The Reaction of 2-Chloroazulene Derivatives with Lithium Acetylide in Liquid Ammonia

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The reaction of diethyl 2-chloroazulene-1,3-dicarboxylate (**1a**) with lithium acetylide in liq ammonia gave diethyl 4- and 6-ethynylazulene-1,3-dicarboxylates by an abnormal substitution reaction. In a similar manner, some 2-chloroazulenes, possessing alkoxycarbonyl and/or cyano substituents at the 1- and 3-positions of azulene nucleus, gave the corresponding 4 (or 8)- and 6-ethynylazulenes. The same type reaction proceeded when lithium phenylacetylide, sodium indenide, and sodium fluorenide were used as the reagents, **1a** giving diethyl 4- and 6-(phenylethynyl)-, 6-(3-indenyl)-, and 6-(9-fluorenyl)azulene-1,3-dicarboxylates, respectively.

The halogeno substituents of haloazulenes are directly replaced by some nucleophilic reagents, such as alkoxides, amines, thiolates, or carbanions derived from active methylene compounds, to give the corresponding "normal substitution products."[1-3] On the other hand, no replacement of the chloro substituent occurred in the reaction of 2-chloroazulene derivatives with Grignard reagents.[4] Addition of the reagents took place at the 4- or 6-position with formation of the dihydrozulene-type addition products, whose dehydrogenation with tetrachloro-*o*-benzoquinone afforded 4- and 6-substituted azulene derivatives in which the chloro substituent at the 2-position remained.

We have recently found a third type of reaction of haloazulene derivatives with nucleophilic reagents; the reaction of 2-chloroazulene derivatives with alkali metal acetylide in liq ammonia yielded 4- and 6-ethynylazulene derivatives by an abnormal substitution reaction.[5] This paper describes the details of the reaction of 2-chloroazulene derivatives with lithium acetylide and its related carbanions in liq ammonia.

Results and Discussion

Diethyl 2-chloroazulene-1,3-dicarboxylate (**1a**),[2] when allowed to react with lithium acetylide in liq ammonia at −40 °C for 1 h, gave a mixture of diethyl 4- (**2a**) and 6-ethynylazulene-1,3-dicarboxylates (**3a**) in good yields. A similar result was obtained with use of sodium acetylide instead of lithium acetylide. 2-Chloroazulenes (**1b**, **1c**, **1d**, and **1e**) also readily reacted with lithium acetylide to give mixtures of isomeric 4-, 6-, and 8-ethynylazulenes (**2b**, **3b**, and **4b**), (**2c** and **3c**), (**2d** and **4d**), and (**2e** and **4e**), respectively. Each product was isolated from a mixture by silica-gel chromatography (Table 1).

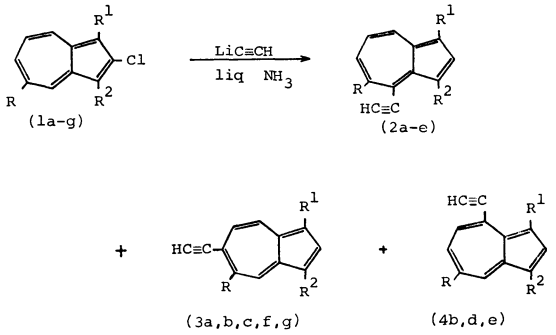
The structures of the ethynylazulene derivatives were determined on the basis of spectral data (Tables 2, 3, and 4), as well as the results of elemental analyses. The electronic spectra indicate that the compounds are azulene derivatives.[6] The presence of the ethynyl group is shown by the sharp absorption bands in IR spectra corresponding to the $\nu_{C\equiv C}$ and $\nu_{\equiv CH}$ (ethynylic). The NMR spectra also reveal the singlets assignable to ethynylic protons. The positions of the substituents in the compound are deduced from the NMR signal patterns corresponding to the ring protons: an AA'BB'-type signal is found in the NMR spectra of symmetrical 6-ethynyl derivatives (**3a**, **c**) and two AB-type signals with long-range coupling in the unsymmetrical 6-ethynyl derivative (**3b**), together with a singlet due to H-2.

