Loss of Nitrogen in Acylation Reactions of 5-Amino-1,2,3,4-thiatriazole. A New Series of Heteropentalenes

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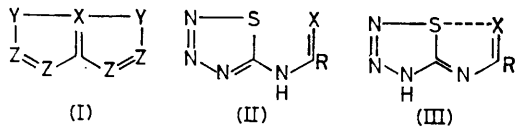
Summary 2,5-Diaryl-1,6-dioxa-6a-thia-3,4-diazapentalenes are obtained when 5-amino-1,2,3,4-thiatriazole is treated with aroyl chlorides and pyridine, but acetylation of 5-amino-1,2,3,4-thiatriazole yields 3,5-diacetamido-1,2,4-thiadiazole.

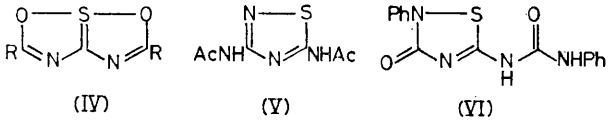
MANY well-defined members of the heteropentalene family have been described during the last decade and, in principle, many more are possible, within the general framework indicated by structure (I; X = S or Se, Y = S, Se, O, or NR, Z = sp^2C or N),[1] although lack of stability may limit the number of possible combinations which can be realized in practice.

In this connexion, we have initiated a study of the thermally unstable 1,2,3,4-thiatriazole system[2] as a potential source of other heterocycles, anticipating, for example, that acylation or thioacylation of 5-amino-1,2,3,4-thiatriazole to give products of type (II: X = O or S) or type (III; X = O or S) might weaken the bonding between sulphur and nitrogen in the thiatriazole ring.

We now report that benzoylation of 5-amino-1,2,3,4-thiatriazole under mild conditions in the presence of pyridine, leads directly to the 2,5-diphenyl derivative (IV; R = Ph; m.p. 189—190 °C) of the hitherto unknown 1,6-dioxa-6a-thia-3,4-diazapentalene system. Three other representatives, (IV; R = *p*-Me·C_6H_4, m.p. 254—255 °C), (IV; R = *p*-MeO·C_6H_4; m.p. 248—250 °C), and (IV; R = *p*-O_2N·C_6H_4; m.p. 282—283 °C), have been similarly prepared, using the appropriate aroyl chlorides.



(I) (II) (III)



(IV) (V) (VI)

The four products have similar u.v. absorption spectra, each with a minor peak (253—275 nm) and a major peak (303—330 nm). In the i.r. spectra, there are no significant bands in the carbonyl region at wavenumbers greater than 1610 cm^{-1}. The ^{13}C n.m.r. spectrum of (IV; R = Ph), and

the ^{13}C and ^{1}H n.m.r. spectra of (IV; R = *p*-Me·C_6H_4) indicate real or time-averaged C_{2v} symmetry. Thus, the six protons of the two methyl groups in (IV; R = *p*-Me·C_6H_4) appear as a sharp singlet (δ 2·45) and, in the ^{13}C spectrum, the signals for the methyl carbon atoms are coincident (δ 21·82). Compound (IV; R = Ph) has been converted into the known 2,5-diphenyl-1,6,6a-trithia-3,4-diazapentalene, m.p. 209—210 °C (lit.[3] m.p. 211 °C), by sulphurisation with phosphorus pentasulphide.

Attempts to prepare the 2,5-dimethyl derivative (IV; R = Me) by similar methods have not been successful. Under a variety of conditions, using either acetyl chloride or acetic anhydride in the presence of pyridine, 5-amino-1,2,3,4-thiatriazole is converted into a sparingly soluble product which has been proved, by an independent synthesis,[4] to be 3,5-diacetamido-1,2,4-thiadiazole (V) and not the isomeric 2,5-diacetamido-1,3,4-thiadiazole.[5]

Formally, compound (V) may be derived from the combination of two Ac·NH·CS·N (or Ac·NH·CNS?) units, with loss of one atom of sulphur. Whatever the mechanism, it is clear that, in this reaction, and in the aroylation reactions described above, acylation of 5-amino-1,2,3,4-thiatriazole is accompanied by loss of nitrogen.

Nitrogen loss also occurs when 5-amino-1,2,3,4-thiatriazole is treated with phenyl isocyanate, but the product, m.p. >330 °C, has not been fully identified; it appears to be an isomer of (IV; R = PhNH) but the i.r. spectrum (doublets at *ca.* 1710 and at *ca.* 1650 cm^{-1}, and a complex pattern of bands in the N–H stretching region) suggests that the material may be a mixture, possibly of the 1,2,4-thiadiazole derivative (VI) and a tautomer. Compound (VI) could arise by rearrangement of (IV; R = PhNH) but could also be formed in a modified reaction sequence.

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