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Studies on Heterocyclic Analogs of Azulenes. XI.[1] Syntheses and Cycloadditions of Cyclohepta[4,5]pyrrolo[1,2-*a*]imidazoles and Cyclohept[*d*]imidazo[1,2-*a*]imidazoles

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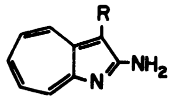
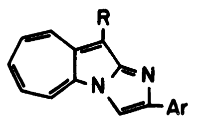
Cyclohepta[4,5]pyrrolo[1,2-*a*]imidazoles (1,3a-diazacyclopent[*a*]azulenes) (**2**) and cyclohept[*d*]imidazo[1,2-*a*]imidazoles (1,3a,9-triazacyclopent[*a*]azulenes) (**6**) were synthesized from 2-aminocyclohepta[*b*]pyrroles and 2-aminocycloheptimidazole, respectively, in moderate to good yields. Reactions of **2** and **6** with reactive acetylenes gave 2-azacyclohepta[*ef*]cycl[3.2.2]azines together with bis(1,3a-diazacyclopent[*a*]azuleno)[1,7]diaza[12]annulenes (**4**) and 2,3-diazacyclohepta[*ef*]cycl[3.2.2]azines together with bis(1,3a,9-triazacyclopent[*a*]azuleno)[1,7]diaza[12]-annulenes (**8**), respectively. Reactions of **2** and **6** with electron deficient olefins gave **4** and **8**, respectively. These reactions proceeded regioselectively *via* 1,10-dipolar intermediates.

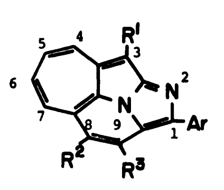
The cyclazine systems have attracted attentions for their interesting physical and chemical properties,[2] whose efficient synthetic method is the cycloaddition to adequate N-bridged heterocycles [*e.g.* cycloaddition of indolizines with dimethyl acetylenedicarboxylate leads to cycl[3.2.2]azines[3-5]]. In the course of our studies on azaazulenes,[6] we investigated the syntheses of cata-condensed 1-azaazulenes and 1,3-diazaazulenes, which would provide a convenient synthetic route to novel cyclazines. In this paper, we report the syntheses and cycloadditions of cyclohepta[4,5]pyrrolo[1,2-*a*]-imidazoles and cyclohept[*d*]imidazo[1,2-*a*]imidazoles, which furnished novel cyclazines and condensed [1,7]-diaza[12]annulenes.



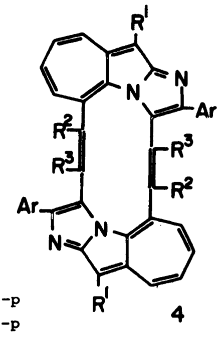
1a: R=H
1b: R=CO_2Et
1c: R=CN



2a: R=H, Ar=Ph
2b: R=H, Ar=C_6H_4Me-p
2c: R=CO_2Et, Ar=Ph
2d: R=CO_2Et, Ar=C_6H_4Me-p
2e: R=CN, Ar=Ph



3



4

3a, 4a: R^1=H, R^2=R^3=E^1, Ar=Ph
3b, 4b: R^1=R^3=H, R^2=E^1, Ar=Ph
3c, 4c: R^1=H, R^2=R^3=E^1, Ar=C_6H_4Me-p
3d, 4d: R^1=R^3=H, R^2=E^1, Ar=C_6H_4Me-p
3e, 4e: R^1=E^2, R^2=R^3=E^1, Ar=Ph
3f, 4f: R^1=R^2=R^3=E^2, Ar=Ph
3g, 4g: R^1=E^2, R^2=E^1, R^3=H, Ar=Ph
3h, 4h: R^1=E^2, R^2=R^3=COPh, Ar=Ph
3i, 4i: R^1=R^2=E^2, R^3=H, Ar=Ph
3j, 4j: R^1=E^2, R^2=R^3=E^1, Ar=C_6H_4Me-p
3k, 4k: R^1=R^2=R^3=E^2, Ar=C_6H_4Me-p
3l, 4l: R^1=R^3=H, R^2=E^1, Ar=C_6H_4Me-p
3m, 4m: R^1=E^2, R^2=R^3=COPh, Ar=C_6H_4Me-p
3n, 4n: R^1=CN, R^2=R^3=E^1, Ar=Ph
3o, 4o: R^1=CN, R^2=E^1, R^3=H, Ar=Ph
3p, 4p: R^1=R^2=R^3=H, Ar=Ph
3q, 4q: R^1=R^2=R^3=H, Ar=C_6H_4Me-p

E^1=CO_2Me, E^2=CO_2Et

Syntheses and Cycloadditions of 1,3a-Diazacyclopent[a]-*azulenes.* Treatment of 2-amino-1-azaazulene (2-aminocyclohepta[*b*]pyrrole) (**1a**)[7,8] with *α*-bromoacetophenone in abs ethanol, followed by the treatment with potassium carbonate in aq ethanol in one pot gave **2a** in a 49% yield. The structure of **2a** was deduced to be 2-phenyl-1,3a-diazacyclopent[*a*]azulene (2-phenylcyclohepta[4,5]pyrrolo[1,2-*a*]imidazole) on the basis of elemental analyses and spectral data. In a similar manner, compounds **2b**—**e** were obtained by the reaction of **1a**—**c** with *α*-bromoacetophenone or 2-bromo-4′-methylacetophenone in abs ethanol or 1-butanol fol-

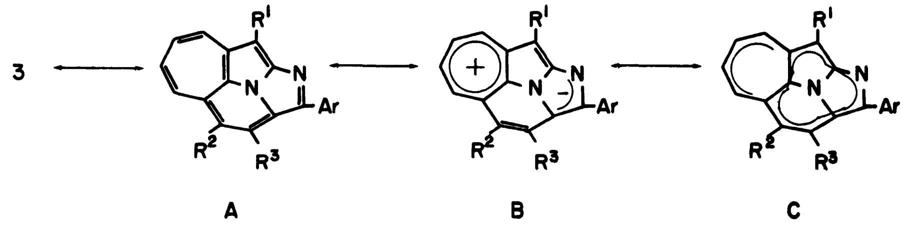
Table 1. Conditions and yields for the reactions of **2** and **6** with reactive acetylenes and electron deficient olefins

Substrate	Reagent	Solvent	Time/h	Product (%)	
2a	DMAD	Benzene	1	**3a** (14)	**4a** (6)
2a	MP	Benzene	20	**3b** (6)	**4b** (25)
2b	DMAD	Benzene	1	**3c** (22)	**4c** (5)
2b	MP	Benzene	27	**3d** (5)	**4d** (34)
2c	DMAD	Benzene	3	**3e** (25)	**4e** (13)
2c	DEAD	MeCN	2	**3f** (18)	**4f** (7)
2c	MP	MeCN	27	**3g** (8)	**4g** (33)
2c	DBA	Benzene	3	**3h** (17)	**4h** (33)
2c	MA	Xylene	7	**3g** (—)	**4g** (43)
2c	EA	Xylene	7	**3i** (—)	**4i** (28)
2d	DMAD	Benzene	3	**3j** (17)	**4j** (8)
2d	DEAD	Benzene	3	**3k** (19)	**4k** (12)
2d	MP	Benzene	24	**3l** (4)	**4l** (41)
2d	DBA	Benzene	3	**3m** (13)	**4m** (23)
2e	DMAD	Benzene	7	**3n** (10)	**4n** (9)
2e	MP	Benzene	120	**3o** (3)	**4o** (16)
6a	DMAD	MeCN	3	**7a** (23)	**8a** (4)
6a	DMAD	Benzene	4	**7a** (29)	**8a** (10)
6a	DEAD	MeCN	2	**7b** (17)	**8b** (6)
6a	MP	MeCN	27	**7c** (43)	**8c** (20)
6a	DBA	MeCN	3	**7d** (36)	**8d** (9)
6a	DMM	MeCN	70	**7a** (—)	**8a** (2)
6a	MA	MeCN	45	**7c** (—)	**8c** (25)
6a	EA	MeCN	48	**7e** (—)	**8e** (25)
6a	AN	MeCN	50	**7f** (—)	**8f** (6)
6b	DMAD	MeCN	2	**7g** (21)	**8g** (3)
6b	DEAD	MeCN	2	**7h** (28)	**8h** (4)
6b	MP	MeCN	27	**7i** (24)	**8i** (8)
6b	DBA	MeCN	3	**7j** (32)	**8j** (3)
6b	EA	MeCN	72	**7k** (—)	**8k** (8)
6b	AN	MeCN	170	**7l** (—)	**8l** (5)

TABLE 2. ELECTRONIC AND IR SPECTRAL DATA OF **3** AND **7**

Compound	λ_{max}/nm (log ϵ)	ν(C=O) or ν(C≡N)/cm^{-1}
3a	249 (4.43), 2.79 (4.52, sh), 291 (4.59), 310 (4.36, sh), 357 (4.48, sh), 373 (4.56), 400 (4.14, sh), 423 (4.10)	1725, 1700
3b	247 (4.33), 278 (4.39, sh), 295 (4.54), 310 (4.37, sh), 358 (4.35, sh), 374 (4.43), 406 (4.08), 428 (4.08)	1710
3c	249 (4.44), 278 (4.43, sh), 290 (4.48), 310 (4.37, sh), 357 (4.42, sh), 375 (4.52), 400 (4.23, sh), 421 (4.09)	1725, 1695
3d	249 (4.45), 273 (4.43, sh), 297 (4.57), 311 (4.45, sh), 360 (4.46, sh), 376 (4.53), 405 (4.22), 427 (4.17)	1710
3e	247 (4.37), 280 (4.45, sh), 292 (4.49), 310 (4.33, sh),381 (4.43) 427 (4.01, sh)	1730, 1705, 1700 (sh)
3f	248 (4.34), 280 (4.46, sh), 292 (4.50), 310 (4.35, sh), 381 (4.43), 427 (4.00, sh)	1730, 1705, 1700 (sh)
3g	245 (4.24), 285 (4.30, sh), 300 (4.53), 310 (4.40, sh), 383 (4.42), 436 (4.21)	1720, 1705
3h[a)]	257 (4.68), 285 (4.45, sh), 323 (4.38), 394 (4.46), 445 (4.09, sh)	1690, 1655
3j	251 (4.43), 278 (4.46, sh), 291 (4.50), 312 (4.35, sh), 384 (4.57), 427 (4.14, sh)	1730, 1720, 1710
3k	251 (4.39), 280 (4.43, sh), 292 (4.45), 312 (4.32, sh), 384 (4.46), 425 (4.13, sh)	1735 (sh), 1720, 1705
3l	250 (4.55), 279 (4.53, sh), 301 (4.68), 313 (4.61, sh), 385 (4.64), 431 (4.18, sh)	1710
3m[a)]	258 (4.59), 285 (4.36, sh), 325 (4.29), 397 (4.40), 445 (4.09, sh)	1690, 1650
3n[a)]	255 (4.35, sh), 282 (4.47), 292 (4.47), 303 (4.43, sh), 317 (4.34), 341 (3.97), 385 (4.42, sh), 399 (4.51), 432 (4.16 sh), 453 (4.09)	2210, 1740, 1720
3o[a)]	257 (4.31), 282 (4.37, sh), 292 (4.44, sh), 305 (4.50), 317 (4.43), 340 (4.02), 382 (4.35, sh), 400 (4.45), 436 (4.00), 461 (3.98)	2230, 1710
7a	237 (4.42), 270 (4.45, sh), 292 (4.57), 380 (4.39), 418 (4.18), 438 (4.16)	1730, 1705
7b	238 (4.14), 269 (4.20, sh), 291 (4.30), 381 (4.05), 419 (3.82), 440 (3.82)	1725, 1695
7c	235 (4.27), 263 (4.23), 292 (4.49), 319 (3.93), 333 (3.95), 373 (4.21), 388 (4.23), 423 (3.97), 446 (4.02)	1715
7d	254 (4.57), 306 (4.33), 385 (4.24), 450 (3.97)	1655
7g	240 (4.33), 270 (4.30, sh), 291 (4.35), 385 (4.29), 417 (4.14), 438 (4.09)	1725, 1700
7h	241 (4.21), 270 (4.23, sh), 291 (4.32), 383 (4.26), 416 (4.09), 437 (4.05)	1740, 1695
7i	241 (4.31), 263 (4.26), 292 (4.45), 321 (4.01), 336 (4.07), 370 (4.33, sh), 381 (4.35), 421 (4.16), 443 (4.19)	1715
7j	253 (4.48), 307 (4.22), 388 (4.22), 445 (4.02)	1650, 1640

