Novel Addition Reactions of New Cyclic Sulphur Ylides, 9-Alkyl-10-cyano-9-thiaphenanthrenes with Acetylenic Electrophiles

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The addition reactions of 10-cyano-9-methyl-9-thiaphenanthrene (**1a**) with dimethyl or diethyl acetylenedicarboxylate afforded the novel spiro products (**2a**) and (**2b**), respectively; these underwent a thermal 1,5-rearrangement to give the corresponding nine-membered sulphur-containing heterocyclic compounds (**4a**) and (**4b**), respectively, while the 9-ethyl derivative (**1b**) gave a seven-membered 1 : 1-adduct (**3**) from the reaction with dimethyl acetylenedicarboxylate.

We have already reported that the reactions of stable cyclic sulphur ylides such as 1- or 2-thianaphthalene derivatives[1] and 10-thia-anthracene derivatives[2] with various kinds of electrophiles afford unusual addition products and provide convenient methods for the synthesis of new sulphur-containing heterocyclic skeletons. This prompted us to investigate the addition reactions of other types of stable cyclic sulphur ylides with electrophiles. In this communication we report the novel addition reactions of new cyclic sulphur ylides, 9-alkyl-10-cyano-9-thiaphenanthrenes (**1**),† which are considered to have the skeletons of both 1- and 2-thianaphthalenes, with acetylenic electrophiles such as dimethyl (DMAD) and diethyl acetylenedicarboxylate (DEAD) to result in the formation of quite different adducts from those obtained from 1- or 2-thianaphthalenes.

10-Cyano-9-methyl-9-thiaphenanthrene (**1a**) was allowed to react with DMAD (1 equiv.) in benzene at 0—10 °C under a nitrogen atmosphere for 8 h to give a 31.3% yield of the novel crystalline spiro compound (**2a**),‡ m.p. 140—141 °C, as pale yellow prisms. The adduct (**2a**) was also obtained in about the

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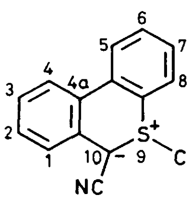
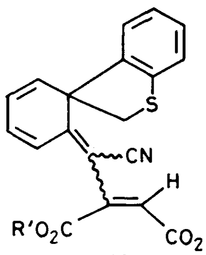
† The 9-thiaphenanthrenes (**1**) were synthesized from the corresponding 9-thiaphenanthrenium salts by deprotonation with triethylamine in ethanol. The details will be reported in a full paper.

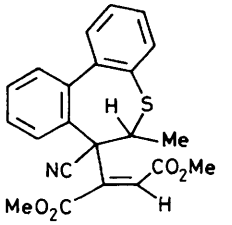
‡ All new compounds gave satisfactory elemental analyses for C, H, and N within ±0.3%.



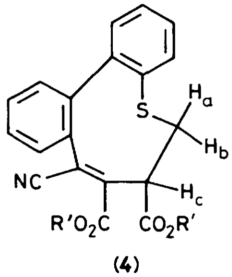
(1)
a; R = H
b; R = Me



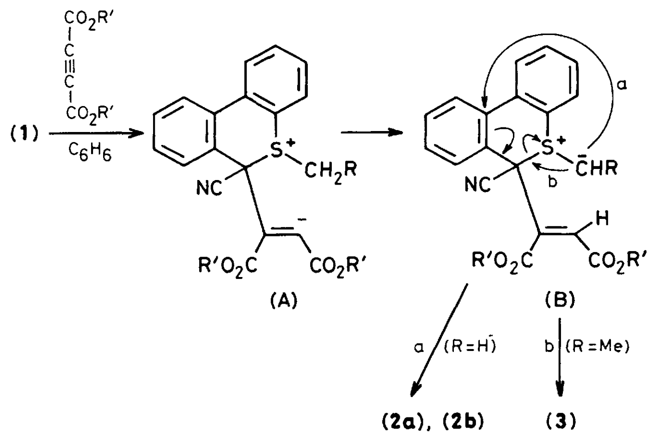
(2)
a; R' = Me
b; R' = Et



(3)



