Studies on Heterocyclic Analogs of Azulene. VI.[1] Cycloadditions of Styryl-substituted Aza Analogs of Azulene with Dimethyl Acetylenedicarboxylate[2]

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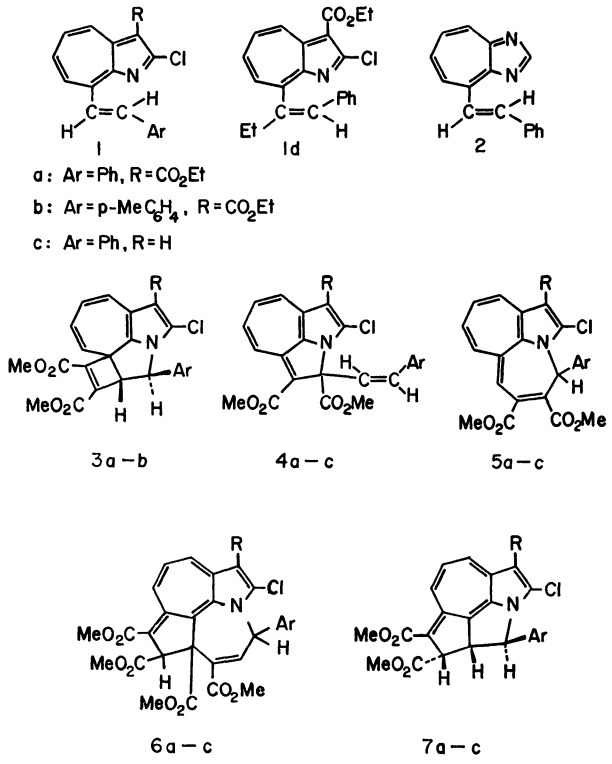
8-[(*E*)-Styryl]-1-azaazulenes stereospecifically react with dimethyl acetylenedicarboxylate to form *trans*-7*H*-6a-azacyclobuta[*j*]cyclopent[*cd*]azulene (**3**), which undergoes thermal rearrangement into 3-[(*E*)-styryl]-3*H*-2a-azacyclopent[*cd*]azulene and 3a,4-dihydro-3*H*-2a-azadicyclopent[*cd, ij*]azulene (**7**), or isomerization into 3*H*-2a-azacyclopenta[*ef*]heptalene by silica gel. Compound **7** is oxidized during the course of reaction to yield 11-oxo-2a*H*-7,10b-methano-2a-azacyclopenta[*ab*]cycloundecene, compound **3** forming 5a,6-dihydro-3*H*-2a-azadicyclopenta[*ef, kl*]heptalene upon reaction with acetylene. The formation of **3** could be accounted for in terms of a symmetry-allowed thermal [$_{\pi}2_{s}+_{\pi}2_{a}+_{\pi}6_{a}$] cycloaddition.

Cycloaddition of nitrogen-heterocycles with alkynes, a versatile synthetic method of heterocycles which are otherwise difficult to obtain,[3] has been utilized recently in the azaazulene[4] and azapentalene ring systems.[5] We report on the cycloaddition of 8-styryl-substituted aza analogs of azulene with dimethyl acetylenedicarboxylate (DMAD).

8-Styryl-1-azaazulenes (**1a**—**d**) and 4-styryl-1,3-diazaazulene (**2**) were prepared by the reaction of the corresponding azaazulene with styrylmagnesium bromide. The (*E*)-configuration about the double bond of compounds **1a**—**c** and **2** follows from the presence of two pairs of 1H doublets at δ 7.5—8.7 (J=17 Hz) in their ^{1}H NMR spectra and an absorption at 970 cm^{-1} in their IR spectra. β-Bromo-β-ethylstyrene required for the preparation of **1d** was synthesized by the decarboxylation of the sodium salt of (*E*)-α,β-dibromo-α-ethylcinnamic acid. The stereochemistry of the styrene thus formed appears to depend on the water content of the solvent.[6] Our conditions (95% ethanol) favor the formation of a (*Z*)-isomer.

Four products were isolated when compound **1a** was heated under reflux with DMAD in benzene. They were characterized as 5-ethyl 8,9-dimethyl 6-chloro-7-phenyl-*trans*-7*H*-6a-azacyclobuta[*j*]cyclopent-[*cd*]azulene-5,8,9-tricarboxylate (**3a**) (24%), 1-ethyl 3,4-dimethyl 2-chloro-3-[(*E*)-styryl]-3*H*-2a-azacyclopent-[*cd*]azulene-1,3,4-tricarboxylate (**4a**) (9%), 1-ethyl 4,5-dimethyl 2-chloro-3-phenyl-3*H*-2a-azacyclopenta[*ef*]-heptalene-1,4,5-tricarboxylate (**5a**) (14%), and 1-ethyl 5,5a,6,7-tetramethyl 2-chloro-3-phenyl-5a,6-dihydro-3*H*-2a-azadicyclopenta[*ef, kl*]heptalene-1,5,5a,6,7-pentacarboxylate (**6a**) (7%), respectively, from consideration of their spectroscopic properties.

The ^{13}C NMR spectrum of **3a** exhibits signals assignable to sp^{3} carbon atoms at δ 56.2 (s, C-9a), 61.5 (d, C-7a), and 65.1 ppm (d, C-7). Two 1H doublets (J=2 Hz) assignable to the H-7a and H-7 protons are observed at δ 3.87 and 5.49, respectively, in its ^{1}H NMR spectrum, whereas the protons at the seven-membered ring are observed at δ 5.60 (d, J=11 Hz, H-1), 6.0—6.3 (m, H-2 and H-3), and 7.22 (d, J=11 Hz, H-4). Large downfield shifts of 0.44 (H-7), 0.36 (H-7a), and 0.97 ppm (H-4) induced on addition of tris(dipivaloylmethanato)europium support these assignments. Further evidence supporting the structure **3a** is the fact that its mass spectrum displays intense



peaks at *m/e* 337 and 339 associated with the loss of dimethyl acetylenedicarboxylate or its equivalent from the molecular ion.[7] The $J_{7,7a}$ value indicates the H-7 and H-7a hydrogens to be situated *trans* to each other in the light of J_{cis} (10—13 Hz) and J_{trans} (2—10 Hz) values reported for the vicinal hydrogens of 2-pyrazolines.[8]

