Synthesis and Chlorinolysis of 2*H*-1,2,3-Benzothiadiazine 1,1-Dioxide

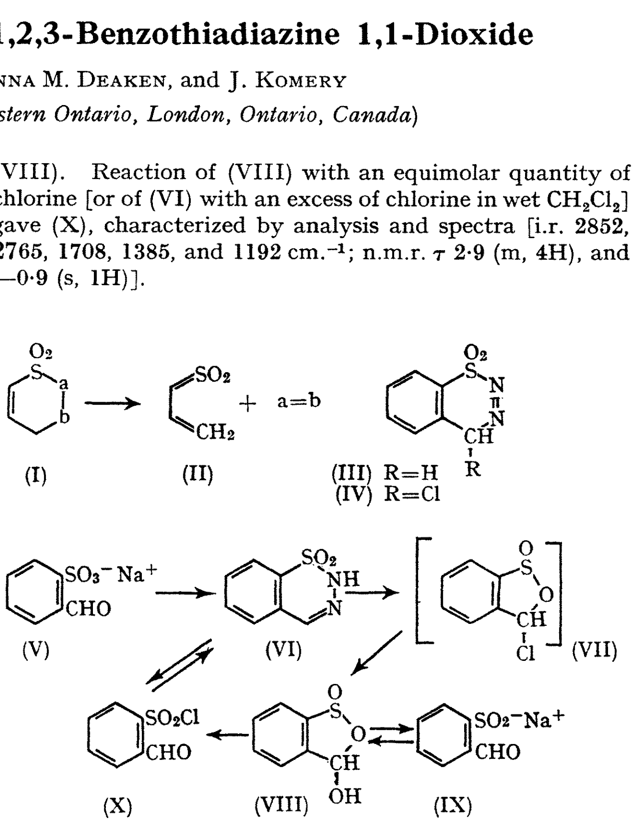
By J. F. KING,* ANNE HAWSON, DONNA M. DEAKEN, and J. KOMERY

(*Department of Chemistry, University of Western Ontario, London, Ontario, Canada*)

IN a preceding Communication[1] we described the generation of a sulphene by an electrocyclic reaction: *i.e.* thermolysis of thiet 1,1-dioxide. This reaction suggests the possibility of the reaction (I) → (II), compound (III), for example, being imagined as a specific substrate for such a process. We report the synthesis of the title compound (VI), the parent compound of a heterocyclic system hitherto known only in the form of 4-hydrazino-derivatives,[2] and describe an interesting reaction of (VI) for which a version of the reaction (I) → (II) may be suggested as the key step.

Reaction of (V) with hydrazine hydrate gave the hydrazone, which, on treatment with PCl$_5$, produced (VI) in yields of up to 80%. Structure (VI) follows from the evidence of elemental analysis, n.m.r. [bands at τ6·9 (1H, N*H*), 2·1 (complex multiplet due to the four ArH) and 2·8 (s, 1H, C*H*=N–), and i.r. spectroscopy [3280 (NH), 1657w (C=N), and 1345vs and 1165vs (SO$_2$)]; direct synthesis from (X) confirms this conclusion.

Treatment of compound (VI) with acid or base failed to give (III). Addition of an equimolar quantity of chlorine in dry methylene chloride to the compound gave a rapid evolution of nitrogen; evaporation of solvent gave an unstable amorphous residue tentatively formulated as the pseudo-acid chloride (VII) on the basis of (a) its i.r. spectrum (which showed no absorption characteristic of SO$_2$, NH, or OH, but did have a band at 1140 cm.$^{-1}$ appropriate to a sulphinic ester), and (b) its further reaction with water to give the pseudo-acid (VIII). Structure (VIII) is shown by elemental analysis, i.r. [bands at 3540 and 3300 (OH), and 1140 (–SO–O), and n.m.r. ([^{2}H$_6$]DMSO) (showing, in addition to the aromatic proton signal, a band of variable shape and chemical shift strongly reminiscent of that found with *o*-formylbenzoic acid[3]). Titration of (VIII) with sodium hydroxide gave an equivalent weight of 171 (calc. 170); evaporation of the solvent gave (IX) as a white residue with peaks at 2750 and 1710 (CHO), and 1045 and 975 cm.$^{-1}$ (SO$_2^-$). Treatment of (IX) with HCl regenerated (VIII). Reaction of (VIII) with an equimolar quantity of chlorine [or of (VI) with an excess of chlorine in wet CH$_2$Cl$_2$] gave (X), characterized by analysis and spectra [i.r. 2852, 2765, 1708, 1385, and 1192 cm.$^{-1}$; n.m.r. τ 2·9 (m, 4H), and —0·9 (s, 1H)].



For the formation of (VIII), we prefer a scheme involving initial *C*-chlorination[4] to form (IV). Fragmentation of (IV) in the fashion (I) → (II) would lead to a sulphene which by the "abnormal" addition in the manner postulated in the accompanying and other communications[1,5,6] would give (VII). We found no product that would result from "normal" cyclization of the sulphene, *i.e.* the four-membered ring sulphone. The considerable angle strain in any transition state leading to that system may well account for the formation of the five-membered ring sulphinate.

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