Dipolar Cycloaddition Reactions of Quinoxalin-3(4*H*)-one 1-*N*-Oxides†

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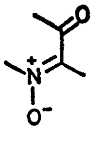
Summary Demonstrating their reactivity as 1,3-dipoles in cycloaddition reactions, quinoxalin-3(4*H*)-one 1-*N*-oxide (**3a**) and its *N*-methyl derivative (**3b**) react with the aryl isocyanates (**4a** and **b**) to give the corresponding 2-arylaminoquinoxalin-3(4*H*)-ones (**6a**—**c**); similarly, reaction with benzyne affords the 2-(*o*-hydroxyphenyl)-quinoxalin-3(4*H*)-ones (**9a** and **b**).



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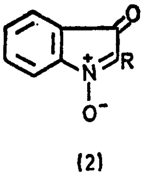

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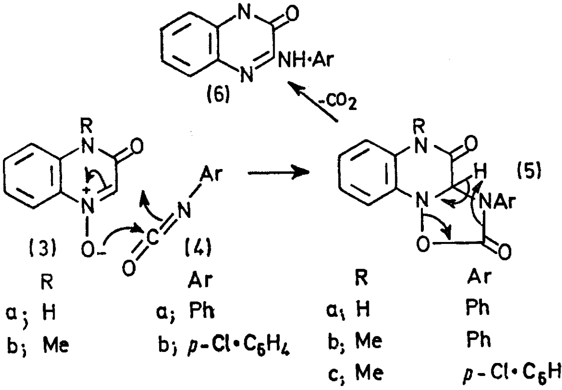
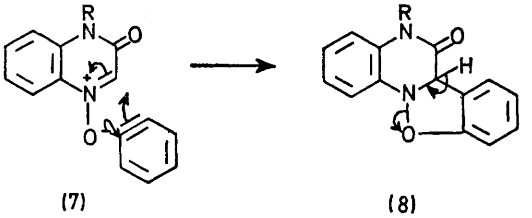
† Satisfactory analyses and spectral data were obtained for all new compounds.

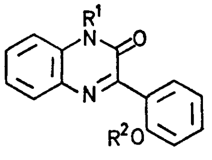
C-Acylnitrones (**1**) show exceptionally fast rates[1] in 1,3-dipolar cycloaddition reactions.[2,3] In this respect, cyclic *C*-acylnitrones are of particular interest because of the stereochemical restraint imposed.[4] Dipolar cycloaddition reactions of substituted cyclic *C*-acylnitrones such as the isatogens (**2**) are well known.[5] However isatogen (**2**; R = H) itself is unknown, and presumably because of the inaccessibility of similar substrates, studies of the cycloaddition reactions of unsubstituted cyclic *C*-acylnitrones do not appear to have been described hitherto. We now report the preliminary results of a general investigation of the 1,3-dipolar reactivity of the readily accessible[6] heterocyclic *C*-acylnitrones (**3a** and **b**).



The quinoxalinone *N*-oxide (**3b**) reacted readily with the isocyanates (**4a**) or (**4b**) to afford the 2-arylaminoquinoxalinones (**6b**) (53%), m.p. 187°, and (**6c**) (56%), m.p. 203°, which were identical with authentic samples prepared by reaction of 2-chloro-4-methylquinoxalin-3(4*H*)-one[7] with aniline and *p*-chloroaniline respectively. The *N*-oxide (**3a**) reacted similarly with phenyl isocyanate to yield the anilinoquinoxalinone (**6a**) (99%), m.p. 252°.

The *N*-oxides (**3a** and **b**) also reacted with benzyne[8] to afford the hydroxyphenylquinoxalones (**9a**) (95%), m.p. 307° and (**9b**) (94%), m.p. 212°. The structures of the products (**9a** and **b**) are based on the unambiguous synthesis of the methoxyphenylquinoxalone (**9c**), m.p. 171°, into which they are converted by methylation. Reaction of *N*-oxides of the types (**3a** and **b**) with arynes is potentially a valuable general route to 2-(*o*-hydroxyaryl)quinoxalin-3(4*H*)-ones.

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	R^1	R^2
a;	H	H
b;	Me	H
c;	Me	Me

By analogy with the known reactions of nitrones with isocyanates[1,3] and with benzyne,[3,9] the reactions of the *N*-oxides (**3a** and **b**) with these reagents are formulated as 1,3-dipolar cycloadditions proceeding by the intermediate formation and subsequent transformation of the cycloadducts (**5**) and (**8**). These reactions demonstrate the potential value of the heterocyclic *C*-acylnitrones (**3a** and **b**) as substrates for the study of the 1,3-dipolar cycloaddition reactions of nitrones.

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