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Cyclooctyne smoothly underwent 1,3-dipolar cycloaddition with pyridinium dicyanomethylides to afford the corresponding indolizines (8-cyano-7-azatricyclo[7.6.0.0^{2,7}]pentadeca-1,3,5,8-tetraenes) in excellent yields.

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Cyclooctyne is the smallest cyclic alkyne that is stable at room temperature and has been prepared by a number of methods which either start from cyclooctene or from cyclooctanone [1-5]. Usually, 1,3-dipolar cycloaddition reactions (HOMO-LUMO controlled) of

dipoles with acetylene and non-activated alkynes either proceed only sluggishly or fails [6]. In spite of high strain and high reactivity of cyclooctyne as well as synthetic potential of its cycloadditions, only a few examples of 1,3-dipolar cycloaddition reactions have been reported [7,8]. Previously we have investigated 1,3-dipolar cycloadditions of pyridinium dicyanomethylides with cyclopropene [9], and with alkyne and related equivalents [10] as well as regioselectivity in the 1,3-dipolar cycloaddition reaction of unsymmetric pyridinium dicyanomethylides with dimethyl acetylenedicarboxylate and methyl propiolate [11]. We now describe in full detail 1,3-dipolar cycloadditions of cyclooctyne with pyridinium dicyanomethylides **1** [12].

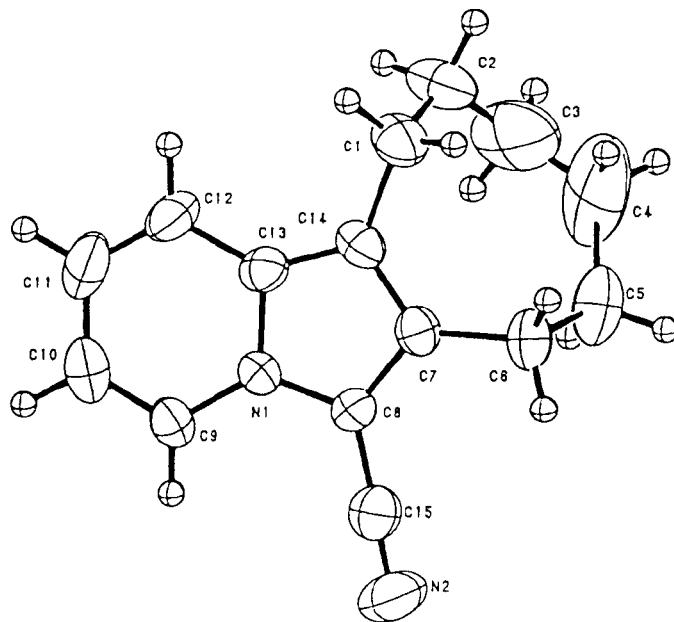
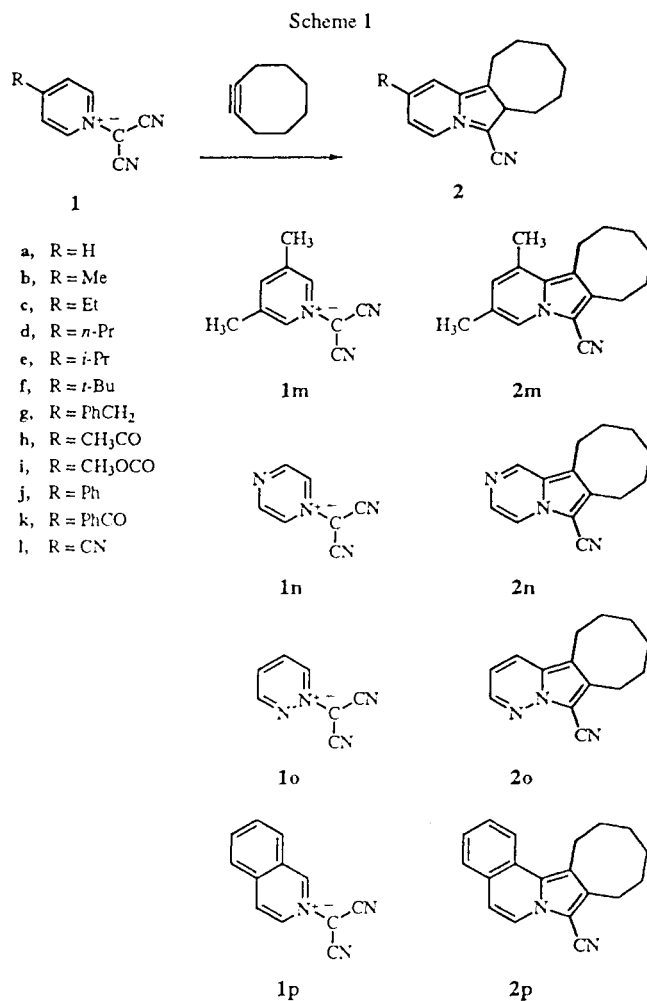


Figure 1. ORTEP Drawing of 8-cyano-7-azatricyclo[7.6.0.0^{2,7}]pentadeca-1,3,5,8-tetraene (**2a**).

