Nonbenzenoid Aromatic Systems. XI.[1] Synthesis and Buffered Acetolysis of 2-(2-Azulyl)ethyl Tosylate and Nosylate

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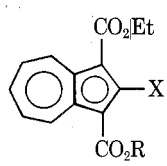
The synthesis of 2-(2-azulyl)ethanol (**1-OH**) was accomplished starting with methyl or ethyl 2-chloro-1-azulenecarboxylate (**6**) and involved nucleophilic substitution at C_2 with sodium methylcyanoacetate followed by lithium iodide ester halogenodealkylation with concomitant bisdecarboxylation to 2-azulylacetonitrile (**10**). Hydrolysis of **10** followed by diborane reduction of the acetic acid **11** gave **1-OH**. The kinetics of buffered acetolysis of **1-OTs** and **1-ONs** were determined. After one solvolytic $t_{1/2}$ **1-OTs** gave 51% **1-OAc** and 34% 2-vinylazulene (**12**). **12** was shown to arise by elimination from both **1-OTs** and **1-OAc**. Similarly **1-ONs** was found to yield 74% **1-OAc** and 11% **12** after one solvolytic $t_{1/2}$. Deuterium labeling with **1-**α,α-d_2-**ONs** established that the major component in k_{solv} of **1-ONs** is k_Δ with only a minor contribution from k_s, and that ion-pair return from the ethylene-2-azulenium ion–nosylate anion pair (**15**) is *not* occurring. These results are discussed in terms of the five nonequivalent azulene ring positions to which the β-ethanol side chain can be attached.

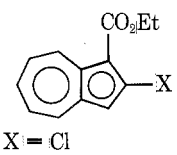
In 1971 we[2] reported preliminary results showing that the 1-azulyl substituent was a "super-participator" in β-arylethyl arenesulfonate solvolyses,[3] showing an acetolysis rate ratio of about 10^5 compared to 2-phenylethyl OTs for the k_Δ process at 25°. Our interest in the azulene ring as a participating aryl group also allows examination of the differences effected by attachment of the β-ethanol side chain to the five nonequivalent ring positions. Our results with 2-(6-azulyl)ethyl arenesulfonate buffered acetolysis showed it to behave solvolytically similar to derivatives of 2-phenylethanol in yielding an ethylenearenonium ion (k_Δ) with competitive elimination to 6-vinylazulene and solvent displacement (k_s).[4] 2-(4-Azulyl)ethyl arenesulfonates behaved similar to the 6 isomers except that the k_Δ process was believed to involve the ring 3 position in an Ar_3-5 mechanism.[4]

One of the reasons for entry into the chemistry of azulene was to determine the effects of the five nonequivalent ring positions in a number of reaction types.[5] In the reaction type of solvolysis of β-arylethyl derivatives, we now wish to report our results for 2-(2-azulyl)ethyl arenesulfonate buffered acetolysis.

Substrate Synthesis. The general Nozoe azulene synthesis was employed for the synthesis of 2-(2-azulyl)ethanol (**1-OH**). 2-Chlorotropone[6] was allowed to condense with 2 equiv of ethyl cyanoacetate with ethanolic sodium ethoxide to yield diethyl 2-amino-1,3-azulenedicarboxylate[8] (**2**) in average 70% yield. Diethyl 2-chloro-1,3-azulenedicarboxylate (**3**) was prepared from **2** by nitrous acid deamination in benzene and hydrogen chloride.[9] Sodium ethylcyanoacetate in ethanol effected nucleophilic displacement at C_2 of **3**, giving diethyl 2-(cyanoethoxycarbonylmethyl)-1,3-azulenedicarboxylate (**4**) in near-quantitative yield. However, considerable difficulties were found when we attempted to convert **4** to 2-azulylacetonitrile (**10**).



2, X = NH_2; R = C_2H_5
3, X = Cl; R = C_2H_5
4, X = $CH(CN)CO_2C_2H_5$; R = C_2H_5
5, X = Cl; R = H



6, X = Cl
7, X = $CH(CN)CO_2CH_3$
8, X = CH_2CN
9, X = $CH(CN)CH_3$

Half-hydrolysis of **3** afforded 2-chloro-3-carboethoxy-1-azuloic acid (**5**) in 66% yield. Thermal, low-pressure decarboxylation gave ethyl 2-chloro-1-azulenecarboxylate (**6**). Nucleophilic displacement at C_2 of **6** occurred with sodium methylcyanoacetate in refluxing dimethylformamide (DMF) to yield ethyl 2-(cyanomethoxycarbonylmethyl)-1-azulenecarboxylate (**7**). **7** was heated under reflux in DMF with lithium iodide (ester halogenodealkylation)[10] for 1.5 hr to yield an inseparable mixture (1:1.6 by NMR integration) of ethyl 2-cyanomethyl-1-azulenecarboxylate (**8**) and ethyl 2-(1-cyanoethyl)-1-azulenecarboxylate (**9**). The apparent origin of **9** was from methylation by liberated methyl iodide of the conjugate base of **8**. Addition of a small amount of acetic acid to a subsequent LiI–DMF halogenodealkylation of **7** gave a 75% yield of **8** free of any contamination by **9**.

When **8** was allowed to react with LiI–DMF–HOAc under nitrogen at reflux for 24 hr, the neutral fraction after work-up contained a small amount of acetonitrile **10** and unreacted **8**. This observation, together with the known faster ester halogenodealkylations of methyl esters compared to ethyl esters,[10] led us to consider the methyl ester corresponding to **6** as starting material. Since the reagents used in the nucleophilic substitution on **6** and the halogenodealkylation of **7** involved the same solvent and were compatible, these two reactions were combined and carried out consecutively in the same flask.

Starting with the methyl ester of **6**, nucleophilic substitution with sodium methylcyanoacetate for 1 hr in DMF under reflux was followed by addition of lithium iodide and a small amount of acetic acid and continued heating under reflux. After 11 hr the optimized yield of **10** was 68%. Using shorter ester halogenodealkylation reaction times afforded acidic products and lower yields of **10** while longer reaction times gave varying amounts of **10** and 2-methylazulene, a product probably arising from hydrolysis and decarboxylation of **10**.