Two pairs of doublets at δ 6.0—7.1 (J=16 Hz) in the ^{1}H NMR spectrum of **4a** shows the presence of an (*E*)-styryl moiety, further confirmed by an IR absorption at 980 cm^{-1}, whereas the ^{1}H NMR spectrum of **5a** displays two 1H singlets at δ 5.31 and 6.11; the former is assigned to a benzylic H-3 proton and the latter to an olefinic H-6 proton. The presence of four aromatic protons in the seven-membered rings of **4a** and **5a**, respectively, is evident from their ^{1}H NMR spectra. The UV spectra of **4a** and **5a** are especially instructive for their structural determinations. The spectrum of **4a** is in line with that of 1-ethyl 3,4-dimethyl 2-chloro-3*H*-2a-azacyclopent[*cd*]azulene-1,3,4-

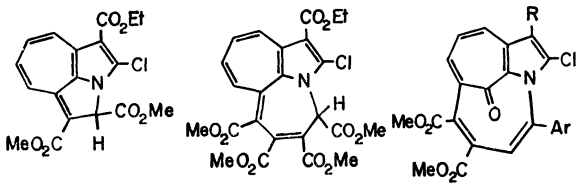
tricarboxylate[4] (**8**) and the spectrum of **5a** is in line with that of 1-ethyl 3,4,5,6-tetramethyl 2-chloro-3*H*-2a-azacyclopenta[*ef*]heptalene-1,3,4,5,6-pentacarboxylate[4] (**9**) except for the presence of additional low-intensity absorptions in the longer wavelength region for **5a**. The ^{13}C NMR spectral features of **4a** and **5a** are also in line with the proposed structures.

The ^1H NMR spectrum of **6a**, 1:2 adduct of **1a** and DMAD, shows the presence of three seven-membered ring protons at δ 6.22 (d, J=6 Hz, H-8), 6.37 (dd, J=10 and 6 Hz, H-9), and 7.39 (d, J=10 Hz, H-10). A singlet at δ 5.71 is assigned to a H-6 proton. There are two pairs of 1H doublets (J=3 Hz) at δ 4.66 and 5.29, the former being assigned to a benzylic H-3 proton and latter to a H-4 one. The ^{13}C NMR spectrum of **6a** exhibits signals assignable to sp^3 carbon atoms at δ 5.60 (s, C-5a), 65.4 (d, C-6), and 68.7 (d, C-3).

Whilst the reaction of **1b** with DMAD in benzene proceeded similarly to produce **3b**, **4b**, **5b**, and **6b**, the reaction of **1c** with DMAD under similar conditions afforded **4c**, **5c**, **6c**, and 4,5-dimethyl 2-chloro-3-phenyl-3a,4-dihydro-3*H*-2a-azadicyclopent[*cd*, *ij*]azulene-4,5-dicarboxylate (**7c**). The seven-membered ring protons of **7c** exhibit signals at δ 6.05 (dd, J=6.5 and 1 Hz, H-6), 6.17 (dd, J=10 and 6.5 Hz, H-7), and 6.84 (d, J=10 Hz, H-8) in its ^1H NMR spectrum. A singlet at δ 6.06 is assignable to a H-1 proton. The H-4 and H-3a protons give rise to the double doublets signals at δ 4.14 (J=8.5 and 1 Hz) and 4.39 (J=8.5 and 2 Hz), respectively. The former shows a long-range coupling with the H-6 proton, and the latter a vicinal coupling with the H-3 proton resonating at δ 5.27 (d, J=2 Hz). The $J_{3,3a}$ value indicates the H-3 and H-3a hydrogens to be situated *trans* to each other in the light of J_{cis} (10—13 Hz) and J_{trans} (2—10 Hz) value reported for the vicinal hydrogens of 2-pyrazolines.[8] The ^{13}C NMR spectrum of **7a** displays sp^3 carbon atoms at δ 42.7 (d, C-3a), 63.0 (d, C-4), and 66.3 (d, C-3).

The reaction of **1a** with DMAD in hot acetonitrile gave a similar result. However, when the reaction was carried out in hot xylene, the yields of the products changed remarkably. Thus, compounds **4a**, **6a**, and **7a** were obtained in 38, 10, and 24% yield, respectively, no compound **3a** being isolated. 1-Ethyl 5,6-dimethyl 2-chloro-3-phenyl-11-oxo-2a*H*-7,10b-methano-2a-azacyclopenta[*ab*]cycloundecene-1,5,6-tricarboxylate (**10a**) was isolated in 6% yield. Compound **10a** was also obtained by the oxidation of **7a** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. Its ^1H NMR spectrum displays signals at δ 7.38 (dd, J=11 and 10 Hz, H-9), 8.79 (d, J=11 Hz, H-10), and 9.10 (d, J=10 Hz, H-8) for the seven-membered ring protons. A low-field resonating singlet at δ 7.42 is assignable to H-4 proton. The UV spectrum (λ_{max} 665 nm) suggests the presence of an extended chlomophore, and a ν(C=O) absorption at 1690 cm^{-1} in its IR spectrum the presence of a conjugated ketone. From the results, the structure was assigned.

Application of the forgoing reactions to the azaazulene (**1d**) possessing a (*Z*)-α-ethylstyryl group at C(8) gave a complicated mixture of products among



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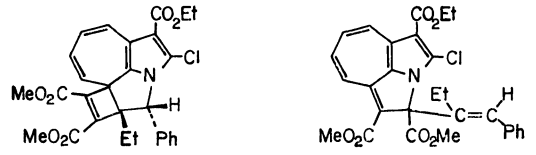
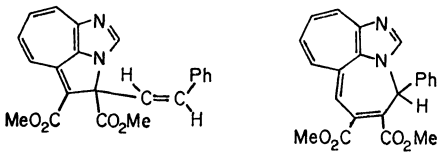


3d 4d



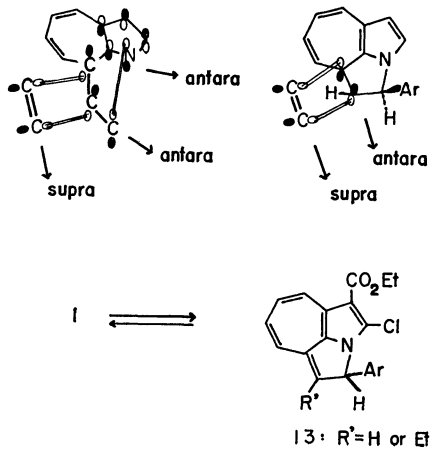
11 12

which the azacyclobuta[*j*]cyclopent[*cd*]azulene (**3d**) and the azacyclopent[*cd*]azulene (**4d**) were identified.