a) Taken for $CHCl_3$ solutions.



lowed by the treatment with potassium carbonate in moderate to good yields.

The compound **2c** was deesterified by hydrolysis with potassium hydroxide followed by decarboxylation with hot hydrobromic acid to give **2a**.

Reactions of **2** with reactive acetylenes gave 1 : 1-adducts (**3**) together with 2 : 2-adducts (**4**). In the reactions of **2** with electron deficient olefins, dehydrogenations were accompanied, and only 2 : 2-adducts (**4**) were isolated. These results were listed in Table 1.

The 1 : 1-adducts (**3**) were highly fluorescent crystals and were characterized as 2-azacyclohepta[*ef*]cycl[3.2.2]azines on the basis of spectroscopic properties (Tables 2, 3, and 6) as well as elemental analyses (Table 7). Deesterification of **3e** and **3j** were attained by hydrolysis with potassium hydroxide followed by heating with copper in quinoline, and compounds **3p** and **3q** were obtained in good yield, respectively. The seven-membered ring protons of **3p** were seen at δ 7.73 (ddd, J=8.0, 7.0, and 1.5 Hz, H-5), 7.78 (ddd, J=8.0, 7.0, and 1.5 Hz, H-6), 8.32 (ddd, J=8.0, 1.5, and 0.5 Hz, H-4), and 8.57 (ddd, J=8.0, 1.5, and 0.5 Hz, H-7) in its 200 MHz ^{1}H NMR spectrum. Two pairs of doublets at δ 7.73 and 7.77 (J=4.0 Hz) were assignable to H-9 and H-8 protons, respectively. Although the low field resonated chemical shift of protons of **3p** intimates that **3p** should be inherently aromatic, the contribution of the resonance form **A** should be predominant, since the coupling constants of seven-membered ring protons imply somewhat of bond-alternation and the value of coupling constant of H-8 and H-9 is rather small (J=4.0 Hz). In the ^{13}C NMR spectrum of **3p**, signals of C-8 and C-9 carbons were seen at δ 113.9 (d) and 110.4 (d) and signals of seven-membered ring carbons (C-4, 5, 6, and 7) were seen at δ 130.5 (d), 123.0 (d), 125.9 (d), and 129.6 (d), respectively, and these observations also accord with the structure.

The 2 : 2-adducts (**4**) were characterized as bis(1,3a-

Table 3. Electronic and IR spectral data of 4 and 8

Compound	λ_{max}/nm (log ϵ)	ν(C=O) or ν(C≡N)/cm^{-1}
4a	268 (4.90), 295 (4.65), 310 (4.58, sh), 360 (4.53), 404 (4.17), 423 (4.13), 523 (3.38, sh), 550 (3.42), 590 (3.31, sh), 640 (2.94, sh)	1725, 1690
4b	222 (4.79), 269 (4.91), 312 (4.76), 322 (4.76), 353 (4.50, sh), 414 (4.18), 436 (4.19), 508 (3.64), 538 (3.64), 580 (3.46, sh), 630 (2.96, sh)	1695
4c	269 (5.05), 305 (4.68), 315 (4.66), 345 (4.55, sh), 407 (4.18), 423 (4.13), 523 (3.63, sh), 550 (3.66), 590 (3.56, sh), 640 (3.19, sh)	1740, 1710
4d	224 (4.83), 270 (4.93), 314 (4.79), 324 (4.78), 355 (4.54, sh), 415 (4.25), 438 (4.25), 511 (3.69), 542 (3.68), 583 (3.50, sh), 635 (3.14, sh)	1695
4e	265 (4.88), 310 (4.40), 329 (4.45), 348 (4.44), 366 (4.45), 413 (4.11), 436 (4.26), 515 (3.63, sh), 547 (3.73), 580 (3.69, sh), 625 (3.37, sh)	1725, 1690
4f	265 (5.02), 308 (4.57), 328 (4.62), 348 (4.61), 365 (4.62), 413 (4.24), 437 (4.38), 517 (3.78, sh), 547 (3.73), 580 (3.81, sh), 625 (3.50, sh)	1730, 1695
4g[a)]	271 (4.87), 320 (4.73), 347 (4.73), 366 (4.60, sh), 425 (4.33), 450 (4.53), 515 (3.80, sh), 539 (3.84), 574 (3.73, sh), 625 (3.26, sh)	1710, 1690
4h	258 (5.07), 351 (4.59), 366 (4.59), 417 (4.18), 441 (4.32), 520 (3.69, sh), 551 (3.77), 587 (3.71, sh), 635 (3.36, sh)	1690, 1665, 1655
4i	232 (4.93), 268 (4.99), 317 (4.79), 343 (4.80), 364 (4.67, sh), 421 (4.42), 445 (4.60), 515 (3.91, sh), 537 (3.95), 572 (3.84, sh), 625 (3.38, sh)	1710, 1690
4j	268 (4.90), 311 (4.53), 330 (4.53), 350 (4.51), 366 (4.51), 416 (4.15), 439 (4.28), 520 (3.70, sh), 550 (3.78), 580 (3.74, sh), 625 (3.47, sh)	1735, 1725, 1690
4k	267 (4.98), 310 (4.61), 331 (4.61), 351 (4.60), 367 (4.61), 416 (4.21), 439 (4.34), 520 (3.76, sh), 552 (3.83), 583 (3.79, sh), 630 (3.51, sh)	1730, 1720, 1695
4l	233 (4.81), 271 (4.85), 319 (4.69), 345 (4.68), 366 (4.58, sh), 425 (4.33), 448 (4.50), 512 (2.77, sh), 542 (3.83), 578 (3.72, sh), 625 (3.29, sh)	1710, 1690
4m	257 (5.03), 353 (4.55), 366 (4.54, sh), 421 (4.16), 443 (4.29), 525 (3.65, sh), 555 (3.73), 590 (3.68, sh), 635 (3.29, sh)	1690, 1660, 1650 (sh)
4n[a)]	267 (4.98), 309 (4.49), 329 (4.51), 350 (4.49), 365 (4.48, sh), 414 (4.21), 436 (4.30), 525 (3.77, sh), 550 (3.82), 585 (3.76, sh), 635 (3.39, sh)	2200, 1725, 1710
4o[a)]	271 (4.85), 319 (4.72), 342 (4.70), 365 (4.59, sh), 422 (4.38), 448 (4.52), 520 (3.79, sh), 543 (3.83), 580 (3.70, sh), 635 (3.20, sh)	2200, 1705
8a	258 (4.73), 293 (4.48), 320 (4.48), 410 (4.15, sh), 424 (4.28), 427 (4.27, sh), 550 (3.60)	1730, 1715
8b	258 (4.86), 293 (4.56), 322 (4.58), 410 (4.35, sh), 425 (4.50), 428 (4.49, sh), 550 (3.75)	1730, 1710
8c	242 (4.63), 260 (4.60), 302 (4.56), 325 (4.55), 417 (4.36, sh), 437 (4.49), 542 (3.65)	1710
8d	255 (4.96), 328 (4.60), 415 (4.31, sh), 433 (4.41), 558 (3.73)	1675, 1660
8e	242 (4.67), 260 (4.65), 302 (4.59), 325 (4.59), 417 (4.39, sh), 437 (4.52), 543 (3.72)	1695
8f	239 (4.43), 254 (4.46), 301 (4.38), 329 (4.33), 417 (4.15, sh), 440 (4.32), 550 (3.45)	2200
8g	257 (4.73), 298 (4.54), 320 (4.49), 410 (4.19, sh), 424 (4.31, sh), 430 (4.32), 552 (3.63)	1730, 1715
8h	255 (4.73), 298 (4.54), 323 (4.52), 410 (4.27, sh), 425 (4.42, sh), 429 (4.43), 553 (3.73)	1735, 1720
8i	243 (4.50), 261 (4.45), 302 (4.41), 327 (4.35), 423 (4.19, sh), 441 (4.30), 546 (3.52)	1700
8j	252 (4.73), 334 (4.32), 420 (4.10, sh), 435 (4.18), 560 (3.44)	1670, 1655
8k	243 (4.69), 262 (4.64), 303 (4.63), 328 (4.61), 422 (4.48, sh), 441 (4.60), 547 (3.75)	1695
8l	241 (4.40), 266 (4.40), 304 (4.37), 335 (4.28), 423 (4.15, sh), 443 (4.31), 555 (3.49)	2200

a) Taken for $CHCl_3$ solutions.

diazacyclopent[*a*]azuleno)[1,7]diaza[12]annulenes by means of their spectroscopic data (Tables 4, 5, and 6) as well as elemental analyses and mass spectra (Table 7). Deesterifications of **4e** and **4j** were attained by hydrolysis with potassium hydroxide followed by decarboxylation with copper in quinoline under heating, and **4p** and **4q** were obtained, respectively. The ^{1}H NMR spectra of **4p** and **4q** show two pairs of doublets at δ 7.05 and 8.03 (J=9.0 Hz) and at δ 7.10 and 8.06 (J=9.0 Hz), respectively, and their IR spectra show absorptions at 725 and 720 cm^{-1}, respectively. These facts denote that the configuration of ethylene bridge of **4** should be cis-one.