Scheme I

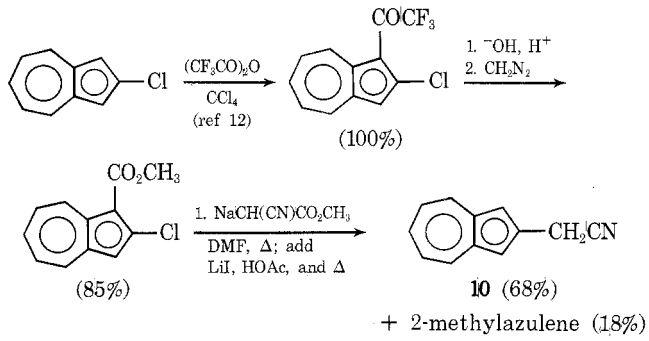


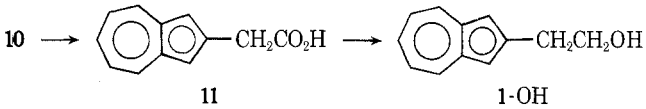
Table I
Buffered Acetolysis Kinetic Data for 2-(2-Azulyl)ethyl Tosylate and Nosylate

Compd	Temp, °C	$10^5 k$, sec^{-1}	Av $10^5 k$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{RONs}/k_{ROTs}
1-OTs	100.0	3.88 ± 0.003	3.92			
		3.96 ± 0.01				
1-ONs	80.0	4.96 ± 0.01	4.98	25.7	−5.8	
		5.00 ± 0.04				
	100.0	37.6 ± 0.2	37.5			9.6
		37.5 ± 0.2				
4-AzEtOTs[a]	100.0		1.23	21.4	−24.1	
4-AzEtONs[a]	100.0		2.17	24.0	−16.1	1.8
6-AzEtOTs[a]	100.0		1.09	23.2	−19.5	
6-AzEtONs[a]	100.0		3.55	23.4	−16.8	3.2
C_6H_5EtOTs[a]	100.0		0.41	24.2	−18.8	
C_6H_5EtONs[a]	100.0		4.66	24.3	−13.6	11.4
p-AnisylEtOTs[a]	100.0		22.2	24.1	−11.2	
p-AnisylEtONs[a]	100.0		293.	23.6	−7.3	13.2

[a] Reference 4.

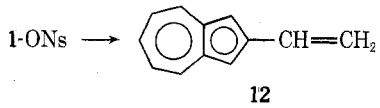
The above experimental results and the availability of quantities of 2-chloroazulene[9] previously prepared for a number of reasons led us to the sequence outlined in Scheme I.

Hydrolysis of **10** using conditions previously employed for hydrolysis of 1-azulylacetonitrile[13] gave 2-azulylacetic acid (**11**) in 89% yield. Diborane reduction of **11** gave 2-(2-azulyl)ethanol, which was purified as the acetate, 2-(2-azulyl)ethyl acetate (**1-OAc**), in 96% yield. The *p*-toluenesulfonate (tosylate) (**1-OTs**) and *p*-nitrobenzenesulfonate (nosylate) (**1-ONs**) esters were prepared by hydrolysis of **1-OAc** to **1-OH** and conversion to the arenesulfonates by standard procedures.[4] Using deuteriodiborane in the reduction of **11**, **1-α,α-d_2-OH** was produced containing 1.84



11 1-OH

deuterium atoms in the α position of the side chain (multiple NMR integrations). Reaction of **1-ONs** with potassium hydroxide in EtOH–THF gave a 96% yield of 2-vinylazulene (**12**).



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Discussion of Kinetic and Product Results from 1-OTs and 1-ONs. The buffered acetolyses of **1-OTs** and **1-ONs** were followed using the conductometric method[14] with the M-D Mini-Cell.[15] The rate constants and activation parameters for these and certain related compounds determined under these conditions are listed in Table I.

The buffered acetolysis of **1-OTs** was complicated by elimination to the 2-vinylazulene (**12**) both from **1-OTs** and the acetolysis product **1-OAc**. An acetolysis stability check on **1-OAc** at 100° for one acetolysis half-life of **1-OTs** gave 76.9% of recovered **1-OAc** and 6.2% of **12**. Assuming that the loss in material balance was due to instability of **12**, the amount of **12** produced from **1-OAc** in 1 half-life was 23.1%. The "1 half-life" preparative scale buffered acetolysis of **1-OTs** gave 52.8% recovered **1-OTs**, 24.1% (51% net) of **1-OAc**, and 15.8% (33.5% net) of **12**. Again assuming that **12** is partially destroyed (polymer) and that **1-OAc** was stable except toward elimination, the amount of **12** produced was 49% of the consumed **1-OTs**. While the ratio of acetate/olefin was larger than had been previously obtained from 2-(4-(**13**) and 2-(6-azulyl)ethyl OTs (**14**) buffered acetolyses,[4] it was evident that attempts to even determine k_{solv} of **1-OTs** let alone dissect it into the k_s and k_Δ components would be difficult.

Table II
Methylene Scrambling in Buffered Acetolysis of 1-α,α-d_2-ONs

	Run	Reaction time ($t_{1/2}$)	Proton content[a] C_α	Proton content[a] C_β	% scramble of C_α and C_β[b]
2-$AzCH_2CD_2ONs$		0	0.18	1.99	
2-$AzCH_2CD_2ONs$	1	1	0.16	2.02	0.0
	2	1	0.16	2.03	0.0
2-$AzCH_2(D_2)$-$CH_2(D_2)OAc$	1	1	1.04	1.10	48.3
	2	1	1.04	1.13	47.5

[a] Calculated by multiple NMR integrations using dioxane or CH_2Cl_2 as an internal proton count standard. [b] Calculated using the equation $[(C_1 - X)/[(C_1 - X) + (C_2 - X)]] \cdot 100$ = % scramble, where C_1 and C_2 are the proton contents of recovered materials at C_α and C_β, respectively, and X is the original proton content at C_α of 1-α,α-d_2-ONs; 50% scramble represents the maximum possible.

The buffered acetolysis of **1-ONs** was then carried out with the hope that with the better leaving group (larger k's) and therefore shorter reaction times (smaller $t_{1/2}$) the contribution of k_{elim} could be reduced. The kinetic data for **1-ONs** are given in Table I and we see that a "normal" k_{RONs}/k_{ROTs} ratio is observed. An acetolysis stability check for **1-OAc** for 1 half-life of **1-ONs** at 100° gave 91.5% recovery of **1-OAc** and 3% of **12**. The "1 half-life" preparative buffered acetolysis of **1-ONs** at 100° afforded 54.3% recovered **1-ONs**, 33.9% (74.2% net) **1-OAc**, and 4.9% (10.7% net) **12**.

The substantial amounts of elimination from **1-OTs**, **1-ONs**, and **1-OAc** in buffered acetolysis, as well as from **13** and **14** and their nosylate and acetate esters, probably reflects the acidities of the C_β–H bonds in these substrates. In contrast, the preparative, buffered acetolysis of 2-(3-nitro-1-azulyl)ethyl OTs at 70° gives a quantitative yield of its acetate.[13] This is qualitatively seen in the HMO anion localization energies at these ring sites.[16] Since deuterium is not lost from the β-methylene of the side chain in the scrambling study with 1-α,α-d_2-ONs (see Table II), equilibrium formation of the C_β carbanion cannot be involved if the elimination is base ($^-$OAc) catalyzed.

