Reactivity of Bicyclo[4.2.2]deca-2,4,7,9-tetraene Derivatives under Conditions of Uniparticulate Electrophilic Addition. The Intramolecular Capture of Zwitterionic Bridged 1,4-Bishomotropylium (Bicyclo[4.3.1]deca-2,4,7-trienyl) Intermediates[1]

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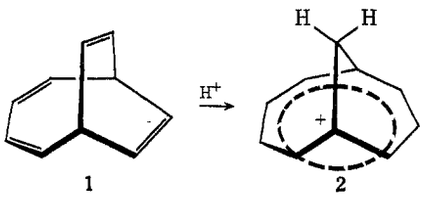
A variety of mono- and disubstituted bicyclo[4.2.2]deca-2,4,7,9-tetraenes have been prepared and their reactivity toward chlorosulfonyl isocyanate compared to that of the parent system. In the latter case, a tricyclic lactam is obtained in which the carbon framework has undergone rearrangement to an unsaturated bicyclo[4.3.1]-decane moiety. Product formation is rationalized in terms of initial stereoselective *N*-(chlorosulfonyl) β-lactam intervention, subsequent ring opening with migration of the butadienyl bridge, and finally intramolecular cyclization to annihilate charge. The driving force for the rearrangement is attributed to 1,4-bishomotropylium cation formation. The symmetrical nature of the zwitterion in the unsubstituted example is lost upon substitution and the directional specificity of the cyclization is revealed in the derivatives. Substituents have a divergent effect on the two possible modes of closure and these results are discussed.

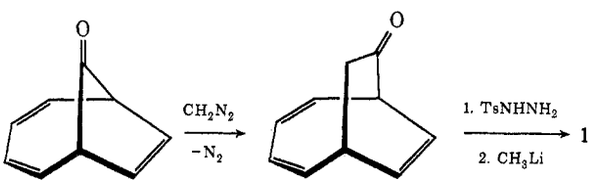
Bicyclo[4.2.2]deca-2,4,7,9-tetraene (**1**) has been discovered to rearrange to bicyclo[4.3.1]deca-2,4,7-trienyl ions when treated with electrophilic reagents. Credit for this discovery is due to Winstein[3] and Schröder,[4] who appear to have investigated independently the generation of **2** under long-life conditions below 0°.[5] Subsequently, Schröder and his coworkers have found that this same skeletal rearrangement accompanies the reaction of **1** with such biparticulate electrophiles[6] as bromine, hydrogen bromide, and mercuric acetate.[7] Current interest in such transformations has been heightened by the awareness that **2** is a bridged, 1,4-



1 **2**

bishomotropylium ion system. Recently, we reported on the generation and intramolecular capture of homo-[8] and 1,3-bishomotropylium cation intermediates[9,10] by treatment of cyclooctatetraenes and *cis*-bicyclo[6.1.0]-nonatrienes, respectively, with uniparticulate electrophilic reagents. The objectives of these studies were to establish whether such processes could function as utilitarian probes of mechanism and stereochemistry, to achieve certain synthetic goals, and to gain some basic information regarding the role of substituents on the reactivity of homoaromatic cations toward nucleophiles. Because of past successes, we have been led to investigate the related chemistry of **2** and herein report the results of this study.

Bicyclo[4.2.2]decatetraene.—Although **1** has been prepared by thermal decomposition of the sodium salt of bicyclo[6.1.0]nonatriene-9-carboxaldehyde tosylhydrazone[11] and by mercuric bromide catalyzed isomerization of bullvalene,[12] we have found it most convenient to prepare this hydrocarbon by diazomethane ring expansion of **3**[13,14] and treatment of the tosylhydrazone



3 **4**

with methyllithium.[15] When a dry methylene chloride solution of **1** was allowed to react with chlorosulfonyl isocyanate (CSI) for 6 hr at room temperature and dechlorosulfonylation was carried out with thiophenol and pyridine[16] or alkaline sodium sulfite solution,[17] tricyclic lactam **5** was obtained in 67% yield. The structure of **5** was established by a combination of spectral and chemical evidence. The compound exhibits an infrared carbonyl stretching band at 1725 cm^{-1}, a maximum at 243 nm (ε 5030) in the ultraviolet region, and the following absorptions in the nmr (100 MHz): δ 7.4 (br, 1, >NH), 5.77-6.4 (m, 5), 5.23 (ddd, J = 9.5, 3.5, and 1.8 Hz, 1), 3.74 (t with additional fine splitting, J = 5 Hz, 1), 3.44 (m, 1), 3.14 (m, 1), and 2.36 (d with additional fine splitting, J = 5 Hz, 1). Spin-decoupling experiments permitted

(1) Unsaturated Heterocyclic Systems. LXXXIX. For the previous paper in this series, see D. J. Pasto, A. F. Chen, G. Ciurdaru, and L. A. Paquette, *J. Org. Chem.*, **38**, 1015 (1973).

(2) Holder of a NATO Postdoctoral Fellowship (1970–1972) administered by the Science Research Council.

(3) M. Roberts, H. Hamberger, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 6346 (1970).

(4) G. Schröder, U. Prange, N. S. Bowman, and J. F. M. Oth, *Tetrahedron Lett.*, 3251 (1970).

(5) The remarkable stability of cation **2** is revealed by the fact that it can be heated to 80° without noticeable change in its nmr features: P. Ahlberg, D. L. Harris, M. Roberts, P. Warner, P. Seidl, M. Sakai, D. Cook, A. Diaz, J. P. Dirlam, H. Hamberger, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 7063 (1972).

(6) L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *ibid.*, **93**, 4503 (1971).

(7) G. Schröder, U. Prange, B. Putze, J. Thio, and J. F. M. Oth, *Chem. Ber.*, **104**, 3406 (1971).

(8) L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 4714 (1969); L. A. Paquette and T. J. Barton, *ibid.*, **89**, 5480 (1967).

(9) L. A. Paquette and M. J. Broadhurst, *ibid.*, **94**, 632 (1972); L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **94**, 630 (1972).

(10) J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *ibid.*, **94**, 2904 (1972).

(11) M. Jones, Jr., and L. T. Scott, *ibid.*, **89**, 150 (1967).

(12) H.-P. Löffler and G. Schröder, *Angew. Chem.*, **80**, 758 (1968); *Angew. Chem., Int. Ed. Eng.*, **7**, 736 (1968).

(13) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 2155 (1972).