The regiochemistry of the reaction was attained by the reaction of **2** with the dissymmetrical acetylene (MP) or olefins (MA or EA). In the ^{1}H NMR spectrum of **3b**, the H-7 proton resonated at rather lower field (δ 9.85) than that of **3p** (δ 8.57), which would be under the deshielding effect of the ester group at C-8. The H-6 proton of **4b** also resonated at lower field (δ 8.30) than that of **4p** (δ 6.90).[9)] It is conceivable that 1,10-dipolar intermediates (**D**), which were produced by the electrophilic attack of the acetylenes at the C-3 position of **2**,[10)] cyclized at C-5 position to give **3** or reacted at C-5 position of another molecule (**D**) each other to give **4**. The reactions of **2** with olefins should proceed in a similar manner with the case of acetylenes, but it is

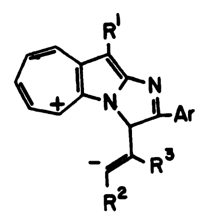
TABLE 4. ^{1}H NMR SPECTRAL DATA OF **3** AND **7**

Compound	H-3	H-4	H-5	H-6	H-7	H-9	Ar	Others		
								CH_3CH_2O	CH_3O	CH_3
3a[a]	8.36s	8.29ddd ($J_{4,5}=J_{6,7}=8.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.5$ Hz, $J_{4,7}=0.5$ Hz)	7.79ddd	7.88ddd	9.66ddd	—	7.55—7.70m (3H) 8.25—8.34m (2H)		4.06s 4.09s	
3b[b]	8.24s	8.25ddd ($J_{4,5}=J_{6,7}=8.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.5$ Hz, $J_{4,7}=0.5$ Hz)	7.70ddd	7.80ddd	9.85ddd	8.18s	7.45—7.65m (3H) 8.30—8.50m (2H)		4.07s	
3c[b]	8.21s	8.17ddd ($J_{4,5}=J_{6,7}=8.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.5$ Hz, $J_{4,7}=0.5$ Hz)	7.66ddd	7.78ddd	9.55ddd	—	7.33d (2H) 8.09d (2H) ($J=8.0$ Hz)		4.07s 4.08s	2.49s
3d[c]	8.13s	8.22ddd ($J_{4,5}=J_{6,7}=8.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.5$ Hz, $J_{4,7}=0.5$ Hz)	7.66ddd	7.80ddd	9,77ddd	8.03s	7.32d (2H) 8.02d (2H) ($J=8.5$ Hz)		4.02s	2.45s
3e[c]	—	8.78ddd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.0$ Hz, $J_{4,7}=0.5$ Hz)	7.78ddd	7.93ddd	9.73ddd	—	7.40—7.75m (3H) 8.15—8.45m (2H)	1.61t 4.78q ($J=7.0$ Hz)	4.03s 4.07s	
3f[c]	—	8.83dd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.0$ Hz)	7.83dd	7.93dd	9.90dd	—	7.50—7.70m (3H) 8.30—8.50m (2H)	1.40t 4.52q ($J=7.0$ Hz) 1.47t 4.55q ($J=7.0$ Hz) 1.60t 4.77q ($J=7.0$ Hz)		
3g[c]	—	8.78dd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.0$ Hz)	7.72dd	7.83dd	9.90dd	8.13s	7.40—7.65m (3H) 8.25—8.50m (2H)	1.62t 4.74q ($J=7.0$ Hz)	4.02s	
3h[c]	—	8.75—9.00m	7.10—8.00m		8.75—9.00m	—	7.10—8.00m (13H) 8.05—8.25m (2H)	1.62t 4.77q ($J=7.0$ Hz)		
3j[a]	—	8.80ddd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.0$ Hz, $J_{4,7}=0.5$ Hz)	7.87ddd	7.91ddd	9.78ddd	—	7.42d (2H) 8.23d (2H) ($J=8.5$ Hz)	1.63t 4.79q ($J=7.0$ Hz)	4.07s 4.08s	2.49s
3k[c]	—	8.79dd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.0$ Hz)	7.80dd	7.92dd	9.82dd	—	7.36d (2H) 8.24d (2H) ($J=8.0$ Hz)	1.43t 4.55q[c] ($J=7.0$ Hz) 1.50t 4.55q[e] ($J=7.0$ Hz) 1.62t 4.77q ($J=7.0$ Hz)		
3l[a]	—	8.87ddd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.5$ Hz, $J_{4,7}=0.5$ Hz)	7.89ddd	7.93ddd	10.05ddd	8.31s	7.43d (2H) 8.41d (2H) ($J=8.5$ Hz)	1.65t 4.80q ($J=7.0$ Hz)	4.10s	2.50s
3m[c]	—	8.70—8.95m	7.00—8.00m		8.70—8.95m	—	7.00—8.00m (12H) 8.07d (2H) ($J=8.0$ Hz)	1.65t 4.79q ($J=7.0$ Hz)		2.37s
3n[d]	—	8.63ddd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.0$ Hz, $J_{4,7}=0.5$ Hz)	7.89ddd	7.99ddd	9.71ddd	—	7.50—7.65m (3H) 8.20—8.35m (2H)		4.05s[e]	
3o[d]	—	8.66ddd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.0$ Hz, $J_{4,7}=0.5$ Hz)	7.90ddd	7.99ddd	10.01ddd	8.34s	7.50—7.65m (3H) 8.40—8.55m (2H)		4.08s[e]	
7a[a]	—	8.40ddd ($J_{4,5}=J_{6,7}=8.5$ Hz, $J_{5,6}=7.5$ Hz, $J_{4,6}=J_{5,7}=2.5$ Hz, $J_{4,7}=0.5$ Hz)	7.85ddd	7.73ddd	9.37ddd	—	7.45—7.65m (3H) 8.15—8.35m (2H)		4.03s[e] 4.05s	

TABLE 4. (Continued)

Compound	H-3	H-4	H-5	H-6	H-7	H-9	Ar	Others		
								CH_3CH_2O	CH_3O	CH_3
7b[c)]	—	8.47dd ($J_{4,5}=J_{6,7}=8.5$ Hz, $J_{5,6}=7.5$ Hz, $J_{4,6}=J_{5,7}=2.0$ Hz)	7.97dd	7.75dd	9.55dd	—	7.45—7.70m (3H) 8.25—8.45m (2H)	1.42t 4.50q (J=7.0 Hz) 1.47t 4.53q (J=7.0 Hz)		
7c[b)]	—	8.60ddd ($J_{4,5}=J_{6,7}=8.5$ Hz, $J_{5,6}=7.5$ Hz, $J_{4,6}=J_{5,7}=2.0$ Hz, $J_{4,7}=0.5$ Hz)	7.88ddd	7.77ddd	9.55ddd	8.03s	7.35—7.60m (3H) 8.25—8.55m (2H)		4.00s[e)]	
7d[b)]	—	8.53ddd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=8.0$ Hz, $J_{4,6}=J_{5,7}=2.0$ Hz, $J_{4,7}=0.5$ Hz)	7.92ddd	7.70ddd	8.72ddd	—	7.10—7.65m (13H) 8.15—8.30m (2H)			
7g[a)]	—	8.50ddd ($J_{4,5}=J_{6,7}=8.5$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.5$ Hz, $J_{4,7}=0.5$ Hz)	7.96ddd	7.85ddd	9.52ddd	—	7.41d (2H) 8.24d (2H) (J=8.5 Hz)		4.07s 4.10s	2.48s
7h[c)]	—	8.50dd ($J_{4,5}=J_{6,7}=8.5$ Hz, $J_{5,6}=7.5$ Hz, $J_{4,6}=J_{5,7}=2.0$ Hz)	7.97dd	7.83dd	9.63dd	—	7.37d (2H) 8.27d (2H) (J=8.5 Hz)	1.47t 4.53q (J=7.0 Hz) 1.50t 4.53q (J=7.0 Hz)		2.48s
7i[a)]	—	8.55ddd ($J_{4,5}=J_{6,7}=8.5$ Hz, $J_{5,6}=7.0$ Hz, $J_{4,6}=J_{5,7}=1.5$ Hz, $J_{4,7}=0.5$ Hz)	8.00ddd	7.90ddd	9.70ddd	8.22s	7.42d (2H) 8.40d (2H) (J=8.5 Hz)		4.10s	2.49s
7j[c)]	—	8.58dd ($J_{4,5}=J_{6,7}=9.0$ Hz, $J_{5,6}=7.5$ Hz, $J_{4,6}=J_{5,7}=1.5$ Hz)	8.00dd	7.77dd	8.78dd	—	7.10—7.80m (12H) 8.23d (2H) (J=8.5 Hz)			2.40s

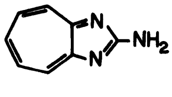
a) At 200 MHz. b) At 90 MHz. c) At 60 MHz. d) At 100 MHz. e) Two peaks are degenerated.



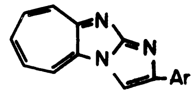
D

obscure which step dehydrogenations occured.

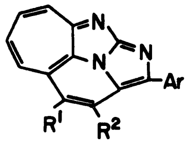
Syntheses and Cycloadditions of 1,3a,9-Triazacyclopent[a]*azulenes.* Treatment of 2-amino-1,3-diazaazulene (2-aminocycloheptimidazole) (**5**)[11] with α-bromoacetophenone in abs ethanol gave 2-amino-1-phenacylcycloheptimidazolium bromide in an 80% yield. Cyclization to 2-phenyl-1,3a,9-triazacyclopent[*a*]azulene (2-phenylcyclohept[*d*]imidazo[1,2-*a*]imidazole) (**6a**) was attained by the treatment of the salt with potassium carbonate in hot aq ethanol in a 76% yield. Similarly, **6b** was obtained by the treatment with 2-bromo-4′-methylacetophenone followed by the treatment with potassium carbonate in a 64% yield. In analogy with the reactions of **2a**, compounds **6a** and **6b** reacted with reactive acetylenes to give 1 : 1-adducts (**7**) and 2 : 2-adducts (**8**), and with electron deficient olefins to give 2 : 2-adducts (**8**). These results were listed in Table 1. The structures of 1 : 1-adducts (**7**) were assigned to 2,3-diazacyclohepta[*ef*]cycl[3.2.2]azines and 2 : 2-adducts to bis(1, 3a, 9-triazacyclopent[*a*]azuleno)[1, 7]diaza[12]-