Table 1
8-Cyano-7-azatricyclo[7.6.0.0^{2,7}]pentadeca-1,3,5,8-tetraene 2

Compound	Yield (%)	Mp (°C)	CN	IR (cm ⁻¹)	CO	¹ H NMR (δ)
2a	97	128.1-128.4	2200			1.29-1.82 (m, 8H, H-11-14), 2.76-2.92 (m, 4H, H-10, 15), 6.67 (dt, J = 7.0, 7.0, 1.4 Hz, 1H, H-5), 6.89 (br t, J = 7.6, 7.0 Hz, 1H, H-4), 7.34 (br d, J = 7.6 Hz, 1H, H-3), 8.12 (br d, J = 7.0, 1H, H-6)
2b	95	100-101	2180			1.25-1.90 (m, 8H, H-11-14), 2.33 (s, 3H, CH ₃), 2.68-2.96 (m, 4H, H-10, 15), 6.47 (dd, 1H, J = 7.0, 1.7 Hz, H-5), 7.66 (br s, 1H, H-3), 7.94 (d, J = 7.0, H-6)
2c	98	55.3-55.7	2180			1.26 (t, J = 7.6 Hz, 3H, CH ₃), 1.31-1.80 (m, 8H, H-11-14), 2.63 (q, J = 7.6 Hz, 2H CH ₂), 2.73-2.90 (m, 4H, H-10, 15), 6.55 (dd, J = 7.0, 1.9 Hz, 1H, H-5), 7.11 (br s, 1H, H-3), 8.04 (t, J = 7.0 Hz, 1H, H-6)
2d	96	oil	2180			0.97 (t, J = 7.4 Hz, 3H, CH ₃), 1.27-1.82 (m, 10H, H-11-14+CH ₂), 2.56 (t, J = 7.4 Hz, 2H, CH ₂), 2.71-2.93 (m, 4H, H-10, 15), 6.53 (dd, J = 6.6, 1.8 Hz, 1H, H-5), 7.10 (br s, 1H, H-3), 8.03 (d, J = 6.6 Hz, 1H, H-6)
2e	94	oil	2180			1.26 (d, J = 7.0 Hz, 6H, CH ₃), 1.30-1.77 (m, 8H, H-11-14), 2.69-2.96 (m, 5H, H-10, 15+CH), 6.58 (dd, J = 7.0, 1.8 Hz, 1H, H-5), 7.12 (br s, 1H, H-3) 8.04 (d, J = 7.0 Hz, 1H, H-6), 1.32 (s, 9H, CH ₃) 1.34-1.78 (m, 8H, H-11-14), 2.74-2.89 (m, 4H, H-10, 15), 6.74 (dd, J = 7.6, 1.9 Hz, 1H, H-5), 7.20 (br s, 1H, H-3), 8.05 (d, J = 7.3 Hz, 1H, H-6)
2f	98	85.2-85.6	2180			1.31-1.82 (m, 8H, H-11-14), 2.69-2.90 (m, 4H, H-10, 15), 3.92 (s, 2H, CH ₂), 6.45 (dd, J = 7.3, 1.9 Hz, 1H, H-5), 7.10-7.38 (m, 6H, H-3+C ₆ H ₅), 8.01 (d, J = 7.3 Hz, 1H, H-6)
2g	91	91.8-92.1	2180			1.32-1.88 (m, 8H, H-11-14), 2.62 (s, 3H, CH ₃), 2.85-2.94 (m, 4H, H-10, 15), 7.24 (dd, J = 7.0, 1.6 Hz, 1H, H-5), 7.99 (br s, 1H, H-3), 8.12 (d, J = 7.0, 1H, H-6)
2h	96	168.5-168.8	2200		1670	1.24-1.80 (m, 8H, H-11-14), 2.82-2.94 (m, 4H, H-10, 15), 3.95 (s, 3H, CH ₃), 7.25 (dd, J = 7.0, 1.6 Hz, 1H, H-5), 8.13 (d, 7.0 Hz, 1H, H-6), 8.15 (br s, 1H, H-3)
2i	90	138.3-138.6	2190		1710	1.33-1.80 (m, 8H, H-11-14), 2.76-2.98 (m, 4H, H-10, 15), 6.99 (dd, J = 7.3, 1.6 Hz, 1H, H-5), 7.34-7.70 (m, 6H, H-3+C ₆ H ₅), 8.19 (dd, J = 7.3, 1.1 Hz, 1H, H-6)
2j	98	163.5-163.9	2190			1.33-1.84 (m, 8H, H-11-14), 2.76-2.97 (m, 4H, H-10, 15), 7.21 (dd, J = 7.3, 1.5 Hz, 1H, H-5), 7.41-7.83 (m, 5H, C ₆ H ₅), 7.85 (br s, 1H, H-3) 8.19 (br s, J = 7.3 Hz, 1H, H-6)
2k	95	130.6-131.0	2180		1650	1.29-1.88 (m, 8H, H-11-14), 2.81-2.96 (m, 4H, H-10, 15), 6.79 (dd, J = 7.2, 1.8 Hz, 1H, H-5), 7.78 (br s, 1H, H-3), 8.17 (dd, J = 7.2, 1.1 Hz, 1H, H-6)
2l	97	197.8-198.2	2190 2210			1.18-1.74 (m, 8H, H-11-14), 2.20 (s, 3H, CH ₃), 2.51 (s, 3H, CH ₃), 2.74-2.93 (m, 4H, H-10, 15), 6.46 (br s, 1H, H-4), 7.79 (br s, 1H, H-6)
2m	98	98.5-98.8	2180			1.32-1.86 (m, 8H, H-11-14), 2.85-2.99 (m, 4H, H-10, 15), 7.73 (d, J = 4.8 Hz, 1H, H-5), 8.01 (d, J = 4.9 Hz, 1H, H-6), 8.83 (s, 1H, H-3)
2n	96	119.3-119.7	2200			