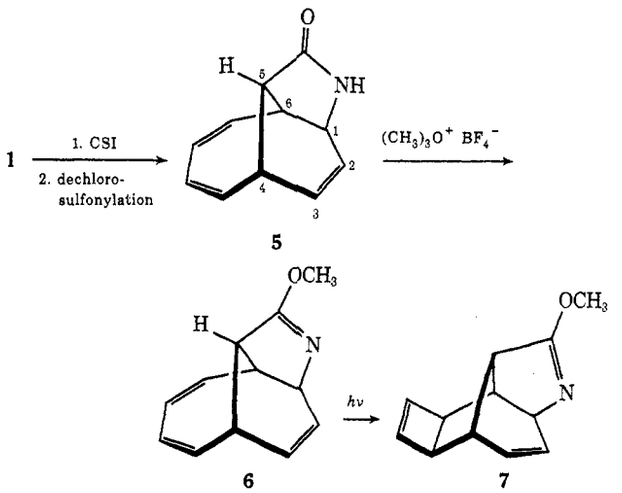
(14) (a) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Schechter, *ibid.*, **94**, 5366 (1972); (b) K. Kurabayashi and T. Mukai, *Tetrahedron Lett.*, 1049 (1972); (c) M. Sakai, R. F. Childs, and S. Winstein, *J. Org. Chem.*, **37**, 2517 (1972).

(15) Studies carried out concurrently with those in the group of Professor H. Shechter: J. B. Press and H. Shechter, *Tetrahedron Lett.*, 2677 (1972).

(16) R. Graf, *Justus Liebigs Ann. Chem.*, **661**, 111 (1963).

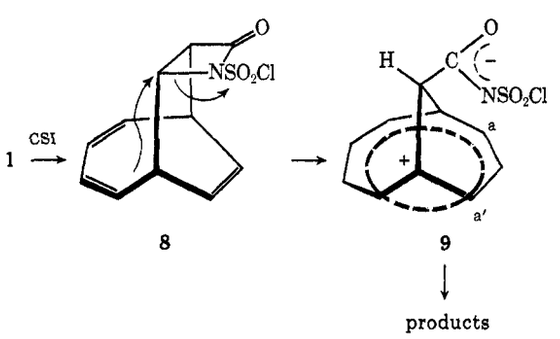
(17) T. Durst and M. J. O'Sullivan, *J. Org. Chem.*, **35**, 2043 (1970).

all proton assignments to be made and showed all coupling constants to be compatible with the assignments (see Experimental Section). Treatment of **5** with trimethyloxonium fluoroborate afforded imino ether **6**, structural assignment to which could be made with confidence on the basis of its spectra. Additionally, triplet-sensitized irradiation of **6** cleanly gave a photoproduct in which the butadiene unit had been isomerized to a cyclobutene ring (*cf.* **7**).[18]



5 **6** **7**

The formation of **5** proceeds analogously to the TCNE reaction with **1**.[19] In both cases, intervention of a zwitterionic 1,4-bishomotropylium ion intermediate (*e.g.*, **9**) appears particularly attractive, since the electrophilic moiety is quite suitably disposed in a geometric sense for ultimate cyclization to product. With particular reference to CSI, the generation of **9**



8 **9**

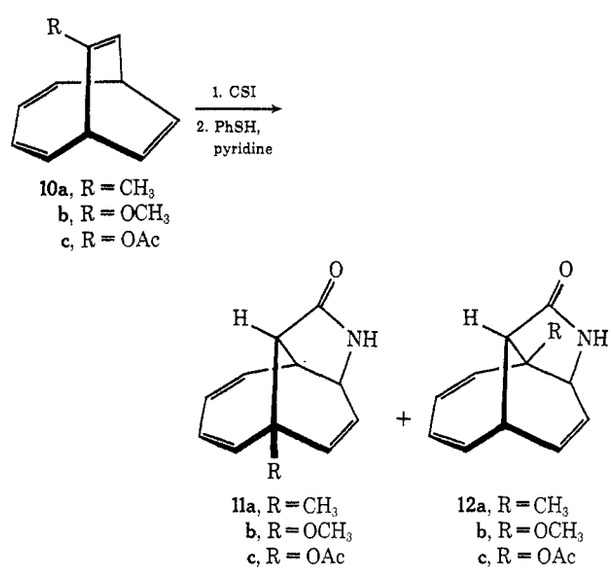
could be preceded by formation of the β-lactam derivative **8**, with subsequent ring opening and rearrangement arising owing to the driving force underlying attainment of the delocalized homoaromatic species. This proposal will subsequently be shown to have basis in fact.

Because of the innate symmetry of **9**, cyclization with charge annihilation can operate at two equivalent sites (a and a′). By making recourse to mono- or higher substitued derivatives of **1**, this symmetry consideration no longer becomes applicable. As a result, the opportunity to examine substituent effects on the direction (in particular) of C—N bond formation is readily available. Accordingly, a quantitative study of product distribution as a function of substitution was next undertaken.

Monosubstituted Bicyclo[4.2.2]decatetraenes.—Of the compounds selected for study, the 7-methyl derivative (**10a**) was synthesized by methylation of **4** and subsequent treatment of its tosylhydrazone with methyllithium; alternatively, **10a** was obtained more conveniently by diazoethane ring expansion of **3** followed by elimination from the tosylhydrazone. Preparation of methoxy tetraene **10b** was effected by O-methylation of the anion of **4** with dimethyl sulfate.[15,20] Enol acetate **10c** was readily available from the reaction of **4** with isopropenyl acetate in the presence of *p*-toluenesulfonic acid.[15]

Each of the purified tetraenes was treated with a slight excess of CSI in methylene chloride at room temperature. It was immediately clear from inspection of aliquots from the trio of reactions that two types of lactam (β and γ) were initially produced. With the passage of time, however, the carbonyl band seen at *ca.* 1825 cm^{-1} gradually disappeared; in contrast, the 1760-cm^{-1} absorption remained. In the case of **10a** and **10b**, the transient *N*-(chlorosulfonyl) β-lactam was no longer present after several hours. The β-lactam derivative arising from **10c** rearranged relatively more slowly, a finding which permitted its ultimate isolation and characterization (*vide infra*).

In each instance, two γ-lactams (**11** and **12**) were formed and their relative percentages were determined by nmr analysis of the nonhydrolyzed *N*-(chlorosulfonyl) derivatives. Control experiments showed that *N*-(chlorosulfonyl) precursors of **11** and **12** were not



10a, R = CH_3
b, R = OCH_3
c, R = OAc

11a, R = CH_3
b, R = OCH_3
c, R = OAc

12a, R = CH_3
b, R = OCH_3
c, R = OAc

interconverted under the reaction conditions. Furthermore, the product distributions were not found to change within experimental error when the cycloadditions were allowed to proceed for varying lengths of time beyond the point at which no β-lactam could be seen. The relevant data have been collected in Table I.

The individual isomers could be distinguished readily by their nmr spectra, which, not unexpectedly, are quite similar within a given lactam series. Particular use was made of the previous spin-decoupling

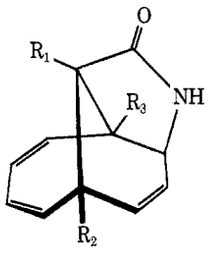
(18) Details of this particular experiment will appear elsewhere at a future date.

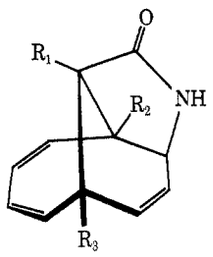
(19) H.-P. Löffler, T. Martini, H. Musso, and G. Schröder, *Chem. Ber.*, **103**, 2109 (1970).