The study was further extended to 4-[(*E*)-styryl]-1,3-diazaazulene (**2**), which gave dimethyl 3-[(*E*)-styryl]-3*H*-1,2a-diazacyclopent[*cd*]azulene-3,4-dicarboxylate (**11**) and dimethyl 3-phenyl-3*H*-1,2a-diazacyclopenta-[*ef*]heptalene-3,4-dicarboxylate (**12**).

The ^1H NMR and ^{13}C NMR spectra of the majority of the compounds are summarized in Tables 1—7.

Mechanistic Discussion. There are two plausible mechanisms leading to the azacyclobuta[*j*]cyclopent-[*cd*]azulene ring system (**3**) from the 8-styryl-1-aza-azulene (**1**): symmetry-allowed thermal [$_\pi2_s+_\pi2_a+_\pi6_a$] cycloaddition,[9] and the thermal [$_\pi2_s+_\pi2_a$] cycloaddition of DMAD with **13**, a valence tautomer of **1**, as shown in the scheme. However, the latter is not preferred, since the cyclobutene ring is disposed *trans* toward the five-membered ring and would have a high torsional energy. The experimental results support the first rationale: (i) the ^1H NMR spectrum of **1** lacks a benzylic proton which would be associated with the structure **13**, (ii) the UV spectrum of **1a**



13: R'=H or Et

Table 1. ^{1}H NMR bands (δ values) of **1a—d** and **2**

Compound	H-2	H-3	H-4	H-5	H-6	H-7	Styryl H-α[a]	Styryl H-β[a]	Styryl Ar	CH_3CH_2[b]
1a			9.37 d; J=11 Hz	7.6—8.0 m		8.25 d; J=11 Hz	8.66 d	7.48 d	7.3—7.5 m (3H) 7.6—8.0 m (2H)	1.46 (3H), 4.44 (2H)
1b			9.42 d; J=10 Hz	7.55—8.1 m		8.28 d; J=10 Hz	8.68 d	7.51 d	2.37 s (3H) 7.18 d (2H)[c] 7.58 d (2H)[c]	1.48 (3H), 4.47 (2H)
1c		7.40 s	8.27 d; J=11 Hz	7.2—7.5 m		8.15 d; J=11 Hz	8.75 d	7.52 d	7.2—7.5 m (3H) 7.53—7.95 m (2H)	
1d			9.4—9.6 m		7.5—7.9 m			6.84—7.0 m	6.7—6.8 m (3H) 6.84—7.0 m (2H)	1.04 (3H), 2.87 (2H)[d] 1.48 (3H), 4.48 (2H)
2	9.07 s		8.87 d; J=11 Hz	7.55—8.1 m	8.2—8.6 m	7.55—8.1 m	8.71 d	7.77 d	7.3—7.5 m (3H) 7.55—8.1 m (2H)	

a) $J_{H\text{-}\alpha,\ H\text{-}\beta}$=17 Hz. b) Multiplicities and $J_{CH_3\text{-}CH_2}$ values are omitted. c) J=8 Hz. d) Double quartets; J=7 and 1 Hz.

Table 2. ^{1}H NMR bands (δ values) of **4a—d** and **11**

Compound	H-1	H-2	H-5	H-6	H-7	H-8	Styryl H-α[a]	Styryl H-β[a]	Styryl Ar	Ester[b] CH_3CH_2O	Ester[b] CH_3O
4a			7.46 d; J=12	6.70 dd; J=12, 8	6.34 dd; J=12, 8	7.62 d; J=12	7.14 d	6.00 d	7.15—7.4 m (5H)	1.40 (3H) 4.36 (2H)	3.76 (3H) 3.79 (3H)
4b			7.46 d; J=11	6.70 dd; J=11, 9	6.33 dd; J=11, 9	7.63 d; J=11	7.08 d	5.97 d	2.30 s (3H) 7.06 d (2H)[c] 7.24 d (2H)[c]	1.40 (3H) 4.36 (2H)	3.74 (3H) 3.78 (3H)
4c	6.34 s		7.41 d; J=12	6.67 dd; J=12, 9	6.21 dd; J=11, 9	6.85 d; J=11	7.16 d	5.98 d	7.2—7.4 m (5H)		3.75 (3H) 3.78 (3H)
4d			7.54 d; J=11	6.70 dd; J=11, 8	6.30 dd; J=11, 8	7.62 d; J=11		6.70[d]	7.27 s (5H)	1.39 (3H) 4.34 (2H)	3.75 (3H) 3.78 (3H)
11		7.41 s	7.25 d; J=10	6.73 t; J=10	6.18 t; J=10	7.10 d; J=10	7.52 d	6.71 d	7.17 s (5H)		3.98 (3H) 4.06 (3H)

a) J=16 Hz. b) Mutiplicities and $J_{CH_3\text{-}CH_2}$ values are omitted. c) J=8 Hz. d) J=2 Hz. The α-ethyl protons are observed at δ 0.72 t (3H) and 2.23 dq (J=8 and 2 Hz).

Table 3. ^{1}H NMR bands (δ values) of **5a—c** and **12**

Compound	H-1	H-2	H-3	H-6	H-7	H-8	H-9	H-10	Ar	Ester[a] CH_3CH_2O	Ester[a] CH_3O
5a			5.31 s	6.11 s	6.52 d; J=10	5.95—6.2 m	6.25—6.5 m	7.38 d; J=11	7.30 s (5H)	1.36 (3H) 4.23 (2H)	3.59 (3H) 3.84 (3H)
5b			5.31 s	6.06 s	6.52 d; J=10	6.0—6.2 m	6.25—6.5 m	7.41 d; J=11	2.32 s (3H) 7.09 d (2H) b) 7.20 d (2H) b)	1.32 (3H) 4.26 (2H)	3.58 (3H) 3.87 (3H)
5c	6.11 s		5.24 s	6.07 s	6.54 d; J=10	5.9—6.15 m	6.3—6.5 m	6.67 d; J=11	7.30 s (5H)		3.57 (3H) 3.88 (3H)
12		7.72 s	5.35 s	6.27 s		6.4—7.0 m		7.1—7.6 m (6H)			3.76 (3H) 3.82 (3H)

a) Multiplicities and $J_{CH_3-CH_2}$ values are omitted. b) J=8 Hz.