Table 1 (continued)

Compound	Yield (%)	Mp (°C)	CN	IR (cm ⁻¹)	CO	¹ H NMR (δ)
2o	97	121.5-121.9	2200			1.26-1.85 (m, 8H, H-11-14), 2.70-2.96 (m, 4H, H-10, 15), 6.70 (dd, J = 8.9, 4.3, 1H, H-4), 7.68 (d, J = 8.9 Hz, 1H, H-3), 8.11 (d, J = 4.3 Hz, 1H, H-5)
2p	96	144.3-144.6	2190			1.22-1.94 (m, 8H, H-11-14), 2.80-3.22 (m, 4H, H-10, 15), 6.88 (d, J = 7.3 Hz, 1H, H-5), 7.20-7.65 (m, 3H, -CH=CH-CH-), 7.93 (d, J = 7.3 Hz, 1H, H-6), 8.25 (d, J = 7.8 Hz, 1H, -CH=)

Table 2

¹³C NMR Data of 8-Cyano-7-azatricyclo[7.6.0.0^{2,7}]pentadeca-1,3,5,8-tetraenes **2**

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-8	C-9	C-10, 11, 12, 13, 14 and 15					CN	C-α	Substituent
2a	114.0	137.9	116.8	120.6	111.8	125.2	93.1	133.7	21.9	24.0	25.5	25.7	30.2	30.7	114.4	
2b	112.6	138.3	115.3	131.4	114.5	124.7	92.3	134.1	21.9	24.1	25.5	25.8	30.2	30.8	114.8	21.1
2c	112.8	137.6	113.8	138.3	113.4	124.9	92.2	134.1	21.9	24.0	25.5	25.7	30.2	30.8	114.8	14.5 28.3
2d	112.7	136.0	114.6	138.1	113.6	124.7	92.1	134.0	21.8	24.0	25.4	25.7	30.1	30.7	114.7	13.6 23.4 37.4
2e	112.9	138.1	112.2	142.0	112.0	124.8	92.0	133.9	21.8	23.9	25.4	25.6	30.0	30.7	114.6	22.9 33.5
2f	113.2	138.1	111.1	144.4	110.9	124.6	91.9	133.7	21.8	23.9	25.4	25.7	30.0	30.7	114.6	30.3 34.4
2g	113.4	138.4	115.4	139.5	113.7	125.1	92.5	133.8	21.9	24.1	25.5	25.7	30.2	30.8	114.6	41.5 126.6 128.7 128.9 134.5
2h	119.5	138.7	119.5	129.1	109.0	124.7	96.0	132.1	22.2	24.0	25.4	25.6	30.4	30.5	113.2	195.3 26.1
2i	118.7	138.6	120.1	122.1	110.7	124.5	95.8	132.3	22.1	24.0	25.5	25.6	30.3	30.6	113.4	165.7 52.4
2j	114.4	138.6	113.7	138.7	111.6	125.3	92.9	133.7	22.0	24.1	25.5	25.7	30.2	30.7	114.8	126.4 127.9 129.0 133.9
2k	119.4	138.9	121.2	129.2	111.5	124.8	96.0	132.1	22.2	24.1	25.5	25.7	30.3	30.6	113.3	194.1 128.5 129.7 132.5 137.4
2l	119.0	139.4	123.5	103.3	131.3	125.5	97.0	131.3	22.1	24.0	25.4	25.5	30.2	30.5	112.5	118.0
2m	113.9	137.9	128.0	121.1	121.0	124.9	92.7	132.2	22.4	24.5	25.1	26.0	31.4	31.7	114.7	17.8 19.4
2n	118.0	137.9	128.9	—	143.0	95.8	128.0	21.7	23.8	25.4	25.5	30.4	30.4	112.3		
2o	114.2	136.0	124.7	112.6	142.2	—	127.2	21.7	23.7	25.4	25.5	30.4	30.5	112.8		
2p	117.5	138.9	128.7	126.2	112.2	127.9	95.3	129.2	23.3	25.0	25.6	26.1	28.5	31.8	114.0	123.0 126.8 127.4 127.3