Table 1. Reaction of 2-chloroazulene derivatives with lithium acetylides

2-Chloro-azulene derivatives	Products (yield/%)		
	4-Ethynyl-	6-Ethynyl-	8-Ethynyl-
1a	**2a** (25.2)	**3a** (35.7)	
1b	**2b** (30.7)	**3b** (25.6)	**4b** (1)
1c	**2c** (44.5)	**3c** (4.9)	
1d	**2d** (73.3)		**4d** (4.5)
1e	**2e** (43.2)		**4e** (14.9)
1f		**3f** (58.3)	
1g		**3g** (39.9)	
1a	**5** (44.8)[a]	**6** (38.3)	

a) (Phenylethynyl)azulene.

On the other hand, a complex multiplet due to the adjacent four-proton system is found in the spectra of 4- (**2a**, **b**, **c**, **d**, **e**) and 8-ethynyl derivatives (**4b**, **d**, **e**), together with a singlet due to H-2 (**2a**, **b**, **c**) or an AB-type signal due to H-2 and H-3 (**2d**, **e** and **4d**, **e**). The structural correlations between pairs of the isomeric 4-ethynyl (**2b**, **d**, **e**) and 8-ethynyl derivatives (**4b**, **d**, **e**) were confirmed by the fact that the NMR peaks corre-



a: R=H, $R^1=R^2=CO_2Et$
b: R=H, $R^1=CO_2Me$, $R^2=CN$
c: R=H, $R^1=R^2=CN$
d: $R=R^2=H$, $R^1=CO_2Et$
e: $R=R^2=H$, $R^1=CN$
f: R=Me, $R^1=R^2=CO_2Et$
g: R=*iso*-Pr, $R^1=R^2=CO_2Et$

Table 2. Electronic spectral data of ethynylazulene derivatives

Compound	Solvent	λ_{max} nm (log ε)				
2a	Cyclohexane	254(4.48)	272(4.32)^{sh}	309(4.50)	320(4.52)	370(3.88)
		388(3.90)	565(2.86)			
3a	Cyclohexane	230(4.57)	270(4.36)	305(4.78)^{sh}	320(5.00)	353(4.17)
		378(3.92)	514(2.68)	540(2.76)	582(2.68)	644(2.27)
2b	Cyclohexane	250(4.39)	263(4.06)	278(4.13)	315(4.31)	360(3.62)
		390(3.65)	540(2.62)^{sh}	558(2.67)	605(2.61)	655(2.26)
3b	Chloroform	260(4.09)	309(4.67)^{sh}	317(4.78)^{sh}	321(4.87)^{sh}	345(4.05)
		353(4.10)	358(4.08)	376(3.61)	545(2.77)	580(2.70)^{sh}
4b	Cyclohexane	265(4.40)	310(4.60)^{sh}	318(4.64)	365(3.95)	383(3.78)
		578(2.81)				
2c	Chloroform	245(4.46)	275(4.33)	310(4.50)	325(4.44)^{sh}	355(3.95)
		365(3.91)	373(3.87)	382(3.99)	440(3.38)	530(2.88)^{sh}
		550(2.90)	560(2.88)	600(2.71)	640(2.39)	650(2.32)^{sh}
3c	Chloroform	260(2.79)	310(4.23)	324(4.36)	353(3.70)	370(3.71)
		380(3.66)	450(2.36)	525(2.48)	570(2.39)	600(2.67)
		620(2.07)	640(1.98)			
2d	Cyclohexane	265(4.38)	304(4.70)	318(4.75)	365(3.77)	375(3.61)
		387(3.65)	576(2.67)	628(2.56)		
4d	Cyclohexane	270(4.49)	305(4.50)	350(3.57)	363(3.65)	380(3.10)
		440(2.30)	550(2.51)	605(2.62)	660(2.50)	
2e	Chloroform	268(4.62)	303(4.72)	317(4.74)	353(3.72)	367(3.78)
		370(3.65)	382(3.58)	460(2.17)	505(2.47)	575(2.70)
		620(2.60)				
4e	Chloroform	272(4.65)	303(4.59)	315(4.58)	350(3.75)	360(3.82)
		378(3.73)	580(2.77)	630(2.68)		
3f	Cyclohexane	237(4.42)	276(4.27)	313(4.70)^{sh}	325(4.84)	355(4.40)
		382(3.82)	552(2.86)	590(2.80)^{sh}	645(2.46)^{sh}	
3g	Cyclohexane	240(4.66)	275(4.40)	318(4.83)^{sh}	323(4.91)	354(4.16)
		383(3.97)	549(2.89)	585(2.83)	645(2.44)	
5	Cyclohexane	255(4.53)	300(4.51)	365(4.36)	570(3.02)	590(3.00)
6	Methanol	235(4.54)	270(4.14)	310(4.43)^{sh}	348(4.70)	530(2.99)