Table 4. ^{1}H NMR bands (δ values) of **6a—c**

Compound	H-1	H-3	H-4	H-6	H-8	H-9	H-10	Ar	Ester[a] CH_3CH_2O	Ester[a] CH_3O
6a		4.46 d; J=3	5.29 d; J=3	5.71 s	6.22 d; J=6	6.37 dd; J=10, 6	7.39 d; J=10	7.2—7.4 m (5H)	1.36 (3H) 4.31 (2H)	3.66 (3H), 3.68 (3H), 3.80 (3H), 3.87 (3H)
6b		4.63 d; J=3	5.27 d; J=3	5.69 s	6.21 d; J=7	6.35 dd; J=10.5, 7	7.39 d; J=10.5	2.35 s (3H) 7.13 s (4H)	1.36 (3H) 4.31 (2H)	3.65 (3H), 3.69 (3H), 3.80 (3H), 3.87 (3H)
6c	6.28 s	4.77 d; J=2	5.30 d; J=2	5.82 s		6.2—6.5 m	6.8—7.2 m	7.43 s (5H)		3.72 (3H), 3.76 (3H), 3.87 (3H), 3.93 (3H)

a) Multiplicities and $J_{CH_3-CH_2}$ values are omitted.

Table 5. ^{1}H NMR bands (δ values) of **7a—c**

Compound	H-1	H-3	H-3a	H-4	H-6	H-7	H-8	Ar	Ester[a] CH_3CH_2O	Ester[a] CH_3O
7a		5.34 d; J=2	4.40 dd; J=8, 2	4.10 dd; J=8, 1.5	6.09 dd; J=7, 1.5	6.31 dd; J=10, 7	7.1—7.4 m (6H)		1.36 (3H) 4.30 (2H)	3.83 (3H) 3.86 (3H)
7b		5.31 d; J=2	4.35 dd; J=8, 2	4.08 dd; J=8, 1.5	6.09 dd; J=7, 1.5	6.31 dd; J=10, 7	7.32 d; J=10	2.35 s (3H) 7.14 s (4H)	1.35 (3H) 4.28 (2H)	3.82 (3H) 3.85 (3H)
7c	6.06 s	5.27 d; J=2	4.39 dd; J=8.5, 2	4.14 dd; J=8.5, 1	6.05 dd; J=6.5, 1	6.17 dd; J=10, 6.5	6.84 d; J=10	7.2—7.4 m (5H)		3.81 (3H) 3.86 (3H)

a) Mutiplicities and $J_{CH_3-CH_2}$ values are omitted.

Table 6. ^{1}H NMR bands (δ values) of **10a—c**

Compound	H-1	H-4	H-8	H-9	H-10	Ar	Ester[a]	
							CH_3CH_2O	CH_3O
10a		7.42 s	9.10 d; J=10	7.38 dd; J=11, 10	8.79 d; J=11	6.85—7.0 m (2H) 7.15—7.3 m (3H)	1.44 (3H) 4.44 (2H)	3.83 (3H), 3.99 (3H)
10b		7.44 s	9.13 d; J=10	7.40 dd; J=11, 10	8.81 d; J=11	2.16 s (3H) 6.8—7.05 m (2H) 7.15—7.3 m (2H)	1.48 (3H) 4.48 (2H)	3.87 (3H), 3.99 (3H)
10c	6.74 s	7.33 s	9.12 d; J=10	7.29 t; J=10	7.98 d; J=10	6.9—7.05 m (2H) 7.1—7.25 m (3H)		3.86 (3H), 3.98 (3H)

a) Multiplicities and $J_{CH_3-CH_2}$ values are omitted.

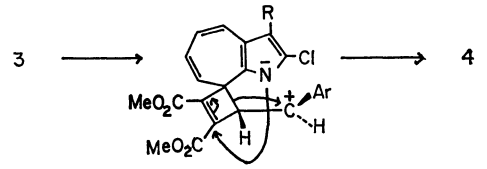
Table 7. ^{13}C Chemical shifts of the compounds (**3a**), (**3b**), (**4a**), (**4c**), (**5a**), (**6a**), and (**7a**)

Carbon	**3a**	**3b**	**4a**	**4c**	**5a**	**6a**	**7a**
1	122.6 d	122.6 d	113.7 s	110.2 d	112.4 s	111.8 s	111.3 s
2	128.4 d	125.6 d	136.2 s	142.5 s	141.1 s	143.0 s	140.2 s
3	123.8 d	123.8 d	77.0 s	76.7 s	69.6 d	68.7 d	66.3 d
3a							42.7 d
4	130.8 d	130.7 d	115.5 s	114.3 s	119.0 s	123.8 d	63.0 d
4a	117.0 s	116.9 s	122.0 s	120.9 s			
5	112.1 s	112.0 s	125.8 d	126.1 d	120.2 s	123.6 s	113.1 s
5a						56.0 s	128.1 s
6	119.9 s	119.8 s	127.1 d	131.0 d	110.6 s	65.4 d	122.9 d
6a					124.2 s		
7	65.1 d	65.2 d	125.8 d	128.0 d	131.6 d	115.1 s	124.0 d
7a	61.5 d	61.3 d				126.5 s	
8	138.7 s	138.1 s	131.6 d	131.6 d	135.3 d	121.3 d	128.3 d
8a			124.4 s	121.8 s			136.0 s
8b			142.9 s	142.7 s			145.9 s
8c							118.2 s
9	139.6 s	138.8 s			136.0 d	127.9 d	
9a	56.2 s	56.1 s					
9b	149.5 s	149.5 s					
10					138.1 d	128.5 d	
10a					125.1 s	139.1 s	
10b					143.0 s	145.5 s	
10c						120.0 s	
C=O	163.4 s	163.3 s	167.1 s	167.8 s	168.5 s	166.3 s	164.8 s
	161.3 s	161.3 s	163.2 s	163.5 s	165.9 s	164.9 s	163.8 s
	160.6 s	160.6 s	162.7 s		162.7 s	164.2 s	163.6 s
						163.5 s	
						163.3 s	
MeO	52.4 q	52.3 q	53.2 q	53.3 q	52.7 q	52.7 q	52.6 q
	52.0 q	52.0 q	51.1 q	50.9 q	51.4 q	52.6 q	52.3 q
						52.4 q	
						52.1 q	
CH_2O	59.9 t	59.8 t	60.4 t		60.3 t	60.2 t	60.0 t
Me	14.4 q	21.1 q	14.4 q		14.2 q	14.4 q	14.4 q
		14.4 q					
-CH=CH-			136.7 d	136.3 d			
			124.4 d	124.2 d			
Phenyl	130.8 s[a]	136.7 s[c]	131.6 s[a]	136.1 s[a]	136.0 s[a]	134.6 s[a]	134.2 s[a]
	129.2 d[b]	129.8 d[b]	128.7 d[d]	128.5 d[e]	129.0 d[d]	129.1 d[b]	129.1 d[b]
	125.6 d[d]	129.1 s[a]	127.1 d[b]	126.8 d[b]	128.2 d[b]	126.4 d[d]	128.6 d[c]
		125.6 d[e]		125.1 d[c]			125.9 d[e]