For example, reactions of pyridinium dicyanomethylide (**1a**, 1.64 mmoles) with cyclooctyne (1.64 mmoles) in refluxing toluene for 1.5 hours gave, after spontaneous dehydrogenation and dehydrocyanation, 97% yield of the indolizine **2a**. The generality of the reactions is illustrated

Table 3

Analytical Data of 8-Cyano-7-azatricyclo[7.6.0.0^{2,7}]pentadeca-1,3,5,8-tetraene **2**

Compound	Found (%)			Elemental Analysis Calcd. (%)			Formula
	C	H	N	C	H	N	
2a	80.41	7.29	12.51	80.32	7.19	12.49	C ₁₅ H ₁₆ N ₂
2b	80.73	7.59	11.76	80.63	7.61	11.76	C ₁₆ H ₁₈ N ₂
2c	81.17	8.10	11.09	80.91	7.99	11.10	C ₁₇ H ₂₀ N ₂
2d	81.28	8.44	10.63	81.16	8.32	10.52	C ₁₈ H ₂₂ N ₂
2e	81.31	8.41	10.59	81.16	8.32	10.52	C ₁₈ H ₂₂ N ₂
2f	81.30	8.59	9.90	81.38	8.63	9.99	C ₁₉ H ₂₄ N ₂
2g	84.29	7.07	8.86	84.04	7.05	8.91	C ₂₂ H ₂₂ N ₂
2h	76.53	6.83	10.52	76.66	6.81	10.52	C ₁₇ H ₁₈ N ₂ O
2i	72.31	6.37	9.87	72.32	6.43	9.92	C ₁₇ H ₁₈ N ₂ O ₂
2j	84.21	6.67	9.31	83.96	6.71	9.33	C ₂₁ H ₂₀ N ₂
2k	80.38	6.09	8.45	80.46	6.14	8.53	C ₂₂ H ₂₀ N ₂ O
2l	76.91	5.94	16.93	77.08	6.07	16.85	C ₁₆ H ₁₆ N ₃
2m	80.67	7.86	10.99	80.91	7.99	11.10	C ₁₇ H ₂₀ N ₂
2n	74.79	6.71	18.62	74.64	6.71	18.65	C ₁₄ H ₁₅ N ₃
2o	74.86	6.71	18.57	74.64	6.71	18.65	C ₁₄ H ₁₅ N ₃
2p	83.14	6.55	10.08	83.18	6.61	10.21	C ₁₉ H ₁₈ N ₂

Table 4
Crystal Data for **2a**

Formula	C ₁₅ H ₁₆ N ₂
Crystal dimensions (mm)	0.36 x 0.50 x 0.56
M (amu)	224.30
Monoclinic space group	P2 ₁ /c (no. 14)
a (Å)	9.568 (4)
b (Å)	9.719 (3)
c (Å)	13.651 (2)
β (degree)	96.45 (2)
U (Å ³)	1261.4 (6)
Z	4
D _c (g cm ⁻³)	1.181
μ (cm ⁻¹)	0.79
F (000)	480
Radiation Mo-Kα, graphite monochromatized	λ = 0.71069 Å
Diffraction	Rigaku AFC5S
Orienting reflections, range	25, 35, 20° < 2θ < 39, 00°
T (K)	293
Scan method	ω-2θ
Data collection range	6.0° < 2θ < 55.0°
No. unique reflections	3075
No. of observed reflections with I > 3σ(I)	1114
No. of parameters	170
R [a]	9.0%
R _w [b]	9.5%
Largest shift/esd, final cycle	0.18
Largest positive peak (e Å ⁻³)	0.43
Largest negative peak (e Å ⁻³)	-0.51
[a] R = [Σ F _o l - F _c l]/Σ F _o l . [b] R _w = {[Σw(F _o l - F _c l) ²]/[Σw(F _o l) ²]} ^{1/2} .	
Weighting scheme: w = 4F _o ² /σ ² (F _o ²).	

