A New Synthesis of 1,2,4-Benzotriazines

By B. ADGER, C. W. REES,* A. A. SALE, and R. C. STORR

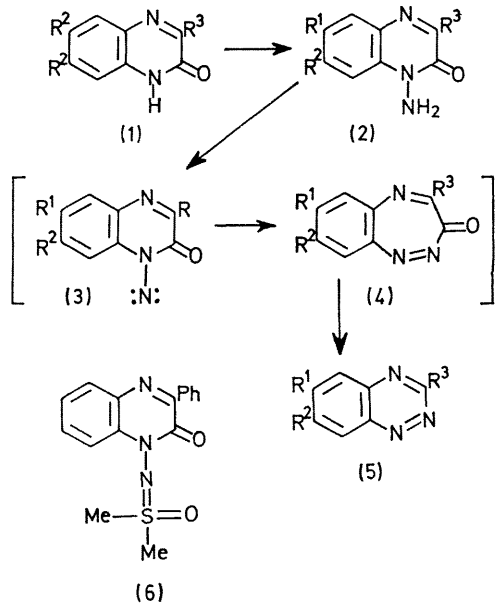
(*The Robert Robinson Laboratories, University of Liverpool, P.O. Box* 147, *Liverpool* L69 3BX)

Summary Oxidation of the readily prepared 1-amino-2-quinoxalones gives 1,2,4-benzotriazines in good yield.

ADDITION of 1-amino-2-quinoxalones (**2**) to lead tetra-acetate (1 mol) in dichloromethane at room temperature gave 1,2,4-benzotriazines (**5**) ($R^1 = R^2 = R^3 = H$; $R^1 = R^2 = H$, $R^3 = Me$; $R^1 = R^2 = H$, $R^3 = Ph$; R^1 or $R^2 = Me$, $R^3 = Ph$†) in 40—70% yields. Oxidative deamination accounts for the other products. 1-Amino-2-quinoxalones (**2**) are readily obtained in high yield (70—80%) by direct amination of the quinoxalones (**1**) with hydroxylamine-*O*-sulphonic acid. In a typical procedure, solid hydroxylamine-*O*-sulphonic acid[1] (0·02 mol) was added in portions during 15—20 min to a solution of the quinoxalone (0·015 mol) and sodium hydroxide (0·04 mol) in water or aqueous ethanol, and the *N*-amino-compound was filtered from the cooled solution. Since the quinoxalones (**1**) are formed rapidly and quantitatively from the appropriate *o*-phenylenediamine and α-keto-acid or -ester,[2] this overall procedure provides a simple and direct route to 1,2,4-benzotriazines. Although these are well known compounds, previous routes to them either involve relatively inaccessible starting materials or, in our experience, are difficult to reproduce.

By analogy with the conversion of 1-amino-2-pyridones into pyridazines,[3] a likely mechanism involves ring expansion of the nitrene (**3**) followed by electrocyclic ring closure of the trienone (**4**) and loss of carbon monoxide. Preliminary attempts to detect or intercept (**4**) by cycloaddition reactions have so far failed, however.

The *N*-nitrene (**3**) ($R^1 = R^2 = H$, $R^3 = Ph$) was trapped as the sulphoximide (**6**) (50%) when the oxidation was carried out in the presence of dimethyl sulphoxide. Pyrolysis of the sulphoximide also gives the benzotriazine but in lower yield. Preliminary experiments[4] show that this reaction sequence can be extended to the formation of 1,2,3-benzotriazines, by the amination of 2-quinazolones followed by oxidation.



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† The reactions were carried out with the isomeric mixture of quinoxalones produced from 3,4-diaminotoluene and benzoylformic acid to give a mixture of isomeric 1,2,4-benzotriazines.

[1] R. Gösl and A. Meuwsen, *Chem. Ber.*, 1959, **92**, 2521.
[2] O. Hinsberg, *Annalen*, 1896, **292**, 245.
[3] C. W. Rees and M. Yelland, *Chem. Comm.*, 1969, 377.
[4] M. Keating, unpublished data.