Cyclization–Hydrolysis of a 1,2,4-Benzothiadiazine 1,1-Dioxide through a Diazonium Intermediate†

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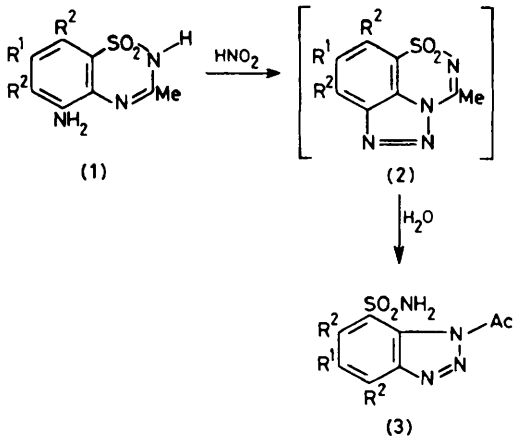
Summary Diazotization of 5-amino-3-methyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxides gave 1-acetyl-7-sulphamoyl-1*H*-benzotriazoles.

BRIDGING of diazonium ions to adjacent nucleophilic nitrogens to generate fused triazolo systems has been observed as a consequence of the treatment of 5-aminobenzomorpholines[1] and 8-amino-4-hydroxyquinolines[2] with nitrous acid. The classic Graebe–Ullmann synthesis of carbazoles also involves a transient benzotriazole which is prepared by internal cyclization of a 2-aminodiphenylamine treated with HNO_2.[3]

We have observed a unique extension of this reaction involving triazolo bridging to a vinylogous sulphonamide with concomitant cleavage of a thiadiazine ring. Thus, treatment of (**1a—c**) (1·0 mmol) with $NaNO_2$ (1·1 mmol) in concn. HCl (5 ml) and water (30 ml) resulted in the formation of stable 1-acetylbenzotriazoles: (**3a**), 76%, m.p. 263—264 °C; (**3b**), 85%, m.p. 261—263 °C; and (**3c**), 50%, m.p. 296—298 °C. No evidence was obtained for normal Sandmeyer behaviour in the presence of such nucleophiles as iodide ion, or for hydrolysis of the presumed diazonium ion to the corresponding phenol.

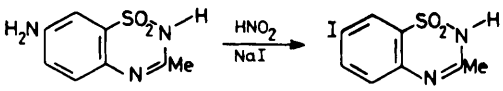
† Taken in part from the doctoral dissertation of E. G. Corley, Lehigh University, 1979.



(1) (2) (3)

a; $R^1 = R^2 = H$
b; $R^1 = Cl$, $R^2 = H$
c; $R^1 = H$, $R^2 = Br$

It appears that formation of the fused triazolobenzo-[1,2,4]thiadiazine 1,1-dioxide (**2**) is a necessary prerequisite for hydrolytic rupture of the heterocyclic ring. We have found that 7-amino-3-methyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide[4] (**4**) diazotizes normally and gives excellent yields of the reported 7-iodo[5] analogue (**5**). Thus, no evidence was obtained for a remote 'resonance activation' of the thiadiazine ring to hydrolytic cleavage by the 7-diazo intermediate.



(4) (5)

The 1-acetylbenzotriazoles displayed the unique high wavenumber carbonyl absorption (1725 ± 5 cm^{-1}) noted for a similar *N*-acetylbenzotriazole[6] and the absence of the amide II band indicated that the amide was tertiary. Solubility in dilute base (10% NaOH) implied the presence of a sulphonamide N–H and the electron impact mass spectrum displayed by (**3a**—**c**) was in accord with that noted for similar acetylbenzotriazoles.[7] Successive loss of 42 (keten equivalent) and 28 (nitrogen) mass units from the parent ions was observed for all products. Satisfactory combustion analyses were obtained for all compounds reported.

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