Table 5
Bond Lengths (Å) and Bond Angles (deg) for **2a**

C(1)-C(2)	1.499(9)	C(9)-C(10)	1.333(8)
C(2)-C(3)	1.46(1)	C(10)-C(11)	1.414(9)
C(3)-C(4)	1.36(1)	C(11)-C(12)	1.363(9)
C(4)-C(5)	1.56(9)	C(12)-C(13)	1.418(8)
C(5)-C(6)	1.518(9)	C(13)-C(14)	1.391(8)
C(6)-C(7)	1.486(8)	C(14)-C(1)	1.508(7)
C(7)-C(8)	1.393(7)	C(14)-C(7)	1.389(7)
C(8)-N(1)	1.377(7)	C(8)-C(15)	1.414(7)
N(1)-C(13)	1.405(6)	C(15)-N(2)	1.140(7)
N(1)-C(9)	1.375(7)		
C(1)-C(2)-C(3)	118.0(5)	C(8)-N(1)-C(13)	107.2(4)
C(2)-C(3)-C(4)	125.6(8)	C(8)-C(15)-N(2)	179.4(7)
C(3)-C(4)-C(5)	126.8(8)	N(1)-C(8)-C(15)	121.4(5)
C(4)-C(5)-C(6)	114.1(6)	N(1)-C(9)-C(10)	119.4(5)
C(5)-C(6)-C(7)	114.8(5)	N(1)-C(13)-C(12)	116.4(5)
C(6)-C(7)-C(8)	125.3(5)	N(1)-C(13)-C(14)	108.1(4)
C(6)-C(7)-C(14)	127.2(5)	C(9)-N(1)-C(13)	122.7(4)
C(7)-C(8)-N(1)	109.1(4)	C(9)-C(10)-C(11)	120.8(5)
C(7)-C(8)-C(15)	129.4(5)	C(10)-C(11)-C(12)	120.2(6)
C(7)-C(14)-C(1)	126.2(5)	C(11)-C(12)-C(13)	120.4(5)
C(7)-C(14)-C(13)	108.0(4)	C(12)-C(13)-C(14)	135.4(5)
C(8)-C(7)-C(14)	107.6(5)	C(13)-C(14)-C(1)	125.8(5)
C(8)-N(1)-C(9)	130.1(4)	C(14)-C(1)-C(2)	113.8(5)

Table 6
Atomic Coordinates ($\times 10^5$) and B(eq) (Å²) for **2a**

	X	Y	Z	B(eq)
N(1)	15531(41)	60592(43)	46586(27)	2.9(2)
N(2)	8079(65)	41934(61)	24896(36)	6.9(3)
C(1)	29271(65)	41206(65)	69193(39)	4.9(3)
C(2)	45006(66)	40270(76)	70646(43)	5.8(4)
C(3)	52011(78)	3339(11)	63058(61)	9.7(6)
C(4)	48018(81)	21244(99)	58684(89)	12.9(7)
C(5)	37974(73)	19221(69)	48926(52)	6.4(4)
C(6)	22854(64)	23463(59)	49655(42)	4.6(3)
C(7)	20640(52)	38510(55)	50666(37)	3.2(2)
C(8)	15696(55)	47349(54)	43019(36)	3.3(3)
C(9)	11390(54)	72650(56)	41846(39)	3.7(3)
C(10)	12361(65)	84449(61)	46859(46)	4.9(3)
C(11)	17310(70)	84662(63)	57015(49)	5.5(3)
C(12)	21045(64)	72718(65)	61844(41)	4.7(3)
C(13)	20432(53)	60042(58)	56677(35)	3.4(3)
C(14)	23439(53)	46393(56)	59146(36)	3.4(3)
C(15)	11545(61)	44368(61)	32974(41)	4.4(3)

the energy difference between dicyanomethylide(LUMO)-cyclooctyne(HOMO) are smaller than those of dicyanomethylide(HOMO)-cyclooctyne(LUMO).

in Table 1. The yields were excellent in all the cases. The elemental analyses as well as ir, ¹H and ¹³C nmr spectra are in agreement with structure **2** (Tables 1-3). Furthermore, the structure **2a** was unambiguously confirmed by an X-ray analysis as shown in Figure 1 (Tables 4-6). The structure shows no marked distortions from typical bond lengths and bond angles, though there was observed the considerable anisotropy of thermal motion of the cyclooctene moiety.

The values of HOMO and LUMO energy of pyridinium dicyanomethylides **1a-l** and cyclooctyne were calculated by semiempirical molecular orbital calculations such as a PM3 method (CACHe) [13]. The results are summarized in Table 7. The reactions are apparently controlled by dipole(LUMO)-cyclooctyne(HOMO) since the values of

EXPERIMENTAL

General.

Melting points were taken on a Yanagimoto micro melting point apparatus and were uncorrected. The ¹H nmr spectra were measured either on a JEOL JNM-EX270 (270 MHz), or JNM-ALPHA500 (500 MHz) instrument. The ¹³C nmr spectra were recorded either on a JNM-EX270 or JNM-ALPHA500 pulsed Fourier-transform spectrometer operating at 67.80 Hz and 125.65 Hz, respectively. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Either partial proton decoupling or DEPT method was used to distinguish between individual carbon atoms. Preparative medium-pressure liquid chromatography was carried out using a column

Table 7

HOMO and LUMO Energies (eV) of Pyridinium Dicyanomethylides **1a-l** and cyclooctyne and Energy Differences (eV) of HOMO (Ylide)-LUMO (Octyne) and LUMO (Ylide)-HOMO (Octyne)

Compound	HOMO energy	LUMO energy	HOMO(Ylide)-LUMO(Octyne)	LUMO(Ylide)HOMO(Octyne)
1a	-8.653	-1.473	9.817	8.693
1b	-8.544	-1.456	9.708	8.710
1c	-8.522	-1.431	9.686	8.735
1d	-8.520	-1.431	9.684	8.735
1e	-8.544	-1.434	9.708	8.732
1f	-8.535	-1.411	9.699	8.755
1g	-8.537	-1.463	9.701	8.703
1h	-8.879	-1.919	10.043	8.247
1i	-8.487	-1.488	9.651	8.678
1j	-8.463	-1.697	9.627	8.469
1k	-8.835	-1.877	9.999	8.289
1l	-9.001	-2.092	10.165	8.074
Cyclooctyne	-10.166	1.164		

(25 x 310 mm) prepacked with silica gel (Lobar, LiChroprep Si60, Merck).