(20) M. J. Goldstein, private communication. The authors thank Professor Goldstein for providing us with the experimental details in advance of publication.

TABLE I

PRODUCT DISTRIBUTIONS OBTAINED UPON CSI ADDITION TO MONO- AND DISUBSTITUTED BICYCLO[4.2.2]DECATETRAENES





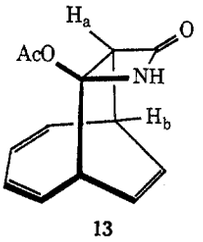
R_1	R_2	R_3	Yield, %[a]	Product distribution, %[a,b]	
H	H	CH_3	73	31.5	68.5
H	H	OCH_3	56.5	54.5	45.5
H	H	OAc	57.5	24	76
CH_3	H	OCH_3	52.5	68.5	31.5

[a] Average of several runs. [b] Analysis by repeated nmr integration of suitable peaks; estimated error, ±4%.

experiments with **5**. In this lactam, H_3 is the olefinic proton which has the most upfield chemical shift in the vinyl region; moreover, it is found in an uncomplicated region of the spectrum and is readily identified. Its appearance in **5** as a doublet of doublets of doublets is due to vicinal coupling with H_2 ($J_{2,3}$ = 9.5 Hz) and H_4 ($J_{3,4}$ = 3.5 Hz) and long-range coupling to H_5 ($J_{3,5}$ = 1.8 Hz). H_2 appears at lowest field and has like multiplicity ($J_{2,3}$ = 9.5 Hz, $J_{1,2}$ = 4.5, $J_{2,4}$ = 2.5 Hz), while H_1 is seen as a broadened triplet. The assignment of structure to lactams **11** is based on the following general spectral characteristics: H_3 appears as a doublet of doublets lacking $J_{3,4}$; H_2 is likewise only a doublet of doublets with $J_{2,4}$ absent; the H_5 absorption consists of a broad doublet ($J \simeq 5$ Hz). These observations are uniquely compatible with substitution of the R group at position 4.

In contrast, lactams **12** share the common features of multiplicities in H_2 and H_3 identical with those in **5**, appearance of H_1 as a broadened doublet, and the collapse of H_5 to a "singlet" with additional long-range coupling (Table II). Furthermore, the ultraviolet spectra of **11** and **12** differ significantly, but remain quite constant within a given set (Table III).

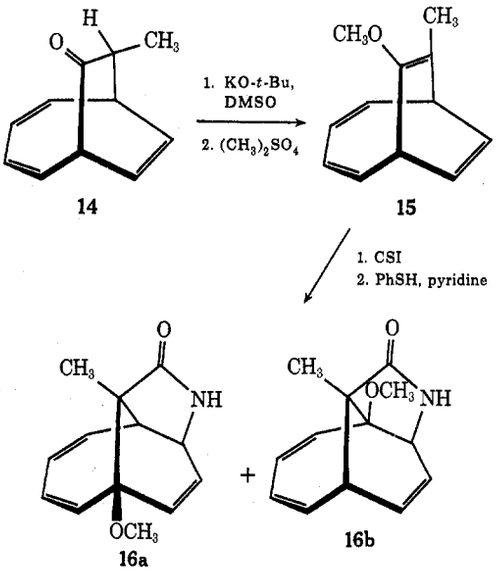
The expectation that a β-lactam could be isolated from the reaction of **10c** with CSI was realized when short reaction times (4–5 min) were employed. Under these conditions, 45.5% of **13** was obtained after cus-



13

tomary reduction with thiophenol and pyridine, together with approximately 20% of a mixture of **11c** and **12c**. From intense carbonyl absorptions at 1770 and 1730 cm^{-1}, the presence of β-lactam and acetate carbonyls could be inferred. The stereochemical relationship of the four-membered heterocyclic ring to the [4.2.2]bicyclic framework is readily ascertained by an examination of the nmr spectrum, which showed a quite narrow singlet absorption for H_a. Dihedral angle measurements made on Dreiding models revealed a relationship between H_a and H_b in **13** such that a small spin–spin interaction is expected; in contrast, a considerably larger coupling constant would seem necessary for the isomeric structure if the Karplus correlation does not break down in such systems. This is unlikely, for, in a mechanistic context, the *N*-(chlorosulfonyl) precursor to **13** can uniquely serve as the source of **11c** and **12c**. This transformation has, in fact, been realized at the experimental level.

Disubstituted Bicyclo[4.2.2]decatetraenes.—Though the results given above provide a sufficiently sharpened view into the reaction to permit several mechanistic conclusions to be drawn, it is to be noted that the substituted etheno bridge has been the site of preferential kinetic attack and that H_5 has invariably been substituted only by hydrogen. With regard to the latter point, 7-methoxy-8-methylbicyclo[4.2.2]-decatetraene (**15**) was prepared by O-methylation of



14 **15** **16a** **16b**

14, the recognized precursor to **10a**. In line with the relative reactivities of **10a** and **10b** and the well-established cationic stabilizing powers of methyl and methoxyl groups, initial attack by the electrophile at the methyl-bearing carbon was anticipated. This would position a methyl group at C_5. Enol ether **15** operates in this manner to produce rapidly a β-lactam (not isolated) which equally rapidly undergoes conversion to five-ring lactams. Reduction and chromatography led to the isolation (52.5% yield) of **16a** and **16b** (initially present in a 31.5:68.5 ratio). Individual identification of the two products was gained by examination of their nmr spectra (Table II), the absence of H_4 in **16a**, for example, resulting in loss of the normal coupling to H_2 and H_3.

Exposure of **17**[21] to the action of CSI under comparable conditions led to the isolation of a sole adduct, the nmr spectrum of which is consistent with struc-

(21) U. Kruerke, *Angew. Chem., Int. Ed. Engl.*, **6**, 79 (1967).

TABLE II
NMR DATA FOR THE TRICYCLIC LACTAMS
(60 MHz, CCl_4–TMS, δ VALUES)