5

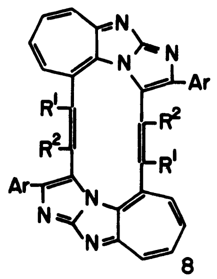


6a: Ar=Ph
6b: Ar=C_6H_4Me-p



7

7a, 8a: $R^1=R^2=E^1$, Ar=Ph
7b, 8b: $R^1=R^2=E^2$, Ar=Ph
7c, 8c: $R^1=E^1$, R^2=H, Ar=Ph
7d, 8d: $R^1=R^2$=COPh, Ar=Ph
7e, 8e: $R^1=E^2$, R^2=H, Ar=Ph
7f, 8f: R^1=CN, R^2=H, Ar=Ph
7g, 8g: $R^1=R^2=E^1$, Ar=C_6H_4Me-p
7h, 8h: $R^1=R^2=E^2$, Ar=C_6H_4Me-p
7i, 8i: $R^1=E^1$, R^2=H, Ar=C_6H_4Me-p
7j, 8j: $R^1=R^2$=COPh, Ar=C_6H_4Me-p
7k, 8k: $R^1=E^2$; R^2=H, Ar=C_6H_4Me-p
7l, 8l: R^1=CN, R^2=H, Ar=C_6H_4Me-p
7m, 8m: $R^1=R^2$=H, Ar=Ph
7n, 8n: $R^1=R^2$=H, Ar=C_6H_4Me-p



8

$E^1=CO_2Me$
$E^2=CO_2Et$

TABLE 5. ^{1}H NMR SPECTRAL DATA OF 4 AND 8[9]

Compound	H-6	H-7	H-8	H-9	H-10	H-olefin	Ar	Others		
								CH_3CH_2O	CH_3O	CH_3
4a[a]	7.35d ($J_{6,7}$=11.5 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=10.5 Hz)	6.80dd	6.46dd	7.55d	7.51s	—	7.35—7.60m (3H) 7.65—7.85m (2H)		3.63s 3.98s	
4b[b]	8.30d ($J_{6,7}$=12.0 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=11.0 Hz)	6.83dd	6.45dd	7.60d	7.35s	8.90s	7.40—7.55m (3H) 8.15—8.30m (2H)		4.00s	
4c[b]	7.27d ($J_{6,7}$=12.0 Hz, $J_{7,8}$=8.5 Hz, $J_{8,9}$=11.0 Hz)	6.72dd	6.37dd	7.48d	7.43s	—	7.25d (2H) 7.63d (2H) (J=8.0 Hz)		3.67s 3.94s	2.42s
4d[b]	8.26dd ($J_{6,7}$=12.0 Hz, $J_{7,8}$=8.0 Hz, $J_{8,9}$=10.0 Hz, $J_{6,8}$=1.0 Hz, $J_{7,9}$=1.5 Hz)	6.80ddd	6.45ddd	7.58dd	7.33s	8.87s	7.33d (2H) 8.15d (2H) (J=8.0 Hz)		4.00s	2.45s
4e[b]	7.80bd ($J_{6,7}$=$J_{8,9}$=10.0 Hz, $J_{7,8}$=7.0 Hz)	7.22dd	6.93dd	8.80bd	—	—	7.45—7.70m (3H) 7.80—7.95m (2H)	1.58t 4.67q (J=7.0 Hz)	3.62s 4.00s	
4f[b]	7.83bd ($J_{6,7}$=11.0 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=10.0 Hz)	7.23dd	6.93dd	8.87bd	—	—	7.40—7.65m (3H) 7.75—7.90m (2H)	0.93t 4.10q (J=7.0 Hz) 1.43t 4.50q (J=7.0 Hz) 1.58t 4.67q (J=7.0 Hz)		
4g[a]	8.38dd ($J_{6,7}$=11.5 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=10.0 Hz, $J_{6,8}$=$J_{7,9}$=1.0 Hz)	6.99ddd	6.77ddd	8.61dd	—	8.82s	7.30—7.60m (3H) 8.15—8.30m (2H)	1.58t 4.58q (J=7.0 Hz)	3.98s	
4h[b]	6.80—8.00m			8.90dm (J=10.0 Hz)	—	—	6.80—8.00m (15H)	1.57t 4.64q (J=7.0 Hz)		
4i[b]	8.57dd ($J_{6,7}$=$J_{8,9}$=11.0 Hz, $J_{7,8}$=9.0 Hz, $J_{6,8}$=$J_{7,9}$=1.5 Hz)	7.21ddd	6.90ddd	8.77dd	—	9.00s	7.45—7.80m (3H) 8.25—8.55m(2H)	1.50t 4.50q (J=7.0 Hz) 1.60t 4.60q (J=7.0 Hz)		
4j[a]	7.63ddd ($J_{6,7}$=12.0 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=10.5 Hz, $J_{6,8}$=$J_{7,9}$=1.0 Hz, $J_{6,9}$=0.5 Hz)	7.06ddd	6.84ddd	8.71ddd	—	—	7.27d (2H) 7.66d (2H) (J=8.0 Hz)	1.56t 4.62q (J=7.0 Hz)	3.46s 3.97s	2.44s
4k[b]	7.71bd ($J_{6,7}$=11.0 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=10.0 Hz)	7.17dd	6.87dd	8.78bd	—	—	7.26d (2H) 7.70d (2H) (J=8.0 Hz)	0.95t 4.10q (J=7.0 Hz) 1.41t 4.47q (J=7.0 Hz) 1.56t 4.62q (J=7.0 Hz)		2.43s
4l[b]	8.18ddd ($J_{6,7}$=11.0 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=10.0 Hz, $J_{6,8}$=1.0 Hz, $J_{7,9}$=1.5 Hz, $J_{6,9}$=0.5 Hz)	6.78ddd	6.53ddd	8.43ddd	—	8.53s	7.20d (2H) 7.98d (2H) (J=8.0 Hz)	1.55t 4.52q (J=7.0 Hz)	3.87s	2.42s
4m[b]	6.80—8.00m			8.92dm ($J_{8,9}$=10.0 Hz)	—	—	6.80—8.00m (14H)	1.57t 4.67q (J=7.0 Hz)		2.24s
4n[c]	7.81ddd ($J_{6,7}$=11.5 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=11.0 Hz, $J_{6,8}$=1.0 Hz, $J_{7,9}$=1.5 Hz, $J_{6,9}$=0.5 Hz)	7.21ddd	7.00ddd	8.01ddd	—	—	7.45—7.60m (3H) 7.70—7.80m (2H)		3.64s 4.00s	
4o[c]	8.67ddd ($J_{6,7}$=12.0 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=11.0 Hz, $J_{6,8}$=1.0 Hz, $J_{7,9}$=1.5 Hz, $J_{6,9}$=0.5 Hz)	7.23ddd	6.99ddd	7.97ddd	—	9.09s	7.35—7.65m (3H) 8.15—8.30m (2H)		4.07s	

Table 5. (Continued)

Compound	H-6	H-7	H-8	H-9	H-10	H-olefin	Ar	Others		
								CH_3CH_2O	CH_3O	CH_3
8a[c)]	8.12dm ($J_{6,7}$=11.0 Hz)	7.30—7.60m		8.32dm ($J_{8,9}$=10.0 Hz)	—	—	7.30—7.60m (3H) 7.80—7.95m (2H)		3.74s 4.00s	
8b[b)]	8.25dm ($J_{6,7}$=10.0 Hz)	7.20—7.70m		8.50dm ($J_{8,9}$=10.0 Hz)	—	—	7.20—7.70m (3H) 7.90—8.20m (2H)	0.97t 4.30q (J=7.0 Hz) 1.45t 4.60q (J=7.0 Hz)		
8c[b)]	8.73dm ($J_{6,7}$=11.0 Hz)	7.25—7.65m		8.13dm ($J_{8,9}$=10.0 Hz)	—	8.97s	7.25—7.65m (3H) 8.15—8.35m (2H)		4.02s	
8d[b)]	8.25dm ($J_{6,7}$=11.0 Hz)	7.10—8.00m		8.47dm ($J_{8,9}$=10.0 Hz)	—	—	7.10—8.00m (15H)			
8e[a)]	8.65dm ($J_{6,7}$=12.0 Hz, $J_{7,8}$=9.0 Hz, $J_{8,9}$=11.0 Hz)	7.13dd	7.29dd	8.10dm	—	8.90s	7.25—7.60m (3H) 8.15—8.25m (2H)	1.53t 4.50q (J=7.0 Hz)		
8f[c)]	7.92dm ($J_{6,7}$=10.0 Hz)	7.30—7.70m		8.35dm ($J_{8,9}$=10.0 Hz)	—	8.68s	7.30—7.70m (3H) 8.20—8.30m (2H)			
8g[b)]	8.20dm ($J_{6,7}$=10.0 Hz)	7.10—7.55m		8.40dm ($J_{8,9}$=10.0 Hz)	—	—	7.35d (2H) 7.82d (2H) (J=8.0 Hz)		3.82s 4.04s	2.47s
8h[b)]	8.17dm ($J_{6,7}$=11.0 Hz)	7.10—7.55m		8.45dm ($J_{8,9}$=10.0 Hz)	—	—	7.43d (2H) 7.93d (2H) (J=8.0 Hz)	1.05t 4.30q (J=7.0 Hz) 1.47t 4.57q (J=7.0 Hz)		2.50s
8i[b)]	8.76dm ($J_{6,7}$=11.0 Hz)	7.10—7.50m		8.22dm ($J_{8,9}$=10.0 Hz)	—	8.98s	7.30d (2H) 8.15d (2H) (J=8.0 Hz)		4.05s	2.42s
8j[b)]	8.23dm ($J_{6,7}$=10.0 Hz)	6.80—8.00m		8.50dm ($J_{8,9}$=10.0 Hz)	—	—	6.80—8.00m (14H)			2.30s
8k[b)]	8.83dm ($J_{6,7}$=11.0 Hz)	7.15—7.50m		8.22dm ($J_{8,9}$=10.0 Hz)	—	9.07s	7.36d (2H) 8.20d (2H) (J=8.0 Hz)	1.53t 4.57q (J=7.0 Hz)		2.44s
8l[b)]	7.93dm ($J_{6,7}$=10.0 Hz)	7.15—7.60m		8.33dm ($J_{8,9}$=10.0 Hz)	—	8.67s	7.37d (2H) 8.20d (2H) (J=8.0 Hz)			

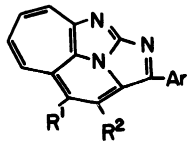
a) At 90 MHz. b) At 60 MHz. c) At 100 MHz.

annulenes on the basis of their spectroscopic properties (Tables 2, 3, 4, 5, and 6) as well as elemental analyses (Table 7).

Compounds **7a** and **7c** were deesterified by the treatment with potassium hydroxide followed by heating with copper in quinoline to give **7m**. Similarly, **7i** was deesterified to give **7n**. In the ^1H NMR spectrum of **7m**, seven-membered ring protons (H-4, H-5, H-6, and H-7) were seen at δ 8.48, 7.80, 7.91, and 8.56, respectively, with the vicinal coupling constants ($J_{4,5}=J_{6,7}=8.5$ Hz and $J_{5,6}=7.0$ Hz). Two pairs of doublets assignable to H-8 and H-9 protons were seen at δ 7.57 and 7.78 ($J=4.0$ Hz), respectively. These facts suggest that the resonance form **E** has large contribution in analogy with the case of **3**.

