Homotropylium Cations. Substituent Control on Their Generation and Subsequent Reactions[1]

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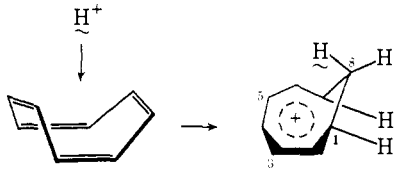
Abstract: When cyclooctatetraene and a number of its monosubstituted derivatives are treated with chlorosulfonyl isocyanate, 1,4 cycloaddition to the eight-membered ring occurs. The structures of the resulting N-(chlorosulfonyl) lactams and their derived products reveal that the electrophilic isocyanate attacks the individual polyene at the carbon atom adjacent to the substituent-bearing carbon to give the more stable classical cation in each instance. By analogy to earlier protonation and chlorination studies, the isocyanate is considered to approach from the *endo* surface of the tub conformation of the polyene. Energy considerations indicate that the intermediate classical cations pass readily by way of low-energy conformational changes to 1-substituted homotropylium cations which subsequently cyclize by means of C–N bond formation. The control which the various substituents at position 1 of the homoaromatic cation exert on the directional specificity of this cyclization reaction is discussed. The conclusions are reached that groups attached to C-1 are unable to interact with the homotropylium cation by resonance and that the inductive effect of the particular substituent is responsible for the appreciable differences in the ratios of the cycloaddition products.

Recent work has established that the $C_8H_9^+$ ion which is generated upon protonation of cyclooctatetraene (COT) in concentrated sulfuric acid is the monohomotropylium cation (**1**).[3,4] In D_2SO_4, considerable stereo-



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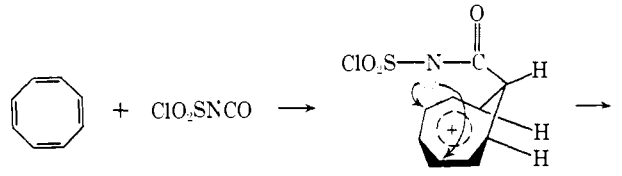
specificity in the protonation is observed at lower temperatures (−15°), the deuterium approaching preferably from the fold of the tub conformation possibly because of the greater electron density on that surface. Subsequent to these important discoveries, a considerable number of monohomotropylium cations have been recognized in a wide range of nmr studies.[5,6] All are capable of sustaining a large induced ring current and are therefore decidedly homoaromatic. The stabilization associated with **1** amounts to a free energy difference of 22.3 kcal/mol relative to the classical planar cyclooctatrienyl cation.[4b]

In view of the appreciable stability of monohomotropylium cations, the possibility exists that many electrophilic additions to COT may proceed by way of such intermediates. Many of the unique features of these reactions would then be more logically interpretable at the mechanistic level. In this context, Huisgen and coworkers have recently established that the chlorination of COT occurs *via endo*-8-chlorohomotropylium cations which suffer kinetically controlled nucleophilic attack by chloride ion at the *endo* side of C-1 to give predominantly *cis*-7,8-dichlorocyclooctatriene.[7] Also, the 1,4-cycloaddition reaction which occurs when COT is treated with chlorosulfonyl isocyanate (**2**) at 50° in the absence of solvent has been rationalized on the basis of intervening dipolar homotropylium cation **3** followed by collapse of **3** *via* either of two equivalent six-centered transition states.[8] In a two-pronged effort to obtain



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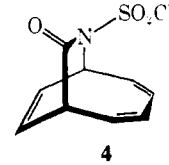

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corroborative evidence for this mechanistic proposal and to develop our knowledge of the chemistry of this interesting six-electron homoaromatic cation, we have extended our studies to include the reaction of several substituted cyclooctatetraenes with **2**. The control which the various substituents exert on the generation of homotropylium cations and the influence of their differing electronic requirements on the cyclization process form the subject of this report.

(1) Unsaturated Heterocyclic Systems. LX. For the previous paper in this series, see L. A. Paquette, S. Kirschner, and J. R. Malpass, *J. Am. Chem. Soc.*, **91**, 3970 (1969).

(2) National Institutes of Health Postdoctoral Fellow, 1967.

(3) (a) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962); (b) C. E. Keller and R. Pettit, *ibid.*, **88**, 604 (1966); (c) C. E. Keller and R. Pettit, *ibid.*, **88**, 606 (1966).

(4) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965); (b) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

(5) (a) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963); (b) H. D. Kaesz, S. Winstein, and C. G. Kreiter, *ibid.*, **88**, 1319 (1966); (c) M. Brookhart, M. Ogliaruso, and S. Winstein, *ibid.*, **89**, 1965 (1967); (d) R. F. Childs and S. Winstein, *ibid.*, **89**, 6348 (1967); (e) W. Merk and R. Pettit, *ibid.*, **90**, 814 (1968); (f) G. D. Mateescu, C. D. Nenitzescu, and G. A. Olah, *ibid.*, **90**, 6235 (1968); (g) O. L. Chapman and R. A. Fugiel, *ibid.*, **91**, 215 (1969).

(6) S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967, pp 5–45.

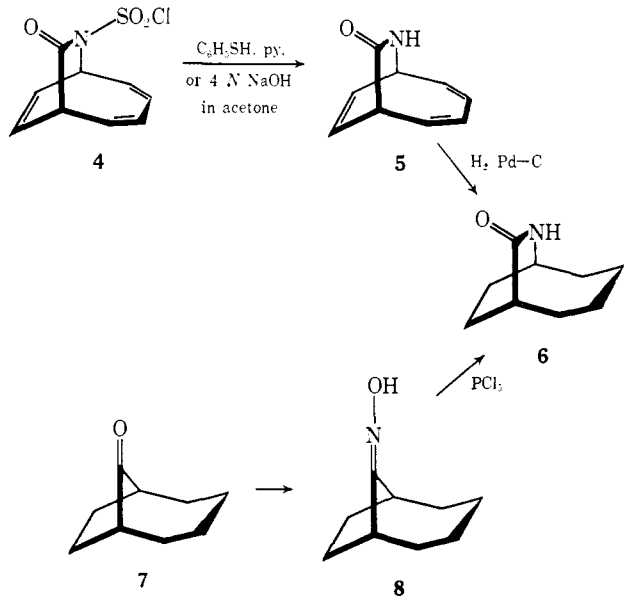
(7) (a) G. Boche, W. Hechtl, H. Huber, and R. Huisgen, *J. Am. Chem. Soc.*, **89**, 3344 (1967); (b) R. Huisgen, G. Boche, and H. Huber, *ibid.*, **89**, 3345 (1967).

(8) L. A. Paquette and T. J. Barton, *ibid.*, **89**, 5480 (1967).

