Novel Addition Products of 2-Aza-1-thiabenzene Derivatives with Methyl Propiolate

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The addition reactions between 2-methyl-1-aza-2-thianaphthalene (**1**) or 9-alkyl-10-aza-9-thiaphenanthrenes (**2**) with methyl propiolate afforded novel 1 : 2-adducts (**3**) or (**4**), respectively, whose structures have been confirmed by an *X*-ray crystal structure determination of (**4a**).

We recently reported the syntheses and some properties of the novel cyclic sulphilimines, 'azathiabenzenes,' in which a sulphur–nitrogen bond forms part of a cyclic conjugated ring system containing six π-electrons, and demonstrated their ylidic properties on the basis of spectral and chemical evidence.[1] Moody *et al.* independently prepared other azathiabenzene derivatives by an alternative method[2] and reported their thermal and nucleophilic reactions.[3]

In continuation of our investigation on the reactivities of this new class of heterocyclic compound based on their ylidic nature, we have now found that a novel addition reaction takes place between 2-methyl-1-aza-2-thianaphthalene (**1**)[1] or 9-alkyl-10-aza-9-thiaphenanthrenes (**2**)[1] and methyl propiolate (MP). Treatment of (**1**) with MP (1.6 equiv.) in dry benzene at room temperature for 160 h afforded a 21% yield of the novel heterocycle (**3**),† m.p. 166—169 °C (decomp.), as yellow columns (from hexane–EtOAc). Microanalytical and mass spectral data (M^+, m/z 331) indicated the molecular formula $C_{17}H_{17}NO_4S$ corresponding to a 1 : 2-adduct of (**1**) and MP. It showed n.m.r. peaks at δ 2.76 (3H, s), 3.78 (3H, s), 3.82 (3H, s), 6.50 (1H, d, J 10 Hz), 7.14 (1H, d, J 10 Hz), 6.95—7.95 (4H, m), 8.39 (1H, d, J 1.5 Hz), and 9.33 (1H, d, J 1.5 Hz) and an i.r. carbonyl absorption at 1660 cm^{-1} (ester), indicating strong delocalization of the ylide carbanion electrons to the ester group. The corresponding 1 : 1-adduct was not obtained even from the reaction with 1 equiv. of MP. It is interesting that this reaction is quite in contrast with the reaction with dimethyl acetylenedicarboxylate (DMAD) which provided only the 1 : 1-adduct.[1]

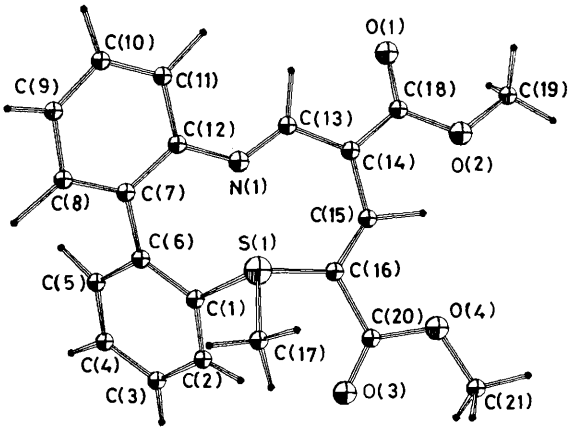
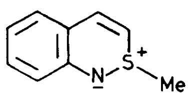
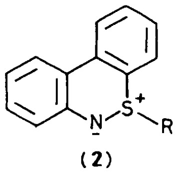


Figure 1. Molecular structure of (**4a**). Selected bond distances (Å) and angles (°) are: S(1) · · · N(1) 2.538(7), S(1)–C(1) 1.815(9), S(1)–C(16) 1.76(1), S(1)–C(17) 1.81(1), N(1)–C(12) 1.37(1), N(1)–C(13) 1.25(1), C(13)–C(14) 1.41(1), C(14)–C(15) 1.45(1), C(15)–C(16) 1.38(1); N(1)–S(1)–C(17) 165.1(4), N(1)–S(1)–C(16) 86.3(3), N(1)–S(1)–C(1) 81.6(3), C(1)–S(1)–C(16) 109.0(4), C(1)–S(1)–C(17) 101.2(4), C(16)–S(1)–C(17) 106.2(4), C(12)–N(1)–C(13) 129.9(8).