The compounds **8c** and **8i** were also deesterified and gave **8m** and **8n**, respectively. In the ^1H NMR spectra of **8m** and **8n**, two pairs of doublets were seen at δ 7.05 and 8.03 ($J=9.0$ Hz) and at δ 6.95 and 7.83 ($J=9.0$ Hz), respectively, and in their IR spectra, absorptions at 710 and 715 cm^{-1}, respectively, were seen. These results show that the configurations of ethylene bridge of **8** should be cis-one in similar to that of **4**.

The regiochemistry of the reaction was again attained by the reaction with dissymmetrical acetylene (MP) or olefins (MA, EA, or AN), and it is conceivable that 1,10-dipolar species should be intermediates.



E

Table 6. ^{13}C NMR spectral data of 3, 4, 7, and 8

Carbon	3e$^{a)}$	3j$^{b)}$	3p$^{b)}$	3q$^{b)}$	7a$^{a)}$	7m$^{b)}$	4e$^{a)}$	4f$^{a)}$	4p$^{b)}$	8b$^{a)}$	8m$^{b)}$
1	146.9s	142.3s	133.5s	132.1s	147.4s	145.8s					
2							140.7s	140.8s	140.8s	151.7s	150.8s
2a	160.2s	159.9s	151.0s	155.8s	163.6s	162.7s					
3	114.7s	113.7s	108.9d	108.6d			134.9s	135.6s	135.6s	150.0s	150.0s
3a	132.6s	130.3s	125.1s	125.1s	130.5s	131.3s					
4	128.3d	127.8d	130.5d	129.7d	133.0d	132.0d					
4a							131.8s	134.4s	131.6s	134.3s	132.2s
5	126.7d$^{f)}$	126.4d$^{f)}$	123.0d$^{f)}$	123.1d$^{f)}$	128.3d$^{f)}$	126.7d$^{f)}$	127.3s	118.4s	119.3s	117.5s	117.0s
6	127.2d$^{f)}$	126.8d$^{f)}$	125.9d$^{f)}$	125.9d$^{f)}$	130.8d$^{c,f)}$	128.7d$^{f)}$	134.5d	134.2d	131.9d	134.4d	133.5d
7	128.7d	128.3d	129.6d	126.7d	130.8d$^{c)}$	130.4d	127.7d$^{f)}$	129.0d$^{f)}$	127.8d$^{f)}$	129.2d$^{c,f)}$	129.9d$^{f)}$
7a	126.5s	123.0s	122.2s	122.3s	118.4s	117.9s					
8	123.5s	122.7s	113.9d	113.9d	129.7s	118.3d	127.5d$^{f)}$	127.7d$^{f)}$	127.6d$^{f)}$	129.2d$^{c,f)}$	129.0d$^{d,f)}$
9	122.9s	115.8s	110.4d	110.3d	128.1s	110.4d	135.1d	134.7d	133.5d	134.7d	134.3d
9a	139.3s	142.3s	139.1s	141.1s	147.4s	147.3s	131.6s	133.2s	130.4s	133.5s	135.1s
9c	130.6s	130.3s	132.0s	130.8s	130.6s	132.4s					
10							105.2s	103.2s	101.0d		
10a							149.3s	148.7s	142.3s	153.0s	151.5s
Olefin							127.2s	125.6d	123.1d	127.3d	123.4d
							121.2s	117.5s	119.3d	116.1s	119.3d
$\underline{C}O_2R$	165.9s	166.0s			165.7s		166.7s	166.3s		166.1s	
	165.3s	165.1s			165.6s		165.8s	164.1s			
	164.4s	164.1s					164.1s				
$O\underline{C}H_2$	62.5t	62.3t					61.2t	60.9t			
Me	52.9q	52.9q		21.6q	53.2q		53.1q	52.4q		52.6q	
	52.4q	52.3q			52.5q		52.8q	14.7q			
	14.5q	21.6q					14.7q				
		14.5q									
Ph	131.8d	138.7s	128.9d$^{c)}$	139.3s	130.1d$^{c)}$	129.2d$^{c)}$	130.1d$^{c)}$	131.3s	128.9d$^{e)}$	129.8d	129.0d$^{d)}$
	130.0d$^{c)}$	129.6d$^{d)}$	128.6d$^{c)}$	129.7d$^{c)}$	129.2d$^{c)}$	128.9d$^{c)}$	128.7d	129.0d$^{c)}$	127.8s	129.1d$^{c)}$	129.0s$^{d)}$
	129.0d$^{c)}$	127.2s	128.0d$^{c)}$	128.6d$^{c)}$	128.0s	123.8s	128.4d$^{c)}$	128.6d	126.9d$^{c)}$	128.5s	128.3d$^{c)}$
	127.8s		126.8d	128.0s	126.6d	123.0d	128.2s	127.9d$^{c)}$		127.6d$^{c)}$	127.1d$^{c)}$

a) At 20 MHz. b) At 25 MHz. c) Two peaks degenerated. d) Four peaks degenerated. e) Three peaks degenerated. f) Assignments may be reversed.

Experimental

Melting points were uncorrected. ^{1}H NMR spectra were taken on JEOL JNM-FX 200 (200 MHz), JEOL JNM FX-100 (100 MHz), Varian EM-390 (90 MHz), and Hitachi R-24B (60 MHz) spectrometers using deuteriochloroform as solvent (TMS as internal standard), unless otherwise stated. ^{13}C NMR spectra were taken on JEOL JNM FX-100 (25 MHz) and Varian FT-80A (20 MHz) spectrometers using deuteriochloroform as solvent (TMS as internal standard). Mass spectra were determined with a Hitachi M-80 instrument by means of field desorption ionization methods. IR spectra were recorded for Nujol mulls and electronic spectra for ethanol solutions, unless otherwise stated. Column chromatography was performed on Kieselgel 60. Recorded yields are based on the material after recrystallization.

Abbreviations. DMAD (dimethyl acetylenedicarboxylate), DEAD (diethyl acetylenedicarboxylate), MP (methyl propiolate), DBA (dibenzoylacetylene), EA (ethyl acrylate), MA (methyl acrylate), DMM (dimethyl maleate), AN (acrylonitrile), TMS (tetramethylsilane).

Materials. 2-Aminocyclohepta[*b*]pyrrole (**1a**)[7,8] and 2-aminocycloheptimidazole (**5**)[11] were prepared as reported.

*Sythesis of **1b**.* A mixture of ethyl 2-chlorocyclohepta[*b*]pyrrole-3-carboxylate (5.00 g, 21.0 mmol) in 20 ml of presaturated ethanolic ammonia in a sealed tube was heated at 160 °C for 3 h. The reaction mixture was poured into water and extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was chromatographed. Elution with benzene–chloroform (1 : 1) gave starting material (0.799 g, 16%). Elution with chloroform–ethyl acetate (2 : 1) gave **1b** (3.50 g, 76%), which crystallized from ethanol as yellow needles (2.79 g, 61%), mp 150—151 °C, (lit,[12,13] mp 150—151 °C); λ_{max} 247 nm (log ε 4.13), 287 (4.55, sh), 293 (4.58), 320 (3.89, sh), 365 (3.85), 424 (3.64, sh), and 432 (3.66); IR 3400, 3250, 3120, and 3050 (NH), and 1655 (ester C=O), and 1630 cm^{-1} (C=N); ^{1}H NMR (60 MHz) $\delta=1.44$ (3H, t, $J=7.0$ Hz, Me), 4.42 (2H, q, $J=7.0$ Hz, OCH_2), 7.10—7.40 (2H, m, $N\underline{H}$, exchangeable), 7.40—7.80 (3H, m, H-5, 6, and 7), 8.02 (1H, dm, $J=10.0$ Hz, H-8) and 8.80 (1H, dm, $J=10.0$ Hz, H-4). Found: C, 66.33; H, 5.52; N, 13.12%. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96%.

*Synthesis of **1c**.* A mixture of 2-chlorocyclohepta[*b*]pyrrole-3-carbonitrile (12.34 g, 65.5 mmol) in 20 ml of presaturated ethanolic ammonia in a sealed tube at 160 °C for 5 h, and worked up as above. Elution with benzene–chloroform (1 : 1) gave starting material (2.36 g, 19%). Elution with chloroform–ethyl acetate (4 : 1) gave **1c** (5.61 g, 51%), which crystallized from ethanol–dichloromethane as yellow needles (4.95 g, 45%), mp 237—238 °C; λ_{max} 242 nm (log ε 4.11, sh), 250 (4.12), 284 (4.53), 291 (4.53), 320 (3.95, sh), 366 (3.86), 423 (3.54), and 433 (3.54); IR 3380, 3300, 3200, and 3150 (NH), and 2200 and 2170 (C≡N), and 1640 cm^{-1} (C=N); ^{1}H NMR (60 MHz) $\delta=5.65$—6.15 (2H, m, $N\underline{H}_2$, exchangeable), 7.45—7.85 (3H, m, H-5, 6, and 7), and 7.90—8.35 (2H, m, H-4 and 8). Found: C, 71.21; H, 3.98; N, 25.00%. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.84%.

*Synthesis of **2a**.* A mixture of **1a** (1.11 g, 7.71 mmol)

Table 7. Analytical data **3**, **4**, **7**, and **8**.