a) C-1. b) C-3 and -5. c) C-4. d) C-2, -4, and -6. e) C-2 and -6.

differs a great deal from that of **8**,[4] (iii) the cycloaddition of 8-[(*E*)-styryl]-1-azaazulene (**1a**—**c**) proceeds stereospecifically producing the *trans*-isomer (**3**) only, (iv) no reaction took place even after heating of **4a** with DMAD for 6 d.

Compound **3a**, when heated under reflux in xylene, gave **4a**, **7a**, and **10a**, whereas compound **3d** underwent rearrangement into **4d** upon heating in a neat state. The results indicate that the azacyclopent[*cd*]azulene (**4**) is the thermal product of the azacyclobuta[*j*]-cyclopent[*cd*]azulene (**3**). Thus we can postulate that **4** was formed by the scission of the bond between nitrogen and benzylic carbon atoms of **3** followed by rapid stereospecific recyclization of the intermediate **14**;[10] the absence of a stereoisomer of **4** in the reaction products supports this assumption.

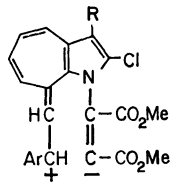


14

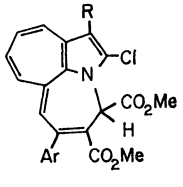
Compound **7** gives **10**, when oxidative cleavage occurs during the reaction, and compound **3** affords **6** upon further reaction with DMAD. However, we have been unable to rationalize the formation of **7** so far.

When a mixture of **3a** and silica gel in benzene was set aside for several days at room temperature, compound **3a** was found to undergo rearrangement into the azacyclopenta[*ef*]heptalene (**5a**) in 56% yield, revealing compound **5** to be a silica gel-induced rearrangement product of **3**.

Dimethyl 5-aryl-3*H*-2a-azacyclopenta[*ef*]heptalene-3,4-dicarboxylate (**16**) to be formed by the intramolecular cyclization of an extended dipolar species[4,11] (**15**) was not detected.



15



16

Experimental

Melting points were uncorrected. ^{1}H NMR spectra were taken with JEOL FX-100 (100 MHz), Hitachi R-40 (90 MHz), or Hitachi R-24B (60 MHz) spectrometers and ^{13}C NMR spectra with JEOL FX-100 or Hitachi R-26 spectrometers (solutions in $CDCl_3$ with Me_4Si as an internal standard). ^{1}H NMR spectral assignments were confirmed by decoupling techniques when necessary. UV spectra were measured for solutions in ethanol unless otherwise stated and IR spectra for Nujol mulls. Kiesel gel 60 was used for chromatography unless otherwise stated. (*E*)-*β*-Bromo-*p*-methylstyrene,[12] (*Z*)-*α*-ethylcinnamic acid[13] (mp 105—107 °C, lit,[14] mp 107 °C), and (*Z*)-*β*-bromo-*β*-ethylstyrene (bp 120—121 °C/17 Torr, lit,[14] bp 126—128 °C/23 Torr) were prepared by the reported methods.