Pyridinium Dicyanomethylides **1a-p** were prepared according to the method by Linn *et al.* who reported pyridinium dicyanomethylide (**1a**) as early as 1965 [14]. The compounds **1b-p** were described by us in the previous reports [9,10] without micro-analytical and spectroscopic data. Therefore, on this occasion, selected physical and spectroscopic data are given as follows.

Compound **1b** was obtained in 85% yield, mp 221-222°; uv (chloroform): λ_{\max} (log ϵ) 406 (4.526), 241 (3.780) nm; ir (potassium bromide disk): 2135, 2170, 2176 cm^{-1} ; ^1H nmr: δ 2.50 (s, 3H, CH_3), 7.41 (d, $J = 6.9$ Hz, 2H, H-3, 5), 8.36 (d, $J = 6.9$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 57.2 (ylidic C), 118.6 (CN), 133.2 (C-2, 6), 128.2 (C-3, 5), 147.2 (C-4), 20.1 (CH_3).

Anal. Calcd. for $\text{C}_9\text{H}_7\text{N}_3$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.74; H, 4.37; N, 26.63.

Compound **1c** was obtained in 65% yield, mp 169-171°; uv (chloroform): λ_{\max} (log ϵ) 405 (4.204), 240 (3.330) nm; ir (potassium bromide disk): 2135, 2174, 2183 cm^{-1} ; ^1H nmr: δ 1.31 (t, $J = 7.6$ Hz, 3H, CH_3), 2.78 (q, $J = 7.6$ Hz, 2H, CH_2), 7.42 (d, $J = 7.0$ Hz, 2H, H-3, 5), 8.37 (d, $J = 7.0$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 57.6 (ylidic C), 118.9 (CN), 133.5 (C-2, 6), 131.3 (C-3, 5), 152.7 (C-4), 26.1 (CH_2), 13.6 (CH_3).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{N}_3$: C, 70.16; H, 5.30; N, 24.54. Found: C, 70.40; H, 5.16; N, 24.56.

Compound **1d** was obtained in 68% yield, mp 119-120°; uv (chloroform): λ_{\max} (log ϵ) 407 (4.069), 242 (3.186) nm; ir (potassium bromide disk): 2125, 2165, 2175 cm^{-1} ; ^1H nmr: δ 0.99 (t, $J = 7.3$ Hz, 3H, CH_3), 1.71 (sextet, $J = 7.3, 7.6$ Hz, 2H, CH_2), 2.70 (t, $J = 7.6$ Hz, 2H, CH_2), 7.39 (d, $J = 7.0$ Hz, 2H, H-3, 5), 8.37 (d, $J = 7.0$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 35.7 (CH_2), 57.6 (ylidic C), 118.7 (CN), 133.4 (C-2, 6), 127.6 (C-3, 5), 151.2 (C-4), 35.7, 22.7 (CH_2), 13.1 (CH_3).

Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_3$: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.06; H, 5.92; N, 22.42.

Compound **1e** was obtained in 72% yield, mp 160-161°; uv (chloroform): λ_{\max} (log ϵ) 408 (4.313), 330 (3.166), 242 (3.687) nm; ir (potassium bromide disk): 2123, 2155 cm^{-1} ; ^1H nmr: δ 1.31 (d, $J = 6.8$ Hz, 6H, CH_3), 3.02 (hept, $J = 6.8$ Hz, 1H, CH), 7.44 (d, $J = 7.0$ Hz, 2H, H-3, 5), 8.38 (d, $J = 7.0$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 57.6 (ylidic C), 119.0 (CN), 133.8 (C-2, 6), 126.0 (C-3, 5), 156.9 (C-4), 32.6 (CH), 22.2 (CH_3).

Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_3$: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.53; H, 5.95; N, 22.75.

Compound **1f** was obtained in 66% yield, mp 139-140°; uv (chloroform): λ_{\max} (log ϵ) 407 (4.395), 320 (2.804), 242 (3.594) nm; ir (potassium bromide disk): 2120, 2180 cm^{-1} ; ^1H nmr: δ 1.36 (s, 9H, CH_3), 7.56 (d, $J = 7.3$ Hz, 2H, H-3, 5), 8.39 (d, $J = 7.3$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 57.7 (ylidic C), 118.8 (CN), 133.4 (C-2, 6), 125.0 (C-3, 5), 159.1 (C-4), 35.2 (C), 29.7 (CH_3).

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{N}_3$: C, 72.34; H, 6.58; N, 21.09. Found: C, 72.62; H, 6.64; N, 21.37.