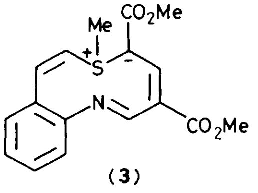


(**1**)

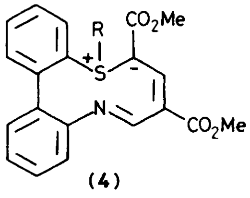


(**2**)

a ; R = Me
b ; R = Et
c ; R = Pr^n

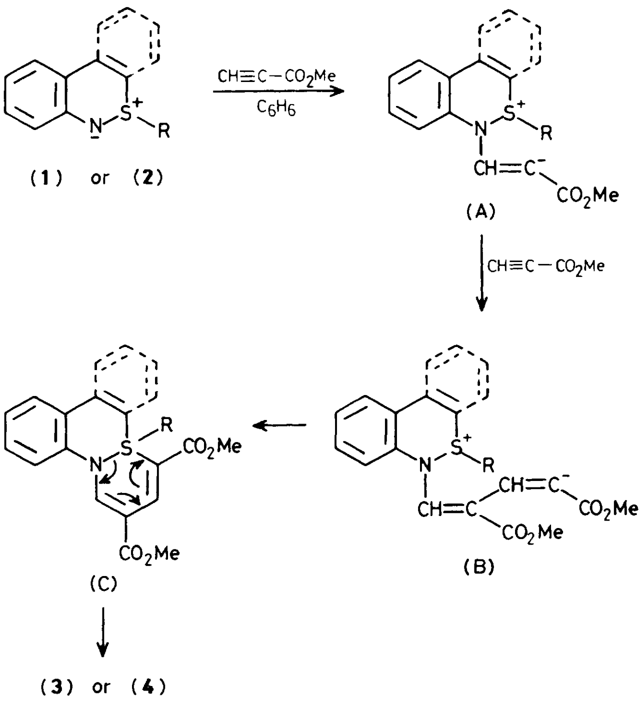


(**3**)



(**4**)

a ; R = Me
b ; R = Et
c ; R = Pr^n



Scheme 1

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† All new compounds gave satisfactory elemental analyses for C, H, and N within ±0.3%.

We next turned our attention to the reaction of 9-alkyl-10-aza-9-thiaphenanthrenes with MP, because 9-methyl-10-aza-9-thiaphenanthrene (**2a**) provided a seven-membered heterocycle as a 1:1-adduct from the reaction with DMAD.[1] 9-Methylazathiaphenanthrene (**2a**) was allowed to react with MP (1.3 equiv.) in benzene at room temperature to give a 14% yield of the novel 1:2-adduct (**4a**), m.p. 178—180 °C (decomp.), as orange prisms (from hexane–CH_2Cl_2), *m/z* 381 (M^+); $\nu_{max.}$ (KBr) 1650 cm^{-1} (ester); ^1H n.m.r. ($CDCl_3$) δ 3.08 (3H, s), 3.80 (3H, s), 7.00—7.95 (8H, m), 8.80 (1H, d, *J* 1.5 Hz), and 9.17 (1H, d, *J* 1.5 Hz); ^{13}C n.m.r. ($CDCl_3$) δ 86.23 (s). Similarly, the 9-ethyl or 9-n-propyl derivatives (**2b**) or (**2c**) also afforded the 1:2-adducts, (**4b**) or (**4c**), as orange prisms in 5 or 10% yields, respectively. The structure of the adduct (**4a**) was confirmed by *X*-ray analysis[‡] (Figure 1).

The *X*-ray structure of (**4a**) shows no planarity of the 10-membered ring in spite of the 10π-electron ring structure, showing lack of aromaticity. Further the possibility of a σ-sulphurane structure (trigonal bipyramidal) is slight, on the basis of the bond angles around sulphur (Figure 1), although the N · · · S distance (2.538 Å) is considerably shorter than the sum of the van der Waals radii of N and S (3.35 Å), indicating some interaction between S and N.

A possible mechanism for the formation of the 1:2-adducts (**3**) and (**4**) is shown in Scheme 1. Nucleophilic attack of cyclic sulphilimines (**1**) and (**2**) on methyl propiolate forms the zwitterionic intermediate (A), whose anion site attacks further another MP molecule to give the second intermediate (B). The intermediate (B) cyclises to yield the final products, with the fission of the S–N bond.

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[‡] *Crystal data:* $C_{21}H_{19}O_4NS$ (**4a**), triclinic, a = 9.835(1), b = 11.096(1), c = 8.924(1) Å, α = 80.62(1), β = 108.77(1), γ = 89.90(1)°, space group $P\bar{1}$, U = 908.2(1) Å^3, Z = 2, D_c = 1.395 g cm^{-3}, crystal dimensions 0.3 × 0.3 × 0.3 mm^3. Intensity data were collected on a Rigaku automatic four-circle diffractometer with graphite monochromated Cu-K_α radiation. The background intensity was counted 5″ both sides of each peak. A total of 1452 independent reflections were measured (up to 2θ = 140°) of which 1304 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the analysis. Corrections were made for Lorentz and polarization factors, but not for absorption effects. The structure was determined by direct methods (MULTAN),[4] and refined by block-diagonal least-squares with anisotropic thermal parameters for the non-hydrogen atoms. All except the methyl hydrogen atoms were located on a difference Fourier map, and several cycles of least-squares refinement were carried out including these hydrogen atoms. The final R value was 0.069. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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