At this point we decided not to concern ourselves with the precise values of the rate constants, k_{elim}, k_Δ, and k_s, in this system. However, the magnitude of the k_Δ/k_s ratio and the rate constant for ion-pair return, $(1 - F)k_\Delta{}^3$, would still

Table III
Comparative Processes in β-Azulylethyl Arenesulfonate Buffered Acetolyses[2,4]

Compd	% C_α-C_β scrambling in RONs[a]	% C_α-C_β scrambling in ROAc[a]	k_{rel}, 100° (RONs)	Amount of k_Δ in k_{solv} of RONs	Amount of k_{elim} in acetolysis of RONs
1-$AzCH_2CH_2OTs$	0[b]	50[b]	3.6×10^4 [f]	Exclusive[b]	None[b]
2-$AzCH_2CH_2ONs$	0[c]	48[c]	17	Major[c]	Minor[c]
4-$AzCH_2CH_2ONs$	0[d]	0[d]	1.0	[d,e]	Significant[d]
6-$AzCH_2CH_2ONs$	12[d]	10[d]	1.6	Minor[d]	Significant[d]

[a] From deuterium labeling results after $t_{1/2}$ for recovered RONs and product ROAc. [b] At 35° with ROTs. [c] At 100°. [d] At 120°. [e] Some amount of k_Δ (Ar_3-5) was probably present but was not observable in these experiments.[4] [f] This value uses the extrapolated k for the ROTs times a factor of 10 as the k_{RONs}/k_{ROTs} ratio.

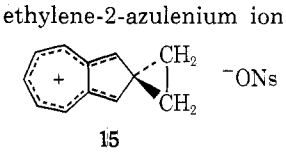
Table IV
HMO Cation Localization Energies[a]

Ring position	L_r^+, β units
1	1.924
2	2.362
4	2.551
5	2.341
6	2.930

[a] Reference 16.

be of interest in the comparisons of the five nonequivalent azulene ring positions to function in these processes. To this end, the buffered acetolysis of 1-α,α-d_2-ONs (prepared from 1-α,α-d_2-OH) was examined over 1 half-life of 1-ONs. Duplicate runs were made and analyses were performed by multiple integrations of the NMR spectra of the isolated products which are listed in Table II.

From the data in Table II we can see that the k_Δ process is the dominant pathway followed in k_{solv} of the buffered acetolysis of 1-ONs with only a minor contribution by solvent displacement, k_s. Also, ion-pair return $(1 - F)k_\Delta$ from the symmetric ethylene-2-azulenium ion pair (**15**) is not



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observed, which requires that $F = 1$ for this system. Special salt effects have been established for several acetate salts in acetolyses.[17,18] That $F = 1$ for 1-ONs compared to $F = 0.76$ for 2-(*p*-anisyl)ethyl OTs under the same conditions at 95°[19] may be due primarily to the presence of nosylate vs. tosylate anions in the respective ion pairs.

The data in Table III compare the four β-azulylethyl arenesulfonates studied to date. While we have only very approximate values of k_Δ for the 2-(4- and 2-(6-azulyl)ethyl nosylates, we can see that the relative abilities of these four azulene ring positions to participate fall in the order 1 > 2 > 6 ~ 4. This is also the order of HMO cation localization energies for these positions[16] listed in Table IV. If this order is to be followed the HMO cation localization energies in Table IV predict that the as yet unknown 2-(5-azulyl)ethyl arenesulfonates should have k_{solv} very similar to that found in 2-ONs. Synthetic efforts are proceeding to test this prediction.

Experimental Section[19]

Diethyl 2-Amino-1,3-azulenedicarboxylate (2).[8] To 150 ml of absolute ethanol was added 5.00 g (0.217 g-atom) of sodium. After the evolution of hydrogen had ceased, 48.5 g (0.428 mol) of ethyl cyanoacetate was added to form a white suspension. To this stirred mixture was added dropwise at 0° 15.0 g (0.107 mol) of 2-chlorotropone[6] in 150 ml of ethanol, and the color changed immediately from white to orange. This mixture was allowed to stand at room temperature for 12 hr, and then was refrigerated for 24 hr. The orange mixture was filtered and the filter cake was washed with benzene. The filtrate and benzene wash solution were evaporated to dryness. The residue was partially dissolved in dichloromethane and filtered again. The filter cake was washed with benzene, and this wash solution combined with the dichloromethane filtrate was evaporated to dryness. The residue was dissolved in ethanol and placed in the refrigerator. Crystallization afforded 22.70 g (74%) of the title compound as orange crystals: mp 92–93° (lit.[8] mp 93–94°); ir (KBr) 2.82 (m, N–H), 2.93 (m, N–H), 6.02 μ (s, C=O); NMR ($CDCl_3$, internal TMS) τ 0.62–1.02 (m, $C_{4,8}$ ring H's, 2), 2.00–2.84 (m, 5), 5.52 (q, J = 7 Hz, $CO_2CH_2CH_3$, 4), and 8.52 (t, J = 7 Hz, $CO_2CH_2CH_3$, 6); λ_{max} (cyclohexane) 315 nm (log ε 4.68), 327 (4.80), 370 (3.83), 392 (3.85), and 456 (3.39).

Anal. Calcd for $C_{16}H_{17}O_4N$: C, 66.88; H, 5.97. Found: C, 66.75; H, 6.05.

Diethyl 2-Chloro-1,3-azulenedicarboxylate (3).[8] Anhydrous HCl (bubbled through concentrated H_2SO_4) was bubbled into 300 ml of dry benzene containing 10.0 g (34.1 mmol) of **2** with ice cooling for 3 hr as red platelets precipitated. The dropwise addition over a 15-min duration of 4.55 g (39.0 mmol) of isoamyl nitrite to this suspension led to color changes from orange to green to blue and finally to red over an 18-hr period. The benzene solution was washed with four 150-ml portions of water and dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed on basic alumina. Elution with 1:1 carbon tetrachloride–benzene removed a diffuse, blue band, followed closely by a broad, red band. Benzene–dichloromethane (1:1) eluted a narrow, orange band and chloroform eluted a yellow band. Only the broad, red band was investigated which gave 10.00 g (96%) of the title compound. Crystallization from ethanol yielded red prisms: mp 75.0–76.0° (lit.[9] mp 77–78°); ir (KBr) 5.95 (s, C=O) and 9.55 μ (s, C–O); NMR (CCl_4, internal TMS) τ 0.25–0.62 (m, $C_{4,8}$ ring H's, 2), 2.07–2.60 (m, $C_{5,6,7}$ ring H's, 3), 5.52 (q, J = 7 Hz, $CO_2CH_2CH_3$, 4), and 8.53 (t, J = 7 Hz, $CO_2CH_2CH_3$, 6); λ_{max} (cyclohexane) 367 nm (log ε 4.26), 298 (4.61), 308 (4.69), 346 (3.75), 353 (3.78), 370 (3.61), 504 (2.67), and 525 (2.66).

