

Studies on Heterocyclic Analogues of Azulene. Part 2.¹ Cycloaddition Reactions of Aza-analogues of Azulene with Dimethyl Acetylenedicarboxylate: Intermediacy of a 1,8-Dipolar Species

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Cyclohepta[*b*]pyrroles (1) and cycloheptimidazole (2) react with dimethyl acetylenedicarboxylate to give 2*H*-2-azacyclopent[*cd*]azulenes (3) and 3*H*-2-azacyclopenta[*ef*]heptalenes (4), and 3*H*-1,2-azacyclopenta[*ef*]heptalene (5), respectively, in low to moderate yields. The formation of these products is explained in terms of 1,8-dipolar cycloaddition reactions.

ALTHOUGH 1,3-² and 1,4-dipolar cycloaddition reactions³ have been widely studied, more extended dipolar cycloaddition reactions are little known; only a few papers record 1,5-⁴ 1,7-⁵ and 1,11-dipolar cycloadditions.^{4,†} In the light of successful cyclisations of azulene^{6a} aceheptylene,^{6b} and a number of pyrroles^{7a} and azoles^{7b} with acetylenic compounds, we envisaged that 1-aza-azulene (cyclohepta[*b*]pyrrole) (1) and 1,3-diaza-azulene (cycloheptimidazole) (2) might produce interesting vinylogous dipolar systems on reaction with acetylenes.

Treatment of ethyl 2-chloro-1-aza-azulene-3-carboxylate (1a) with an excess of dimethyl acetylenedicarboxylate in benzene under reflux gave two products. One

1 H singlet at δ 5.78 [C(3)H] in addition to signals for two methyl groups and one ethyl group; assignment of the δ 7.59 signal to the C(8) proton was made by reference to the spectrum of the aza-azulene (1a), in which the C(4) proton signal is observed at lowest field.

The other product (14%) was the 1:2 adduct. Comparison of the ¹³C n.m.r. spectrum of this adduct with that of the aza-azulene (1a) and off-resonance decoupling (Table) revealed that of the thirteen ring carbon atoms only one gives a resonance assignable to an *sp*³ carbon atom; thus ring closure took place at the seven-membered ring of compound (1a) with concomitant loss of a hydrogen atom. The ¹H n.m.r. spectrum allows the

¹³C Chemical shifts of the compounds (1a), (1b), (4a), (4b), and (5)

Carbon	(1a)	(1b)	(4a)	(4b)	(5)			
1			111.3s	109.6d				
2	158.9s	157.9s	143.0s	143.9s	140.9d			
3	111.9s	112.2d	55.5d	55.7d	57.2d			
3a	146.9s	147.2s						
4	137.9d	135.4d	118.8s	116.3s	116.1s			
5	133.0d	130.0d	126.5s ^a	124.4s ^b	131.2s			
6	137.0d	134.5d	125.9s ^a	122.7s ^b	125.5s			
6a			126.5s ^a	127.7s	140.9s			
7	133.0d	130.3d	127.2d	126.1d	127.4d			
8	139.5d	137.6d	128.6d	129.5d	131.2d			
8a	156.7s	156.1s						
9			127.8d	128.7d	130.2d			
10			131.2d	131.1d	132.2d			
10a			129.8s	131.1s	144.2s			
10b			141.5s	142.2s	145.3s			
C=O	162.9s		162.6s	164.7s	165.5s	167.1s	165.4s	167.2s
OMe			166.2s	166.5s	167.1s	167.4s	167.2s	167.2s
			52.2q	52.9q	52.1q	52.7q	52.7q	53.4q
			52.9q	53.5q	52.7q	53.4q	53.4q	53.7q
OCH ₂	60.6t		60.6t					
Me	14.3q		14.2q					

^{a,b} Assignments may be reversed.