(4)
a; R' = Me
b; R' = Et



Scheme 1

same yield using ethanol as the solvent. Elemental analyses and mass spectral data (M^+, m/z 379) indicate a molecular formula of $C_{21}H_{17}NO_4S$ corresponding to a 1 : 1-adduct of (**1a**) and DMAD. The i.r. spectrum showed characteristic absorption bands at 2197 cm^{-1} for the cyano group and at 1735 cm^{-1} for the two ester groups. The ^{1}H n.m.r. spectrum (400 MHz) had characteristic resonances at δ (CDCl$_3$) 6.01 (dd, J 9.3, 5.8 Hz), 6.24 (d, J 9.3 Hz), 6.53 (dd, J 10.7, 5.8 Hz), and 7.00 (d, J 10.7 Hz) attributable to the four olefinic protons of the cyclohexadiene ring in addition to the two methylene proton signals at δ 3.34 and 3.81 (each d, J 12.2 Hz). The maleate structure was determined from the ^{1}H n.m.r. chemical shift (δ 5.20)[2,3] of the olefinic proton. The spiro structure of (**2a**) was also supported by its ^{13}C n.m.r. spectrum, showing the quaternary carbon at δ (CDCl$_3$) 57.23 together with the methylene carbon at δ 45.42 (t). The geometry of the exocyclic double bond bearing CN and the maleate group could not be established by ^{1}H n.m.r. spectroscopy. A similar reaction of (**1a**) with DEAD afforded a 23.4% yield of the corresponding spiro compound (**2b**) as a yellow oil. To our knowledge, the formation of spiro compounds analogous to (**2a**) or (**2b**) has not previously been observed in the reactions of cyclic sulphur ylides with electrophiles.

The 9-ethyl derivative (**1b**), however, gave a different reaction. Treatment of (**1b**) with DMAD (1 equiv.) under similar reaction conditions (as above) afforded a 38% yield of a seven-membered dibenzothiepine derivative, (**3**) m.p. 113 °C, as colourless crystals. Its ^{1}H n.m.r. spectrum showed a methyl proton signal at δ (CDCl$_3$) 1.58 as a doublet (J 7 Hz) and a methine proton signal at δ 4.09 as a quartet (J 7 Hz) coupled with the methyl group. The ^{13}C n.m.r. spectrum indicated the existence of a quaternary carbon at δ (CDCl$_3$) 57.21 and a tertiary carbon at δ 52.43. The fumarate structure was determined on the basis of the ^{1}H n.m.r. chemical shift (δ 6.06)[3] of the olefinic proton, though the reason why the fumarate compound was yielded preferentially in this case is not clear at present.

We next turned our attention to the thermal rearrangements of (**2a**), (**2b**), and (**3**) in order to investigate the possibility of their ring expansion reactions to lead to new sulphur-containing heterocyclic compounds. Thus, on heating a benzene solution in a sealed tube up to 200 °C for 4 h (**1a**) underwent a thermal 1,5-rearrangement to afford a 95% yield of the ring-expanded product (**4a**) m.p. 154—155 °C, as colourless crystals [i.r. 2205 (CN), 1745, 1730 cm^{-1} (ester), ^{1}H n.m.r. (CDCl$_3$, 400 MHz) δ 2.95 (dd, J 15.4, 9.2 Hz, H_a), 3.51 (dd, J 15.4, 1.1 Hz, H_b), 3.67 (dd, J 9.2, 1.1 Hz, H_c), 3.67 (s, OMe), 3.75 (OMe), and 7.26—7.71 (8H, m, ArH); ^{13}C n.m.r. (CDCl$_3$) δ 34.9 (t), 51.9 (d); m/z 379 (M^+)]. A similar 1,5-rearrangement of the spiro compound (**2b**) under the same conditions gave the ring-expanded product (**4b**) as an oil in 90% yield. The benzothiepine derivative (**3**), however, completely degraded under the above conditions and no products were isolated.

A plausible mechanism for the formation of (**2a**), (**2b**), and (**3**) is depicted in Scheme 1. The nucleophilic attack of (**1a**) or (**1b**) onto the electron-deficient acetylene forms the zwitterionic intermediate (A), which gives the sulphonium ylide intermediate (B) upon intramolecular proton abstraction from the proximate alkyl group. The attack of the carbanion site of the ylide intermediate (B; R = H) on the aromatic carbon (C-4a) together with the cleavage of the C-10–S bond gives (**2a**) or (**2b**) (path a, Sommelet–Hauser type rearrangement). In contrast, the intermediate (B; R = Me) undergoes Stevens-type rearrangement to result in the formation of the ring-expansion product (**3**) (path b), presumably because the steric effect of the S-substituent prevents the ylide carbanion from attacking the aromatic ring. A similar ring expansion reaction leading to the seven-membered ring of the analogous exocyclic ylides to (B) was recently observed by Benati *et al.*[4]

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