

Oxazolo[3,2-c]- and Thiazolo[3,2-c]-[1,2,3]-benzotriazinium Salts

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THE synthesis of oxazolo[3,2-c]- and thiazolo[3,2-c]-[1,2,3]-benzotriazinium salts (Ia), new resonance-stabilized 14π -electron systems, is reported.[†] Treatment of the sodium salt of 3,4-dihydro-4-oxo-1,2,3-benzotriazine with α -halogeno-ketones yielded *N*- β -oxoalkyl derivatives (II), which are formulated as *N*-substituted rather than *O*-substituted compounds on the assumption that the mode of substitution observed previously,^{1,2} is general. Cyclization of these derivatives with cold concentrated sulphuric acid³ yielded the oxazolotriazinium salts (Ia; X=O) which were isolated as their fluoroborates and chlorides in *ca.* 80% yield.

The infrared spectra of these salts show no significant absorption in the carbonyl region but the presence of a diazo-band at 2300 cm^{-1} (KBr) indicates that the diazo-form (Ib) is probably in equilibrium with the form (Ia). This is not surprising since other condensed 1,2,3-triazines behave as the corresponding diazo-isomers in their reactions.^{4,5}

The n.m.r. spectra of these products are also consonant with their formulation as (I). Thus the spectrum of (I; X=O, Y=BF₄⁻, R¹=Me, R²=H), measured in trifluoroacetic acid with tetramethylsilane as an external standard, shows a singlet at δ 2.15 corresponding to the protons of the methyl group, and an aromatic multiplet in the region δ 8.4—7.1 equivalent to 5 protons.

The mechanism of cyclisation may be viewed as a protonation of the carbonyl oxygen atom in

(II) and rearrangement of electrons with concomitant cyclisation. The resulting alcohol (IV) would then be expected to dehydrate readily in the concentrated acid. Such a reaction would be similar to the dehydration of 1,4-diketones to yield furan derivatives.⁶

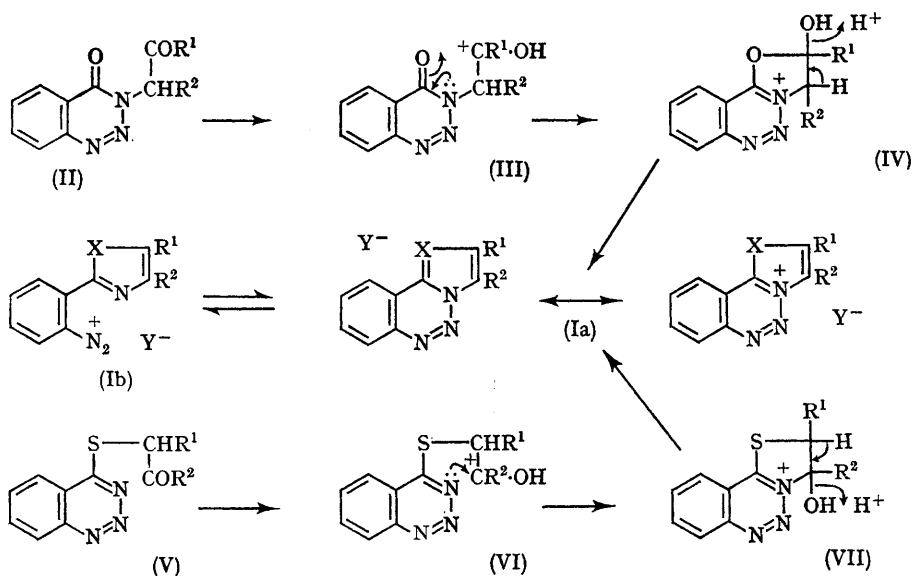
Similarly, the keto-sulphides formed by the reaction of α -halogeno-ketones with the anion of 4-mercapto-1,2,3-benzotriazine and tentatively formulated as S-alkyl derivatives (V)⁷ were cyclised by cold concentrated sulphuric acid treatment to the thiazolotriazinium salts (I; X=S), which were isolated as their fluoroborates. The n.m.r. spectra of these salts likewise indicate delocalisation of charge from nitrogen to sulphur. Thus the n.m.r. of (I; X=S, Y=BF₄⁻, R¹=H, R²=Me) shows but a single unsplit peak at δ 2.3 for the methyl group with the correct ratio (3:5) to the aromatic multiplet at δ 8.5—7.5.

By analogy with the formation of the oxazolotriazinium system, this reaction may be considered as a special case of aromatic cyclodehydration⁸ in which acid-catalysed attack of the carbonyl group occurs on an aromatic heterocyclic nitrogen atom rather than on carbon. While it would be expected that the conjugate acid (VI) would cyclise readily, the great ease with which the protonation of the triazine nitrogen is likely to take place, almost certainly causes the reaction to proceed by a concerted mechanism, involving a non-classical cation.

Prolonged treatment of (I; X=O, Y=BF₄⁻,

[†] The following salts were prepared: (I) X=O, R¹=Me, Ph, C₆H₄·Br-*p*; R²=H; Y=BF₄⁻ and Cl⁻.
X=S, R¹=H; R²=Me, Ph, C₆H₄·Br-*p*; Y=BF₄⁻.

All of the above compounds gave satisfactory analytical data.



$R^1=Ph$, $R^2=H$) under reflux with aqueous ethanol afforded 2,5-diphenyloxazole,⁹ whereas similar treatment of (I; $X=S$, $Y=BF_4^-$, $R^1=H$, $R^2=Ph$) yielded 2,4-diphenylthiazole,¹⁰ a fact which unambiguously shows that the original

alkyl derivatives of 4-mercapto-1,2,3-benzotriazine are S-alkyl, and not N-alkyl, derivatives.

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