(2%) was the 1:1 adduct, as revealed by elemental analysis. The structure (3a) was assigned on the basis of the ¹H n.m.r. spectrum, which has two 1 H doublets at δ 7.45 [C(5)H] and 7.59 [C(8)H] (*J* 11 Hz) and two 1 H double doublets at δ 6.30 [C(6)H] and 6.69 [C(7)H] (*J* 11 and 9 Hz) assignable to four aromatic protons, a

structure (4a) to be assigned, with the C(7) and C(10) proton signals appearing as double multiplets at δ 6.83 and 7.83 (*J* 10 Hz), the C(8) and C(9) proton signals as double double doublets at δ 6.50 and 6.57 (*J* 10, 7.5 and 4 Hz), and the C(3) proton signal at δ 6.80.

2-Chloro-1-aza-azulene (1b) similarly reacts with the

† For the definition of cycloaddition we follow Huisgen^{2b} rather than Reimlinger.^{4a}

¹ Part 1, N. Abe, *Heterocycles*, 1976, **4**, 221.

² R. Huisgen, *Angew. Chem.*, (a) 1963, **75**, 604; (b) 1968, **80**, 329.

³ R. Huisgen, *Topics Heterocyclic Chem.*, 1969, 223.

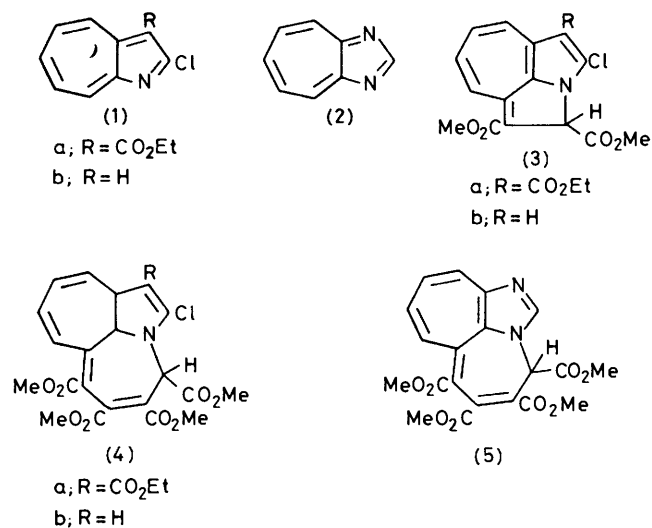
⁴ (a) H. Reimlinger, *Chem. Ber.*, 1970, **103**, 1900; (b) S. F. Gait, M. J. Rance, C. W. Rees, R. W. Stephenson, and R. C. Storr, *J.C.S. Perkin I*, 1975, 556.

⁵ D. J. Cram and R. D. Partos, *J. Amer. Chem. Soc.*, 1963, **85**, 1273.

⁶ (a) K. Hafner, H. Diehl, and H. U. Süss, *Angew. Chem. Internat. Edn.*, 1976, **15**, 104; (b) K. Hafner, H. Diehl, and W. Richarz, *ibid.*, p. 108.

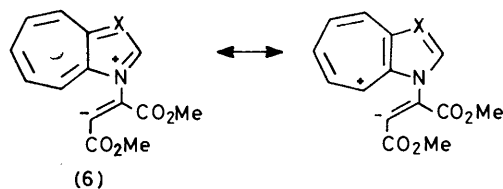
⁷ (a) R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125; (b) P. J. Abott, R. M. Acheson, U. Eisner, D. J. Watkin, and J. R. Carruthers, *J.C.S. Perkin I*, 1976, 1269, and previous papers from this group.

acetylene producing a 1 : 2 adduct (4b) and an unstable 1 : 1 adduct (3b), whereas 1,3-diaza-azulene (2) reacts



with the acetylene at room temperature to afford a 1 : 2 adduct only, whose structure was established as (5) from ¹H and ¹³C n.m.r. spectra (Table).

In these reactions, the electrophilic acetylene attacks the ring nitrogen, to give a dipolar species (6) whose



sextet formulation bears a positive and a negative charge at the 1- and 8-positions of the formal azatetraene system; hence the species may be regarded as 1,8-dipolar. Cycloaddition of this zwitterion followed by a hydrogen shift produces compound (3), whereas cycloaddition with a further molecule of dimethyl acetylenedicarboxylate followed by hydrogen shift leads to compound (4) or (5).