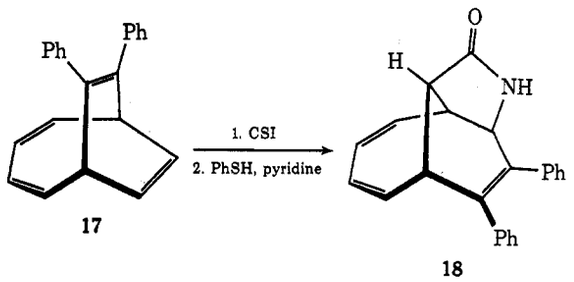
Compd	H_1	H_2	H_3	H_4	H_5	H_6	Other olefinic protons
5	3.74 (br t)[a] J = 5 Hz	6.3 (m)	5.23 (ddd) J = 9.5, 3.5, 1.8 Hz	3.44 (m)	2.36 (br d)[a] J = 5 Hz	3.14 (m)	5.77–6.1 (m)
11a	3.71 (t) J = 5 Hz	6.11 (dd) J = 9.0, 5.3 Hz	5.09 (d)[a] J = 9.0 Hz		2.22 (br d)[a] J = 5 Hz	3.17 (m)	5.45–5.9 (m) (1.38, s, $-CH_3$)
11b	3.75 (br t)[a] J = 5 Hz	6.31 (dd) J = 9.0, 5.0 Hz	5.18 (d)[a] J = 9.0 Hz		2.73 (br d)[a] J = 5 Hz	3.18 (m)	5.95 (br s) (3.53, s, $-OCH_3$)
11c	3.82 (br t)[a] J = 4.5 Hz	6.38 (dd) J = 9.2, 5.5 Hz	5.24 (d)[a] J = 9 Hz		3.3 (m)[b]	3.3 (m)[b]	5.65–6.3 (m) (2.11, s, $-COCH_3$)
12a	3.4 (m)[b]	6.3 (ddd) J = 9.0, 5.5, 2.0 Hz	5.16 (d)[a] J = 9.0 Hz	3.4 (m)[b]	2.27 (m)		5.7–6.15 (m) (1.30, s, $-CH_3$)
12b	3.55 (m)[b]	6.28 (ddd) J = 9.3, 5.8, 2.0 Hz	5.21 (d)[a] J = 9.3 Hz	3.55 (m)[b]	2.78 (m)		5.95 (m) (3.25, s, $-OCH_3$)
12c	4.32 (m)	6.30 (m)	5.30 (dd)[a] J = 9.5, 3.0 Hz	3.50 (m)	3.0 (m)		6.0 (m) (2.02, s, $-COCH_3$)
16a	3.74 (t) J = 5 Hz	6.36 (dd) J = 9.5, 5.5 Hz	5.36 (d) J = 9.5 Hz			2.78 (m)	5.98 (br s) (3.42, s, $-OCH_3$; 1.04, s, $-CH_3$)
16b	3.77 (d) J = 6.0 Hz	6.2 (ddd) J = 9.5, 6.0, 2.0 Hz	5.18 (dd)[a] J = 9.5, 3.5 Hz	3.25 (m)			6.0 (m) (3.32, s, $-OCH_3$; 1.14, s, $-CH_3$)

[a] Additional fine coupling is present. [b] Overlapping peaks.

TABLE III
ULTRAVIOLET DATA FOR THE TRICYCLIC LACTAMS
(C_2H_5OH SOLUTION)

Compd	λ_{max}	ε	Compd	λ_{max} (ε)
5	243	5030	11a	257.5 infl (3620), 248 (5310), 244 (5125)
11a	245	4680	12b	261 infl (3250), 251.5 (4980), 246 (4950)
11b	245	4200	12c	262.5 infl (3280), 251 (5400), 246 (5360)
11c	242.5	4620	16b	262 infl (3250), 253 (4910), 246.5 (4850)
16a	244	4250		

ture **18**. In particular, the lactam has only four olefinic protons (δ 5.73–6.3, m), the remaining four tetrahe-



17 **18**

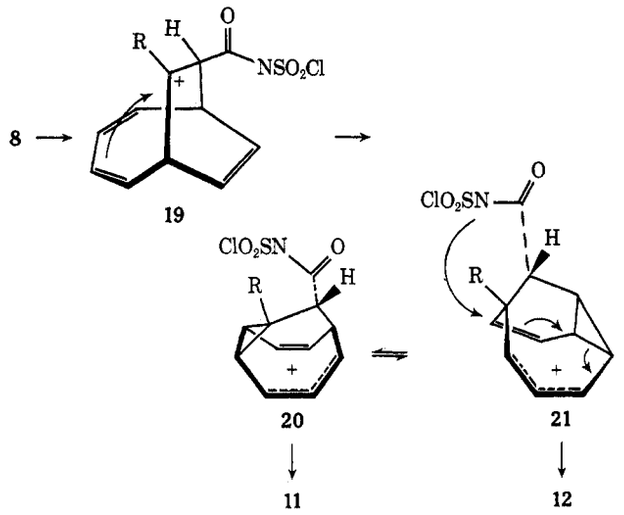
drally bound hydrogens appearing at 4.22 (d, J = 4.5 Hz), 4.0 (d, J = 8 Hz), 3.45 (m), and 2.77 (m). Furthermore, the observation of the following electronic spectrum [$\lambda_{max}^{C_2H_5OH}$ 271 nm (sh, ε 6110), 238 (sh, 13,200), and 226 (18,200)] requires the presence of a stilbene chromophore. The lack of reactivity of the phenyl-substituted double bond in **17** is not unexpected in view of the fact that stilbene fails to react with CSI.[16]

Discussion

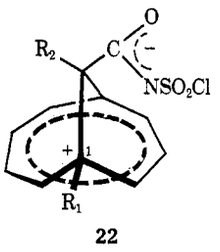
Mechanistic Considerations.—The experimental results show that the bicyclo[4.2.2]decatetraene ring system reacts with CSI to give initially a β-lactam intermediate which arises from approach of electrophile to the polyene from the direction of the etheno (rather than butadieno) bridge. Such high levels of stereoselectivity very likely arise because of steric factors and are well precedented in a number of related structural types.[14,15] Whether β-lactam formation involves a two-step ionic mechanism or a more concerted [$_\pi 2_a + {}_\pi 2_s$] process is uncertain.

The structurally rearranged nature of the γ-lactams, in combination with the fact that two isomeric products arise in the unsymmetrical examples, argue convincingly for the intervention of carbonium ion intermediates. Isomerization reactions of *N*-(chlorosulfonyl) β-lactams by cationic pathways have been reported previously on many occasions. In a formal sense, a 1,2 shift of the conjugated diene unit is involved followed by cyclization to either of two possible positions (*cf.* **8** and **9**). This bond reorganization can be viewed as the result of the rearrangement sequence outlined below. The observed product ratios now might be interpreted as reflecting the relative capability of the R group to stabilize a cyclopropane ring.

However, the accumulated evidence[3–5] obtained from protonation studies of **1** attests convincingly to the fact that cations of type **20** and **21** are less thermodynamically stable than the related homoaromatic bicyclo[4.3.1]deca-2,4,7-trienyl cations. Consequently, we have assumed that a true cyclopropane bond likewise is not present in those transient intermediates which arise from CSI addition and that the