Table 3. IR spectral data of ethynylazulene derivatives (KBr tablet, in cm^{-1})

Compound	$\nu_{C\equiv CH}$	$\nu_{C\equiv C}$	$\nu_{C\equiv N}$	COOR			
2a	3230	2090		1690	1200	1049	1031
3a	3230	2090		1690	1190	1044	
2b	3250	2100	2220	1696	1210	1040	
3b	3260	2090	2200	1697	1210	1041	
4b[a)]	3250	2100	2220	1725			
2c	3230	2090	2220				
3c	3260	2100	2220				
2d	3300	2090		1685	1220	1042	
4d	3330	2100		1710	1210	1025	
2e	3270	2090	2200				
4e	3240	2090	2220				
3f	3250	2090		1680	1210	1040	1028
3g	3250	2090		1680	1200	1041	1028
5		2200		1712	1210	1040	
				1690	1190	1017	
6		2208		1684	1203	1037	

a) In chloroform.

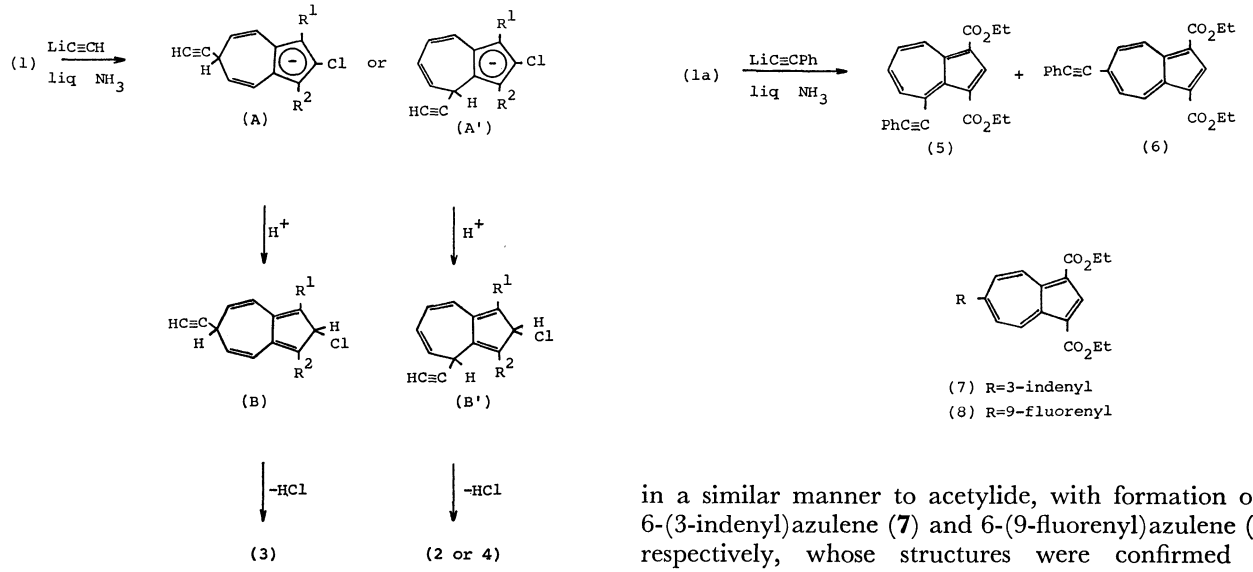
sponding to H-8 of 4-ethynyl derivatives are found at lower field, because of the diamagnetic anisotropy due to the CO_2R or CN group in the peri-position, than those corresponding to H-4 of 8-ethynyl derivatives. In a similar manner to that of **1a**, 5-alkyl-2-chloroazulenes (**1f**[7] and **1g**[8]) also reacted with lithium acetylide to give the 6-ethynylazulenes (**3f**) and (**3g**), respectively. In these cases only 6-ethynyl derivatives, whose structures were confirmed by spectral data (Tables 2, 3, and 4), were obtained in spite of the presence of the alkyl group at the 5-position of the azulene nucleus.