Results

Cyclooctatetraene. The present research began with cyclooctatetraene in an attempt to gain insight into the reactivity of the parent polyunsaturated hydrocarbon toward chlorosulfonyl isocyanate (CSI, **2**). It was noted by reference to the work of Graf[9] that CSI adds readily to a variety of olefins at −70° to 0° in an inert solvent such as CCl_4 or CH_2Cl_2. Cyclooctatetraene, however, was found not to react under these conditions; at room temperature cycloaddition did occur but the rate of the process was very slow and impractical from the synthetic viewpoint.[10] However, slow addition of CSI to COT in the absence of solvent at 50° led in 73% yield to N-(chlorosulfonyl) lactam **4**. Reduction of **4** proceeded smoothly with thiophenol and pyridine in acetone at 0° or with aqueous 4 *N* sodium hydroxide in acetone with loss of the chlorosulfonyl group to yield **5** (Scheme I), the structure of which was deduced from its

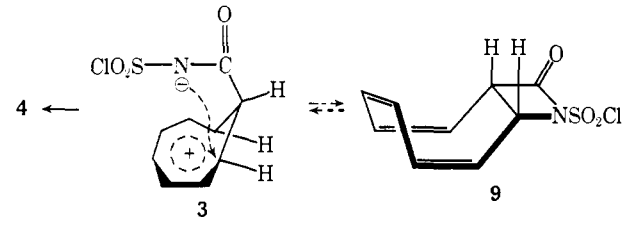
Scheme I



4 5 6 7 8

spectral properties and by its catalytic reduction with the absorption of 3 mol of hydrogen to **6**. Independent synthesis of **6** was achieved in low yield by oximation and subsequent Beckmann rearrangement of the known bicyclo[4.2.1]nonan-9-one (**7**).[11]

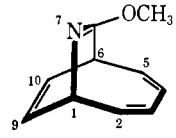
The mechanistic pathway proposed earlier[8] assumes approach of CSI toward the inside fold of the tub conformation of COT and ultimate electrophilic attack to form dipolar homotropylium cation **3**. Although the collapse of **3** *via* a six-centered transition state to give **4** was expected to be faster than the alternative four-center pathway leading to **9**, the marked proclivity of CSI for $(2 + 2)\pi$ cycloaddition to olefins[9] and dienes[12] and the demonstrated propensity of chloride ion to attack 8-chlorohomotropylium cations exclusively at C-1[7] prompted a search for the possible intervention of **9**.



4 ← 3 ⇌ 9

Since the subsequent rearrangement of **9** to **4** would very likely proceed by heterolytic C–N bond cleavage back to **3**, the transient formation of **9** would not vitiate the original proposal. Rather, it would merely require expansion of the concept to include sequential rapid kinetically controlled cyclization to **9**, reionization to **3**, and less rapid thermodynamically controlled azabicyclo-[4.2.2]decatrienone production. To this end, a 1.6 *M* solution of COT in CCl_4 containing an equivalence of CSI was heated at 75–80° and aliquots were periodically removed and examined by infrared spectroscopy. As the reaction progressed (slowly), there was observed only the development of the 1730-cm^{-1} band characteristic of **4**. Therefore, if **9** were produced in this reaction, its rate of conversion to **4** must be sufficiently rapid on the absolute scale to preclude its isolation.

Exposure of **5** to trimethyloxonium fluoroborate led to the isolation of imino ether **10**. This tetraene was characterized by an ultraviolet absorption maximum in acetonitrile at 271 mμ (ε 2000) and a 100-MHz nmr spectrum which showed a methoxyl group singlet at δ 3.52, a one-proton doublet of doublet signal ($J_{5,6}$ = 8.8 Hz; $J_{6,10}$ = 5.2 Hz) at 3.38 for H-6, a second doublet of doublets ($J_{1,2}$ = 8.4 Hz, $J_{1,9}$ = 4.4 Hz) at 4.27 attributable to H-1, and a complex vinyl proton multiplet of area 6 in the 5.43–6.42 region.[13]



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Methylcyclooctatetraene (11) reacted with 1 molar equiv of CSI in methylene chloride solution at 20° to give in 97% yield a solid mixture of two 1,4-addition products which were subjected directly to hydrolysis and treatment with trimethyloxonium fluoroborate. There was produced with high recovery a mixture of imino ethers **14** and **15** in an average ratio of 65:35 (Scheme II). Although the two isomers could not be separated by gas chromatographic techniques on a wide variety of columns, treatment of an ether solution of the mixture with methanolic 60% perchloric acid caused the perchlorate salt of **15** to crystallize preferentially. Regeneration of the free base from this purified salt gave **15** as a low-melting white solid; basification of the mother liquors from the perchlorate crystallization yielded an oil, crystallization of which from ether–pentane at −15° afforded **14**. The major isomer (**14**) exhibited an ultraviolet spectrum in acetonitrile solution which showed a lone maximum at 269 mμ (ε 2700); in **15**, this band was bathochromically shifted to 273 mμ (ε 4400). Because these absorptions arise chiefly from $\pi \rightarrow \pi^*$ excitation of the diene chromophore in the tetraenes and since the at-

(9) R. Graf, *Ann.*, **661**, 111 (1963).

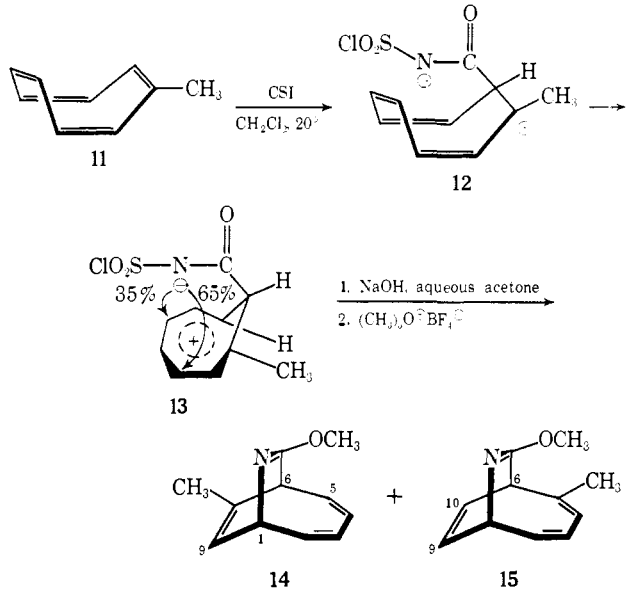
(10) Subsequent to our preliminary communication on this subject,[8] P. Wegener [*Tetrahedron Letters*, 4985 (1967)] reported the isolation of **4** in 40% yield by reaction of neat COT and CSI in 1:1 molar proportions at room temperature.

(11) C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960). We are indebted to Professor Gutsche for a generous sample of ketone **7**.

(12) E. J. Moriconi and W. C. Meyer, *Tetrahedron Letters*, 3823 (1968).

(13) As noted earlier,[8] the 60-MHz spectrum of **10** suffers from the fact that the methoxyl signal overlaps with the absorption due to H-6.

Sechme II



tachment of an alkyl group to the diene segment can be expected to displace λ_{max} to longer wavelengths by approximately 5 mμ, these observations indicate that the methyl group in **15** is positioned on the larger bridge. This conclusion is supported by 100-MHz nmr analysis which established further that the methyl substituent is attached to C-5. Thus, the doublet of doublets at δ 4.32 attributable to the bridgehead proton adjacent to nitrogen was coupled to the extent of 4.6 and 8.0 Hz to H-9 and H-2, respectively. The bridgehead proton at C-6, however, appeared only as a doublet at δ 3.35 with J = 5.5 Hz; on the basis of the fact that the bridgehead protons consistently show larger vicinal coupling to the neighboring diene proton than to the nearest proton on the ethylene bridge (see Table I),[14] it follows that the methyl group in **15** is at C-5. Conversely, compound **14** displayed a spectrum in which H-1 (δ 4.24) appeared as a doublet of doublets (J = 5.0 and 8.0 Hz) and H-2 (δ 3.48) was seen as a doublet with a substantially larger coupling constant (8.7 Hz).