Anal. Calcd for $C_{16}H_{15}O_4Cl$: C, 62.65; H, 4.93. Found: C, 63.00; H, 5.00.

Diethyl 2-(Cyanoethoxycarbonylmethyl)-1,3-azulenedicarboxylate (4).[9] To 10 ml of absolute ethanol was added 383 mg (16.65 mg-atom) of sodium. When the sodium had dissolved, 1.880 g (16.65 mmol) of ethyl cyanoacetate was added to form a white suspension. To this mixture, 1.278 g (4.17 mmol) of **3** was added. The mixture was heated under reflux for 1 hr, diluted with 50 ml of water, acidified with 6 *N* hydrochloric acid, and extracted with three 50-ml portions of ether. The combined ethereal extracts were dried ($MgSO_4$), the solvent volume was reduced, and the residue was chromatographed on basic alumina. Elution with ether developed a large, red band that afforded 1.520 g (95%) of the title compound. Crystallization from 1:1 ether–hexanes yielded small, red plates: mp 113.5–114.0° (lit.[9] mp 116–117°); ir (neat film) 4.52 (w, C≡N), 5.75 (s, C=O), 5.90 (s, C=O), and 9.70 μ (s, C–O); NMR ($CDCl_3$, internal TMS) τ 0.05–0.38 (m, $C_{4,8}$ ring H's, 2), 1.87–2.47 (m, $C_{5,6,7}$ ring H's, 3), 2.97 (s, $CHCNCO_2C_2H_5$, 1), 5.20–5.93 (m, $CO_2CH_2CH_3$, 6), and 8.33–9.88 (m, $CO_2CH_2CH_3$, 9); λ_{max} (cyclohexane) 273 nm (log ε 4.31), 294 (4.48), 304 (4.59), 338 (3.66), 367 (3.79), 511 (2.75), 538 (2.73), and 587 (2.35).

Anal. Calcd for $C_{21}H_{21}O_6N$: C, 65.78; H, 5.52. Found: C, 65.55; H, 5.65.

2-Chloro-3-carboethoxy-1-azuloic Acid (5).[9] To 760 mg (2.48 mmol) of **3** in 8 ml of ethanol was added 170 mg (3.0 mmol) of potassium hydroxide in 2 ml of water. This mixture was heated under reflux with stirring for 15 min, diluted with 100 ml of water, and extracted with four 100-ml portions of ether to remove unreacted **3**. These extracts were dried (Na_2SO_4), and the solvent volume was reduced to yield 240 mg of unreacted material. The aqueous layer was acidified with 10% hydrochloric acid and extracted with six 100-ml portions of ether. These extracts were dried (Na_2SO_4), and the solvent volume was reduced to yield 456 mg (66%, 97% net) of the title compound. Crystallization from methanol afforded pink

granules: mp 206–207° (sealed capillary) (lit.[9] mp 193° dec); ir (KBr) 5.95 (m, C=O), 6.05 (s, C=O), and 9.50 μ (m, C–O); NMR (DMSO-d_6, internal TMS) τ −3.12 (broad s, CO_2H, 1), 0.22–0.75 (m, $C_{4,8}$ ring H's, 2), 1.73–2.33 (m, $C_{5,6,7}$ ring H's, 3), 5.53 (q, J = 7 Hz, $CO_2CH_2CH_3$, 4), and 8.57 (t, J = 7 Hz, $CO_2CH_2CH_3$, 6); λ_{max} (95% ethanol) 270 nm (log ε 4.33), 295 (4.60), 302 (4.64), 350 (3.81), 366 (3.77), and 498 (2.75).

Anal. Calcd for $C_{14}H_{11}O_4Cl$: C, 60.33; H, 3.98. Found: C, 60.10; H, 4.00.

Ethyl 2-Chloro-1-azulenecarboxylate (6).[9] A sublimation tube containing 327 mg (1.17 mmol) of **5** was heated to 250° (200 Torr) for 3 hr. The red-violet oil that collected on the condenser was removed and chromatographed on basic alumina. Elution with hexanes afforded a violet band that gave 38 mg of 2-chloroazulene. Hexanes–dichloromethane (1:1) eluted a broad red-violet band that gave 220 mg (80%) of the title compound, a red-violet oil: ir (neat film) 5.92 (s, C=O) and 9.58 μ (s, C–O); NMR (CCl_4, internal TMS) τ 0.80–1.10 (m, C_8 ring H, 1), 1.77–2.10 (m, C_4 ring H, 1), 2.23–2.90 (m, $C_{5,6,7}$ ring H's, 3), 3.00 (s, C_3 ring H, 1), 5.58 (q, J = 7 Hz, $CO_2CH_2CH_3$, 4), and 8.57 (q, J = 7 Hz, $CO_2CH_2CH_3$, 6). For analysis a trinitrobenzene complex was prepared and crystallized from 1:1 ethyl acetate–hexanes to yield long, fine, yellow needles: mp 85.0–85.5°; λ_{max} (cyclohexane) 293 nm (log ε 4.76), 305 (4.79), 342 (3.87), 354 (3.93), 369 (3.62), 522 (2.62), 550 (2.59), and 595 (2.23).

Anal. Calcd for $C_{19}H_{14}O_8N_3Cl$: C, 50.96; H, 3.15. Found: C, 51.10; H, 3.30.