From the results, it was found that the reaction of 2-chloroazulenes (**1a—g**) with lithium acetylide in liq ammonia gave no 2-ethynylazulene derivatives, normal substitution product, but 4(or 8)- and 6-ethynylazulenes, abnormal substitution products, which were formed in such a way that the reagent entering into a position not that at which the leaving chloro substituent was attached. A mechanism for this abnormal substitution reaction seems to involve the additional-elimination process (Scheme 1). The acetylide attacks 2-chloroazulenes (**1**) at the 4(or 8) or 6-position of the azulene nucleus to give an anionic intermediate (**A** or **A'**) of a cyclopentadienide structure. Such attack of the reagent would be facilitated by the aid of electron-withdrawing alkoxycarbonyl or cyano groups at the 1- and/or 3-positions, because of stabilization of the anion (**A** or **A'**). This is supported by the fact that 2-chloroazulene did not react with acetylide under the same conditions.

TABLE 4. NMR SPECTRAL DATA OF ETHYNYLAZULENE DERIVATIVES
(at 60 MHz, in $CDCl_3$, Chemical shifts in δ/ppm from TMS, J/Hz)

Compound	C≡CH	Ring protons							$J_{2,3}$	$J_{4,5}$	$J_{7,8}$	OCH_2-CH_3 J=7.0 (Others)
		H_2	H_3	H_4	H_5	H_6	H_7	H_8				
2a	3.77s	8.58s			7.50	—	7.90m	9.80m				4.49q 1.40t 1.42t
3a	3.47s	8.78s		9.63d	7.83d		7.83d	9.63d		11.0	11.0	4.43q 1.46t
2b	4.07s	8.58s			7.80	—	7.95m	9.82m				(3.98s OCH_3)
3b[a]	3.56s	8.52s		8.62d	7.86dd		7.92dd	9.63d		10.2	10.5	(3.96s OCH_3)
4b	3.88s	8.30s		8.77m	7.63	—	8.00m					(3.95s OCH_3)
2c[b]	4.15s	8.36s			7.66	—	8.00m	8.76d			9.3	
3c	4.18s	8.28s		8.34d	7.59d		7.59d	8.34d		10.0	10.0	
2d	3.58s	8.27s	7.51d		7.20	—	7.57m	9.63m	4.0			4.38q 1.43t
4d	3.78s	8.23d	7.40d	8.53d	7.33	—	7.60m		4.0	11.0		4.40q 1.43t
2e	3.76s	8.10d	7.55d		7.35	—	7.80m	8.67d	4.0		10.0	
4e	3.96s	8.12d	7.33d	8.46d	7.23	—	7.78m		4.0	10.0		
3f	3.76s	8.76s		9.80s			7.88d	9.46d			10.5	4.43q 1.45t (2.90s CH_3 on C-5)
3g	3.71s	8.80s		10.27s			7.92d	9.45d			11.0	4.42q 1.43t 4.43q 1.45t (4.02sept 1.46d $CH(CH_3)_2$)
5		8.56s			7.28	—	7.87m	9.76m				4.40q 1.42t on C-1 4.29q 1.29t on C-3 (7.2—7.8 C_6H_5)
6		8.60s		9.85d	8.00d		8.00d	9.45d		11.0	11.0	4.50q 1.40t (7.4—7.7 C_6H_5)