Table I. Nmr Spectral Comparison of the 8-Methoxy-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraenes ($CDCl_3$ Solutions)[a]

Compd	δ, H-1 (m)[b]	$J_{1,2}$, Hz	$J_{1,9}$, Hz	δ, H-6 (m)[b]	$J_{5,6}$, Hz	$J_{6,10}$, Hz
10	4.27 (dd)	8.4	4.4	3.38 (dd)	8.8	5.2
14	4.24 (dd)	8.0	5.0	3.48 (d)	8.7	
15	4.32 (dd)	8.0	4.6	3.35 (d)		5.5
18	4.40 (dd)	8.0	5.0	3.57[c]		~5.0
19	4.35 (dd)	8.0	6.0	3.65[c]	c	
24	4.55 (dd)	8.0	5.5	4.15 (d)	8.5	
25	4.49 (dd)	7.8	4.5	4.10 (d)		5.5
28	4.53 (dd)	8.0	5.4	4.13 (d)	8.5	
29	4.50 (dd)	7.6	4.7	4.08 (d)		5.1
33	4.56 (t)	~6.0	~6.0	4.10 (d)		5.6

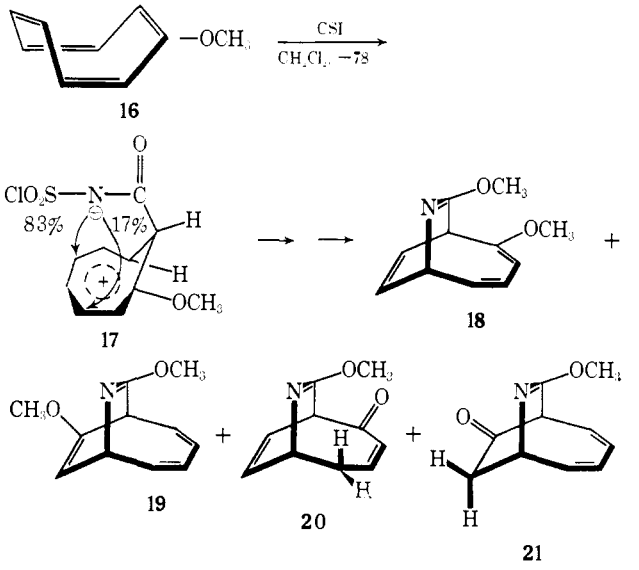
[a] The numbering system employed may be found in formulas **10**, **14**, and **15**. [b] Multiplicity of the absorption: d = doublet; dd = doublet of doublets; t = triplet. [c] Absorption of H-6 in these cases is overlapped by the methoxyl peaks.

(14) This general conclusion has been established by extensive double resonance studies on the various tetraenes described in this paper. For economy of space, the detailed analyses are not discussed; however, the spectra will be made available to interested parties on request.

The above data clearly indicate that the isocyanate attacks **11** to produce the most stable classical carbonium ion (**12**); irreversible low-energy conformational change in **12** with development of delocalization interaction and accompanying stabilization gives a 1-methylhomotropylium cation bearing an *endo*-ClO_2SN^-CO– residue at C-8 (**13**). This zwitterion is seen to be partitioned unequally in the C–N bond-forming step, cyclization to C-3 being favored by a factor approaching 2:1.

Methoxycyclooctatetraene. Addition of CSI to methoxycyclooctatetraene (**16**) occurred with exceptional ease, being complete within 4 hr at −78° in methylene chloride solution. Sequential treatment of the crude addition product as above gave in 62% over-all yield a mixture of four imino ethers (Scheme III). The major product (55%) was readily identified

Scheme III



as **18** on the basis of its ultraviolet and nmr spectra (Table I). The minor component (4%) exhibited an ultraviolet spectrum which denoted that the methoxyl substituent was not situated on the diene segment. The close correspondence of its nmr spectrum with that of **14**, and appropriate double resonance studies,[19] unambiguously defined the structure as **19**. The infrared spectrum of **20** (28%) showed a strong band at 1647 cm^{-1}, while that of **21** (13%) displayed intense peaks at 1727 and 1672 cm^{-1} (in Nujol). Significantly, whereas **20** exhibited only a single peak in the ultraviolet at 221 mμ (ε 5400, hexane), ketone **21** gave evidence of two absorption bands at 264 (ε 3500) and 273 mμ (ε 3300, hexane). As expected from **20**, its nmr spectrum displayed a complex four-proton multiplet at δ 5.6–6.2 due to the vinyl protons, a 1:3:3:1 quartet with spacings of 4.0 Hz centered at δ 4.54 due to H-1, a doublet (J = 5.5 Hz) at 4.10 for H-6, and a complex AB quartet (J_{AB} = 21 Hz, Δ_{AB} = 23.5 Hz) centered at 3.00 for the methylene group. Double-resonance studies confirmed that spin–spin coupling of the methylene protons at C-2 to H-1 (J = 4.0 Hz in each case) and to the vinyl proton at position 3 (J = 2.0 and 3.0 Hz) was operative. Substantiation for structure **21** was likewise found in its nmr spectrum which showed H-1 as a complex "triplet," spin decoupling of which revealed the following cou-

pling constants: $J_{1,2}$ = 6 Hz and $J_{1,9}$ = 6.0 and 2.0 Hz. In addition, the vinyl protons were seen as complex patterns at δ 6.28 (1 H) and 5.6–5.9 (3 H), and the methylene protons appeared as an AB quartet (J_{AB} = 18 Hz, Δ_{AB} = 21 Hz) centered at δ 2.65 which was complicated because of the differing spin–spin interactions of the two protons with H-1 (J = 6.0 and 2.0 Hz). The H-6 absorption was partially obscured by the methoxyl singlet.

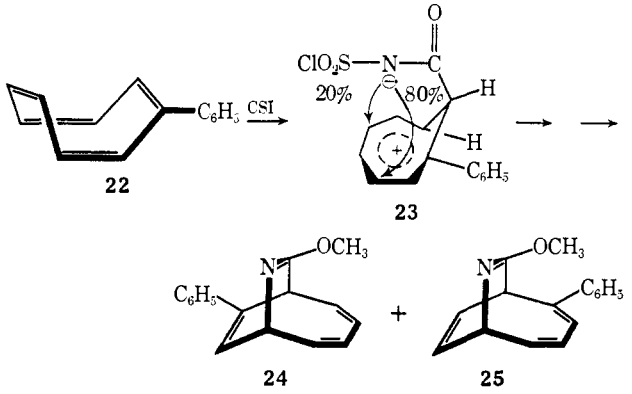
Modifications in the work-up procedure caused changes in the proportions of **18**:**20** and **19**:**21**, thereby indicating that the carbonyl containing imino ethers were the results of vinyl ether hydrolysis in the course of this operation. These additional experiments were further revealing: in the several runs, the percentage ratio of (**18** + **20**) : (**19** + **21**) remained constant (83:17) within a 3% maximum deviation limit. Additionally, this percentage isomer distribution was not altered for reactions conducted over a 100° temperature range (−78 to +20°).

In view of the high reactivity of methoxycyclooctatetraene (**16**), its reaction with CSI could be conveniently monitored at low temperatures. When CSI was added to a solution of **16** in methylene chloride precooled to approximately −75° in a low-temperature infrared cell and the reaction was allowed to proceed at that temperature with repeated scanning of the 1600–1900-cm^{-1} region, no band characteristic of an intermediate β-lactam was seen. Rather, the 1730-cm^{-1} band of the six-ring lactams gradually intensified.