Ethyl 2-(Cyanomethoxycarbonylmethyl)-1-azulenecarboxylate (7). To 260 mg (5.8 mmol) of a 57% oil dispersion of sodium hydride in 10 ml of dry (distilled from BaO) DMF was added dropwise 2.0 ml of methyl cyanoacetate. After bubbles of hydrogen had ceased to be evolved, 212 mg (0.905 mmol) of **6** in 10 ml of dry DMF was added, and this mixture was heated for 1 hr at 150°. This mixture was cooled, diluted with 100 ml of water, and extracted with 50 ml of ether. The ethereal extract was discarded, and the aqueous layer was acidified with 5% hydrochloric acid and extracted with three 50-ml portions of ether. The combined ethereal extracts were washed with 100 ml of water and dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed on basic alumina. Benzene eluted a narrow, yellow band that was not investigated, and 9:1 chloroform–ethanol eluted a violet band that afforded 165 mg (61%) of the title compound. Crystallization from ethanol yielded violet crystals: mp 130–132°; ir (KBr) 5.70 (s, C=O), 5.98 (s, C=O), and 9.68 μ (s, C–O); NMR ($CDCl_3$, internal TMS) τ −0.03 to 0.57 (m, C_8 ring H, 1), 1.50–1.75 (m, C_4 ring H, 1), 2.02–2.82 (m, $C_{3,5,6,7}$ ring H's, 4), 4.15 (s, CH, 1), 5.67 (q, J = 7 Hz, $CO_2CH_2CH_3$, 2), 6.28 (s, CO_2CH_3, 3), and 8.67 (t, J = 7 Hz, $CO_2CH_2CH_3$, 3); λ_{max} (CH_2Cl_2) 290 nm (log ε 4.68), 302 (4.79), 338 (3.89), 347 (3.84)(sh), 365 (3.95), 528 (2.76), 550 (2.74)(sh), and 600 (2.37)(sh).

Anal. Calcd for $C_{17}H_{15}O_4N$: C, 68.67; H, 5.09; N, 4.71. Found: C, 68.37; H, 5.20; N, 4.55.

Ethyl 2-Cyanomethyl-1-azulenecarboxylate (8). To 100 mg (0.336 mmol) of **7** in 10 ml of dry (distilled from BaO) DMF was added 400 mg (2.35 mmol) of lithium iodide dihydrate[10] and 1.0 ml of acetic acid. This mixture was heated for 1 hr at 140°, cooled, diluted with 100 ml of water, and extracted with three 50-ml portions of ether. The combined ethereal extracts were washed with 100 ml of water and dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed on basic alumina. Dichloromethane–ether (1:1) eluted a red-violet band that afforded 60 mg (75%) of the title compound. Crystallization yielded violet crystals: mp 90–91°; ir (KBr) 5.92 (s, C=O) and 9.50 μ (C–O); NMR ($CDCl_3$, internal TMS) τ 0.37–0.63 (m, C_8 ring H, 1), 1.57–1.83 (m, C_4 ring H, 1), 2.03–2.83 (m, $C_{3,5,6,7}$ ring H's, 4), 5.58 and 5.70 (superimposed q, J = 7 Hz, and s, $CO_2CH_2CH_3$ and CH_2CN, 4), and 8.53 (t, J = 7 Hz, $CO_2CH_2CH_3$, 3); λ_{max} (CH_2Cl_2) 291 nm (log ε 4.76), 302 (4.77), 338 (3.77), 349 (3.77), 366 (3.89), 525 (2.69), 550 (2.65)(sh), and 600 (2.26)(sh).

A second reaction with the above conditions and without the addition of acetic acid was allowed to occur. An inseparable mixture of the title compound and ethyl 2-(1-cyanoethyl)-1-azulenecarboxylate (**9**) was obtained as identified by NMR spectroscopy.

2-Chloroazulene.[9] This was obtained by thermal decarboxylation of 2-chloro-1,3-azulenedicarboxylic acid.[9] From 500 mg (1.63 mmol) of diethyl 2-chloro-1,3-azulenedicarboxylate (**3**) after saponification the crude, dry diacid (410 mg, 100%) was heated in a large sublimer at 260° (200 Torr). Chromatography of the sublimate on basic alumina and hexanes elution gave 260 mg (98%) of the title compound. Crystallization from methanol gave violet needles: mp 90.0–90.5° (lit.[9] mp 91–92°); ir (CCl_4) no characteristic absorptions; NMR (CCl_4, internal TMS) τ 1.83–2.22 (m, $C_{4,8}$ ring H's, 2) and 2.42–3.20 (m, $C_{1,3,5,6,7}$ ring H's, 5); λ_{max} (cyclohexane) 276 nm (log ε 5.06), 285 (5.09), 303 (4.01), 330 (3.93), 344 (4.04), 357 (3.68), 551 (2.53), 592 (2.48), 615 (2.21), 635 (2.09), and 650 (2.10).

Anal. Calcd for $C_{10}H_7Cl$: C, 73.85; H, 4.34. Found: C, 74.00; H, 4.48.

2-Chloro-1-trifluoroacetylazulene. From the procedure of Anderson[12] for the trifluoroacetylation of azulene, 1.0 ml of trifluoroacetic anhydride was added to 780 mg (4.81 mmol) of 2-chloroazulene in 10 ml of carbon tetrachloride, and within 2 min the color changed from violet to red. This mixture was stirred for 3 hr, diluted with 50 ml of 5% aqueous sodium bicarbonate, and extracted into two 100-ml portions of ether. The combined ethereal extracts were washed with 100 ml of water and dried (Na_2SO_4), and the solvent volume was reduced. The residue was chromatographed on deactivated (3% water) basic alumina. Dichloromethane developed a single, broad, violet band that was eluted with chloroform to afford 1.240 g (100%) of the title compound. Crystallization from ethanol afforded large, red plates: mp 88.0–88.5°; ir (KBr) 6.12 μ (s, C=O); NMR ($CDCl_3$, internal TMS) τ 0.43–0.77 (m, C_8 ring H, 1), 1.50–1.85 (m, C_4 ring H, 1), 1.87–2.67 (m, $C_{5,6,7}$ ring H's, 3), and 2.77 (s, C_3 ring H, 1); λ_{max} (CH_2Cl_2) 275 nm (log ε 4.44), 323 (4.61), 376 (4.15)(sh), 392 (4.13)(sh), and 495 (2.95).

Anal. Calcd for $C_{12}H_6F_3ClO$: C, 55.72; H, 2.34. Found: C, 55.55; H, 2.46.

Methyl 2-Chloro-1-azulenecarboxylate. To 1.900 g (7.35 mmol) of 2-chloro-1-trifluoroacetylazulene in 30 ml of ethanol was added 1.80 g (32.1 mmol) of potassium hydroxide in 30 ml of water. This mixture was heated under reflux for 1 hr as the color changed from red to violet, diluted with 100 ml of water, and extracted with 100 ml of ether. The ethereal extract was discarded and the aqueous portion was acidified with 5% hydrochloric acid. This acidified portion was extracted with five 200-ml portions of ethyl acetate and dried (Na_2SO_4) and the solvent volume was reduced to yield 1.440 g (95%) of crude 2-chloro-1-azuloic acid.