Multiplicity, s: singlet; d: doublet; t: triplet; q: quartet; sept: septet; m: multiplet.
a) 100 MHz. b) Pulse Fourier transform mode.



Scheme 1. A mechanism for the reaction of 2-Chloroazulene derivatives with lithium acetylide.

Dehydrochlorination from the protonated intermediate (**B** or **B'**), produced from the anion (**A** or **A'**) afforded 4(or 8)-ethyl- (**2** or **4**) or 6-ethynylazulenes (**3**). The same type of reaction proceeded when lithium phenylacetylide was used as a reagent instead of lithium acetylide; **1a** easily reacted with this reagent to give 4-(phenylethynyl)- (**5**) and 6-(phenylethynyl)azulene (**6**) in 44.8 and 38.3% yields, respectively. The structures of these products were determined on the basis of spectral data (Tables 2, 3, and 4).

Sodium indenide and fluorenide also reacted with **1a** in a similar manner to acetylide, with formation of a 6-(3-indenyl)azulene (**7**) and 6-(9-fluorenyl)azulene (**8**), respectively, whose structures were confirmed by spectral data (Experimental).

It is evident that such bulky groups could attack only the less hindered 6-position rather than the more hindered 4(or 8)-position with two ethoxycarbonyl groups in the peri-position.

Experimental

Melting points are uncorrected. The electronic spectra were measured on a Hitachi EPS-3 Spectrometer and IR spectra on a Shimadzu IR-27 infracord. The NMR spectra were measured with a Varian A-60D Spectrometer; in some cases on a JNM-100 instrument in the Fourier transform mode. TMS was used as an internal standard. The mass spectra were recorded on Hitachi RMU-6 mass spectrometer

at 25 eV. The THF employed was distilled from calcium hydride before use.

*Methyl 2-Chloro-3-cyanoazulene-1-carboxylate (**1b**).* Dry HCl gas was bubbled into a benzene solution (600 ml) of methyl 2-amino-3-cyanoazulene-1-carboxylate[9] (4.5 g, 19.9 mmol) at 5 °C for 15 min. To the solution was added isopentyl nitrite (4.5 g) with stirring. After stirring for 2 d at room temp, water (600 ml) was added to the mixture. The reaction mixture was extracted with benzene. The organic layer was washed with water, satd. $NaHCO_3$ aq, dried (Na_2SO_4), and evaporated to give a reddish brown residue. Chromatography (alumina, with benzene) of the residue gave **1b** (4.3 g, 87.95 mmol), red prisms (from ethanol), mp 207—209 °C; λ_{max} (chloroform), nm (log ε): 297 (4.89), 307 (4.98), 353 (4.15), 370 (3.99), 496 (3.09), 510 (3.08); IR (KBr) 2210 (C≡N), 1690 cm^{-1} (C=O); NMR ($CDCl_3$): δ 4.03 (s, CO_2Me), 7.67—8.27 (m, H-5,6, and 7), 8.72 (dm, J=10 Hz, H-4), 9.75 (dm, J=10 Hz, H-8). Found: C, 63.48; H, 3.14; N, 5.56%. Calcd for $C_{13}H_8ClNO_2$: C, 63.55; H, 3.28; N, 5.70%.