As before, these results can be uniquely interpreted to mean that initial attack of CSI occurs on the *endo* surface of C-2 in **16** to give the most stable classical cation which rapidly passes to **17**. However, bonding to C-5 is now favored by a factor of 4 over bonding to C-3.

Phenylcyclooctatetraene. The reaction of phenylcyclooctatetraene (**22**) with CSI proceeded in a manner similar to that of the methyl and methoxy derivatives although somewhat more sluggishly (neat at 55° or refluxing methylene chloride for 20 hr; see Scheme IV).

Scheme IV

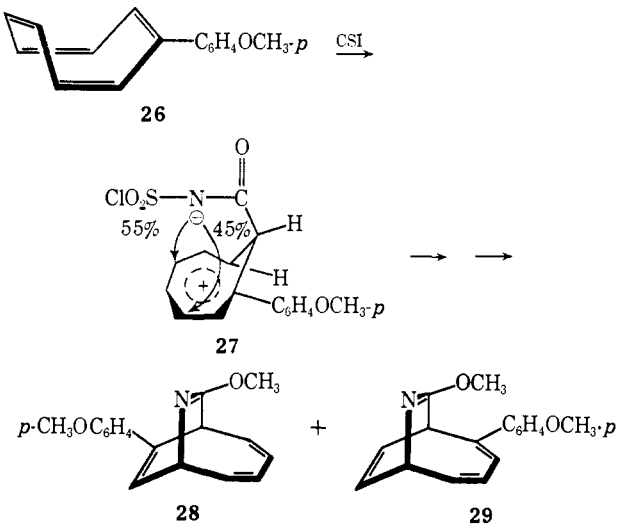


Preparative-scale vpc served to separate the resulting two imino ethers. Inspection of the nmr spectrum of the major (80%) product revealed that the absorption at δ 4.15 assignable to H-6 appeared as a doublet with J = 8.5 Hz (see Table I). Additionally, its lone ultraviolet maximum (in hexane) was seen at 246.5 mμ (ε 13,900). These data signify that the phenyl substituent occupies position 10 and characterize the substance as **24**. The fact that the minor isomer showed H-6 as a doublet (J = 5.5 Hz) at δ 4.10 and exhibited a single ultraviolet maximum in hexane at 299 mμ (ε 10,000) indicates clearly that the phenyl group is at C-5 and therefore that **25** was produced in low yield (20%).

In **23**, a strong preference for ultimate bonding of nitrogen to C-3 is observed; this behavior parallels closely the reactivity demonstrated by methyl derivative **13**.

***p*-Methoxyphenylcyclooctatetraene.** Because of the contrasting reactivity of the methyl- and phenyl-substituted homotropylium cations **13** and **23** on the one hand and methoxy derivative **17**, an examination of the reaction of *p*-methoxyphenylcyclooctatetraene (**26**) with CSI was deemed important for the purpose of mechanistic rationalization. This polyene (**26**) was obtained with difficulty (3% yield) upon treatment of cyclooctatetraene with *p*-anisyllithium. Reaction of **26** with CSI in methylene chloride solution was slow at 0°, but was complete within 6 hr at room temperature (Scheme V). Direct hydrolysis afforded a quantitative crude

Scheme V

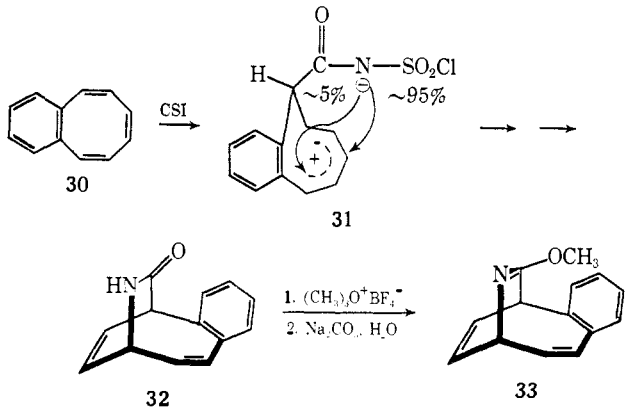


yield of two amides. Subsequent treatment with Meerwein's reagent gave the corresponding imino ethers **28** and **29** in 74% yield. It was not possible to separate these isomers by vpc even on an analytical scale; however, small quantities of the amides could be separated by fractional crystallization and each was converted separately to **28** and **29**. Also, the higher melting imino ether (**28**) could be obtained in a pure state by fractional crystallization of the imino ether mixture. Nmr (Table I) and ultraviolet data (see Experimental Section) were sufficient to characterize these products unequivocally.

The ratio of the two products was determined by careful integration of the pair of four-proton AB quartets due to the two types of aromatic protons in the amide and imino ether mixtures. In several experiments, the percentage of **28** (and its derived amide) was seen to be 45 ± 3%. Clearly, therefore, the *p*-methoxyl function is capable of exerting an effect which promotes increased cyclization to C-5 in homotropylium cation **27**. Although the high preference (80%) exhibited by methoxyl derivative **17** for bonding to C-5 is not seen, a substantial shift in that direction relative to phenyl derivative **23** (20%) is to be noted. This order of magnitude was expected for **27** in view of the fact that the methoxyl group is insulated from the cationic center by the phenyl ring.

Benzocyclooctatetraene.[15] Benzocyclooctatetraene (**30**) also undergoes the interesting transformation to an azabicyclo[4.2.2]octatetraene when treated with CSI at 82° in the absence of solvent for 3 hr (Scheme VI).

Scheme VI



30 31 32 33

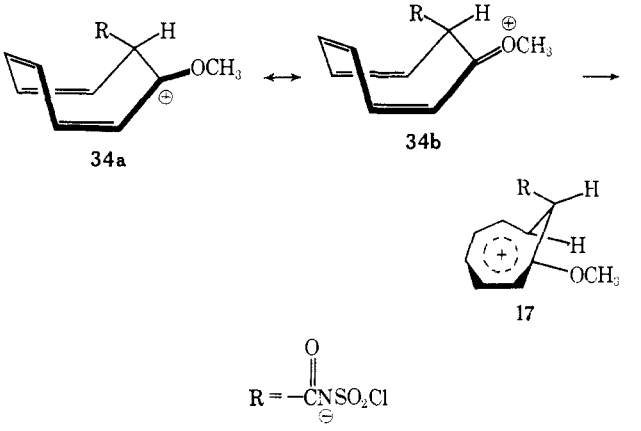
Hydrolysis of the resulting brown oily solid with aqueous sodium hydroxide in acetone afforded in 82% yield the amide **32**. The assigned structure follows from the ultraviolet spectrum which consisted solely of a styrene chromophore and from the nmr spectrum which displayed the bridgehead protons as a broad multiplet in the δ 4.1–4.4 region. The precise magnitude of the spin–spin coupling constants associated with the bridgehead protons was clarified by conversion to **33**. The nmr spectrum of this substance clearly revealed H-1 as a triplet (J = 6 Hz) at δ 4.56 and H-6 as a doublet (J = 5.6 Hz) at δ 4.10. Consequently, the phenyl ring must be fused to positions 4 and 5.

Careful nmr analysis of the unpurified amide indicated that an upper limit of 7% cyclization to C-3 could have occurred. However, the limited availability of this minor product precluded its isolation and characterization. Electrophilic attack of CSI on **30** therefore proceeds to give dipolar benzohomotropylium cation **31**, collapse of which occurs chiefly by bonding to C-5.