To 1.590 g (7.7 mmol) of crude 2-chloro-1-azuloic acid in 500 ml of ethyl acetate was added an excess of an ethereal diazomethane solution. This mixture was allowed to stand for 30 min, the solvent volume was reduced, and the residue was chromatographed on basic alumina. Benzene eluted a narrow, yellow band that was not investigated and a broad, red band that afforded 1.470 g (87%) of the title compound. Dichloromethane eluted a narrow, yellow-orange band that was not investigated. Crystallization from ethanol gave the product as fine, red needles: mp 86.0–86.5°; ir (KBr) 5.92 (s, C=O) and 9.55 μ (s, C–O); NMR ($CDCl_3$, internal TMS) τ 0.38–0.72 (m, C_8 ring H, 1), 1.57–1.87 (m, C_4 ring H, 1), 2.05–2.67 (m, $C_{5,6,7}$ ring H's, 3), 2.78 (s, C_3 ring H, 1), and 6.02 (s, CO_2CH_3, 3); λ_{max} (CH_2Cl_2) 294 nm (log ε 4.72), 304 (4.77), 340 (3.81), 350 (3.84), 366 (3.51), 515 (2.72), 538 (2.70)(sh), and 590 (2.28)(sh).

Anal. Calcd for $C_{12}H_9O_2Cl$: C, 65.32; H, 4.11. Found: C, 65.62; H, 3.97.

2-Azulylacetonitrile (10). To a suspension of 200 mg (4.75 mmol) of a 57% oil dispersion of sodium hydride in 10 ml of dry DMF (distilled from BaO) was added dropwise 600 mg (6.07 mmol) of methyl cyanoacetate. After bubbles of hydrogen had ceased to evolve, 420 mg (1.90 mmol) of methyl 2-chloro-1-azulenecarboxylate in 10 ml of dry DMF was added, and this mixture was heated at 140–150° for 1 hr. After this mixture was allowed to cool to room temperature, 2.0 ml of acetic acid and 3.40 g (20 mmol) of crushed lithium iodide dihydrate[10] were added. This mixture was heated to 140–150° under a dry, nitrogen atmosphere with stirring for 11 hr, diluted with 100 ml of water, and extracted with three 100-ml portions of ether. The combined extracts were washed with two 100-ml portions of water and dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed on basic alumina. A violet band eluted with 1:1 benzene–hexanes that afforded 50 mg (18%) of 2-methylazulene. Benzene eluted a narrow, yellow band that was not investigated and a broad, violet band that yielded 215 mg (68%) of the title compound. Crystallization from 1:1 ether–hexanes afforded violet crystals: mp 95.0–95.5°; ir (KBr) 4.44 μ (m, C≡N); NMR ($CDCl_3$, internal TMS) τ 1.62–1.90 (m, $C_{4,8}$ ring H's, 2), 1.97–3.03 (m, $C_{1,3,5,6,7}$ ring H's, 5), and 5.92 (s, CH_2CN, 2); λ_{max} (CH_2Cl_2) 276 nm (log ε 4.79), 283 (4.81), 300 (3.87)(sh), 326 (3.63), 340 (3.79), 560 (2.58), 595 (2.52), and 655 (2.11)(sh).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.42; N, 8.38. Found: C, 85.96; H, 5.35; N, 8.20.

2-Azulylacetic Acid (11). Forty milliliters of 50% aqueous ethanol and 1.350 g (24.1 mmol) of potassium hydroxide were heated

under a continuous, dry, oxygen-free, nitrogen sweep with stirring for 2 hr. To this mixture was added 280 mg (1.675 mmol) of **10** in 2.5 ml of THF. This mixture was heated under gentle reflux for 7 hr, diluted with 100 ml of water, and extracted with 50 ml of ether. The ethereal extract was discarded and the aqueous portion was acidified with 5% hydrochloric acid. The acidified layer was extracted with two 50-ml portions of ether. The ethereal extracts were combined and dried (Na_2SO_4), and the solvent volume was reduced to yield 295 mg (89%) of the title compound. Crystallization from 4:1 ether–hexanes afforded violet plates: mp 128–129°; ir (KBr) 5.90 μ (s, C=O); NMR ($CDCl_3$, internal TMS) τ −0.32 (broad s, CO_2H, 1), 1.67–1.93 (m, $C_{4,8}$ ring H's, 2), 2.47–3.17 (m, $C_{1,3,5,6,7}$ ring H's, 5) and 5.98 (s, CH_2CO_2H, 2); λ_{max} (CH_2Cl_2) 277 nm (log ϵ 4.79), 285 (4.83), 298 (3.73)(sh), 327 (3.60), 342 (3.73), 564 (2.53), 605 (2.48)(sh), and 660 (2.07)(sh); mass spectrum (70 eV, heated inlet) *m/e* (rel abundance) 186 ($M\cdot^+$, 8), 185 (58), 142 (76), 141 (100), and 115 (34).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.29; H, 5.49.

2-(2-Azulyl)ethyl Acetate (1-OAc). A mixture of 250 mg (1.26 mmol) of acid **11** and 366 mg (9.60 mmol) of $NaBH_4$ in 30 ml of dry THF was stirred at room temperature until hydrogen evolution ceased. To this mixture was added dropwise 5 ml of boron trifluoride etherate in 25 ml of dry THF over a period of 30 min. After 60 min of additional stirring, 10 ml of 10% hydrochloric acid was added dropwise and then the mixture was diluted with 100 ml of ether and 50 ml of water. The layers were separated and the extraction was repeated twice with 100-ml portions of ether. The combined ethereal extracts were washed with 100 ml of 5% aqueous sodium bicarbonate and 100 ml of water and dried (Na_2SO_4). The solvent volume was reduced and the residue was chromatographed with chloroform on basic alumina. A single, violet band eluted which was contaminated with impurity as determined by NMR.

This crude alcohol was stirred with 3 ml of dry pyridine and 1 ml of reagent grade acetic anhydride for 2 hr at 0°, protected from atmospheric moisture. This mixture was diluted with 100 ml of ice-cold 10% hydrochloric acid and 50 ml of ether. The layers were separated and the ethereal layer was washed with four 100-ml portions of 10% hydrochloric acid and one 100-ml portion of water. The ethereal layer was dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed on basic alumina with 1:1 carbon tetrachloride–dichloromethane. A single violet band eluted that afforded 260 mg (96%) of **1-OAc** as a violet oil: ir (neat film) 5.75 (s, C=O) and 9.60 μ (s, C–O); NMR (CCl_4, internal TMS) τ 1.75–2.03 (m, $C_{4,8}$ ring H's, 2), 2.33–3.17 (m, $C_{1,3,5,6,7}$ ring H's, 5), 5.60 (t, J = 6.5 Hz, CH_2CH_2OAc, 2), 6.73 (t, J = 6.5 Hz, CH_2CH_2OAc, 2) and 8.00 (s, O_2CCH_3, 3); mass spectrum (70 eV, heated inlet) *m/e* (rel abundance) 214 ($M\cdot^+$, 47), 155 (22), 154 (100), 153 (13), 141 (24), 115 (13), and 43 (34).