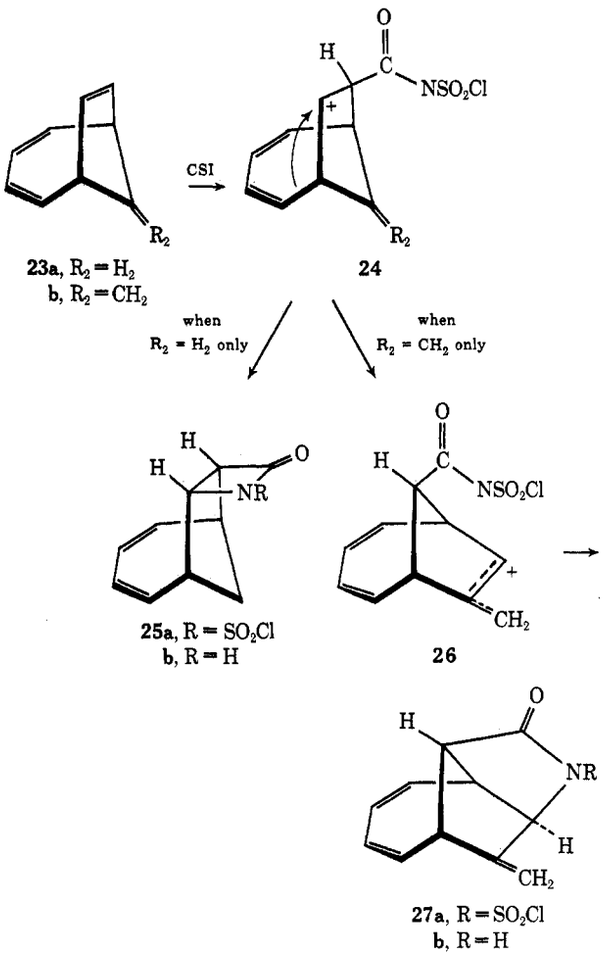


product distribution arises from differing rates of cyclization in 22.

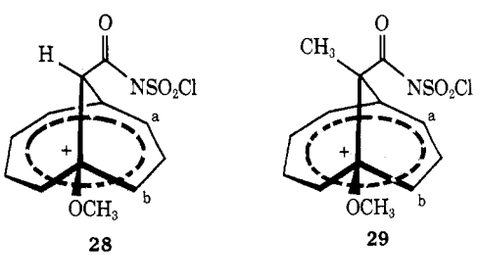


The fundamental underlying importance of charge delocalization to the successful realization of skeletal rearrangement in these systems is revealed experimentally by the contrasting behavior of structurally related hydrocarbons **23a** and **23b**. At 25°, cycloaddition of CSI to **23a** took place, giving only **25a**, dechlorosulfonylation of which led to the ready isolation of **25b** (80% yield). The exo stereochemistry of **25b** was revealed by the virtual lack of spin–spin coupling between the >CHCO– and >CHN< protons and their adjoining bridgehead counterparts, a result in keeping with the *ca.* 90° dihedral angle separating them. Comparable exclusive exo attack has been observed previously with norbornene and norbornadiene derivatives.[22,23] 9-Methylenebicyclo[4.2.1]nonatriene (**23b**) does not share with **23a** an inability to undergo bond reorganization under these conditions. Rather, **27b** is obtained as the major constituent of a reaction mixture containing a number of rearrangement products.[24]

Substituent Effects.—As established above, the positions occupied by the R substituent in lactams **11**, **12**, and **16** necessitate that the initial bonding of the isocyanate occur so as to generate the most stable bicyclo[4.2.2]trienyl cation. The β-lactams which arise from this step of the sequence could result from a "quasiconcerted" cycloadditive process, in which some charge separation develops. To arrive at the 1,4-bishomotropylium ion intermediate, substantial cationic character must become localized at that carbon



atom bearing the R group.[25] A 1,2 shift of the diene bridge subsequently gives **22** in which the lone substituent is bonded to C_1. Because of its attachment to a tetrahedral center, the substituent cannot be expected to exert any π-electron conjugative effect on the two possible modes of ring closure. Rather, the observed differences (Table I) must be attributed to inductive and field influences, steric effects, or a combination of these three factors. That steric effects may not be inconsequential in certain cases is reflected in the behavior of zwitterions **28** and **29**. In **28**, closure to



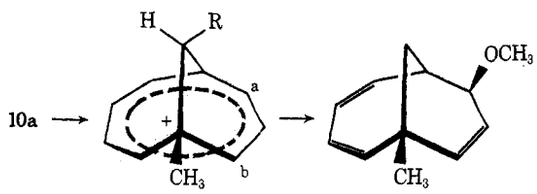
carbon a occurs to the extent of 45.5%; the additional methyl group in **29** clearly disfavors this pathway (now only 31.5%). Molecular models suggest that the methyl and methoxyl groups are in closer spatial proximity in **16a** than in **16b**.

When attention is focused uniquely on the series

(22) E. J. Moriconi and W. C. Crawford, *J. Org. Chem.*, **33**, 370 (1968).
(23) L. A. Paquette and T. J. Barton, unpublished observations.
(24) L. A. Paquette and M. J. Broadhurst, *J. Org. Chem.*, **38**, 1893 (1973).

(25) For convenience in discussion, the R groups under consideration are those which can stabilize positive charge. When the substituent is not carbonium ion stabilizing, the other bridge is preferentially attacked by the electrophile.[26]
(26) G. Schröder, U. Prange, and J. F. M. Oth, *Chem. Ber.*, **105**, 1854 (1972).

10a–10c, the net substituent contributions are seen to be rather divergent. The propensity of **30a** to cyclize preferably away from the methyl group has been encountered also by Schröder.[26] Subsequent to the completion of this work, he and his coworkers have described the protonation and alkaline methanol quench of **10a**. The only product isolated was **31**,



30a, R = $CONSO_2Cl$
b, R = H

31

but, since the yield was unfortunately only 15%, little can be said about the *overall* chemical fate of **30b** under such circumstances. Nevertheless, these data can be explained in terms of a model in which the dipolar influence of the methyl group, whether through space or σ bonds, renders the proximate site of attack less electron deficient. Consequently, C–N bond formation at the alternative more positive ring carbon (to give **11a**) is kinetically preferred.

On this basis, the more electronegative methoxyl group would be expected to transmit an electrical effect such that positive charge should be greatest in the vicinity of this substituent. This influence is opposite to that exerted by methyl. Accordingly, **12b** should dominate the product composition. At the experimental level, this lactam is formed in 54.5% relative yield.

At first sight, the acetoxyl group would appear to be an anomaly, for the results indicate it to exert an effect more similar to methyl than to methoxyl. However, if the polarization of the carbonyl group is considered and if, as now believed,[27] the propagation efficiency of a polar group resides chiefly in its field effect, then the electronegative carbonyl oxygen atom could exert an untoward influence on the $-CO\overline{N}SO_2Cl$ moiety.

In summary, the results collected in Table I and the necessarily tentative theoretical suggestions advanced above reveal that substituents exert phenomenologically interesting control on the directional specificity of intramolecular charge annihilation in homoaromatic bicyclo[4.3.1]deca-2,4,7-trienyl zwitterions.

Experimental Section

Melting points are corrected. Proton magnetic resonance spectra were obtained with Varian A-60A and HA-100 spectrometers and apparent coupling constants are cited. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Reaction of Bicyclo[4.2.2]deca-2,4,7,9-tetraene (1) with CSI. A. Thiophenol–Pyridine Work-Up.—A solution of 0.4 ml (4.8 mmol) of CSI in 5 ml of dry methylene chloride was added dropwise under nitrogen to 520 mg (4.0 mmol) of **1** dissolved in 10 ml of the same solvent. After 6 hr the reaction was complete (ir analysis). The solvent was evaporated and the residual pale yellow, viscous oil was dissolved in acetone and treated with thiophenol and pyridine at 0° in the usual way.[16] Chromatography on Florisil gave 461 mg (67%) of **5** as colorless crystals, mp 190.5–191°, from methylene chloride–ether, $\nu_{max}^{CHCl_3}$ 1715 cm^{-1}.