Syntheses of ***1*** *and* ***2***. A solution of ethyl 2-chloro-1-azaazulene-3-carboxylate (1.00 g) in tetrahydrofuran (30 ml) was slowly added to the Grignard solution prepared from magnesium (0.412 g), (*E*)-*β*-bromostyrene (3.11 g), and tetrahydrofuran (30 ml). The mixture was stirred for 5 min, hydrolyzed with methanol (8 ml) and 2 N-hydrochloric acid (40 ml), and extracted with benzene. The benzene solution was washed with dilute aqueous sodium hydroxide solution, stirred overnight with tetrachloro-*o*-benzoquinone (2.00 g), the solvent was evaporated, and alumina chromatography of the residue with benzene afforded **1a** (0.846 g, 59%). Crystallization from cyclohexane–dichloromethane gave yellow prisms, mp 161—162 °C, UV_{max} 225 nm (log *ε* 4.51), 295 (4.50), 322^{sh} (4.43), 392 (4.47), and 445^{sh} (3.59); IR 1700 (C=O) and 970 cm^{-1} (*trans* CH=CH). Found: C, 71.21: H, 4.74; Cl, 10.32; N, 3.92%. Calcd for $C_{20}H_{16}ClNO_2$: C, 71.11; H, 4.77; Cl, 10.50; N, 4.15%. By this procedure we made the following: (i) **1b** [81%, mp 147—148 °C (from cyclohexane–dichloromethane), UV_{max} 226 nm (log *ε* 4.41), 236 (4.41), 287^{sh} (4.40), 297 (4.41), 322^{sh} (4.31), 403 (4.43), and 455^{sh} (3.78); IR 1690 (C=O) and 970 cm^{-1} (*trans* CH=CH). Found: C, 71.81; H, 5.06; Cl, 10.18; N, 3.73%. Calcd for $C_{21}H_{18}ClNO_2$: C, 71.69; H, 5.16; Cl, 10.08; N, 3.98%.]; (ii) **1c** [62%, mp 90—91 °C (from petroleum ether), UV_{max} 247 nm (log *ε* 4.38), 282 (4.34), 325 (4.31), 385 (4.37), and 467 (3.36); IR 960 cm^{-1} (*trans* CH=CH). Found: C, 77.10; H, 4.54; Cl, 13.35; N, 5.23%. Calcd for $C_{17}H_{12}ClN$: C, 76.84; H, 4.55; Cl, 13.34; N, 5.27%.]; (iii) **1d** [81%, mp 128—129 °C (from cyclohexane–dichloromethane), UV_{max} 236 nm (log *ε* 4.55) 288 (4.66), 323 (4.10), 366^{sh} (3.46), and 442 (3.17); IR 1690 (C=O) and 835 cm^{-1} (trisubstituted ethylene). Found: C, 72.06; H, 5.75; Cl, 9.85; N, 3.70%. Calcd for $C_{22}H_{20}ClNO_2$: C, 72.23; H, 5.51; Cl, 9.69; N, 3.83%.]; (iv) **2** [87%, mp 148—149 °C (from cyclohexane–dichloromethane), UV_{max} 256 nm (log *ε* 4.41), 292^{sh} (4.23), 371 (4.31), and 433 (4.04); IR 965 cm^{-1} (*trans* CH=CH). Found: C, 82.77; H, 5.44; N, 11.85%. Calcd for $C_{16}H_{12}N_2$: C, 82.72; H, 5.21; N, 12.06%].

Reaction of ***1a*** *with DMAD*. (*a*): A solution of compound **1a** (0.25 g) and DMAD (1.052 g) in benzene (30 ml) was heated under reflux for 48 h and the solvent was evaporated. Chromatography of the residue with benzene gave **4a** [0.033 g (9%), red prisms (from cyclohexane), mp 172—173 °C, UV_{max} 252 nm (log *ε* 4.72), 375 (4.17), 393 (4.13), 440 (3.78), 468 (3.71), 502 (3.51), and 537 (3.06); IR 1750, 1700, and 1675 (C=O) and 980 cm^{-1} (*trans* CH=CH). Found: C, 64.91; H, 4.82; Cl, 7.50; N, 2.82%. Calcd for $C_{26}H_{22}ClNO_6$: C, 65.07; H, 4.62; Cl, 7.39; N, 2.92%]. Further elution afforded a mixture of products, which were fractionally crystallized from cyclohexane–dichloromethane to give **3a** [0.085 g (24%), yellow prisms (from petroleum ether–dichloromethane), mp 168—169 °C, UV_{max} 226^{sh} nm (log *ε* 4.51) and 290 (3.83); IR 1735, 1722, and 1690 cm^{-1} (C=O); ^{1}H NMR *δ*=1.35 (3H, t, *J*=7 Hz, Me), 3.70 (3H, s, Me), 3.87 (3H, s, Me), 3.87 (1H, d, *J*=2 Hz, H-7a), 4.28 (2H, q, *J*=7 Hz, CH_2), 5.49 (1H, d, *J*=2 Hz, H-7), 5.60 (1H, d, *J*=11 Hz, H-1), 6.0—6.3 (2H, m, H-2 and 3), 6.85—7.05 (2H, m, phenyl), 7.15—7.3 (3H, m, phenyl), 7.22 (1H, d, *J*=11 Hz, H-4); MS *m/e* 481 and 479 (M^+), 339 and 337 (M^+—DMAD). Found: C, 65.33; H, 4.77; Cl, 7.59; N, 2.88%. Calcd for $C_{26}H_{22}ClNO_6$: C, 65.07; H, 4.62; Cl, 7.39; N, 2.92%] and **5a** [0.05 g (14%), brown needles (from ethanol), mp 148—149 °C (dec), UV_{max}

228 nm (log ε 4.54), 260 (4.28), 434 (4.38), 492sh (3.95), 530 (3.74), and 570 (3.43); IR 1725, 1705, and 1700 cm^{-1} (C=O). Found: C, 65.33; H, 4.68; Cl, 7.25; N, 2.86%. Calcd for $C_{26}H_{22}ClNO_6$: C, 65.07; H, 4.62; Cl, 7.39; N, 2.92%]. Elution with chloroform gave a red oil, which solidified upon trituration with petroleum ether to give **6a** (0.034 g, 7%). Crystallization from ethanol afforded yellow prisms, mp 157—158 °C, UV_{max} 238 nm (log ε 4.28), 288 (3.84), 327 (3.91), and 380 (3.64); IR 1735, 1725, and 1705 cm^{-1}. Found: C, 61.79; H, 4.65; Cl, 5.51; N, 2.14%. Calcd for $C_{32}H_{28}ClNO_{10}$: C, 61.79; H, 4.54, Cl, 5.70; N, 2.25%.

(*b*): A solution of compound **1a** (0.50 g) and DMAD (2.10 g) in xylene (30 ml) was heated under reflux for 24 h and the solvent evaporated. Chromatography of the residue with benzene gave **4a** (0.27 g, 38%) followed by **7a** [0.17 g (24%), yellow needles (from ethanol), mp 177—178 °C, UV_{max} 263 nm (log ε 4.07), 323 (3.95), and 394 (3.58); IR 1735, 1710, and 1690 cm^{-1} (C=O). Found: C, 65.14; H, 4.49; Cl, 7.18; N, 2.87%. Calcd for $C_{26}H_{22}ClNO_6$: C, 65.07; H, 4.62; Cl, 7.39; N, 2.92%]. Further elution gave **10a** (0.046 g, 6%), which crystallized as blue prisms from ethanol, mp 187—188 °C, UV_{max} ($CHCl_3$) 267 nm (log ε 4.54), 301 (4.23), 313 (4.24), 349 (4.63), 391 (3.88), and 665 (3.30); IR 1715, 1690, and 1680 cm^{-1} (C=O). Found: C, 63.24; H, 4.02; Cl, 7.34, N, 2.73%. Calcd for $C_{26}H_{20}ClNO_7$: C, 63.23; H, 4.08; Cl, 7.18; N, 2.84%. Benzene–chloroform (1:1) eluted **6a** (0.088 g, 10%).