For analysis a 1,3,5-trinitrobenzene complex was prepared and crystallized from 1:1 ethyl acetate–hexanes to afford bronze-colored crystals: mp 80.5–81.0°; λ_{max} (CH_2Cl_2) 276 nm (log ϵ 4.75), 285 (4.82), 300 (3.73), 329 (3.55), 343 (3.69), 560 (2.47), 602 (2.42), and 665 (1.99)(sh).

Anal. Calcd for $C_{20}H_{17}O_8N_3$: C, 56.21; H, 4.01. Found: C, 56.06; H, 4.11.

2-(2-Azulyl)ethanol (1-OH). A mixture of 260 mg (1.21 mmol) of **1-OAc** in 8 ml of ethanol and 500 mg (8.9 mmol) of potassium hydroxide in 2 ml of water was stirred at 0° for 1 hr. This mixture was diluted with 100 ml of ice-cold water and extracted with two 50-ml portions of ether. The combined ethereal layers were dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed on basic alumina. Dichloromethane developed a broad, blue band that was eluted with chloroform to afford 218 mg (98%) of the title compound. Crystallization from carbon tetrachloride yielded long, violet needles: mp 97.0–97.5°; ir (KBr) 3.06 (s, O–H) and 9.50 μ (s, C–O); NMR (CCl_4, internal TMS) τ 1.75–2.05 (m, $C_{4,8}$ ring H's, 2), 2.52–3.20 (m, $C_{1,3,5,6,7}$ ring H's, 5), 6.05 (t, J = 6 Hz, CH_2CH_2OH, 2), 6.87 (t, J = 6 Hz, CH_2CH_2OH, 2), and 8.57 (broad s, OH, 1); λ_{max} (CH_2Cl_2) 276 nm (log ϵ 4.76), 286 (4.83), 301 (3.73), 330 (3.61), 343 (3.70), 561 (2.47), 602 (2.41), and 660 (1.97)(sh); mass spectrum (70 eV, heated inlet) *m/e* (rel abundance) 172 ($M\cdot^+$, 79), 155 (30), 154 (22), 142 (37), 141 (100), 139 (21), 129 (76), 128 (18), and 115 (50).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.40; H, 7.10.

2-(2-Azulyl)ethyl Tosylate (1-OTs). To 195 mg (1.13 mmol) of **1-OH** in 3.0 ml of dry ether was added 232 mg (1.22 mmol) of sublimed tosyl chloride and 200 mg (3.58 mmol) of crushed potassium hydroxide. The mixture was allowed to stir at 0°, protected from atmospheric moisture, for 6 hr, and diluted with 100 ml of ether and 200 ml of ice-cold water. The layers were separated and the aqueous portion was extracted with a second 100 ml of ether. The combined ethereal extracts were washed twice with 100-ml portions of water and dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed on deactivated (6% water) basic alumina. Dichloromethane eluted a broad, violet band, followed by a narrow, violet band. The narrow, violet band yielded 15 mg of unreacted **1-OH**. The broad, violet band afforded 340 mg (92%, 100% net) of the title compound, a violet oil that crystallized upon standing. Crystallization from ethyl acetate gave long, violet needles: mp 105.0–106.0°; ir (KBr) 7.38 (s, S–O) and 8.42 μ (s, S–O); NMR ($CDCl_3$, internal TMS) τ 1.67–2.08 (m, $C_{4,8}$ ring H's, 2), 2.13–3.09 (m, 9), 5.60 (t, J = 7 Hz, CH_2CH_2OTs, 2), 6.68 (t, J = 7 Hz, CH_2CH_2OTs, 2), and 7.62 (s, tosyl CH_3, 3); λ_{max} (CH_2Cl_2) 277 nm (log ϵ 4.69), 285 (4.76), 300 (3.73)(sh), 329 (3.54), 343 (3.66), 564 (2.46), 605 (2.40), and 660 (2.00)(sh); mass spectrum (70 eV, heated inlet) *m/e* (rel abundance) 326 ($M\cdot^+$, 0.6), 172 (86), 154 (24), 108 (20), 107 (30), 91 (62), and 45 (100).

Anal. Calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56. Found: C, 69.91; H, 5.62.

2-(2-Azulyl)ethyl Nosylate (1-ONs). To 65 mg (0.378 mmol) of **1-OH** in 3 ml of dry THF was added 17 mg of a 57% oil dispersion of sodium hydride. This mixture was allowed to stir overnight at room temperature as a violet precipitate separated. The mixture was cooled to 0° and 110 mg (0.40 mmol) of recrystallized *p*-nitrobenzenesulfonyl chloride was added. After 4 hr of stirring at 0°, 50 ml of ice-cold water and 50 ml of ether were added, the layers were separated, and the aqueous layer was extracted with two additional 50-ml portions of ether. The combined ethereal layers were washed with 100 ml of water and dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed on deactivated (3% water) basic alumina. Dichloromethane eluted a blue band and chloroform eluted a second blue band. The second band afforded 30 mg of unreacted alcohol, and the first band yielded 63 mg (47%, 87% net) of the title compound. Crystallization from 1:1 ethyl acetate–hexanes gave copper-colored prisms: mp 128.0–128.8°; ir (KBr) 7.32 (s, S–O), 7.42 (s, S–O), and 8.42 μ (s, S–O); NMR ($CDCl_3$, internal TMS) τ 1.70–3.07 (m, 11), 5.47 (t, J = 6.5 Hz, CH_2CH_2ONs, 2) and 6.67 (t, J = 6.5 Hz, CH_2CH_2ONs, 2); λ_{max} (CH_2Cl_2) 278 nm (log ϵ 4.70), 285 (4.73), 300 (4.08)(sh), 314 (3.87)(sh), 342 (3.66), 563 (2.49), 605 (2.44)(sh), and 665 (1.99)(sh).

Anal. Calcd for $C_{18}H_{15}NO_5S$: C, 60.49; H, 4.23. Found: C, 60.21; H, 4.13.