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.08. Found: C, 76.27; H, 6.37; N, 8.09.

The following double irradiation experiments confirmed the structural assignment. Irradiation of the NH proton resulted in removal of fine coupling from H_1 which appeared as a triplet (J = 5 Hz); no other alterations were noted. Saturation slightly to lower field of the main olefinic absorption removed the major coupling (J = 9.5 Hz) from H_3 and collapsed H_1 to a doublet (J = 4 Hz). These observations suggested that both H_1 and H_3 are strongly coupled to the same olefinic region with little change elsewhere except for removal of some fine splitting from H_5 and narrowing of the multiplet due to H_4. When H_5 was saturated, H_3 appeared as a doublet of doublets (J = 9.5 and 3.5 Hz), H_6 developed triplet characteristics (J = 3.5 Hz), and H_4 lost some of its original fine coupling. The long-range coupling between H_3 and H_4 can be rationalized in terms of W coupling and has been observed for a number of structurally related compounds.[28]

Simultaneous irradiation of H_1 and H_4 resulted in collapse of the lowest field vinyl proton (H_2) to a doublet (J = 9.5 Hz) while H_3 appeared as a doublet of doublets (J = 9.5 and 1.8 Hz). Consequently, H_2 and H_3 are strongly coupled. When H_4 was saturated, H_2 was seen as a doublet of doublets ($J_{2,3}$ = 9.5, $J_{1,2}$ = 4.5 Hz) and H_3 appeared as a broadened doublet (J = 9.5 Hz). Thus, H_2 and H_4 interact long range to the extent of *ca.* 2.5 Hz. Finally, irradiation of H_6 led to the simplification of H_5 (now a broadened singlet).

B. Alkaline Sodium Sulfite Work-Up.—A solution of 1.3 g (1 mmol) of **1** and 0.9 ml (1.05 mmol) of CSI in 40 ml of methylene chloride was stirred at 25° under nitrogen for 23 hr. The solvent was evaporated and the residue was taken up in ether (20 ml). This solution was added dropwise with vigorous stirring to 30 ml of 2% sodium sulfite solution. Portions of 10% potassium hydroxide solution were added throughout the addition in order to maintain pH 7–8. Upon completion of the addition, the solution was stirred for 30 min, during which time the product began to crystallize. The total reaction mixture was extracted with methylene chloride (3 × 30 ml) and the combined extracts were dried and evaporated. A white, crystalline solid was obtained which was washed with ether and filtered. The colorless crystals so obtained (1.056 g, 61%) were identical with the sample of **5** obtained above and were of almost analytical purity, mp 187–189°.

O-Methylation of 5.—Lactam **5** (865 mg, 5.0 mmol) was dissolved in 50 ml of dry methylene chloride and treated with 1.0 g (6.6 mmol) of trimethyloxonium fluoroborate under nitrogen. The mixture was stirred at 25° for 12 hr, washed twice with saturated sodium bicarbonate solution and once with brine, dried, and evaporated. The resulting pale yellow oil (930 mg) was subjected to molecular distillation at 70° (0.3 mm) from which was obtained 821 mg (88%) of a colorless liquid which slowly crystallized on cooling to 0°: $\delta_{max}^{CDCl_3}$ 5.8–6.3 (m, 5, olefinic), 5.0 (br d, 1, H_3), 4.0 (m, 1, H_1), 2.95–3.45 (m, 2, H_4 and H_6), and 2.4 (m, 1, H_5).

The perchlorate of **7** was obtained as colorless needles, mp 193–193.5°, from methylene chloride–ether, ν_{max}^{KBr} 1660 cm^{-1}, $\lambda_{max}^{C_2H_5OH}$ 247 nm (ϵ 4725).

Anal. Calcd for $C_{12}H_{14}ClNO_5$: C, 50.09; H, 4.91; N, 4.87. Found: C, 50.02; H, 4.85; N, 4.84.

7-Methylbicyclo[4.2.2]deca-2,4,7,9-tetraene (10a).—To a solution of 5.0 g (0.038 mol) of **3** in 200 ml of methanol was added an ethereal solution of diazoethane (400 ml, prepared from 30 g of *N*-ethyl-*N*-nitrosourea) and the mixture was maintained at 0° overnight in the dark. After removal of the solvent, there remained 5.20 g of pale orange liquid, vpc analysis (5% SE-30, 130°) of which indicated the presence of **14** as the one major product.

A 530-mg sample of the crude ring-expanded ketone and 700 mg of *p*-toluenesulfonylhydrazine dissolved in 50 ml of ethanol was treated with 4 drops of concentrated hydrochloric acid and kept at 5° for 24 hr. The solution was concentrated to *ca.* 20 ml and the tosylhydrazone was allowed to crystallize during 6 days at 5°.

(27) For leading references, see (a) L. M. Stock, *J. Chem. Educ.*, **49**, 400 (1972); (b) R. Golden and L. M. Stock, *J. Amer. Chem. Soc.*, **94**, 3080 (1972); (c) C. L. Liotta, W. F. Fisher, E. L. Slightom, and C. L. Harris, *ibid.*, **94**, 2129 (1972); (d) C. L. Liotta, W. F. Fisher, G. H. Greene, Jr., and B. L. Joyner, *ibid.*, **94**, 4891 (1972); (e) C. F. Wilcox and C. Leung, *ibid.*, **90**, 336 (1968); (f) D. S. Noyce and G. A. Selter, *J. Org. Chem.*, **36**, 3458 (1971).

(28) See, for example, M. Jones, Jr., *J. Amer. Chem. Soc.*, **89**, 4236 (1967).

There was obtained 600 mg (52.5%) of colorless crystals, mp 152–154° dec, from ether–methylene chloride.

Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.84; H, 6.08; N, 8.51.

To a suspension of 3.0 g (9.1 mmol) of pure tosylhydrazone in 90 ml of dry ether was added with stirring 60 ml of methyllithium (*ca.* 1.0 *M*). The clear orange solution so obtained became cloudy and then clear red during 12 hr at room temperature. With ice cooling, water was added dropwise. The ether layer was separated, washed with saturated sodium chloride solution, dried, and evaporated. The crude orange-yellow oil (1.9 g) was chromatographed on Florisil (pentane elution) to furnish 0.87 g (66.4%) of **10a** as a clear, colorless oil. An analytical sample was prepared by vpc purification, $\delta_{TMS}^{CDCl_3}$ 5.2–6.45 (br m, 7 H, olefinic), 2.85–3.35 (br m, 2, bridgehead), and 1.78 (s with additional fine coupling, 3 H, methyl).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.37. Found: C, 91.38; H, 8.61.