Compound **1g** was obtained in 66% yield, mp 163-164°; uv (chloroform): λ_{\max} (log ϵ) 411 (4.356), 320 (3.253), 242 (3.642), 260 (3.114) nm; ir (potassium bromide disk): 2125, 2156 cm^{-1} ; ^1H nmr: δ 4.06 (s, 2H, CH_2), 7.15 (d, $J = 6.8$ Hz, 2H, H-3, 5), 7.3-7.4 (m, 5H, Ar), 8.35 (d, $J = 6.8$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 57.5 (ylidic C), 118.3 (CN), 137.7 (C-2, 6), 128.1 (C-3, 5), 149.3 (C-4), 40.5 (CH_2), 128.6, 128.4, 126.4, 133.3 (each Phenyl-C).

Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{N}_3$: C, 77.23; H, 4.75; N, 18.01. Found: C, 77.46; H, 4.56; N, 18.02.

Compound **1h** was obtained in 90% yield, mp 191-192°; uv (chloroform): λ_{\max} (log ϵ) 465 (4.094), 350 (2.559), 250 (3.235) nm; ir (potassium bromide disk): 2126, 2155, 1678 cm^{-1} ; ^1H nmr: δ 2.63 (s, 3H, CH_3), 7.95 (d, $J = 7.3$ Hz, 2H, H-3, 5), 8.45 (d, $J = 7.3$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 60.3 (ylidic C), 116.4 (CN), 131.9 (C-2, 6), 125.6 (C-3, 5), 137.1 (C-4), 193.8 (CO), 26.0 (CH_3).

Anal. Calcd. for $\text{C}_{10}\text{H}_7\text{N}_3\text{O}$: C, 64.86; H, 3.81; N, 22.69. Found: C, 65.02; H, 3.60; N, 22.75.

Compound **1i** was obtained in 68% yield, mp 220-221°; uv (chloroform): λ_{\max} (log ϵ) 454 (4.315), 348 (2.892), 253 (3.607), 242 (3.543) nm; ir (potassium bromide disk): 2145, 2172, 1734 cm^{-1} ; ^1H nmr: δ 3.99 (s, 3H, CH_3), 8.04 (d, $J = 7.0$ Hz, 2H, H-3, 5), 8.44 (d, $J = 7.0$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 60.3 (ylidic C), 116.3 (CN), 131.9 (C-2, 6), 126.6 (C-3, 5), 131.1 (C-4), 162.4 (CO), 42.8 (OCH_3).

Anal. Calcd. for $\text{C}_{10}\text{H}_7\text{N}_3\text{O}_2$: C, 59.70; H, 3.51; N, 20.89. Found: C, 59.79; H, 3.26; N, 21.07.

Compound **1j** was obtained in 84% yield, mp >300°; uv (chloroform): λ_{\max} (log ϵ) 439 (4.221), 350 (2.855), 248 (3.556), 282 (3.520), 260 (3.523) nm; ir (potassium bromide disk): 2140, 2175 cm^{-1} ; ^1H nmr: δ 7.54-7.57 (m, 3H, Ar), 7.64-7.68 (m, 2H, Ar), 7.78 (d, $J = 7.2$ Hz, 2H, H-3, 5), 8.47 (d, $J = 7.2$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 61.5 (ylidic C), 118.0 (CN), 133.1 (C-2, 6), 126.5 (C-3, 5), 144.1 (C-4), 133.9 (*ipso*-C), 130.2 (*o*-CH), 129.1 (*m*-CH), 124.3 (*p*-CH).

Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{N}_3$: C, 76.70; H, 4.14; N, 19.17. Found: C, 76.85; H, 3.98; N, 19.07.

Compound **1k** was obtained in 62% yield, mp 223-224°; uv (chloroform): λ_{\max} (log ϵ) 467 (4.467), 350 (2.971), 260 (3.891), 275 (3.709), 241 (3.833) nm; ir (potassium bromide disk): 2128, 2170, 1650 cm^{-1} ; ^1H nmr: δ 7.56 (q, $J = 7.3, 7.6$ Hz, 2H, Ar), 7.69 (d, $J = 7.3$ Hz, 1H, Ar), 7.76 (d, $J = 7.6$ Hz, 2H, Ar), 7.89 (d, $J = 7.3$ Hz, 2H, H-3, 5), 8.47 (d, $J = 7.3$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 60.6 (ylidic C), 116.5 (CN), 133.2 (C-2, 6), 131.9 (C-3, 5), 138.0 (C-4), 190.9 (CO), 135.2 (*ipso*-C), 129.2 (*o*-CH), 128.5 (*m*-CH), 127.1 (*p*-CH).

Anal. Calcd. for $\text{C}_{15}\text{H}_9\text{N}_3\text{O}$: C, 72.87; H, 3.67; N, 17.00. Found: C, 73.09; H, 3.64; N, 17.04.