Reaction of ***1b*** *with DMAD.* (*a*): A solution of compound **1b** (0.50 g) and DMAD (2.02 g) in benzene (30 ml) was heated and worked-up as for **1a**. Elution with benzene gave **4b** [0.069 g (10%), red prisms (from cyclohexane), mp 198—199 °C, UV_{max} 253 nm (log ε 4.73), 375 (4.14), 394 (4.11), 441 (3.71), 470 (3.66), 503 (3.45), and 542 (3.00); IR 1750, 1695, and 1675 (C=O) and 980 cm^{-1} (*trans* CH=CH). Found: C, 65.83; H, 4.94; Cl, 7.25; N, 2.57%. Calcd for $C_{27}H_{24}ClNO_6$: C, 65.65; H, 4.90; Cl, 7.18; N, 2.84%]. Elution with benzene–chloroform (1:1) afforded a mixture of products, which was fractionally crystallized to yield **3b** [0.385 g (55%), yellow prisms (from cyclohexane), mp 151—152 °C, UV_{max} 240 nm (log ε 4.17) and 293 (3.82); IR 1735, 1720, and 1683 cm^{-1} (C=O); ^{1}H NMR δ=1.34 (3H, t, *J*=7 Hz, Me), 2.30 (3H, s, Me), 3.68 (3H, s, Me), 3.81 (1H, d, *J*=2 Hz, H-7a), 3.85 (3H, s, Me), 4.27 (2H, q, *J*=7 Hz, CH_2), 5.60 (1H, d, *J*=2 Hz, H-7), 5.60 (1H, d, *J*=10 Hz, H-1), 6.0—6.25 (2H, m, H-2 and 3), 6.84 (2H, d, *J*=8 Hz, phenyl), 7.08 (2H, d, *J*=8 Hz, phenyl), 7.18 (1H, d, *J*=10 Hz, H-4). Found: C, 65.72; H, 4.82; Cl, 7.44; N, 2.59%. Calcd for $C_{27}H_{24}ClNO_6$: C, 65.65; H, 4.90; Cl, 7.18; N, 2.84%] and **5b** [0.02 g (3%), brown needles (from ethanol), mp 116—118 °C, UV_{max} 260sh nm (log ε 4.20), 447 (3.92), 487sh (3.75), 530 (3.02), and 575 (2.97); IR 1735 and 1705 cm^{-1} (C=O). Found: C, 65.81; H, 4.95; Cl, 7.02; N, 2.54%. Calcd for $C_{27}H_{24}ClNO_6$: C, 65.65; H, 4.90; Cl, 7.18; N, 2.84%]. Elution with benzene–chloroform (1:2) gave **6b** (0.058 g, 6%). Crystallization from ethanol gave yellow needles, mp 175—176 °C, UV_{max} 262sh (log ε 4.12), 326 (3.92), and 385 (3.65); IR 1735, 1727, and 1705 cm^{-1} (C=O). Found: C, 62.02; H, 4.65; Cl, 5.78; N, 2.11%. Calcd for $C_{33}H_{30}ClNO_{10}$: C, 62.32; H, 4.75; Cl, 5.57; N, 2.20%.

(*b*): A solution of compound **1b** (0.25 g) and DMAD (1.01 g) in xylene (30 ml) was heated and worked-up as for **1a**. Elution with benzene gave **4b** (0.166 g, 47%), **7b** [0.038 g (11%), yellow needles (from ethanol), mp 188—189 °C, UV_{max} 238 nm (log ε 4.13), 264sh (4.05), 324 (3.90), and 395 (3.59); IR 1735, 1710, and 1690 cm^{-1} (C=O). Found: C, 65.59; H, 4.80; Cl, 7.19; N, 2.73%. Calcd for $C_{27}H_{24}ClNO_6$: C, 65.65; H, 4.90; Cl, 7.18; N, 2.84%] and **10b** [0.019 g (5%), blue needles (from ethanol), mp 191—192 °C, UV_{max} ($CHCl_3$) 269 nm (log ε 4.54), 301 (4.17), 313 (4.19), 351 (4.65), 390 (3.98), and 665 (3.18); IR 1725, 1690, and 1680 cm^{-1} (C=O). Found: C, 63.93; H, 4.32; Cl, 6.78; N, 2.88%. Calcd for $C_{27}H_{22}ClNO_7$: C, 63.85; H, 4.37; Cl, 6.98; N, 2.76%], successively. Elution with benzene–chloroform (1:1) gave **6b** (0.075 g, 17%).

Reaction of ***1c*** *with DMAD.* (*a*): A solution of compound **1c** (0.50 g) and DMAD (2.67 g) in benzene (30 ml) was heated and worked-up as for **1a**. Elution of benzene gave starting material **1c** (0.025 g) first. Further elution yielded four products: (i) **7c** [0.013 g (2%), yellow needles (from cyclohexane), mp 167—168 °C, UV_{max} 268 nm (log ε 4.10), 337 (3.85), and 415 (3.60); IR 1735 and 1710 cm^{-1} (C=O). Found: C, 67.89; H, 4.35; Cl, 8.97; N, 3.20%. Calcd for $C_{23}H_{18}ClNO_4$: C, 67.73; H, 4.45; Cl, 8.69; N, 3.43%]; (ii) **4c** [0.317 g (41%), red prisms (from cyclohexane), mp 133—134 °C, UV_{max} 242 nm (log ε 4.71), 282sh (4.24), 292sh (4.14), 375 (4.14), 395 (4.13), 438 (3.80), 466 (3.79), 498 (3.63), and 535 (3.20); IR 1757 and 1670 (C=O) and 965 cm^{-1} (*trans* CH=CH). Found: C, 68.03; H, 4.57; Cl, 8.68; N, 3.35%. Calcd for $C_{23}H_{18}ClNO_4$: C, 67.73; H, 4.45; Cl, 8.69; N, 3.43%]; (iii) **5c** [0.196 g (26%), brown prisms (from cyclohexane), mp 205 °C (dec), UV_{max} 215 nm (log ε 4.58), 250sh (4.34), 285sh (4.15), 440 (4.34), 456 (4.34), 488sh (4.13), 527 (3.97), 565 (3.69), and 618 (3.13); IR 1727 and 1695 cm^{-1} (C=O). Found: C, 67.71; H, 4.60; Cl, 8.63; N, 3.39%. Calcd for $C_{23}H_{18}ClNO_4$: C, 67.73; H, 4.45; Cl, 8.69; N, 3.43%]; (iv) **6c** [0.164 g (16%), yellow prisms (from cyclohexane), mp 182.5—184 °C, UV_{max} 337 nm (log ε 3.75) and 400 (3.52); IR 1735, 1728, and 1707 cm^{-1} (C=O). Found: C, 63.32; H, 4.24; Cl, 6.56; N, 2.51%. Calcd for $C_{29}H_{24}ClNO_8$: C, 63.34; H, 4.40; Cl, 6.45; N, 2.55%].