Reaction of 7-Methylbicyclo[4.2.2]deca-2,4,7,9-tetraene (10a) with CSI.—A solution of 290 mg (2.0 mmol) of **10a**[15] and 0.18 ml (2.0 mmol) of CSI in 10 ml of dry methylene chloride was stirred rapidly at 25° under nitrogen. Infrared analysis of aliquots revealed the presence of intense new carbonyl bands at 1825 and 1760 cm^{-1}; however, after 7 hr only the 1760-cm^{-1} band remained. The solvent was evaporated; nmr analysis of the residue showed the presence of two components in the ratio of 68.5:31.5. The predescribed pyridine–thiophenol work-up gave 282 mg (73%) of the lactam mixture. Crystallization from methylene chloride–ether gave the major isomer (**11a**) as colorless crystals, mp 163.5–164.5°, $\nu_{max}^{CHCl_3}$ 1705 cm^{-1}.

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: 76.98; H, 6.89; N, 7.43.

The mother liquors from several such runs were combined and chromatographed on Florisil. The minor isomer (**12a**) was eluted first with chloroform, colorless needles, mp 170.5–172.5°, $\nu_{max}^{CHCl_3}$ 1705 cm^{-1}.

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.76; H, 6.88; N, 7.59.

Reaction of 7-Methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (10b) with CSI.—A solution of 158 mg (1.0 mmol) of **10b**[15,20] and 0.1 ml (1.4 mmol) of CSI in 10 ml of methylene chloride was stirred at 25° under nitrogen for 7 hr. The solvent was evaporated and the residue showed two methoxyl peaks (ratio 54.5:45.5) in its nmr spectrum. Processing as before gave 115 mg (56.5%) of the lactam mixture. Careful chromatography on Florisil ($CHCl_3$ elution) enabled **12b** (more rapidly moving) to be separated from **11b**. Recrystallization of the minor isomer (**11b**) from methylene chloride–ether gave colorless crystals (38 mg, 18.5%), mp 154–154.5°, $\nu_{max}^{CHCl_3}$ 1705 cm^{-1}.

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.72; H, 6.48; N, 6.85.

Lactam **12b** was likewise recrystallized from methylene chloride–ether, 50 mg (24%), colorless crystals, mp 193–194°, $\nu_{max}^{CHCl_3}$ 1705 cm^{-1}.

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.55; H, 6.57; N, 6.81.

Reaction of 7-Acetoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (10c) with CSI. A. Long Reaction Time.—The enol acetate (**10c**, 270 mg, 1.5 mmol)[15] was dissolved in 15 ml of dry methylene chloride and 0.18 ml (2.0 mmol) of CSI was added in one portion with stirring under nitrogen. After 13 hr at 25°, the solvent was evaporated and nmr analysis indicated the presence of two components in a 76:24 ratio. The customary thiophenol–pyridine reduction and filtration through a short column of Florisil gave 193 mg (57.5%) of a lactam mixture. Recrystallization from methylene chloride–ether furnished a pure sample of the major product (**11c**, 128 mg, 38%) as colorless prisms, mp 193.5–194°, $\nu_{max}^{CHCl_3}$ 1735 and 1705 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.26; H, 5.61; N, 6.04.

Like purification of the minor product (**12c**) led to its isolation as colorless crystals, mp 187.5–188.5°; $\nu_{max}^{CHCl_3}$ 1735 and 1705 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.40; H, 5.67; N, 6.12.

B. Brief Reaction Period.—CSI (0.25 ml, 0.3 mmol) was added to a solution of 453 mg (0.25 mmol) of **10c** in 7 ml of methylene chloride. After stirring for 4 min, the solvent was evaporated and the residue was immediately dissolved in acetone and treated with thiophenol and pyridine at 0° in the usual way. Chromatography on Florisil and elution with pentane–chloroform (1:1) yielded 344 mg of colorless, oily β-lactam **13** which on crystallization gave 250 mg (45.5%) of colorless crystals: mp 159.5–160.5°; $\nu_{max}^{CHCl_3}$ 1770 and 1730 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 273 nm (ε 3150), 263 (5110), 253.5 (4890), and 246 (sh, 3730); $\delta_{TMS}^{CDCl_3}$ 7.3 (br s, >NH), 5.65–6.4 (m, 6, olefinic), 3.9 (m 1, bridgehead), 3.36 (s, >CHCO–), 3.16 (m, 1 bridgehead), and 2.08 (s, 3, $-COCH_3$).

Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.55; H, 5.75; N, 5.95.

7-Methoxy-8-methylbicyclo[4.2.2]deca-2,4,7,9-tetraene (15).—A dry 500-ml three-necked flask was fitted with a thermometer, two 10-ml addition funnels (fitted with nitrogen inlet), a mechanical stirrer, and a connection to the house vacuum *via* a stopcock. The flask was charged with 200 ml of dry dimethyl sulfoxide and 4.6 g of potassium *tert*-butoxide. The addition funnels contained 2.0 g of somewhat impure **14** and 4 ml of dimethyl sulfate. The system was degassed three times, filled with nitrogen, and cooled to 0°. The ketone was added during 30 sec and the resulting red solution was stirred for 3 min. At 0°, the dimethyl sulfate was added rapidly. The solution was stirred for 20 min at 0° and for 1.5 hr at room temperature, after which it was poured into 500 ml of 2 *M* sodium hydroxide solution. The product was extracted with pentane (10 × 100 ml) and the combined pentane extracts were washed four times with water and dried. Evaporation of the solvent gave a yellow oil (1.7 g), chromatography of which on alumina (activity I) using pentane–2% ether as eluent gave 0.83 g (38%) of **15**: ν_{max}^{neat} 1700 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 256.5 nm (ε 3360) and 248.5 (3300); $\delta_{TMS}^{CDCl_3}$ 5.5–6.54 (m, 6, olefinic), 3.50 (s, 3, $-OCH_3$), 2.92–3.5 (m, 2, bridgehead), and 1.7 (s, 3, $-CH_3$).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.09. Found: C, 82.60; H, 8.05.

Reaction of 7-Methoxy-8-methylbicyclo[4.2.2]deca-2,4,7,9-tetraene (15) with CSI.—Treatment of 340 mg (2.0 mmol) of **15** with 0.18 ml (2.0 mmol) of CSI in 20 ml of dry methylene chloride as above gave an *N*-(chlorosulfonyl) γ-lactam mixture in a ratio of 68.5:31.5. The usual chlorodesulfonylation and Florisil chromatography yielded 223 mg (52.5%) of a solid mixture of **16a** and **16b**. When the mixture was rechromatographed on Florisil (chloroform elution), separation of the two components was readily effected. The first isomer to elute was **16b**, which crystallized from methylene chloride–ether as colorless needles (143 mg, 43%), mp 189.5–190.5°, $\nu_{max}^{CHCl_3}$ 1705 cm^{-1}.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.59; H, 6.92; N, 6.37.