*2-Chloro-1,3-dicyanoazulene (**1c**).* A mixture of 1,3-dicyano-2-hydroxyazulene[10] (100 mg, 0.54 mmol), $POCl_3$ (5 ml), and a trace of pyridine was heated in a sealed tube at 150 °C for 8 h. After distillation of excess $POCl_3$, the residue was treated with ice and water, and extracted with a large amount of chloroform. The organic extract was washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed on alumina with chloroform to give **1c** (84 mg, 73.4%), red prisms (from ethanol), mp over 300 °C. $\lambda_{max}^{chloroform}$ nm (log ε): 297 (4.70), 310 (4.83), 347 (3.89), 353 (3.89), 372 (3.71), 498 (2.86), 520 (2.85). IR (KBr): 2200 cm^{-1} (C≡N). Found: C, 67.67; H, 3.32; N, 13.36%. Calcd for $C_{12}H_5ClN_2$: C, 67.78; H, 3.37; N, 13.18%.

*2-Chloro-1-cyanoazulene (**1e**).* A mixture of **1b** (2.0 g) and 75% H_2SO_4 (40 ml) was heated at 70 °C until the evolution of CO_2 ceased, and the mixture was poured into ice and water, and then extracted with chloroform. The organic layer was washed with satd. NaCl aq, dried (Na_2SO_4), and concentrated to give a red residue. Chromatography of the residue on alumina with chloroform gave **1e** (1.3 g, 85%), red needles (from ethanol), mp 160—162 °C. $\lambda_{max}^{chloroform}$ nm (log ε): 290 (4.78), 303 (4.88), 340 (3.74), 353 (3.86), 365 (3.47), 520 (2.72), 550 (2.69). IR (KBr): 2200 cm^{-1} (C≡N). NMR ($CDCl_3$): δ 7.30 (s, H-3), 7.67—8.07 (m, H-5—7), 8.50 (dm, J=10 Hz, H-4), 8.70 (dm, J=10 Hz, H-8). Found: C, 70.74; H, 3.81; N, 7.49%. Calcd for $C_{11}H_6NCl$: C, 70.63; H, 3.21; N, 7.45%.

Reaction of 2-Chloroazulene Derivatives with Lithium Acetylides: General Procedure. The reaction of 2-chloroazulene derivatives with alkali metal acetylides was carried out as follows: A stream of acetylene gas was introduced into a blue colored fresh lithium metal in liq ammonia at −40 °C until the blue color of the solution disappeared. After stirring for 5 min, a solution of the 2-chloroazulene derivatives in dry THF was added to the solution of lithium acetylide. The mixture was kept at −40 °C for 1 h with stirring. Methanol was then added and excess ammonia was removed by evaporation at room temperature. The residue was mixed with ice-water, acidified slightly with 6 mol dm^{-3} HCl and extracted with benzene. The organic extract was washed with satd. $NaHCO_3$ aq, water, and dried (Na_2SO_4). The benzene solution, after concentration to a small volume, was chromatographed (silica gel, with benzene as an eluent). The yields of the ethynylazulene derivatives are given in Table 1, their electronic spectral data in Table 2, IR spectral data in Table 3, and NMR spectral data in Table 4.

*Reaction of **1a**[2] with Lithium Acetylide.* A solution of **1a** (550 mg, 1.8 mmol) in dry THF (30 ml) was treated with a lithium acetylide solution, prepared from lithium metal (69 mg, 10 mmol), liq NH_3 (20 ml) and gaseous acetylene. The reaction mixture was worked up. The first elution from chromatography afforded **3a** as reddish violet crystals (190 mg, 35.7%), which were recrystallized from ethanol to give reddish violet needles, mp 164—165 °C (Found: C, 73.14; H, 5.62%. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%). The second elution gave **2a**, blue crystals (134 mg, 25.2%), which were recrystallized from ethanol to give blue prisms, mp 81—82 °C (Found: C, 72.65; H, 5.54%. Calcd for $C_{18}H_{16}O_4$: C,72.96; H, 5.44%). Treatment of **1a** (1.50 g, 4.89 mmol) with a sodium acetylide solution (prepared from 500 mg of sodium metal, 30 ml of liq NH_3, and acetylene) gave **3a** (580 mg, 40.0%) and **2a** (610 mg, 42.1%).