(*b*): A solution of compound **1c** (0.30 g) and DMAD (1.60 g) in xylene (30 ml) was heated and worked-up as for **1a**. Elution with benzene gave **7c** (0.036 g, 8%), **4c** (0.28 g, 61%), and **10c** [(0.014 g (3%), blue prisms (from ethanol), mp 207—208 °C, UV_{max} ($CHCl_3$) 273 (log ε 4.32), 301 (4.01), 314 (4.04), 353 (4.33), 398 (3.88), 410sh (3.84), and 665 (3.37); IR 1730, 1720, and 1690 cm^{-1} (C=O). Found: C, 65.62; H, 3.91; Cl, 8.36; N, 3.07%. Calcd for $C_{23}H_{16}ClNO_5$: C, 65.49; H, 3.82; Cl, 8.40; N, 3.32%], successively. Elution with benzene–chloroform (1:1) gave **6c** (0.025 g, 4%).

Reaction of ***1d*** *with DMAD.* (*a*): A solution of compound **1d** (0.40 g) and DMAD (1.55 g) in benzene (30 ml) was heated and worked-up as for **1a**. Elution with benzene gave **4d** [0.006 g (1%), red prisms (from petroleum ether), mp 113—114 °C, UV_{max} 246 nm (log ε 4.77), 252sh (4.77), 374 (4.14), 392 (4.10), 439 (3.72), 467 (3.69), 500 (3.51), and 537 (3.10); IR 1730 and 1695 (C=O) and 830 cm^{-1} (trisubstituted ethylene). Found: C, 66.04; H, 5.27; Cl, 7.01, N, 2.71%. Calcd for $C_{28}H_{26}ClNO_6$: C, 66.21; H, 5.16; Cl, 6.98; N, 2.76%]. Further elution afforded **3d** [0.247 g (45%), yellow needles (from petroleum ether), mp 141—142 °C, UV_{max} 238 nm (log ε 4.12) and 291 (3.79); IR 1730 and 1710 cm^{-1} (C=O); ^{1}H NMR δ=0.83 (3H, t, *J*=7 Hz, Me), 1.33 (3H, t, *J*=7 Hz, Me), 1.58 (2H, q, *J*=7 Hz, CH_2), 3.68 (3H, s, Me), 3.85 (3H, s, Me), 4.27 (2H, q, *J*=7 Hz, CH_2), 5.27 (1H, s, H-7), 5.54 (1H, d, *J*=9 Hz, H-1), 6.0—6.5 (2H, m, H-2 and 3), 7.1—7.4 (6H, m, H-4 and phenyl). Found: C, 65,91; H, 5.19; Cl, 7.27; N, 2.74%. Calcd for $C_{28}H_{26}ClNO_6$: C, 66,21; H, 5.16; Cl, 6.98; N, 2.76%]. Elution

with chloroform gave an unidentified red compound (0.127 g).

(*b*): A solution of compound **1d** (0.20 g) and DMAD (0.78 g) in xylene (30 ml) was heated and worked up as for **1a** to yield **4d** (0.009 g, 3%), **3d** (0.042 g, 15%), and a red compound (0.039 g).

Reaction of 2 with DMAD. A solution of compound **2** (0.50 g) and DMAD (3.059 g) in benzene (50 ml) was heated under reflux for 1 h, the solvent was evaporated, and the residue was chromatographed with benzene–chloroform (1:1) to give **11** (0.064 g, 8%), which crystallized from ethanol as yellow needles, mp 184—186 °C (dec), UV_{max} 233 (log ε 4.54), 291 (4.46), 354 (3.95), 370^{sh} (3.94), 415 (3.84), 441 (3.96), 466 (3.92), and 497 (3.67); IR 1725 and 1700 (C=O) and 970 cm^{-1} (*trans* CH=CH). Found: C, 70.49; H, 4.77; N, 7.20%. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48%. Elution with benzene–chloroform (1:2) gave **12** (0.138 g, 17%). which crystallized from cyclohexane as red prisms, mp 167—168 °C (dec), UV_{max} 293 nm (log ε 3.98) and 455 (3.64); IR 1720 cm^{-1} (C=O). Found: C, 70.73; H, 4.88; N, 7.29%. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48%.

Thermal Rearrangement of 3. (*a*): A solution of compound **3a** (0.10 g) in xylene (30 ml) was heated under reflux for 24 h. The work-up gave **4a** (0.04 g, 40%), **7a** (0.02 g, 20%), and **10a** (0.006 g, 6%).

(*b*): Compound **3d** (0.06 g) was heated at 200 °C in a neat state for 10 min and chromatographed. Elution with benzene gave **4d** (0.036 g, 60%).

Oxidation of 7a. A mixture of compound **7a** (0.04 g), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.019 g) in xylene (10 ml) was heated under reflux for 24 h, the solvent was evaporated, and the residue was chromatographed on alumina. Elution with benzene gave **10a** (0.007 g, 17%).

Rearrangement of 3 on Silica Gel. A mixture of compound **3a** (0.05 g) and silica gel (10 g) in benzene was left to stand at room temperature for five days and then chromatographed. Elution with benzene–chloroform (1:1) gave **5a** (0.028 g, 56%). In a similar mannar, a mixture of compound **3b** (0.10 g) and silica gel (20 g) gave **5b** (0.06 g, 60%).

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