2-Vinylazulene (12). To 55 mg (0.142 mmol) of **1-ONs** in 5 ml of absolute ethanol and 2 ml of THF was added at 0° under stirring 200 mg (3.58 mmol) of crushed potassium hydroxide. This mixture was stirred for 1 hr and diluted with 100 ml of ether and 100 ml of water. The layers were separated and the aqueous layer was extracted with a second 100-ml portion of ether. The combined, blue extracts were dried (Na_2SO_4), the solvent volume was reduced, and the residue was chromatographed with carbon tetrachloride on basic alumina. A single, blue band eluted that yielded 21 mg (96%) of the title compound. Crystallization from hexanes afforded blue plates: mp 104.5–106.0°; ir (KBr) 12.15 (s) and 13.78 μ (s); NMR ($CDCl_3$, internal TMS) τ 1.67–1.97 (m, $C_{4,8}$ ring H's, 2), 2.17–3.30 (m, 6), and 3.80–4.67 (m, 8 lines, 2); λ_{max} (cyclohexane) 281 nm (log ϵ 4.62), 291 (4.72), 302 (4.61), 319 (3.60), 334 (3.49), 349 (3.63), 364 (3.90), 374 (3.60), 382 (4.09), 580 (2.47), 600 (2.41), 613 (2.42), 626 (2.47), 645 (2.23)(sh), 664 (2.12), and 690 (2.21).

For analysis a trinitrobenzene complex was prepared and crystallized from ethanol–hexanes (1:1) to yield brown needles, mp 106.0–107.0°.

Anal. Calcd for $C_{18}H_{13}O_6N_3$: C, 58.86; H, 3.57. Found: C, 58.73; H, 3.72.

Kinetic Method. The method previously described[14,15] was used with some modifications. A Beckman differential reading thermometer, calibrated in 0.01°, was used, in conjunction with ASTM thermometers, to monitor temperature variations and to obtain the $10t_{1/2}$ point at a temperature representative of the points taken during the first 2 half-lives. The constant-temperature bath cover and perimeter were insulated to prevent heat loss. Temperature changes of ±0.002° were then detectable and could be approximated, and temperature variations were normally about ±0.003° during a typical solvolytic run. There was no observable change noted in the conductance readings between the $10t_{1/2}$ point and subsequent points when the readings were taken at the same temperature.

All kinetic runs were made with 1.0×10^{-3} M ROTs (RONs) and 1.2×10^{-3} M potassium acetate. Infinity ($10t_{1/2}$) titers of these solutions gave the following percent reaction: **1**-OTs (100°), 94.2%; **1**-ONs (80°), 97.3%; **1**-ONs (100°), 97.8%.

All preparative scale buffered acetolyses were determined using 0.010 M ROTs and 0.012 M potassium acetate. The solutions were sealed in flasks and placed in the constant-temperature bath for the allotted time. After removal from the bath and quenching in ice–water, the contents were poured from the flasks into water and extracted with methylene chloride which was washed with water, 5% aqueous $NaHCO_3$, and water and dried (Na_2SO_4). Evaporation of the solvent and chromatography of the residue then gave the products.

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Registry No.—**1**-OH, 54798-03-7; **1**-OTs, 54798-04-8; **1**-ONs, 54798-05-9; **1**-OAc, 54798-06-0; **1**-OAc 1,3,5-trinitrobenzene complex, 54798-07-1; **2**, 3806-02-8; **3**, 36044-40-3; **4**, 54832-62-1; **5**, 54798-08-2; **6**, 54522-71-3; **6** 1,3,5-trinitrobenzene complex, 54798-09-3; **7**, 54798-10-6; **8**, 54798-11-7; **10**, 54798-12-8; **11**, 54798-13-9; **12**, 53477-10-4; **12** 1,3,5-trinitrobenzene complex, 54798-14-0; ethyl cyanoacetate, 105-56-6; 2-chlorotropone, 3839-48-3; 2-chloroazulene, 36044-31-2; 2-chloro-1-trifluoroacetylazulene, 54798-15-1; methyl 2-chloro-1-azulenecarboxylate, 54798-16-2; 2-chloro-1-azuloic acid, 54798-17-3; *p*-nitrobenzenesulfonyl chloride, 98-74-8; tosyl chloride, 98-59-9.

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Molecular Rearrangements. XII.[1a] Reactions of 2-Chlorobicyclo[2.2.1]hept-2-ene *exo*-Oxide and 2-Chlorobicyclo[2.2.2]oct-2-ene Oxide with Lithium Diethylamide

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The reactions of two bicyclic α-chloro epoxides, 2-chlorobicyclo[2.2.1]hept-2-ene *exo*-oxide (**2**) and 2-chlorobicyclo[2.2.2]oct-2-ene oxide (**3**), with lithium diethylamide have been investigated. With **2**, refluxing benzene–ether and ether (0 to −15°) were examined as solvents while, with **3**, only refluxing benzene–ether was studied. From **2** the major product was tricyclo[2.2.1.$0^{2,6}$]heptan-3-one (**4**). The amount of the minor product, tricyclo[2.2.1.$0^{2,6}$]heptan-3-ol (**5**), was solvent and base concentration dependent. Using **2**-*3-d* in ether, no deuterium was found in **4** and none at C_3 of **5**. While the formation of **4** can be readily rationalized as involving transannular insertion by the α-keto carbene formed by α elimination at C_3 of **2**, the pathway **2** → **5** is unclear. From **3**, two major products, tricyclo[3.2.1.$0^{2,7}$]octan-6-one (**15**) and *N,N*-diethylbicyclo[2.2.1.]heptane-7-carboxamide (**16**), and two minor products, 3-chlorobicyclo[2.2.2]octan-2-one (**13**) and bicyclo[2.2.2]octanone (**14**), were isolated. Ketone **15** and amide **16** are believed derived from the α-keto carbene, **15** by transannular insertion and **16** by Wolff ring contraction, while ketones **13** and **14** probably arise via thermal rearrangement of **3**. These results are compared with those from other methods of generating the respective bicyclic α-keto carbenes or carbenoids. The site specificity in these conversions of bicyclic α-chloro epoxides **2** and **3** to tricyclic ketones **4** and **15**, respectively, may prove synthetically useful.

The reactions of strong bases with acyclic, cyclic, and bicyclic epoxides have been studied by a number of researchers,[2] notably Cope, Crandall, and Rickborn. The major types of processes observed were α elimination (yielding insertion and ketone products), β elimination, and nucleophilic epoxide ring opening. The extent of involvement of these processes was dependent on structural effects in both the epoxide and the base.

Our interests in the chemistry of α-chloro epoxides[1,3] led us to consider how the α-chloro substituent might effect the outcome of such strong base reactions. Using (*Z*)-2-chlorobutene oxide (**1**) as an example, the conceivable pathways are listed in Scheme I. Nouri-Bimorghi[4] reported that varying amounts of β elimination (pathway a) and nucleophilic epoxide ring opening (pathway e) were observed when three acyclic α-chloro epoxides were allowed to react