EXPERIMENTAL

M.p.s were determined for samples in capillary tubes unless otherwise stated. ¹H N.m.r. spectra were taken with a Varian HA-100 spectrometer at 100 MHz and ¹³C n.m.r. spectra with a Hitachi R-26 spectrometer (solutions in CDCl₃ with tetramethylsilane as internal standard). U.v. spectra were measured for solutions in chloroform and i.r. spectra for Nujol mulls. Chromatography was performed on Kieselgel 60.

Reaction of Ethyl 2-Chloro-1-aza-azulene-3-carboxylate (1a) with Dimethyl Acetylenedicarboxylate.—A mixture of compound (1a)⁸ (2.00 g) and the acetylene (4.00 g) in benzene (40 ml) was heated under reflux for 9 h. The solvent was removed under reduced pressure and the residue chromatographed with benzene to give 1-ethyl 3,4-dimethyl 2-chloro-

⁸ T. Nozoe, S. Seto, S. Matsumura, and T. Terasawa, *Chem. and Ind.*, 1954, 1357.

3H-2a-azacyclopent[cd]azulene-1,3,4-tricarboxylate (3a) (0.056 g, 2%), which crystallised from cyclohexane as orange prisms, m.p. 177—178° (Found: C, 57.1; H, 4.4; N, 3.8. C₁₈H₁₆ClNO₆ requires C, 57.2; H, 4.3; N, 3.7%), λ_{max} 255 (log ε 4.51), 273 (4.15), 285sh (4.03), 372 (4.17), 392 (4.13), 416 (3.70), 443 (3.74), 472 (3.71), 507 (3.53), and 545 nm (3.06), ν_{max} 1 740, 1 690, and 1 670 cm⁻¹ (C=O), δ 1.42 (3 H, t, J 7 Hz), 3.78 (3 H, s), 3.80 (3 H, s), 4.37 (2 H, q, J 7 Hz), 5.78 (1 H, s), 6.30 (1 H, dd, J 11 and 9 Hz), 6.69 (1 H, dd, J 11 and 9 Hz), 7.45 (1 H, d, J 11 Hz), and 7.59 (1 H, d, J 11 Hz). Elution with benzene-chloroform (1 : 1) gave the starting material (0.83 g) and elution with benzene-chloroform (1 : 2) yielded 1-ethyl 3,4,5,6-tetramethyl 2-chloro-3H-2a-azacyclopent[ef]heptalene-1,3,4,5,6-pentacarboxylate (4a) (0.61 g, 14%), which crystallised from cyclohexane as red prisms, m.p. 133—134° (Found: C, 55.2; H, 4.3; Cl, 7.2; N, 2.7. C₂₄H₂₂ClNO₁₀ requires C, 55.4; H, 4.3; Cl, 6.8; N, 2.7%), λ_{max} 257sh (log ε 4.37) and 448 nm (3.85), ν_{max} 1 750, 1 730, 1 712, and 1 693 cm⁻¹ (C=O), δ 1.38 (3 H, t, J 7 Hz), 3.76 (3 H, s), 3.77 (3 H, s), 3.82 (3 H, s), 3.83 (3 H, s), 4.40 (2 H, q, J 7 Hz), 6.50 (1 H, ddd, J 10, 7.5, and 4 Hz), 6.57 (1 H, ddd, J 10.5, 7.5, and 4 Hz), 6.80 (1 H, s), 6.83 (1 H, dm, J 10 Hz), and 7.83 (1 H, dm, J 10.5 Hz).

