[4+6]π Cycloadditions of Thiadiazole 1,1-Dioxides to 6-Dimethylaminofulvene: A Synthesis of a Diaza-azulene

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Summary Treatment of 2,5-bis(alkylsulphinyl)-1,3,4-thiadiazole 1,1-dioxides with 6-dimethylaminofulvene in acetone gave 5,6-diaza-azulenes in good yields; solvent effects support a concerted mechanism for the formation of the cycloadducts.

THERE is much interest in the [4+6]π cycloaddition reactions of dienes and fulvenes. In particular, a new general azulene synthesis has been reported by the cycloadditions of thiophen 1,1-dioxides to 6-dimethylaminofulvene.[1] During the study of the frontier orbital-controlled cycloadditions of electron-accepting heterodienes,[2] we found that cycloaddition of the 1*H*-2,5-bis(alkylsulphinyl)-1,3,4-thiadiazole 1,1-dioxides with 6-dimethylaminofulvene gave the 4-alkylsulphinyl-7-dimethylaminosulphinyl-5,6-diaza-azulenes.

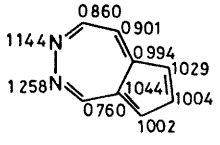
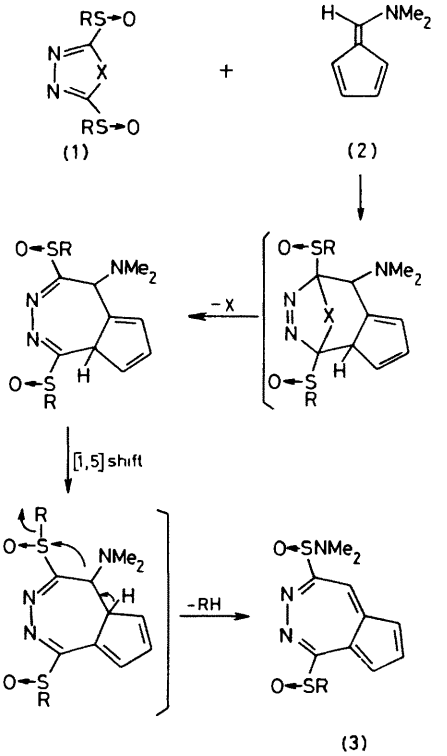


FIGURE.

The cycloaddition of the heterodiene (**1a**)† with (**2**) at room temperature in acetone gave, after 0·5 h, the cycloadduct (**3a**), m.p. 179 °C, $C_{11}H_{13}N_3O_2S_2$ as yellow crystals in 60% yield, M^+ *m/z* 283 (rel. int. 30%). The structure of (**3a**) was determined from the spectroscopic data. The resonances due to the dimethylamino-group, at δ 3·34 and 3·44, could be readily distinguished from that due to the methyl-group at δ 3·40, because of the characteristic broad



SCHEME.

a; R = Me, X = SO_2
b; R = Et, X = SO_2
c; R = $PhCH_2$, X = SO

† Compounds (**1a**), (**1b**), and (**1c**) were obtained by oxidation of the corresponding 2,5-dialkylthio-1,3,4-thiadiazoles with H_2O_2: (**1a**), $C_4H_6N_2O_4S_3$, m.p. 181 °C; (**1b**) $C_6H_{10}N_2O_4S_3$, m.p. 130·5 °C; and (**1c**) $C_{16}H_{14}N_2O_3S_3$, m.p. 203 °C. All compounds gave satisfactory analyses.

singlet signal of the dimethylamino-group The data indicate the loss of one methyl group originating from the 1 : 1 adduct Furthermore, a signal at δ 9·00 is due to the resonance of a ring proton, since the spectral pattern was unchanged by deuterium exchange This abnormal downfield signal must be due to 8-H, by comparison with the signal of corresponding ring proton of azulene [3] A comparison of the completely decoupled and off-resonance ^{13}C-n m r spectra provides further evidence for the structure of diaza-azulene (**3a**) resonances due to 4 sp^2 carbons are observed at δ 122·1, 122·5, 128·1, and 153·5 p p m , each coupled with one proton, while resonances due to 4 sp^2 carbons at δ 113·2, 119·9, 161·7, and 171·5 p p m are assigned to nonprotonated carbons These chemical shifts were correlated with π-electron densities (Figure) calculated using the PPP SCF MO method [4] Similar reactions of (**2**) with the heterodiene (**1b**)† in acetone at room temperature overnight and the heterodiene (**1c**)† in chloroform at 50 °C for 7 h, afforded the diaza-azulenes (**3b**) ($C_{12}H_{15}N_3O_2S_2$, m p 161 °C) and (**3c**) ($C_{17}H_{17}N_3O_2S_2$, m p 179 °C), respectively, as yellow crystals in moderate yields The spectral data of these adducts [(**3b**) and (**3c**)] are similar overall to those of (**3a**), indicating their skeletal resemblance

Since the heterodienes (**1a**), (**1b**), and (**1c**) are electron-deficient dienes, the heterodiene LUMO–6-dimethylaminofulvene HOMO interaction is expected to be more predominant than the reverse interaction The small decrease in the rate of cycloaddition with increasing solvent polarity supports a concerted mechanism The solvent effect on the cycloaddition of (**1a**) with (**2**) at 34·1 °C is shown by the following rate constants 4·43 × 10^{-3} s^{-1} in chloroform, 1·35 × 10^{-3} s^{-1} in acetone, and 2·36 × 10^{-3} s^{-1} in dimethyl sulphoxide

A reasonable mechanism for the formation of the diaza-azulenes‡ would involve the loss of SO_2 from the initial 1 : 1 adduct followed by a [1,5] sigmatropic shift and an S_N2-like intramolecular attack by the dimethylamino-group on the alkylsulphinyl-group, and further subsequent elimination of an alkane as shown in the Scheme

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‡ There is no evidence that the positions of the SOR and $SONMe_2$ groups should be reversed in the 5,6-diaza-azulenes The S_N2-like intramolecular attack of the dimethylamino-group on the alkylsulphinyl-group would be expected to be preferred to intermolecular addition which would lead to an alternative structure

[1] (a) S E Reiter, L C Dunn, and K N Houk, *J Am Chem Soc* , 1977, **99**, 4199, (b) D Mukherjee, L C Dunn, and K N Houk, *ibid* , 1979, **101**, 251, (c) D Copland, D Leaver and W B Menzies, *Tetrahedron Lett* , 1977, 639

[2] (a) T Sasaki, K Kanematsu, and T Kataoka *J Org Chem* , 1975, **40**, 1201, (b) depending on the reaction conditions, similar reaction of 6-dimethylaminofulvene with 3 6-diphenyl-1 2,3 4-tetrazine afforded 5-dialkylaminoethylene-1,4-diphenyl-5*H*-cyclopenta[d]pyridazine (see M Bachmann and H Nenhoeffen *Justus Liebig's Ann Chem* 1979, 675)

[3] D Meuche, B B Molloy, D H Reid, and E Heilbronner *Helv Chim Acta* 1963, **46**, 2483

[4] R G Parr 'The Quantum Theory of Molecular Electronic Structure,' Benjamin, New York, 1963