Compound	Appearance	Mp θ_m/°C	Formula	Found (%)			Calcd (%)			M/*m*/*e* (M$^+$)
				C	H	N	C	H	N	
3a	Yellow needles[a]	178—180	$C_{23}H_{16}N_2O_4$	72.09	4.11	7.22	71.87	4.20	7.29	384
3b	Yellow needles[b]	213—214	$C_{21}H_{14}N_2O_2$	77.56	4.24	8.37	77.29	4.32	8.58	
3c	Yellow needles[b]	218—219	$C_{24}H_{18}N_2O_4$	72.10	4.59	7.03	72.35	4.55	7.03	
3d	Yellow needles[b]	242—243	$C_{22}H_{16}N_2O_2$	77.42	4.63	8.08	77.63	4.74	8.23	
3e	Yellow needles[a]	192—194	$C_{26}H_{20}N_2O_6$	68.34	4.27	5.91	68.42	4.42	6.14	456
3f	Yellow needles[b]	114—115	$C_{28}H_{24}N_2O_6$	69.37	4.95	5.57	69.41	4.99	5.78	
3g	Yellow needles[c]	162—163	$C_{24}H_{18}N_2O_4$	72.39	4.41	7.02	72.35	4.55	7.03	
3h	Yellow needles[a]	255—256	$C_{36}H_{24}N_2O_4$	78.76	4.23	5.01	78.82	4.41	5.11	
3j	Yellow prisms[a]	211.5—213	$C_{27}H_{22}N_2O_6$	68.67	4.62	5.87	68.93	4.71	5.95	
3k	Yellow needles[a]	198—199	$C_{29}H_{26}N_2O_6$	70.11	5.15	5.48	69.87	5.26	5.62	
3l	Yellow needles[a]	202—204	$C_{25}H_{20}N_2O_4$	72.74	4.70	6.63	72.80	4.89	6.79	
3m	Yellow needles[a]	222.5—223	$C_{37}H_{26}N_2O_4$	79.02	4.65	4.88	78.99	4.66	4.98	
3n	Yellow needles[a]	219—220	$C_{24}H_{15}N_3O_4$	70.62	3.52	10.28	70.41	3.69	10.26	
3o	Yellow needles[b]	293—295	$C_{22}H_{13}N_3O_2$	74.98	3.65	12.16	75.20	3.73	11.96	
4a	Violet needles[a]	199—201	$C_{46}H_{32}N_4O_8$	71.98	4.04	7.10	71.87	4.20	7.29	768
4b	Brown needles[b]	193—194	$C_{42}H_{28}N_4O_4$	77.39	4.29	8.40	77.29	4.32	8.58	
4c	Violet needles[b]	222—223	$C_{48}H_{36}N_4O_8$	72.36	4.43	6.87	72.35	4.55	7.03	
4d	Brown needles[b]	225—226	$C_{44}H_{32}N_4O_4$	77.77	4.66	8.32	77.63	4.74	8.23	
4e	Violet needles[a]	187—188	$C_{52}H_{40}N_4O_{12}$	68.40	4.29	6.08	68.42	4.42	6.14	912
4f	Violet needles[c]	250—251	$C_{56}H_{48}N_4O_{12}$	69.39	4.91	5.54	69.41	4.99	5.78	
4g	Violet needles[c]	195—197	$C_{48}H_{36}N_4O_8$	72.41	4.48	6.75	72.35	4.55	7.03	796
4h	Violet needles[a]	253—254	$C_{72}H_{48}N_4O_8$	78.90	4.45	5.26	78.82	4.41	5.11	
4i	Violet needles[a]	198—200	$C_{50}H_{40}N_4O_8$	73.05	4.68	6.52	72.80	4.89	6.79	
4j	Violet needles[a]	218—219.5	$C_{54}H_{44}N_4O_{12}$	69.14	4.72	5.87	68.93	4.71	5.95	
4k	Violet needles[a]	215—217	$C_{58}H_{52}N_4O_{12}$	69.75	5.17	5.63	69.87	5.26	5.62	
4l	Brown needles[b]	209—210	$C_{50}H_{40}N_4O_8$	72.94	4.78	6.93	72.80	4.89	6.79	
4m	Brown needles[a]	227—231	$C_{74}H_{52}N_4O_8$	78.43	4.59	4.90	78.99	4.66	4.98	
4n	Brown needles[a]	204—205	$C_{48}H_{30}N_6O_8$	70.27	3.48	10.05	70.41	3.69	10.26	
4o	Brown needles[b]	271—272	$C_{44}H_{26}N_6O_4$	74.92	3.45	12.07	75.20	3.73	11.96	
7a	Yellow needles[a]	215—216	$C_{22}H_{15}N_3O_4$	68.50	3.88	10.85	68.57	3.92	10.90	385
7b	Yellow needles[a]	159—161	$C_{24}H_{19}N_3O_4$	69.46	4.50	10.09	69.72	4.63	10.16	
7c	Yellow needles[a]	246—248	$C_{20}H_{13}N_3O_2$	73.52	3.87	12.98	73.39	4.00	12.84	327
7d	Yellow needles[a]	249—250	$C_{32}H_{19}N_3O_2$	80.38	3.86	8.66	80.49	4.01	8.80	
7g	Yellow needles[a]	238—242	$C_{23}H_{17}N_3O_4$	69.09	4.23	10.61	69.17	4.29	10.52	
7h	Yellow needles[a]	205—206	$C_{25}H_{21}N_3O_4$	70.37	4.80	9.75	70.25	4.95	9.83	
7i	Yellow needles[a]	245—246	$C_{21}H_{15}N_3O_2$	73.86	4.44	12.16	73.89	4.43	12.31	
7j	Yellow needles[a]	245—246	$C_{33}H_{21}N_3O_2$	80.39	4.11	8.29	80.64	4.31	8.55	
8a	Violet needles[a]	223—224	$C_{44}H_{30}N_6O_8$	68.48	3.88	10.69	68.57	3.92	10.90	770
8b	Violet needles[a]	152—155	$C_{48}H_{38}N_6O_8$	69.74	4.50	10.02	69.72	4.63	10.16	
8c	Violet needles[a]	196—198	$C_{40}H_{26}N_6O_4$	73.15	3.96	12.75	73.39	4.00	12.84	654
8d	Brown needles[a]	248—249	$C_{64}H_{38}N_6O_4\cdot$ EtOH	79.81	3.97	8.31	79.67	4.32	8.20	
8e	Violet needles[a]	198—199	$C_{42}H_{30}N_6O_4$	74.16	4.38	12.38	73.89	4.43	12.31	
8f	Brown needles[a]	>300	$C_{38}H_{20}N_8$	77.51	3.25	18.87	77.54	3.42	19.04	
8g	Violet needles[a]	216—218	$C_{46}H_{34}N_6O_8\cdot$ 1/2 EtOH	68.65	4.09	9.91	68.69	4.54	10.23	
8h	Violet needles[a]	184—185	$C_{50}H_{42}N_6O_8$	70.38	5.11	9.57	70.25	4.95	9.83	
8i	Violet needles[a]	221—223	$C_{42}H_{30}N_6O_4$	73.98	4.18	12.10	73.89	4.43	12.31	
8j	Violet needles[a]	249—250	$C_{66}H_{42}N_6O_4$	80.36	4.17	8.45	80.46	4.31	8.55	
8k	Violet needles[a]	198—199	$C_{44}H_{34}N_6O_4$	74.14	4.65	11.47	74.35	4.82	11.82	
8l	Violet needles[a]	292—293	$C_{40}H_{24}N_8$	78.07	3.84	17.87	77.91	3.92	18.17	

a) Recrystallized from ethanol. b) Recrystallized from cyclohexane-dichloromethane. c) Recrystallized from cyclohexane.

and α-bromoacetophenone (1.50 g, 7.73 mmol) in abs ethanol (30 ml) was heated under reflux for 8 h. To this mixture, water (10 ml) and potassium carbonate (2.13 g, 15.4 mmol) were added, and the mixture was heated under reflux for 1 h and evaporated to dryness under reduced pressure. The residue was dissolved into water and extracted with chloroform. The extract was washed with water, dried over Na_2SO_4, evaporated, and the residue was chromatographed. Elution with benzene–chloroform (1 : 1) gave **2a** (1.205 g, 64%), which was crystallized from cyclohexane–dichloromethane to give brown prisms (0.925 g, 49%), mp 147—148 °C; λ_{max} 247 nm (log ε 4.28), 260 (4.23, sh), 320 (4.61), 340 (4.45, sh), 384 (3.57), 404 (3.63), 429 (3.58), 470 (2.70), 505 (2.76), 545 (2.74), 587 (2.61, sh), and 650 (2.28, sh); IR 740 and 690 cm^{-1} (phenyl); ^{1}H NMR (60 MHz) δ=6.80 (1H, s, H-10), 6.65—7.10 (3H, m, H-6, 7, and 8), 7.30—7.60 (3H, m, phenyl), 7.60—7.90 (2H, m, H-5 and 9), 7.97 (1H, s, H-3), and 7.90—8.20 (2H, m, phenyl); δ (CF_3CO_2H)=7.15 (1H, s, H-10), 7.45—8.30 (8H, m, H-6, 7, 8, and phenyl), 8.35 (1H, s, H-3), 8.53 (1H, dm, J=9.0 Hz, H-9), and 8.69 (1H, dm, J=9.0 Hz, H-5). Found: C, 83.47; H, 4.85; N, 11.32%. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.59; N, 11.47%.

Synthesis of **2b**. A mixture of **1a** (0.500 g, 3.47 mmol) and 2-bromo-4′-methylacetophenone (0.730 g, 3.51 mmol) in abs ethanol (20 ml) was heated under reflux for 10 h. Water (5 ml) and potassium carbonate (0.960 g, 6.96 mmol) were added to this mixture, then the mixture was heated under reflux for 1 h and worked up as above. Chloroform eluted **2b** (0.569 g, 63%), which was crystallized from cyclohexane–dichloromethane to give brown scales (0.425 g, 47%), mp 165—166 °C; λ_{max} 250 nm (log ε 4.28), 264 (4.28), 325 (4.61), 345 (4.48, sh), 385 (3.60), 405 (3.64), 429 (3.55), 470 (2.75), 505 (2.79), 545 (2.77), 587 (2.65, sh), and 650 (2.39, sh); IR 820 cm^{-1} (phenyl); ^{1}H NMR (90 MHz) δ=2.35 (3H, s, Me), 6.72 (1H, s, H-10), 6.50—7.00 (3H, m, H-6, 7, and 8), 7.14 (2H, d, J=8.0 Hz, H-*m*-phenyl), 7.31 (1H, dm, J=9.5 Hz, H-5), 7.54 (1H, dm, J=10.5 Hz, H-9), 7.76 (2H, d, J=8.0 Hz, H-*o*-phenyl), and 7.82 (1H, s, H-3). Found: C, 83.59; H, 5.23; N, 10.65%. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84%.

Synthesis of **2c**. A mixture of **1b** (4.240 g, 19.6 mmol) and α-bromoacetophenone (4.190 g, 21.6 mmol) in 1-butanol (30 ml) was heated under reflux for 20 h, then evaporated to dryness. To the residue, water (40 ml), ethanol (60 ml), and potassium carbonate (5.400 g, 39.3 mmol) were added, and the mixture was heated under reflux for 1 h, and evaporated. The residue was dissolved into water and extracted with chloroform. The extract was washed, dried (Na_2SO_4), and evaporated. The residue was chromatographed. Elution with benzene–chloroform gave **2c** (2.603 g, 42%), which was crystallized from cyclohexane–dichloromethane to give brown needles (1.887 g, 30%), mp 160—161 °C; λ_{max} 253 nm (log ε 4.41), 280 (4.09, sh), 340 (4.36), 355 (4.33, sh), 442 (3.60), 455 (3.59, sh), 530 (2.76, sh), 575 (2.56, sh), and 640 (1.98, sh); IR 1685 (ester C=O), and 740 and 695 cm^{-1} (phenyl); ^{1}H NMR (60 MHz) δ=1.57 (3H, t, J=7.0 Hz, Me), 4.60 (2H, q, J=7.0 Hz, OCH_2), 7.25—7.65 (6H, m, H-6, 7, 8, and phenyl), 7.93 (1H, dm, J=10.0 Hz, H-5), 8.07 (1H, s, H-3), 7.95—8.20 (2H, m, phenyl), and 9.33 (1H, dm, J=10.0 Hz, H-9). Found: C, 75.78; H, 4.92; N, 8.86%. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86%. Elution with chloroform–ethyl acetate (2 : 1) gave **1b** (1.725 g, 41%).