Discussion

From the synthetic viewpoint, the present results encompass over-all 1,4 cycloaddition of CSI to the cyclooctatetraene system. Prior to our preliminary report of this reaction,[8] only four examples of 1,4 addition to cyclooctatetraene had been described, all of which were free-radical reactions.[16] More recently, however, benzyne[17] and 4-phenyl-1,2,4-triazoline-3,5-dione[18] have been shown to undergo related reactions.

At the mechanistic level, the high yields observed in the production of the various N-(chlorosulfonyl) lactams require a high order of specificity for *endo* attack by the electrophilic isocyanate upon the eight-membered polyenes. This conclusion agrees entirely with earlier deuteration and chlorination studies.[7] As established above, the positions occupied by the substituent groups in the six-ring lactams and the corresponding imino ethers attest to the fact that the initial bonding of the isocyanate takes place to produce the most stable classical cation. These observations are helpful when one considers the relative rates of the various cycloadditions studied, as estimated qualitatively from the temperatures necessary to achieve effective condensation. For example, methoxycyclooctatetraene was the most reactive derivative examined, and this accelerative effect must result because of an increase in the rate of formation of the derived carbonium ion in the rate-determining step. For closely related reactions, a difference in rate of formation of carbonium ions is largely determined by a difference in the energy of activation. Because stabilization of the cation by charge dispersal stabilizes the incipient carbonium ion of the transition state, **16** is expected to react more rapidly than the remaining cyclooctatetraenes studied due to the intervention of a resonance hybrid composed of structures **34a** and **34b**.[19] Judging from the considerably greater stability of homotropylium cations,[4b] intermediates of type **34** would pass



34a 34b 17

readily by way of a low-energy conformational change to **17** in order to develop the 1,7 interaction necessary for homoaromaticity. The initially formed N-(chlorosulfonyl) lactams appear not to be subject to equilibration. Furthermore, inspection of molecular models leaves no doubt that the 1 substituent can exert little, if any, steric effect on either cyclization pathway. The wide differences in directional specificity of ring closure of the homotropylium cations, summarized in Table II,

Table II. Comparison of Directional Specificity in the Ring Closure of the Various Homotropylium Cation Intermediates

Structure	Substituent	% cyclization to C-3[a]	% cyclization to C-5[a]
31	1,2-(CH=CH)$_2$	5	95
17	1-OCH$_3$	17	83
27	1-C$_6$H$_4$OCH$_3$-*p*	45	55
13	1-CH$_3$	65	35
23	1-C$_6$H$_5$	80	20

[a] The numbering system employed is that of the homotropylium cation (see **1**).

must therefore be the result of inductive effects, resonance effects, or a combination of these two factors.

(15) A portion of this work appears in the following preliminary communication: L. A. Paquette and J. R. Malpass, *J. Am. Chem. Soc.*, **90**, 7151 (1968).

(16) (a) J. L. Kice and T. S. Cantrell, *ibid.*, **85**, 2298 (1963); (b) T. S. Cantrell, *J. Org. Chem.*, **32**, 911 (1967); (c) A. G. Anastassiou, *J. Am. Chem. Soc.*, **87**, 5512 (1965); (d) H. Schechter, J. J. Gardikes, T. S. Cantrell, and G. V. D. Tiers, *ibid.*, **89**, 3005 (1967).

(17) E. Vedejs, *Tetrahedron Letters*, 2633 (1968).

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(19) Obviously, this discussion does not give sufficient consideration to the differences in ground-state free energies of the monosubstituted cyclooctatetraenes. In the present instance, overestimation or underestimation of the accelerative effect of the particular substituent is not the major question at issue (see below); however, since this very qualitative consideration gives the expected reactivity order, it is of some utility.

It often is difficult to disentangle inductive effects from other influences, particularly in those instances where direct transmission between the substituent and a conjugated system is possible. In connection with the present study, the previously unexamined question of the degree of electronic interaction which a 1 substituent can transmit to the "pseudoaromatic" sextet of electrons which comprise the homotropylium cation necessarily demands attention.

In benzohomotropylium cation **31**, the benzene ring which is fused to the 1,2 positions is forced to adopt a coplanar, or nearly coplanar, orientation relative to the seven carbon atoms which constitute the cyclic carbonium ion. As a result, C-3 is more or less typically benzylic in nature and can be visualized to be endowed with less positive character than C-5. The observed results are best accommodated by the entirely logical supposition that intramolecular cyclization to C-5 is kinetically preferred because of the relatively greater electron deficiency at that site.

Monomethylhomotropylium cation **13** is a species in which precisely opposite influences are exerted. Thus, the methyl substituent at C-1 will most certainly induce a higher concentration of positive charge at that site since it is a tertiary center. Because C-3 will in turn be more electropositive than C-5 by virtue of its closer proximity to C-1, cyclization to position 3 is favored. To a first approximation, therefore, the marked propensity of methoxyl-substituted cation **17** for cyclization to C-5 is dictated by the adverse inductive effect which is transmitted by the oxygen atom directly to C-1 and less directly to C-3. The important point established by this example is that there is actually no resonance interaction between the methoxyl group and the homotropylium cation. If such an effect were significant, then allowance would have to be made for the fact that considerable buildup of positive charge at C-1 would ensue and a preference for cyclization to C-3 would be demonstrated. This is not seen. The above conclusion is fundamental to homotropylium ion chemistry and may perhaps be made most clear by making reference to structures **34** and **17** above. Focusing attention initially on **17**, we see that resonance interaction of the methoxyl oxygen with the cation would necessarily require rehybridization of C-1. As portrayed, this change is tantamount to forcing loss of homoconjugative stabilization and conformational readjustment of the system back to **34**. As already noted, there is substantial (approximately 22 kcal/mol) driving force operating in the direction which favors formation of the homoaromatic cation. It is certainly unlikely that resonance interaction by a methoxyl or any other group will provide sufficient stabilization to deter the irreversible passage to the localized cation.

Phenyl derivative **23** is controlled by similar energetics. However, although electron delocalization into the benzene ring and attendant change in geometry will not occur, there is free rotation about the C-1 phenyl bond and the phenyl ring can be expected to align itself in the manner most suitable for maximum overlap with the C-1–C-7 bond. Such an arrangement would again favor enhanced carbonium ion character at C-1 and preferred bonding to C-3 as observed. In a system such as **27** in which the phenyl ring bears a *p*-methoxy substituent, the inductive effect of the methoxyl group would be expected to direct cyclization to C-5. Quite clearly, this is observed; however, the insulation provided by the intervening benzene ring not unexpectedly lessens the directive capability of the oxygenated functionality.

In summary, the results collected in Table II and the theoretical points raised above have been considered to reflect the inability of a substituent at C-1 to interact with the homotropylium cation by resonance. On the other hand, the inductive effect of the particular substituent is noted to cause appreciable differences in the directional specificity of the ring closure. Since the changes which affect the cyclization ratios can be understood without resorting to a consideration of electronic transmission through the 1,7 bond, additional studies will be required to shed light on this point, and these are now in progress.