From the later fractions, there was obtained 60 mg (14%) of **16a**, mp 171–172.5°, from methylene chloride–ether, $\nu_{max}^{CHCl_3}$ 1705 cm^{-1}.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.77; H, 7.01; N, 6.47.

Reaction of 7,8-Diphenylbicyclo[4.2.2]deca-2,4,7,9-tetraene (17) with CSI.—A solution of 200 mg (0.7 mmol) of **17**[21] and 0.065 ml (0.77 mmol) of CSI in 10 ml of dry methylene chloride was stirred at room temperature for 22 hr, evaporated, and hydrolyzed with sodium sulfite solution as above. The product was extracted into methylene chloride and, after drying and evaporation, was obtained as fine, colorless needles (122 mg, 53%), mp 215.5–216.5°, from methylene chloride–ether, $\nu_{max}^{CHCl_3}$ 1705 cm^{-1}.

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89. Found: C, 84.53; H, 5.85.

Reaction of Bicyclo[4.2.1]nona-2,4,7-triene (23a) with CSI.—Hydrocarbon **23a** (470 mg, 0.4 mmol)[29] was dissolved in methylene chloride (7 ml) and treated with CSI (0.35 ml, 0.42 mmol) under nitrogen with stirring. After 14 hr, only *N*-(chlorosulfonyl) β-lactam carbonyl absorption was visible in the infrared. The solution was evaporated and the residue was treated with thiophenol and pyridine in acetone at 0°. After chromatography on Florisil (chloroform–pentane, 1:1, used for elution), 517 mg (80%) of a colorless oil was obtained which appeared homogeneous (nmr analysis). Trituration with ether–pentane at −78° and recrystallization from this solvent system gave **25b** as colorless crystals: mp 76–78°; $\nu_{max}^{CHCl_3}$ 1750 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 275.5 nm (ε 2950), 264.5 (5500), 255 (5600), and 248 (sh, 4240); $\delta_{TMS}^{CDCl_3}$ 7.1 (br, 1 >NH), 5.8–6.6 (m, 6, olefinic), 3.88 (d, J = 3.5 Hz, 1), 3.5 (m, 1), 2.3–3.1 (m, 3), and 1.85 (d, J = 11.5 Hz).

(29) T. J. Katz and S. Cerefice, *Tetrahedron Lett.*, 2561 (1969).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.59; H, 6.80; N, 8.74.

β-Lactam **25b** is unstable, since originally colorless crystals become yellow and partly insoluble over a period of a few days. In the noncrystalline state, polymerization is particularly rapid.

Registry No.—**1**, 15677-13-1; **3**, 34733-74-9; **5**, 38910-79-1; **7**, 38910-80-4; **7** perchlorate, 38910-81-5; **10a**, 37494-24-9; **10b**, 36629-02-4; **10c**, 36629-05-7; **11a**, 38910-85-9; **11b**, 38910-86-0; **11c**, 38910-87-1; **12a**, 38910-88-2; **12b**, 38910-89-3; **12c**, 38910-90-6; **13**, 38910-91-7; **14**, 38910-92-8; **14** tosylhydrazone, 38974-04-8; **15**, 38910-93-9; **16a**, 38910-94-0; **16b**, 38898-33-8; **17**, 14690-42-7; **18**, 38898-35-0; **23a**, 38898-36-1; **25b**, 38898-37-2; CSI, 1189-71-5.

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Uniparticulate Electrophilic Addition as a Probe of Possible Bicycloaromatic and Antibicycloaromatic Carbonium Ion Character. Reactions of Chlorosulfonyl Isocyanate with Exocyclic Methylene Precursors to Such Cations[1]

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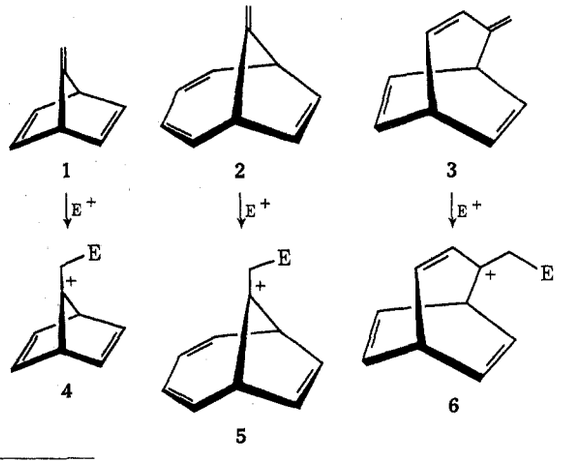
Received January 3, 1973

Synthesis of the methylene polyolefins 9-methylenebarbaralane (**10**), 2-methylenebicyclo[3.2.2]nona-3,6,8-triene (**3**), 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (**2**), and their benzologs, as well as 7-methylenenorbornadiene (**1**) and 7-methylenequadricyclane (**8**), has been achieved and the reactions of these hydrocarbons with chlorosulfonyl isocyanate studied. The systems examined were those which upon attack at the methylene group would lead to the generation of possible bicycloaromatic (*e.g.*, **4**) or antibicycloaromatic (*e.g.*, **5**, **6**) zwitterionic intermediates. Possible mechanistic pathways leading to the products are proposed and conclusions relating to stabilization and destabilization of the relevant cations are drawn.

The concept of bicycloaromaticity, initially formalized in 1967,[3] relates to possible extensive charge delocalization in tricyclic ions containing three π bridges in a longicyclic topology.[4] Of interest because it extends the phenomenon of homoaromaticity[5] to a third dimension, this theory has received an ever increasing amount of attention since its introduction. To this time, the several relevant cations which have been studied have been generated either solvolytically (short-life conditions)[6] or by protonation in superacidic media at low temperatures (long-life conditions).[7] Access to anions has been gained by the action of sodium–potassium alloy on a suitable methoxyl precursor[6g,8] and by deprotonation.[9] In this paper, we present yet another way to assess the possible bicyclo- or antibicycloaromatic character of cationic species which relies upon the generation and capture of these elusive intermediates with the uniparticulate electrophile[10] chlorosulfonyl isocyanate (CSI).

In earlier work, the necessity of a suitable reference system for evaluation of the level of bicycloaromatic character in each individual ion under study has presented certain problems. Originally, Goldstein and Odell[6a] resorted to a compound possessing the same number of trigonal carbon atoms and π electrons. More recently, Grutzner and Winstein[6h] selected a homoaromatic reference system in which interaction operates between two bridges isolated from the third. The ideal situation is, of course, one in which the identical geometry is available to both the standard and potentially bicycloaromatic entity.

In view of the practicality of synthesizing alicyclics **1–3** and related exocyclic methylene hydrocarbons, we have entertained the possibility of employing each of these hydrocarbons as its own standard of reference. Were electrophilic attack to occur at the exocyclic



(1) Unsaturated Heterocyclic Systems. XC. Preceding contribution in this series: L. A. Paquette and M. J. Broadhurst, *J. Org. Chem.*, **38**, 1886 (1973).

(2) Holder of a NATO Postdoctoral Fellowship (1970–1972) administered by the Science Research Council.

(3) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

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