Reaction of 2-Chloro-1-aza-azulene (1b) with Dimethyl Acetylenedicarboxylate.—A mixture of compound (1b)⁸ (1.00 g) and the acetylene (4.00 g) in benzene (80 ml) was heated under reflux for 5 h and worked up as above. Elution with benzene afforded an oil (0.12 g), which partly solidified on trituration with petroleum (b.p. 30—60 °C) to afford dimethyl 2-chloro-3H-2a-azacyclopent[cd]azulene-3,4-dicarboxylate (3b) (0.06 g, 3%). Repeated recrystallisations from petroleum (b.p. 30—60 °C)-dichloromethane gave the pure compound as red prisms (0.005 g), m.p. 155—156° (hot-stage) (Found: *m/e* 307.042. C₁₅H₁₂ClNO₄ requires *M*, 307.042), λ_{max} 255 (log ε 4.17), 273 (3.83), 283 (3.74), 373 (3.79), 394 (3.76), 415 (3.42), 431 (3.45), 459 (3.41), 492 (3.23), and 530 nm (2.78), ν_{max} 1 727 and 1 690 cm⁻¹ (C=O), δ 3.75 (3 H, s), 3.79 (3 H, s), 5.77 (1 H, s), 6.17 (1 H, dd, J 11 and 9 Hz), 6.24 (1 H, s), 6.65 (1 H, dd, J 12 and 9 Hz), 6.81 (1 H, d, J 11 Hz), and 7.41 (1 H, d, J 12 Hz). The benzene-chloroform (2 : 1) eluate gave the starting material (0.35 g), and elution with benzene-chloroform (1 : 3) afforded tetramethyl 2-chloro-3H-2a-azacyclopent[ef]heptalene-3,4,5,6-tetracarboxylate (4b) (0.82 g, 30%), which crystallised from cyclohexane as red prisms, m.p. 164—165° (Found: C, 56.1; H, 4.0; Cl, 8.1; N, 2.8. C₂₁H₁₈ClNO₈ requires C, 56.3; H, 4.05; Cl, 7.9; N, 3.1%), λ_{max} 320 (log ε 3.56) and 467 nm (3.76), ν_{max} 1 743, 1 725sh, 1 715, and 1 690sh cm⁻¹ (C=O), δ 3.72 (3 H, s), 3.76 (s, 3 H), 3.79 (3 H, s), 3.80 (3 H, s), 6.28 (1 H, ddd, J 12, 8, and 4.5 Hz), 6.38 (1 H, s), 6.43 (1 H, ddd, J 11.5, 8, and 4 Hz), 6.61 (1 H, s), 6.78 (1 H, dm, J 12 Hz), and 6.79 (1 H, dm, J 11.5 Hz).

Reaction of 1,3-Diaza-azulene (2) with Dimethyl Acetylenedicarboxylate.—A mixture of compound (2)⁹ (1.25 g) and the acetylene (5.50 g) in benzene (70 ml) was stirred at room temperature for 5 h. The dark red solution was evaporated under reduced pressure; chromatography of the residue with benzene-chloroform (1 : 8) gave tetramethyl 3H-1,2a-diazacyclopent[ef]heptalene-3,4,5,6-tetracarboxylate (5) (0.53 g, 14%), which crystallised from cyclohexane as red prisms, m.p. 197—198° (Found: C, 57.9; H, 4.4; N,

⁹ T. Nozoe, T. Mukai, and I. Murata, *J. Amer. Chem. Soc.*, 1954, **76**, 3352.

6.45. $C_{20}H_{18}N_2O_8$ requires C, 58.0; H, 4.4; N, 6.8%), λ_{max} . 280 (log ϵ 4.01) and 450 nm (3.99), ν_{max} . 1 742, 1 727, 1 715, and 1 705 cm^{-1} (C=O), δ 3.76 (3 H, s), 3.78 (3 H, s), 3.82 (3 H, s), 3.83 (3 H, s), 6.27 (1 H, s), 6.48 (1 H, ddd, J 11, 6, and 2 Hz), 6.58 (1 H, ddd, J 12, 6, and 2 Hz), 6.92 (1 H, dm, J 12 Hz), 7.11 (1 H, dm, J 11 Hz), and 7.71 (1 H, s). Elution with chloroform gave the starting material (0.18 g).

When this reaction was carried out in benzene under reflux for 20 min, the yield of the compound (5) was 2%.

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