Experimental Section[20]

Addition of CSI to Cyclooctatetraene. Cyclooctatetraene (20.8 g, 0.20 mol) was heated with stirring under nitrogen to 50° and 22.6 g (0.16 mol) of chlorosulfonyl isocyanate was added dropwise during 1 hr. Upon completion of the addition, the mixture was stirred at this temperature for an additional 6.5 hr or until a small aliquot failed to evolve gas when added to water.[21] The dark reaction mixture was cooled to room temperature and poured directly into 250 ml of water to precipitate a crude yellow solid. This material was filtered, washed thoroughly with water, and dried to give 28.5 g (72.5%) of **4**, mp 82–84.5°. Repeated recrystallization of this solid from acetone–ether gave pure white microcrystals, mp 85.0–86.5°; ν_{max}^{Nujol} 1730 (>C=O), 1368, and 1182 cm^{-1} (-SO_2Cl).

Anal. Calcd for $C_9H_8ClNO_3S$: C, 44.00; H, 3.28; N, 5.70. Found: C, 44.15; H, 3.35; N, 5.75.

7-Azabicyclo[4.2.2]deca-2,4,9-trien-8-one (5). A. With Thiophenol and Pyridine. To an ice-cooled magnetically stirred solution of **4** (38.8 g, 0.158 mol) and thiophenol (35.2 g, 0.32 mol) in 50 ml of acetone was added dropwise 16.0 g (0.20 mol) of pyridine. After the completion of the pyridine addition, a few drops of water caused immediate precipitation of crystalline phenyl disulfide (mp 59–60°) which was filtered and washed with water. The combined filtrate and washings were concentrated under reduced pressure, heated with 1 l. of water, and decanted from additional oily phenyl disulfide. Cooling of the aqueous solution to room temperature followed by filtration served to remove most of the remaining disulfide. The aqueous solution was extracted with methylene chloride (three 200-ml portions) and the combined organic layers were dried, filtered, and evaporated. The resulting white solid was recrystallized from acetone–ether to give 22.8 g (98%) of **5** as white crystals, mp 139–140°; ν_{max}^{Nujol} 1667 cm^{-1} (>C=O); $\lambda_{max}^{CH_3CN}$ 266 mμ (ε 3100); $\delta_{TMS}^{CDCl_3}$ 8.07 (broad peak, 1 H, >NH), 5.93 (multiplet, 6 H, vinyl protons), 4.07 (broadened quartet, 1 H, proton at C-1), and 3.63 (broadened multiplet, 1 H, proton at C-6).

Anal. Calcd for C_9H_9NO: C, 73.41; H, 6.16; N, 9.56. Found: C, 73.38; H, 6.20; N, 9.37.

B. With Sodium Hydroxide in Aqueous Acetone. Cyclooctatetraene (26.0 g, 0.25 mol) was converted to **4** as above with 28.3 g (0.20 mol) of CSI. The excess cyclooctatetraene was removed at 50° (2 mm). The resulting dark solid was dissolved in 35 ml of acetone and this solution was added in portions to a solution of 100 ml of water and 50 ml of acetone. The pH of this solution was maintained between 5 and 8 by dropwise addition of 4 *N* sodium hy-

(20) Melting points are corrected and boiling points are uncorrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The nmr spectra were determined with Varian A-60, A-60A, and HA-100 spectrometers purchased with funds made available through the National Science Foundation. The mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV.

(21) We have observed on several occasions that, if the scale of this reaction is increased to above the 0.5-mol level, the mixture will explode violently 1–3 hr after the completion of the addition with extensive spewing of black tar and broken glass. This problem has been avoided by controlling the addition of CSI over 5–6 hr. However, it would be our recommendation that the cycloaddition not be performed on a scale above twice that illustrated and that the researcher take adequate measures to protect himself with a safety shield, etc.

droxide solution. Filtration of the deposited sodium sulfate[22] followed by methylene chloride extraction (three 100-ml portions) of the filtrate and processing as in part A yielded 18.8 g (65%) of **5**, mp 138–140°.

7-Azabicyclo[4.2.2]decan-8-one (6). A. Hydrogenation of 5. A solution of 195 mg (1.32 mmol) of **5** in 17 ml of tetrahydrofuran was hydrogenated over 10% palladium on charcoal at atmospheric pressure. When the uptake of hydrogen ceased, the catalyst was filtered, and the filtrate was evaporated under reduced pressure. The residue was triturated with hexane to give 140 mg (69%) of **6** as a white crystalline solid, mp 157–159°.

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.15. Found: C, 70.54; H, 9.89; N, 9.00.

B. From Bicyclo[4.2.1]nonan-9-one (7). **7**[13] was oximated in the usual manner to give white crystals of **8**, mp 130–131°. Treatment of 120 mg of **8** with a slight excess of phosphorus pentachloride in ether (15 ml) at room temperature for 2 hr, followed by washing of the ethereal solution with water and saturated sodium bicarbonate solution, gave 15 mg of crude white solid, mp 70–110°. Sublimation of this product gave 8 mg of white solid, mp 145–153°, whose infrared spectrum was superimposable upon that of the material isolated above.

8-Methoxy-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraene (10). A solution of 14.72 g (0.10 mol) of **5** and 18.45 g (0.13 mol) of trimethyloxonium fluoroborate[23] in 150 ml of dry methylene chloride was stirred at room temperature for 10 hr. After careful addition of 40 ml of 50% potassium carbonate solution, stirring was continued for 1 hr. The mixture was filtered, and the filtrate was dried and concentrated. The residue was filtered through a small amount of neutral alumina (ether solution) and crystallized from pentane at 0°. There was obtained 13.06 g (81%) of pale yellow solid, mp 47–50°. Sublimation of this material followed by recrystallization from pentane gave pure **10** as white crystals, mp 50.5–52.0°; ν_{max}^{Nujol} 1672 cm^{-1} (imino ether); $\lambda_{max}^{CH_3CN}$ 271 mμ (ε 2000).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.83; N, 8.69. Found: C, 74.37; H, 6.92; N, 8.73.

Methylcyclooctatetraene (11). To a solution of cyclooctatetraenyllithium[24] (0.0273 mol) in anhydrous ether (50 ml) at −70° under nitrogen was added methyl iodide (7.05 g, 0.0497 mol) in 15 ml of ether. The mixture was stirred as it was allowed to warm to room temperature overnight. After dilution with 75 ml of ether, the organic solution was washed twice with water, dried, and evaporated. The residue was distilled through a Vigreux column and the fraction of bp 72–75° (72 mm) was collected giving **11** of 97% purity (vpc analysis), 2.1 g (66%), $n^{22}D$ 1.5265.[25]

Addition of CSI to 11. A solution of 5.52 g (0.0467 mol) of **11** and 6.60 g (0.0467 mol) of CSI in 15 ml of dry methylene chloride was prepared at 0° and allowed to warm to room temperature where it was stirred for 9 hr. The mixture was diluted with methylene chloride, washed with ice water (two 30-ml portions), and evaporated to give a mixture of N-(chlorosulfonyl) lactams as a faintly brown crystalline solid, 11.7 g (97%), mp 74–82°. Nmr analysis indicated the presence of two adducts in the ratio of 35:65. A pure sample of the mixture, mp 97–98° dec, was obtained by recrystallization from acetone–ether–pentane; $\nu_{max}^{CH_2Cl_2}$ 1730 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}ClNO_3S$: C, 46.25; H, 3.88; N, 5.39. Found: C, 46.40; H, 3.95; N, 5.32.