Reaction of **1b** (1.000 g, 4 mmol) in dry THF (50 ml) with lithium acetylide (prepared from 110 mg of Li, 30 ml of liq NH_3, and acetylene) yielded 245 mg (25.6%) of methyl 3-cyano-6-ethynylazulene (**3b**), violet needles, mp over 300 °C, from ethanol (Found: C, 76.97; H, 3.79; N, 6.03%. Calcd for $C_{15}H_9NO_2$: C, 76.58; H, 3.86; N, 5.96%), 295 mg (30.7%) of methyl 3-cyano-4-ethynylazulene-1-carboxylate (**2b**), violet needles, mp over 300 °C, from ethanol (Found: C, 76.45; H, 3.54; N, 6.02%. Calcd for $C_{15}H_9NO_2$: C, 76.58; H, 3.86; N, 5.96%), and 10 mg (1%) of methyl 3-cyano-8-ethynylazulene-1-carboxylate (**4b**), violet needles, mp over 300 °C, from ethanol[mass: *m/e* 235 (M^+, 100%)].

Reaction of 2-chloro-1,3-dicyanoazulene (**1c**) (426 mg, 2 mmol) with lithium acetylide (prepared from 42 mg of Li, 30 ml of liq NH_3, and acetylene) yielded 20 mg (4.9%) of 1,3-dicyano-6-ethynylazulene (**3c**), red prisms, mp over 300 °C, from ethanol (Found: C, 83.54; H, 3.02; N, 13.72%. Calcd for $C_{14}H_6N_2$: C, 83.15; H, 2.99; N, 13.85%) and 180 mg (44.5%) of 1,3-dicyano-4-ethynylazulene (**2c**), reddish violet prisms, mp over 300 °C, from ethanol (Found: C, 82.83; H, 3.06; N, 14.03%. Calcd for $C_{14}H_6N_2$: C, 83.15; H, 2.99; N, 13.85%).

Reaction of **1d** (702 mg, 3 mmol) in dry THF (30 ml) with lithium acetylide (prepared from 63 mg of Li, 20 ml of liq NH_3, and acetylene) gave 492 mg (73.2%) of ethyl 4-ethynylazulene-1-carboxylate (**2d**), violet needles, mp 60—61 °C, from light petroleum ether [mass: *m/e* 244 (M^+, 82.6%), 179 (M^+ −45, 100%), 152 (42.1%)] and 30 mg (4.5%) of ethyl 8-ethynylazulene-1-carboxylate (**4d**), blue oil [mass: *m/e* 244 (M^+, 100%)].

Reaction of **1e** (760 mg, 4 mmol) in dry THF (30 ml) with lithium acetylide (prepared from 100 mg of Li, 30 ml of liq NH_3, and acetylene) afforded 307 mg (43.2%) of 1-cyano-4-ethynylazulene (**2e**), blue needles, mp 150—153 °C, from ethanol [mass: *m/e* 177 (M^+, 100%)] and 107 mg (14.9%) of 1-cyano-8-ethynylazulene (**4e**), blue needles, mp 85—86 °C, from ethanol [mass: *m/e* 177 (M^+, 100%)].

Reaction of diethyl 2-chloro-5-methylazulene-1,3-dicarboxylate (**1f**)[7] (115 mg, 0.36 mmol) in 20 ml of THF with lithium acetylide (prepared from 10 mg of Li) yielded 965 mg (58.3%) of diethyl 6-ethyl-5-methylazulene-1,3-dicarboxylate (**3f**), reddish violet needles, mp 169—170 °C, from ethanol (Found: C, 73.31; H, 5.84%. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85%).

Reaction of diethyl 2-chloro-5-isopropylazulene-1,3-dicarboxylate (**1g**)[8] (1.050 g, 3 mmol) in 30 ml of THF with lithium acetylide (prepared from 63 mg of Li) yielded 407 mg (39.9%) of diethyl 6-ethynyl-5-isopropylazulene-1,3-dicarboxylate (**3g**), reddish violet needles, mp 122—123 °C, from ethanol (Found: C, 74.29; H, 6.43%. Calcd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55%).