Synthesis of **2d**. A mixture of **1b** (4.463 g, 20.6 mmol) and 2-bromo-4′-methylacetophenone (4.645 g, 20.6 mmol) in 1-butanol (30 ml) was heated under reflux for 20 h and evaporated. To this residue, water (10 ml), ethanol (90 ml), and potassium carbonate (5.710 g, 41.3 mmol) were added, and the mixture was heated under reflux for 1 h, and worked up as for **2c**. Elution with benzene–chloroform (1 : 1) gave **2d** (4.127 g, 60.5%), which was crystallized from cyclohexane–dichloromethane to give brown needles (2.475 g, 36%), mp 133—134 °C; λ_{max} 254 nm (log ε 4.42), 280 (4.11, sh), 347 (4.47), 360 (4.45, sh), 445 (3.68), 455 (3.68, sh), 530 (2.85, sh), 590 (2.53, sh), and 630 (2.19, sh); IR 1680 (ester C=O) and 810 cm^{-1} (phenyl); ^{1}H NMR (60 MHz) δ=1.53 (3H, t, J=7.0 Hz, Me), 2.38 (3H, s, Me), 4.55 (2H, q, J=7.0 Hz, OCH_2), 7.23 (2H, d, J=8.0 Hz, H-*m*-phenyl), 7.25—7.60 (3H, m, H-6, 7, and 8), 7.85 (1H, dm, J=10.0 Hz, H-5), 7.93 (2H, d, J=8.0 Hz, H-*o*-phenyl), 7.97 (1H, s, H-3), and 9.25 (1H, dm, J=10.0 Hz, H-9). Found: C, 76.64; H, 5.67; N, 8.09%. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.35; H, 5.49; N, 8.48%. Elution with chloroform–ethyl acetate (2 : 1) gave **1b** (1.581 g, 36%).

Synthesis of **2e**. A mixture of **1c** (1.210 g, 7.16 mmol) and α-bromoacetophenone (1.930 g, 7.16 mmol) in 1-butanol (30 ml) was heated under reflux for 100 h, and evaporated under reduced pressure. To the residue, ethanol (90 ml), water (10 ml), and potassium carbonate (1.980 g, 14.3 mmol) were added, and the mixture was heated under reflux for 1 h, and worked up as for **2c**. Elution with benzene–chloroform (1 : 1) gave **2e** (0.608 g, 32%), which was crystallized from ethanol–dichloromethane to give brown prisms (0.291 g, 15%), mp 256—257 °C; λ_{max} ($CHCl_3$) 247 nm (log ε 4.43), 280 (4.18, sh), 342 (4.45), 355 (4.42, sh), 435 (3.62), 457 (3.63), 507 (2.95, sh), 546 (2.83, sh), 595 (2.65, sh), and 650 (2.29, sh); IR 2200 (C≡N), and 740 and 695 cm^{-1} (phenyl); ^{1}H NMR (60 MHz) δ (CF_3CO_2D)=7.50—7.95 (5H, m, phenyl), 8.20—8.60 (3H, m, H-6,7, and 8), 8.54 (1H, s, H-3), 9.05 (1H, dm, J=10.0 Hz, H-5), and 9.18 (1H, dm, J=10.0 Hz, H-9). Found: C, 80.27; H, 3.93; N, 15.43%. Calcd for $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60%.

Deesterification of **2c**. A mixture of **2c** (0.316 g, 1.00 mmol) and potassium hydroxide (0.56 g, 10.0 mmol) in ethanol (30 ml)–water (20 ml) was heated under reflux for 1 h. The reaction mixture was diluted with water and acidified with 1 M aq hydrochloric acid (1 M=1 mol dm^{-3}). The resulted precipitate was filtered and dried to give the corresponding carboxylic acid [0.262 g, 90%, mp 181—182 °C (decomp)]. A suspension of the carboxylic acid (0.140 g, 0.49 mmol) in 48% hydrobromic acid (10 ml) was heated under reflux for 1 h, then poured into water, and neutralized with sodium carbonate, and extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed with benzene–chloroform (1 : 1) to give **2a** (0.037 g, 31%).

General Procedure for the Reactions of **2** *with Acetylenes.* A mixture of **2** (2.00 mmol), the acetylene (4.00 mmol), and the solvent (30 ml) was heated under reflux under the conditions specified in Table 1, and evaporated under reduced pressure. Chromatography of the residue with benzene–chloroform (1: 1) gave **3** and **4**, successively. Analytical data are listed in Table 7 and spectroscopic data in Tables 2—5, and 6.

General Procedure for the Reactions of **2** *with Olefins.* A mixture of **2** (2.00 mmol), the olefin (20.0 mmol), and the solvent (30 ml) was heated under reflux under the conditions specified in Table 1 and evaporated to dryness under the reduced pressure. Chromatography of the residue with benzene–chloroform (1 : 1) gave **4**. Analytical data are listed in Table 7 and spectroscopic data in Tables 4, 5, and 6.

Deesterification of **3** *and* **4**. A solution of **3e** (0.190 g, 0.42 mmol) and potassium hydroxide (0.90 g, 16 mmol) in ethanol (40 ml)–water (20 ml) was heated under reflux for 3 h. The reaction mixture was poured into water (250 ml), acidified with 1 M aq hydrochloric acid, and resulted precipitate was filtered to give the corresponding tricarboxylic acid (0.147 g, 88%, mp>300 °C). A mixture of the carboxylic acid (0.147 g, 0.37 mmol) and copper-powder (0.10 g) in quinoline (5 ml) was heated under reflux for 1 h. The reaction mixture was filtered off, and copper-powder was washed with chloroform. The combined filtrate was washed with 1 M aq hydrochloric acid followed by water, dried (Na_2SO_4), and evaporated. The residue was chromatographed with chloroform to give **3p** (0.098 g, 99%), which crystallized from cyclohexane as yellow needles (0.074 g, 75%), mp 197—199 °C; λ_{max} 239 nm (log ε 4.36), 260 (4.34, sh), 270 (4.40, sh), 281 (4.51, sh), 288 (4.54), 295 (4.47, sh), 320 (3.75), 357 (4.26), 374 (4.36), 417 (3.95), and 440 (4.07); ^{1}H NMR (200 MHz) δ=7.50—7.70 (3H, m, phenyl), 7.73 (1H, ddd, J=8.0, 7.0, and 1.5 Hz, H-5), 7.73 (1H, d, J=4.0 Hz, H-9), 7.77 (1H, d, J=4.0 Hz, H-8), 7.78 (1H, ddd, J=8.0, 7.0, and 1.5 Hz, H-6), 8.32 (1H, ddd, J=8.0, 1.5, and 0.5 Hz, H-4), 8.33 (1H, s, H-3), 8.45—8.55 (2H, m, phenyl), and 8.57 (1H, ddd, J=8.0, 1.5, and 0.5 Hz, H-7). Found: C, 84.75; H, 4.58; N, 10.28%. Calcd for $C_{19}H_{12}N_2$:

C, 85.05; H, 4.51; N, 10.44%.

In a similar manner, **3j**, **4e**, and **4j** gave **3q** (85%), **4p** (54%), and **4q** (50%), respectively.

3q: Yellow needles (from cyclohexane), mp 235 °C; λ_{max} 242 nm (log ε 4.71), 260 (4.65, sh), 271 (4.60, sh), 280 (4.69, sh), 290 (4.77), 300 (4.77), 323 (4.15), 359 (4.59), 375 (4.66), 415 (4.26), and 438 (4.36); ^{1}H NMR (60 MHz) δ=2.46 (3H, s, Me), 7.35 (2H, d, *J*=8.0 Hz, H-*m*-phenyl), 7.60—7.90 (4H, m, H-5, 6, 8, and 9), 8.22 (1H, dm, *J*=9.0 Hz, H-4), 8.25 (1H, s, H-3), 8.35 (2H, d, *J*=8.0 Hz, H-*o*-phenyl), and 8.50 (1H, dm, *J*=9.0 Hz, H-7). Found: C, 85.11; H, 4.83; N, 9.91%. Calcd for $C_{20}H_{14}N_2$: C, 85.09; H, 5.00; N, 9.92%.

4p: Violet needles (from cyclohexane–dichloromethane), mp 157—158 °C; λ_{max} 237 nm (log ε 4.77), 262 (5.01), 285 (4.38, sh), 344 (4.60), 360 (4.51), 384 (4.21, sh), 403 (4.46), 427 (4.46), 485 (3.58, sh), 515 (3.70), 547 (3.70), 590 (3.50), and 645 (2.94, sh); IR 725 cm^{-1} (*cis* HC=CH); ^{1}H NMR (60 MHz) δ=6.23 (2H, ddd, *J*=10.5, 8.0, and 2.0 Hz, H-8), 6.73 (2H, ddd, *J*=10.5, 8.0, and 2.5 Hz, H-7), 6.90 (2H, dd, *J*=10.5 and 2.0 Hz, H-6), 7.05 (2H, d, *J*=9.0 Hz, H–olefin), 7.27 (2H, s, H-10), 7.15—7.60 (6H, m, phenyl), 7.60 (2H, dd, *J*=10.5 and 2.5 Hz, H-9), 8.03 (2H, d, *J*=9.0 Hz, H–olefin), and 8.05—8.30 (4H, m, phenyl). Found: C, 85.27; H, 4.47; N, 10.56%. Calcd for $C_{38}H_{24}N_4$: C, 85.05; H, 4.51; N, 10.44%.

4q: Dark green needles (from cyclohexane), mp 159.5—162 °C; λ_{max} 240 nm (log ε 4.75), 264 (4.98), 287 (4.44, sh), 345 (4.55), 363 (4.48), 386 (4.27, sh), 406 (4.41), 428 (4.38), 487 (3.57, sh), 520 (3.62), 553 (3.63), 592 (3.47), and 650 (3.03, sh); IR 720 cm^{-1} (*cis* HC=CH); ^{1}H NMR (60 MHz) δ=2.42 (6H, s, Me), 6.27 (2H, ddd, *J*=10.5, 8.0, and 2.0 Hz, H-8), 6.69 (2H, ddd, *J*=10.5, 8.0, and 2.0 Hz, H-7), 6.90 (2H, d, *J*=9.0 Hz, H–olefin), 7.27 (4H, d, *J*=8.0 Hz, H-*m*-phenyl), 7.33 (2H, s, H-10), 7.41 (2H, dd, *J*=10.5 and 2.0 Hz, H-9), 8.06 (2H, d, *J*=9.0 Hz, H–olefin), and 8.09 (4H, d, *J*=8.0 Hz, H-*o*-phenyl). Found: C, 84.91; H, 4.98; N, 9.64%. Calcd for $C_{40}H_{28}N_4$: C, 85.09; H, 5.00; N, 9.92%.

