

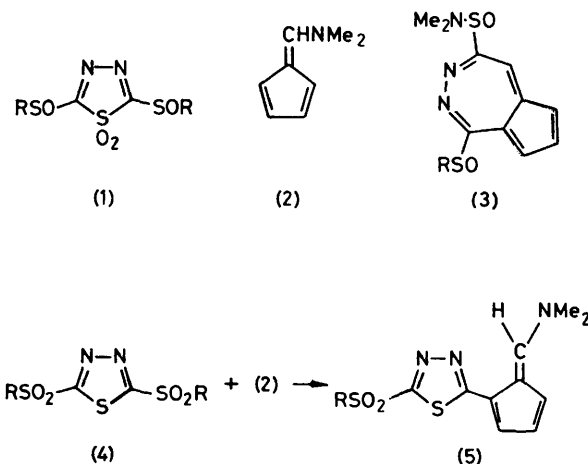
Comments on a Reported Synthesis of 5,6-Diaza-azulenes

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Summary A reported reaction of 2,5-bis(alkylsulphinyl)-1,3,4-thiadiazole 1,1-dioxides with 6-dimethylaminofulvene involved 2,5-bis(alkylsulphonyl)-1,3,4-thiadiazoles as reactants, and proceeded in a way entirely different from the one suggested.

A RECENT note¹ describing the synthesis of some interesting diaza-azulenes (**3**) by cycloaddition, followed by group migration and elimination, of the bis-sulphoxides (**1**) to 6-dimethylaminofulvene (**2**) contained some features which we felt deserved further investigation. Although the initial stages seemed unexceptional, the final step was a most unusual concerted migration of the dimethylamino group and displacement of a sulphanyl methyl as CH_3^- . Furthermore, the sharp, high melting-points, and the method of synthesis, of the sulphoxides (**1**) seemed incompatible with their formulation. Peroxide oxidation of 2,5-bis(alkylthio)-1,3,4-thiadiazoles has been reported earlier^{2,3} to produce bis-sulphones (**4**), and the melting-point of the bis-methylsulphone (**4**; R = Me) (171–173 °C,² 177–178 °C⁴) is close to that reported¹ for the thiadiazole dioxide (**1**; R = Me) (181 °C).



We suggest that the reactions observed by Mori and Kanematsu¹ involved alkylsulphinyl displacement by the nucleophilic fulvene molecule from the bis-sulphones (**4**).

All the properties they report for the diaza-azulenes (**3**) are compatible also with the fulvene structure (**5**). In particular, (a) the low-field proton at δ 9.00, assigned¹ to 8-H of (**3**), is correct for the fulvene 6-proton of (**5**), deshielded by the adjacent heterocyclic ring, (b) the dimethylamino-group signal (whether a 'broad singlet' or a doublet with peaks at δ 3.34 and 3.44, is not made clear) reveals slow exchange which is characteristic of 6-dimethylaminofulvenes substituted by electron-withdrawing groups,⁵ rather than dimethylsulphinamides, which only seldom show non-

equivalent methyl groups and then only at much lower temperatures,⁶ and (c) the ¹³C-n.m.r. details quoted¹ for compound (**3**) are also completely consistent with structure (**5**; R = Me).

We acknowledge courteous correspondence with Professor K. Kanematsu, who has informed us that he agrees with these conclusions.

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⁶ H. J. Jakobsen, A. Senning, and S. Kaae, *Acta Chem. Scand.*, 1971, **25**, 3031.