole were synthesised, for comparison, by a known method from pyrrolylpotassium and the corresponding arylsulphonyl chloride.[4]

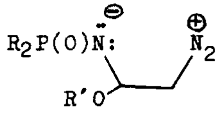
Formation of the pyrrole derivative (XIII)

Formation of the pyrrolidine ring may be envisaged to have taken place by any of the following routes: The azide (I) may add slowly across the double bond of the vinyl ether (II) to give rise to a triazoline ring (III, Scheme 2) in a fashion characteristic of 1,3-dipolar cycloaddition.[5] This triazoline may equilibrate with the zwitter ion (XI). In the presence of an excess of the vinyl ether (a fairly good nucleophile) this intermediate may undergo a rapid reaction with a second molecule of the former to give eventually the pyrrolidine (XIII). In the absence of an excess of the vinyl ether, the zwitter ion (XI) may interact with itself to give rise, after loss of nitrogen, to the dimer (IV) or a polymer (V) as it is reported.[1] Zwitter ions such as (XVII)[2], (XVIII)[6], and (XIX)[7], are postulated as intermediates during several reactions.

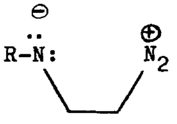


a) R = C_6H_5 ; b) R = p-$CH_3C_6H_4$; c) R' = n-C_4H_9 ; d) R' = i-C_4H_9 .

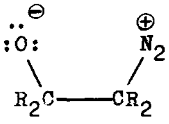
(Scheme 2)



(XVII)



(XVIII)



(XIX)

The other possibility for the formation of the pyrrolidine ring is <u>via</u> an unstable sulphonylaziridine. However, little data are available as to allow a decision about the mechanism or the nature of the intermediates involved.

Conversion of the pyrrolidine derivative (XIII) into the pyrrole (XV) occurs after elimination of two molecules of the alcohol (XVI), successively *via* the pyrroline (XIV), or in one step. This process, which is catalysed by heat or by acid, is probably assisted by the gain in stability as a result of aromatization to the pyrrole ring.

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