*Synthesis of **6a***. A mixture of **5** (2.00 g, 13.8 mmol) and α-bromoacetophenone (2.74 g, 14.1 mmol) in abs ethanol (50 ml) was heated under reflux for 7 h, then cooled overnight to give 2-amino-1-phenacycloheptimidazolium bromide (3.74 g, 80%), which crystallized from ethanol as colorless prisms (mp 230—231 °C. Found: C, 55.64; H, 4.33; N, 11.96%. Calcd for $C_{16}H_{14}BrN_3O$: C, 55.83; H, 4.10; N, 12.21%). A mixture of the salt and potassium carbonate (3.25 g, 24.1 mmol) in ethanol (90 ml)–water (10 ml) was heated under reflux for 2 h, and worked up as for **1a**. Elution with chloroform–ethyl acetate (4 : 1) gave **6a** (2.19 g, 76%), which was crystallized from ethanol to give brown needles (1.970 g, 68%), mp 244—245 °C; λ_{max} 232 nm (log ε 4.50), 245 (4.42, sh), 334 (4.70), 421 (3.62), and 428 (3.60, sh); IR 735 and 685 cm^{-1} (phenyl); ^{1}H NMR (100 MHz) δ=7.20—7.50 (3H, m, phenyl), 7.55—7.80 (3H, m, H-6, 7, and 8), 7.94 (1H, s, H-3), 7.90—8.05 (2H, m, H-*o*-phenyl), 8.05 (1H, dm, *J*=11.0 Hz, H-5), and 8.40 (1H, dm, *J*=11.0 Hz, H-9), δ (CF_3CO_2D)=7.50—7.90 (5H, m, phenyl), 8.43 (1H, s, H-3, exchangeable), 8.60—9.00 (3H, m, H-6, 7, and 8), and 9.20—9.60 (2H, m, H-5 and 9). Found: C, 78.52; H, 4.49; N, 17.21%. Calcd for $C_{16}H_{11}N_3$: C, 78.35; H, 4.52; N, 17.13%.

*Synthesis of **6b***. A mixture of **5** (2.00 g, 13.8 mmol) and 2-bromo-4′-methylacetophenone (2.94 g, 13.8 mmol) in abs ethanol (40 ml) was heated under reflux for 5 h, then cooled overnight. Resulted precipitates were collected by filtration to give 2-amino-1-(*p*-methylphenacyl)cycloheptimidazolium bromide (3.82 g, 77%), which crystallized from ethanol as colorless needles [mp 257 °C (decomp). Found: C, 56.76; H, 4.43; N, 11.88%. Calcd for $C_{17}H_{16}BrN_3O$: C, 57.00; H, 4.50; N, 11.73%]. A mixture of the salt (4.65 g, 13.0 mmol) and potassium carbonate (3.59 g, 26.0 mmol) in ethanol (225 ml)–water (25 ml) was heated under reflux for 2 h and worked up as for **1a**. Elution with chloroform gave **6b** (2.786 g, 83%), which was crystallized from ethanol–dichloromethane to give brown needles (1.903 g, 57%), mp 272—275 °C (decomp); λ_{max} 235 nm (log ε 4.42), 255 (4.31), 338 (4.60), 423 (3.56), and 428 (3.54, sh); IR 820 cm^{-1} (phenyl); ^{1}H NMR (60 MHz) δ (CF_3CO_2D)=2.48 (3H, s, Me), 7.41 (2H, d, *J*=8.0 Hz, H-*m*-phenyl), 8.03 (2H, d, *J*=8.0 Hz, H-*o*-phenyl), 8.37 (1H, s, H-3, exchangeable), 8.65—9.00 (3H, m, H-6, 7, and 8), and 9.20—9.60 (2H, m, H-5 and 9). Found: C, 78.77; H, 5.18; N, 15.94%. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.20%.

*General Procedure for the Reactions of **6** with Acetylenes.* A mixture of **6** (2.00 mmol), the acetylene (4.00 mmol), and the solvent (50 ml) was heated under reflux under the conditions specified in Table 1 and evaporated to dryness under reduced pressure. Chromatography of the residue with benzene–chloroform (1 : 1) gave **7** and **8**, successively. Analytital data are listed in Table 7 and spectroscopic data in Tables 2, 3, 4, 5, and 6.

*General Procedure for the Reactions of **6** with Olefins.* A mixture of **6** (1.00 mmol), the olefin (10.0 mmol), and the solvent (30 ml) was heated under reflux under the conditions specified in Table 1 and evaporated to dryness under reduced pressure. Chromatography of the residue with benzene–chloroform (1 : 1) gave **8**. Analytical data are listed in Table 7 and spectroscopic data in Tables 4 and 5.

*Deesterification of **7** and **8**.* A solution of **7a** (0.400 g, 1.04 mmol) and potassium hydroxide (0.58 g, 10.4 mmol) in ethanol (30 ml)–water (20 ml) was heated under reflux for 2 h. The reaction mixture was poured into water (200 ml), acidified with 1M aq hydrochloric acid. Resulted precipitate was filtered to give the corresponding dicarboxylic acid as yellow powder (0.350 g, 97%, mp>300 °C). A mixture of the carboxylic acid (0.350 g, 0.98 mmol) and copper-powder (0.10 g) in quinoline (5 ml) was heated under reflux for 1 h and worked up as for **3p**. Elution with chloroform gave **7m** (0.175 g, 66%), which was crystallized from ethanol–dichloromethane to give yellow needles (0.142 g, 54%), mp 204—206 °C; λ_{max} 234 nm (log ε 4.35), 261 (4.38), 282 (4.43), 291 (4.40), 322 (3.93), 335 (4.01), 364 (4.23), 380 (4.21, sh), 438 (4.08), and 462 (4.15); IR 745 and 680 cm^{-1} (phenyl); ^{1}H NMR (200 MHz) δ=7.57 (1H, d, *J*=4.0 Hz, H-8), 7.63 (1H, s, H-3), 7.58—7.70 (3H, m, phenyl), 7.78 (1H, d, *J*=4.0 Hz, H-9), 7.80 (1H, ddd, *J*=8.5, 7.0, and 1.5 Hz, H-5), 7.91 (1H, ddd, *J*=8.5, 7.0, and 2.0 Hz, H-6), 8.48 (1H, ddd, *J*=8.5, 2.0, and 0.5 Hz, H-4), 8.50—8.57 (2H, m, phenyl), and 8.56 (1H, ddd, *J*=8.5, 1.5, and 0.5 Hz, H-7). Found: C, 80.04; H, 3.85; N, 15.53%. Calcd for $C_{18}H_{11}N_3$: C, 80.28; H, 4.12; N, 15.60%.

In a similar manner, **7c**, **7i**, **8c**, and **8i** gave **7m** (94%), **7n** (44%), **8m** (51%), and **8n** (55%), respectively.

7n: Yellow needles (from cyclohexane–dichloromethane), mp 213—215 °C; λ_{max} 237 nm (log ε 4.36), 262 (4.39), 285 (4.36), 294 (4.37), 327 (3.98, sh), 340 (4.10, sh), 367 (4.33), 377 (4.32, sh), 440 (4.07), and 460 (4.20); IR 825 and 815 cm^{-1} (phenyl); ^{1}H NMR (60 MHz) δ=2.44 (3H, s, Me), 7.31 (2H, d, *J*=8.0 Hz, H-*m*-phenyl), 7.51 (1H, d, *J*=8.5 Hz, H-8), 7.50—8.00 (3H, m, H-5, 6, and 7), 8.32 (1H, d, *J*=8.5 Hz, H-9), 8.34 (2H, d, *J*=8.0 Hz, H-*o*-phenyl), and 8.43 (1H, dm, *J*=10.0 Hz, H-4). Found: C, 80.26; H, 4.43; N, 14.82%. Calcd for $C_{19}H_{13}N_3$: C, 80.55; H, 4.62; N, 14.83%.

8m: Brown needles (from cyclohexane–dichloromethane), mp 224—225 °C; λ_{max} 238 nm (log ε 4.91), 250 (4.87, sh), 266 (4.75, sh), 277 (4.66, sh), 328 (4.70), 340 (4.66, sh), 415 (4.53, sh), 437 (4.70), 525 (3.78, sh), 555 (3.81), 585 (3.72, sh), and

640 (3.25, sh); IR 740 and 680 (phenyl), and 710 cm^{-1} (*cis* HC=CH); ^{1}H NMR (60 MHz) δ=6.23 (2H, ddd, J=10.5, 8.0, and 2.0 Hz, H-8), 6.73 (2H, ddd, J=10.5, 8.0, and 2.5 Hz, H-7), 6.90 (2H, ddd, J=10.5, 2.0, and 0.5 Hz, H-6), 7.05 (2H, d, J=9.0 Hz, H-olefin), 7.27 (2H, s, H-10), 7.15—7.60 (6H, m, phenyl), 7.60 (2H, ddd, J=10.5, 2.5, and 0.5 Hz, H-9), 8.03 (2H, d, J=9.0 Hz, H-olefin), and 8.05—8.30 (4H, m, phenyl). Found: C, 80.02; H, 3.97; N, 15.30%. Calcd for $C_{36}H_{22}N_6$: C, 80.28; H, 4.12; N, 15.60%.

8n: Dark brown needles (from cyclohexane–dichloromethane), mp 216—217 °C; λ_{max} 239 nm (log ε 4.86), 250 (4.79, sh), 266 (4.66, sh), 281 (4.42), 335 (4.65), 343 (4.62, sh), 418 (4.51, sh), 440 (4.69), 530 (3.78, sh), 560 (3.82), 595 (3.72, sh), and 647 (3.26, sh); IR 810 (phenyl) and 715 cm^{-1} (*cis* HC=CH), ^{1}H NMR (60 MHz) δ=2.37 (6H, s, Me), 6.60—7.15 (6H, m, H-6, 7, and 8), 6.95 (2H, d, J=9.0 Hz, H-olefin), 7.14 (4H, d, J=8.0 Hz, H-*m*-phenyl), 7.75 (2H, dm, J=10.0 Hz, H-9), 7.83 (2H, d, J=9.0 Hz, H-olefin), and 7.93 (4H, d, J=8.0 Hz, H-*o*-phenyl). Found: C, 80.41; H, 4.49; N, 14.55%. Calcd for $C_{38}H_{26}N_6$: C, 80.55; H, 4.62; N, 14.83%.

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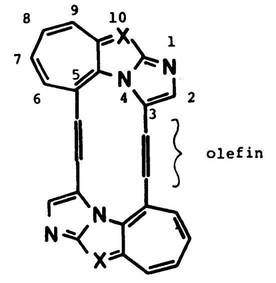

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