The crude sample (11.6 g) was dissolved in the minimum amount of acetone; this solution was added dropwise during 90 min to a stirred solution of 30 ml of water and 15 ml of acetone. Sodium hydroxide solution (4 *N*) was added at such a rate to maintain pH 6–8. The reaction was exothermic and the temperature was kept reasonably constant by the addition of small quantities of ice. The pH was finally adjusted to 7 and the mixture was extracted with methylene chloride (five 100-ml portions). The combined organic layers were dried, filtered, and evaporated to give 6.53 g (90%) of the amide mixture as an almost colorless crystalline solid, mp 140–170°; $\nu_{max}^{CH_2Cl_2}$ 3390 (>NH) and 1672 cm^{-1} (>C=O). Nmr analysis at this stage likewise showed the two amides to be in the ratio of 35:65. A small sample was recrystallized five times from methanol–ether–pentane to give colorless microcrystals, mp 190–193°; $\lambda_{max}^{CH_3CN}$ 260 mμ (ε 3000).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.97; H, 6.89; N, 8.67.

A solution of 6.334 g (0.0393 mol) of this amide mixture and 7.58 g (0.051 mol) of trimethyloxonium fluoroborate in 10 ml of dry methylene chloride was processed in the previously described fashion (3-hr reaction time) to give 6.30 g (92%) of a mixture of **14** and **15** as an almost colorless oil. The nmr spectrum showed two singlets at δ 1.80 and 2.04 in a ratio of 64:36. The isomers appeared as a single peak on a wide variety of vpc columns.

A portion of this imino ether mixture (285 mg) in ether was treated with 60% perchloric acid (258 mg) in methanol, and sufficient methanol was added to produce a homogeneous solution (total solvent 0.5 ml). Upon scratching, crystals formed; these were removed by centrifugation and recrystallized from methanol to give 104 mg of colorless rhombs, mp 148–150°. Further recrystallization from ethanol afforded pure **15** perchlorate, mp 158.5–159°.

Anal. Calcd for $C_{11}H_{14}ClNO_5$: C, 47.92; H, 5.12; N, 5.08. Found: C, 48.38; H, 5.18; N, 4.99.

Treatment with aqueous base gave **15** in 97% yield; after recrystallization from pentane at −20°, this crystalline imino ether melted at 35–36.5°; $\nu_{max}^{CHCl_3}$ 1670 and 1640 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 273 mμ (ε 4400).

The mother liquors from the perchlorate precipitation were similarly neutralized and the liberated yellow oil was scratched in ether at −78°. Oily crystals formed, and the mother liquors were decanted at −78°. These crystals were used to seed the bulk of the imino ether mixture (4.3 g) dissolved in an ether–pentane solution at −15°. A total of 1.1 g of **14**, mp 50–53°, was obtained over several days. Recrystallization from pentane at −20° gave colorless microneedles, mp 53–54°; $\nu_{max}^{CHCl_3}$ 1685 and 1665 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 269 mμ (ε 2700).

Anal. Calcd for $C_{10}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.24; H, 7.50; N, 8.01.

The mother liquors from this crystallization were employed as an additional source of **15** perchlorate.

Addition of CSI to 16. Chlorosulfonyl isocyanate (9.67 g, 0.068 mol) was added dropwise under nitrogen during 30 min to a stirred solution of **16**[26] in 35 ml of dry methylene chloride cooled to −78°. The mixture was stirred at this temperature for 7 hr, poured into water (50 ml), and extracted with methylene chloride (two 120-ml portions). Processing as above gave 17.8 g (95%) of the crude N-(chlorosulfonyl) lactam mixture, $\nu_{max}^{CHCl_3}$ 1730 cm^{-1}. Hydrolysis with aqueous sodium hydroxide as before gave an oily brown solid which upon fractional crystallization in methanol–ether yielded two crops of crystals: i, mp 195–215°; ii, mp 101–145°. Each amide sample was treated separately with trimethyloxonium fluoroborate in methylene chloride solution. Vpc analysis on different columns[27a,b] clearly indicated the presence of four components.

Seeding of fraction i in ether at −20° with a few crystals of **20** obtained by preparative vpc succeeded in the deposition of additional **20**. After recrystallization from ether at −20°, pure **20** melted at 77–78°; ν_{max}^{Nujol} 1647 cm^{-1}; λ_{max}^{hexane} 221 mμ (ε 5400); *m/e* 177.

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.85; H, 6.33; N, 7.64.

The mother liquors from this crystallization were now enriched in **18**. Treatment with 60% perchloric acid in methanol–ether in the predescribed manner gave an immediate precipitate, mp 152–153.5°. Regeneration of the free base gave a colorless oil which crystallized when cooled. Recrystallization from pentane afforded **18** as colorless plates, mp 79–79.5°; ν_{max}^{Nujol} 1675 and 1642 cm^{-1}; λ_{max}^{hexane} 274 mμ (ε 6000); *m/e* 191.

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.12; H, 6.92; N, 7.61.

Careful preparative vpc[27a] of fraction ii led to the isolation of **19** and **21**. Pure **19** was obtained by recrystallization from ether at −20°, mp 79–79.5°; ν_{max}^{Nujol} 1678 and 1653 cm^{-1}; λ_{max}^{hexane} 268 mμ (ε 3000); *m/e* 191.

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.22; H, 6.86; N, 7.26.

(22) As the sodium sulfate does not always precipitate, this step can be sometimes eliminated.

(23) H. Meerwein, *Org. Syn.*, **46**, 120 (1966).

(24) A. C. Cope, M. Burg, and S. W. Fenton, *J. Am. Chem. Soc.*, **74**, 174 (1952).

(25) Keller and Pettit[3b] have also prepared **11** through reaction of cyclooctatetraenyllithium with methyl iodide, but no procedure is given.

(26) Prepared in 77% yield by the method of J. F. M. Oth, R. Merenyi, T. Martini, and G. Schröder, *Tetrahedron Letters*, 3087 (1966).

(27) (a) 5% Carbowax 20M on Chromosorb W; 10 ft × 0.25 in. aluminum tubing; 155°; (b) 5% SE 30 on Chromosorb W; 10 ft × 0.25 in. aluminum tubing; 172°; (c) 10% SF 96 on Chromosorb G; 5 ft × 0.25 in. aluminum tubing; 180°.

A purified sample of **21** was prepared by recrystallization from ether–pentane, mp 67.5–68.5°; ν_{max}^{Nujol} 1727 and 1672 cm^{-1}; λ_{max}^{hexane} 264 (ε 3500) and 273 mμ (ε 3300); *m/e* 177.

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 68.13; H, 6.41; N, 7.75.

With the isolation and characterization of the four components in the reaction mixture, the reaction was repeated at several temperatures (−78°, 0°, 20°, etc) and worked up under several different sets of conditions. The imino ether mixture was finally analyzed in each run by nmr spectroscopy to determine the product ratios.

Addition of CSI to 22. In a typical reaction, a solution of 1.0 g of phenylcyclooctatetraene[28] and 0.78 g of CSI in 8 ml of methylene chloride was refluxed for 20 hr. Hydrolysis of the crude N-(chlorosulfonyl) lactam mixture gave 0.83 g (67%) of the amide mixture. Treatment of a 635-mg sample of this material with 0.46 g of trimethyloxonium fluoroborate afforded 526 mg (78%) of **24** and **25** after rapid filtration of the crude product through a small column of alumina (ether elution). Vpc analysis[27c] established the ratio of the two components to be 80:20.