Compound **1l** was obtained in 40% yield, mp 215°; uv (chloroform): λ_{\max} (log ϵ) 272 (4.502) nm; ir (potassium bromide disk): 2153, 2180, 2225 cm^{-1} ; ^1H nmr: δ 7.64 (d, $J = 7.3$ Hz, 2H, H-3, 5), 8.40 (d, $J = 7.3$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 62.1 (ylidic C), 115.5 (CN), 131.6 (C-2, 6), 129.7 (C-3, 5), 115.8 (C-4), 112.2 (CN).

Anal. Calcd. for $\text{C}_9\text{H}_4\text{N}_4$: C, 64.28; H, 2.40; N, 33.32. Found: C, 64.35; H, 2.20; N, 33.21.

Compound **1m** was obtained in 63% yield, mp 256-257°; uv (chloroform): λ_{\max} (log ϵ) 407 (4.147), 256 (3.768), 250 (3.710) nm; ir (potassium bromide disk): 2110, 2145, 2172 cm^{-1} ; ^1H nmr: δ 2.39 (s, 6H, CH_3), 7.19 (s, 1H, H-4), 8.14 (s, 2H, H-2, 6); ^{13}C nmr: δ 57.5 (ylidic C), 118.3 (CN), 136.3 (C-2, 6), 137.5 (C-3, 5), 130.3 (C-4), 17.6 (CH_3).

Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{N}_3$: C, 70.16; H, 5.30; N, 24.54. Found: C, 70.44; H, 5.10; N, 24.53.

Compound **1n** was obtained in 61% yield, mp 258-260°; uv (chloroform): λ_{\max} (log ϵ) 433 (4.014), 255 (3.854) nm; ir (potassium bromide disk): 2270, 2295 cm^{-1} ; ^1H nmr: δ 8.19 (d, $J = 4.9$ Hz, 2H, H-3, 5), 8.61 (d, $J = 4.9$ Hz, 2H, H-2, 6); ^{13}C nmr: δ 65.8 (ylidic C), 114.7 (CN), 123.3 (C-2, 6), 148.1 (C-3, 5).

Anal. Calcd. for $C_7H_4N_4$: C, 58.63; H, 2.52; N, 38.82 Found: C, 58.49; H, 2.80; N, 38.87.

Compound **1o** was obtained in 42% yield, mp 206-207°; uv (chloroform): λ_{max} (log ϵ) 428 (3.608), 240 (2.741) nm; ir (potassium bromide disk): 2260, 2285 cm^{-1} ; 1H nmr: δ 7.06 (dd, $J = 5.4, 7.8$ Hz, 1H, H-5), 7.69 (dd, $J = 7.0, 7.8$ Hz, 1H, H-4), 8.48 (d, $J = 7.0$ Hz, 1H, H-3), 8.65 (d, $J = 5.4$ Hz, 1H, H-6); ^{13}C nmr: δ 66.0 (ylidic C), 115.6 (CN), 151.7 (C-3), 134.1 (C-4), 121.7 (C-5), 130.1 (C-6).

Anal. Calcd. for $C_7H_4N_4$: C, 58.63; H, 2.52; N, 38.82. Found: C, 58.52; H, 2.73; N, 38.85.

Compound **1p** was obtained in 64% yield, mp 258-259°; uv (chloroform): λ_{max} (log ϵ) 450 (4.184), 381 (3.956), 310 (3.773), 299 (3.608), 242 (3.883), 272 (3.507), 263 (3.571), 250 (3.657) nm; ir (potassium bromide disk): 2123, 2155 cm^{-1} ; 1H nmr: δ 7.78-7.81 (m, 2H, H-8, 9), 7.87-7.92 (m, 3H, H-4, 6, 7), 8.36 (d, $J = 7.0$ Hz, 1H, H-3), 8.99 (br s, 1H, H-1); ^{13}C nmr: δ 58.3 (ylidic C), 120.0 (CN), 133.5 (C-2), 128.3 (C-3), 127.8 (C-4), 127.4 (C-5), 130.5 (C-6), 126.7 (C-7), 131.5 (C-8), 118.3 (C-9), 132.3 (C-10).

Anal. Calcd. for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.41; H, 3.48; N, 21.60.

General Procedure for the Reactions of Dicyanomethylides **1a-p** with cyclooctyne.

A mixture of **1** (0.50 mmole) and cyclooctyne (0.11 g, 1.00 mmole) was heated in refluxing toluene (10 ml) for 6-24 hours. After evaporation of the solvent *in vacuo*, the residue was chromatographed on silica gel (30 g) with hexane-dichloromethane (1:1) to give the corresponding indolizines **2**. The results are summarized in Tables 1-3.

Crystal Structure Determination.

Summary of the crystal data and structure refinement details are given in Table 5. The structure was solved by a direct method [15], and refined by full matrix least squares. The atoms other than hydrogen were refined anisotropically. The atomic scattering factors for all atoms and the anomalous dispersion correction factors for atoms other than hydrogen were taken from the literature [16-18]. All calculations were performed using the TEXSAN [19] crystallographic software package of the Molecular Structure Corporation.

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