Cycloaddition of 8-Styrylcyclohepta[*b*]pyrroles with Dimethyl Acetylenedicarboxylate. Formation and Thermal Rearrangement of the 7*H*-6a-Azacyclobuta[*j*]cyclopenta[1,2,3-*cd*]azulene Ring System

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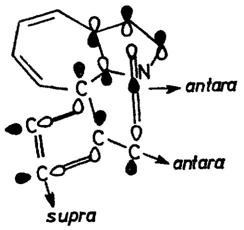
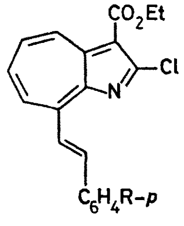
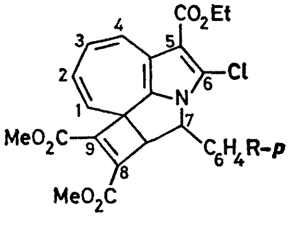
Summary The cycloaddition of 8-styrylcyclohepta[*b*]pyrroles with dimethyl acetylenedicarboxylate gives the 7*H*-6a-azacyclobuta[*j*]cyclopenta[1,2,3-*cd*]azulene ring system, which rearranges thermally into the 3*H*-2a-azacyclopenta[*cd*]azulene ring system.

CYCLOADDITIONS of the aza-analogues of azulene[1] and pentalene[2] with dimethyl acetylenedicarboxylate (DMAD) are now receiving attention. We describe here the reaction of 8-styrylcyclohepta[*b*]pyrroles (**1**) with DMAD to give the 7*H*-6a-azacyclobuta[*j*]cyclopenta[1,2,3-*cd*]azulene ring

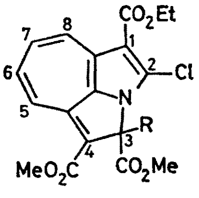




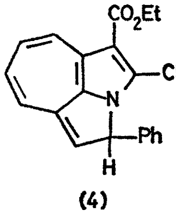
(1)
a; R = H
b; R = Me



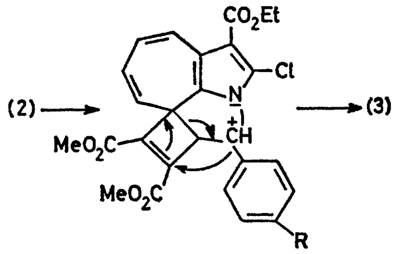
(2)
a; R = H
b; R = Me



(3)
a; R = PhCH=CH
b; R = p-MeC$_6$H$_4$CH=CH
c; R = H



(4)



SCHEME

system (**2**) and its thermal rearrangement into the 3*H*-2a-azacyclopenta[*cd*]azulene ring system (**3**); the formation of (**2**) may be explained in terms of a symmetry-allowed thermal [$_{\pi}2_s + {}_{\pi}2_a + {}_{\pi}6_a$] cycloaddition as shown in the Scheme.[3]†

When compound (**1a**) was heated with an excess of DMAD in benzene under reflux for 48 h, two 1 : 1 adducts (**2a**),‡ m.p. 168—169 °C, yellow prisms (24%) and (**3a**),‡ m.p. 172—173 °C, red prisms (9%) were isolated together with other products by silica gel chromatography.

The ^{13}C n.m.r. spectrum (CDCl$_3$) of (**2a**) exhibits signals assignable to sp^3 carbon atoms at δ 56·19 (s, C-9a), 61·45 (d, C-7a), and 65·10 p.p.m. (d, C-7), respectively. Two 1H doublets (*J* 2 Hz) assignable to the 7a-H and 7-H protons are observed at δ 3·87 and 5·49, respectively, in the 90 MHz ^{1}H n.m.r. spectrum (CDCl$_3$), whereas the seven-membered ring protons are observed at δ 5·60 (d, *J* 11 Hz, 1-H), 6·0—6·3 (m, 2- and 3-H), and 7·22 (d, *J* 11 Hz, 4-H). Large downfield shifts of 0·44 (7-H), 0·36 (7a-H), and 0·97 p.p.m. (4-H) induced on addition of tris(dipivaloylmethanato)europium support these assignments. Further evidence in support of structure (**2a**) is provided by its mass spectrum which displays intense peaks at *m/e* 337 and 339 associated with the loss of dimethyl acetylenedicarboxylate or its equivalent from the molecular ion.[4]

The u.v. spectrum [λ_{max} (EtOH) 252 (log ε 4·72), 375 (4·17), 393 (4·13), 440 (3·78), 468 (3·71), 502 (3·51), and 537 nm (3·06)] of (**3a**) closely resembles that of (**3c**)[1] and the observation of two 1H doublets (*J* 16 Hz) at δ 6·00 and 7·14 in its n.m.r. spectrum shows the presence of a styryl unit. Other ^{1}H and ^{13}C n.m.r. spectral features are completely in accordance with structure (**3a**).

The reaction of (**1b**) with DMAD proceeds in a similar way to afford compounds (**2b**),‡ m.p. 151—152 °C (55%) and (**3b**),‡ m.p. 198—199 °C (10%).

Compound (**2a**), when heated in xylene under reflux for 24 h, was found to rearrange to (**3a**) in 40% yield. This shows that (**3**) isolated during the reaction of (**1**) with DMAD is a thermal product of (**2**) and may be formed by the scission of the bond between nitrogen and the benzylic-carbon atoms of (**2**).

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† The tautomeric equilibrium of (**1**) with (**4**) and the cycloaddition of (**4**) with DMAD to give (**2**) is another mechanistic possibility. However, this is unlikely because the ^{1}H n.m.r. spectrum of (**1**) lacks a benzylic proton which would be associated with structure (**4**), the u.v. spectrum of (**1**) is quite different from that of (**3c**), and no reaction took place even after prolonged heating of (**3a**) with DMAD in benzene.

‡ Satisfactory microanalytical data have been obtained.

[1] N. Abe, Y. Tanaka, and T. Nishiwaki, *J.C.S. Perkin I*, 1978, 429.

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[3] Symmetry-allowed, thermal, three-component cycloadditions are known: T. Machiguchi, Y. Yamamoto, M. Hoshino, and Y. Kitahara, *Tetrahedron Letters*, 1973, 2627; T. Kaneda, T. Ogawa, and S. Misumi, *ibid.*, p. 3373; D. J. Pasto and J. K. Borchardt, *J. Amer. Chem. Soc.*, 1974, **96**, 6944.

[4] R. M. Acheson and G. Procter, *J.C.S. Perkin I*, 1977, 1924.