Separation of the isomers by preparative vpc[27a] was achieved with difficulty. The minor product (**25**) exhibited the slightly shorter retention time and was obtained as white crystals, mp 102–103°, from ether–pentane at −20°; ν_{max}^{Nujol} 1675 and 1645 cm^{-1}; λ_{max}^{hexane} 299 mμ (ε 10,000).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37. Found: C, 80.83; H, 6.34.

The major product (**24**) was obtained as colorless crystals, mp 73–74°, from ether–pentane at −20°; ν_{max}^{Nujol} 1675 and 1645 cm^{-1}; λ_{max}^{hexane} 246.5 mμ (ε 13,900).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.62; H, 6.29; N, 5.63.

***p*-Methoxyphenylcyclooctatetraene (26).** To a solution of *p*-anisyllithium [prepared from 49.4 g (0.264 mol) of *p*-bromoanisole and 4.0 g (0.58 g-atom) of lithium wire] in 210 ml of ether was added 55 g (0.53 mol) of cyclooctatetraene at room temperature. The contents were gradually heated, and the ether was collected by distillation. The bath temperature was finally adjusted to 110° and maintained there for 4 hr. The orange-yellow mixture was cooled in ice; 150 ml of ether was added, followed by the cautious addition of ice water. The organic phase was washed with additional water and dried. The ether was evaporated and the residual oil was carefully distilled. A golden yellow viscous oil (7.5 g) of bp 135–150° (0.45 mm) was collected. When scratched in methanol–acetone, there was deposited a small amount of crystalline solid, mp 122–124°, which exhibited only methoxyl and aromatic protons in the nmr and which was not further examined. The remaining oil was heated at reflux for 1 hr in absolute ethanol (70 ml) containing 7.5 g of silver nitrate. After cooling, solid material (6.7 g) was slowly deposited over a period of 6 days. The crude complex was treated with excess ammonium hydroxide solution and extracted into ether. There was obtained a yellow oil which crystallized when cooled; however, thin layer chromatography clearly indicated the presence of two components.

Careful "dry-column" chromatography[29] on 330 g of alumina (activity I) using hexane–ether (85:15) separated two yellow bands, and subsequent elution with the same solvent mixture afforded two compounds. The first was a yellow crystalline compound (520 mg), mp 124–125°, recrystallizable from hexane, which was characterized as bicyclooctatetraenyl.[30] The second band was obtained as yellow crystals (1.6 g), mp 64–65°, and was characterized as **26**; λ_{max}^{hexane} 254 mμ (ε 17,000) with tailing well into the visible region; $\delta_{TMS}^{CDCl_3}$ 7.32 and 6.83 (two doublets of the AB pattern, J = 8.9 Hz, 4 H, aromatic protons), 6.00 (broad multiplet, 7 H, vinyl protons), and 3.77 (singlet, 3 H, $-OCH_3$).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.48; H, 6.67.

Addition of CSI to 26. A solution of 305 mg (1.45 mmol) of **26** in 1.4 ml of dry methylene chloride cooled to 0° was treated dropwise under nitrogen with 0.125 ml (*ca.* 1.50 mmol) of CSI by means of a syringe. The mixture was stirred at room temperature overnight. The solvent was evaporated in a stream of dry nitrogen and the remaining dark brown syrup was taken up in dry acetone and hydrolyzed with 4 *N* sodium hydroxide solution. There was obtained 368 mg (100%) of brown crystals, the nmr of which clearly demonstrated the presence of two amides in a ratio of 55:45. Treatment of a 276-mg sample of this mixture with 330 mg of trimethyloxonium fluoroborate gave 215 mg of colorless crystals. This mixture of imino ethers was likewise found by nmr analysis to be composed of two components in the same ratio as above. Attempts to separate the two components by fractional crystallization of their perchlorate salts or by preparative scale vpc were not successful.

Repeated crystallization of the amide mixture from ethanol did, however, give the pure 10-*p*-methoxyphenyl derivative, mp 198.5–199.5°; ν_{max}^{Nujol} 3220, 1678, and 1632 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 255 mμ (ε 20,500); $\delta_{TMS}^{CDCl_3}$ 4.20 (complex multiplet, 2 H, H-1 and H-6).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.56; H, 6.07; N, 5.50.

Reaction of this amide (36 mg) with trimethyloxonium fluoroborate (46 mg) in methylene chloride as before afforded 36 mg (95%) of **28** as colorless plates, mp 147–149°, from pentane; ν_{max}^{Nujol} 1672 and 1608 cm^{-1}; λ_{max}^{hexane} 256 mμ (ε 18,300).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.29; H, 6.47; N, 4.97.

Concentration of the mother liquors from the amide crystallization resulted in the slow deposition of colorless needles of the 5-*p*-methoxyphenyl amide. Recrystallization of this material from ethanol gave pure amide, mp 169–169.5°; ν_{max}^{Nujol} 3170, 1680, and 1613 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 308 mμ (ε 17,150); $\delta_{max}^{CDCl_3}$ 4.20 (complex multiplet, 2 H, H-1 and H-6).

Exposure of this amide (24 mg) to trimethyloxonium fluoroborate (35 mg) in the usual manner gave 19 mg of **29** as colorless needles, mp 85–86°, from hexane; ν_{max}^{Nujol} 1677 and 1612 cm^{-1}; λ_{max}^{hexane} 307 mμ (ε 15,300).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41. Found: C, 76.69; H, 6.77.

Addition of CSI to 30. A 379-mg (2.46 mmol) sample of **30**[31] was placed in a 5-ml, pear-shaped flask and was warmed to 75° with magnetic stirring under nitrogen. At this point, 251 μl. (*ca.* 425 mg, 3.0 mmol) of CSI was slowly added by means of a syringe during 15 min. The temperature was raised to 82° and stirring was continued for 3 hr. The brown solid thus obtained was hydrolyzed directly with aqueous sodium hydroxide in acetone to give 394 mg (82%) of crude **32**, mp 200–210°. Recrystallization from methanol acetone gave colorless crystals, mp 226–227°, whose spectroscopic properties (ir and nmr) were identical with the crude material; $\nu_{max}^{CH_2Cl_2}$ 3390 and 1680 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 269 mμ (ε 9700); $\delta_{TMS}^{CDCl_3}$ *ca.* 7.3 (complex multiplet, 5 H, aromatic protons and >NH), 5.6–6.6 (complex multiplet, 4 H, vinyl protons), and 4.1–4.4 (broad multiplet, 2 H, H-1 and H-6).

Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.33; H, 5.65; N, 7.07.

The crude amide of mp 200–210° (287 mg, 1.46 mmol) was treated as above with 324 mg (2.18 mmol) of trimethyloxonium fluoroborate in 25 ml of methylene chloride. There was obtained 295 mg (96%) of golden yellow oil which was crystallized and recrystallized from ether–pentane at −20° to give pure **33**, mp 76–80°; ν_{max}^{Nujol} 1678 and 1647 cm^{-1}; λ_{max}^{hexane} 273.5 mμ (ε 8500).

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.49; H, 6.25; N, 6.45.

Acknowledgment. We wish to thank the Alfred P. Sloan Foundation and the National Science Foundation (Grant GP-8678) for financial support. We are also grateful to Badische Anilin und Soda Fabrik for the generous gift of cyclooctatetraene which made this work possible.

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(31) We acknowledge with gratitude the generosity of Professor Rowland Pettit who provided us with the sample of benzocyclooctatetraene.