Reaction of **1a** (3.00 g, 9.79 mmol) in 50 ml of THF with

phenylacetylide (prepared from 207 mg (29.5 mmol) of Li, 4.0 g of phenylacetylene, 30 ml of liq NH_3) gave 1.394 g (38.3%) of diethyl 6-(phenylethynyl)azulene-1,3-dicarboxylate (**6**), reddish violet needles, mp 160—161 °C, from ethanol (Found: C, 77.24; H, 5.73%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%) and 1.631 g (44.8%) of diethyl 4-(phenylethynyl)-azulene-1,3-dicarboxylate (**5**), bluish violet needles, mp 104—105 °C, from ethanol (Found: C, 77.24; H, 5.37%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%).

Diethyl 6-(3-Indenyl)azulene-1,3-dicarboxylate (7). A solution of **1a** (352 mg, 1.1 mmol) in 30 ml of THF was added with stirring to a solution of sodium indenide prepared from 138 mg of Na, 20 ml of liq NH_3, and 700 mg of indene in 50 ml of THF at −40 °C. After being stirred for 90 min, the reaction mixture was quenched with 30 ml of MeOH and worked up. The first elution from chromatography gave unreacted indene. The second elution gave 222 mg (52.3%) of **7**, red prisms, mp 130—131 °C, from ethanol, $\lambda_{max}^{chloroform}$ nm (log ε): 247 (4.48), 268 (4.44), 309 (4.63), 348 (4.39), 372 (4.29), 516 (2.91), 552 (2.80 sh), 605 (2.42 sh); IR (KBr): 1680 (C=O), 1195 (C–C(=O)–O), 1039 (O–C–C) cm^{-1}; NMR ($CDCl_3$): δ 1.45 (t, J=7.0 Hz, 2 $OCH_2\underline{CH_3}$), 4.45 (q, J=7.0 Hz, 2 $OC\underline{H_2}CH_3$), 3.58 (2H, d, J=2.0 Hz, H-1′), 6.80 (d, J=2.0 Hz, H-2′), 7.67—7.25 (4H, m, phenyl protons), 7.97 (br d, J=11.0 Hz, H-5,7), 8.83 (s, H-2), 9.80 (br d, J=11.0 Hz, H-4,8). Found: C, 77.34; H, 5.76%. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74%.

Diethyl 6-(9-Fluorenyl)azulene-1,3-dicarboxylate (8). A solution of **1a** (306 mg, 1 mmol) in 20 ml of THF was added with stirring to a solution of sodium fluorenide prepared from 75 mg of Na, 20 ml of liq NH_3, and 500 mg of fluorene in 20 ml of THF at −40 °C. After being stirred for 1h, the reaction mixture was worked up. The first elution from the chromatography gave 108 mg (18.5%) of **8**, red prisms, mp 192—193 °C, from cyclohexane. λ_{max}^{MeCN} nm (log ε): 233 (4.71), 270 (4.66), 310 (4.79), 375 (3.42), 500 (2.88). IR (KBr): 1684 (C=O), 1208 (C–C(=O)–O), 1028 (O–C–C) cm^{-1}. NMR ($CDCl_3$): δ 1.40 (t, J=7.0 Hz, 2 $OCH_2\underline{CH_3}$), 4.36 (q, J=7.0 Hz, 2 $OC\underline{H_2}CH_3$), 5.18 (s, H-9′), 7.00—7.37 (6H, m, H-2′—7′), 7.83 (m, H-1′, 8′), 7.35 (br d, J=11.0 Hz, H-5,7), 8.76 (s, H-2), 9.51 (br d, J=11.0 Hz, H-4,8). Found: C, 79.60; H, 5.49%. Calcd for $C_{29}H_{24}O_4$: C, 79.79; H, 5.54%.

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