Stereochemical and Substituent Effects in Chlorosulfonyl Isocyanate Additions to *cis*-Bicyclo[6.1.0]nonatrienes[1]

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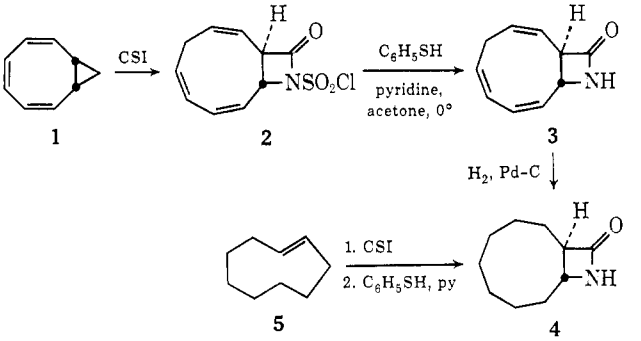
Abstract: Reaction of *cis*-bicyclo[6.1.0]nonatriene, two anti-9-substituted derivatives, and several ring-methylated congeners with chlorosulfonyl isocyanate has been found to produce *trans*-10-azabicyclo[7.2.0]undeca-2,5,7-trien-11-ones. The related syn-9-substituted isomers fail to undergo cycloaddition. The ready cyclopropane ring opening which accompanies reaction of the triene systems is not shared by the diene and monoene (vinylcyclopropane) of comparable ring size. The structures of the products were elucidated by chemical, spectral, and X-ray methods. The overall reaction pathway and particularly the impressive stereocontrol observed with the anti-9-substituted derivatives are interpreted in terms of electrophilic attack at C_3 in the folded conformation of the triene to arrive at an intermediate *trans*-1,3-bishomotropylium ion. Subsequent C–N bond formation leads to the trans-fused bicyclic β-lactam products.

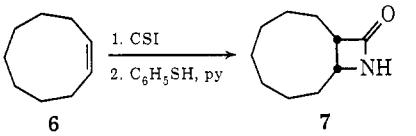
In the preceding paper,[5] it was shown that a most powerful way to derive fundamental information about the carbonium ion behavior of *cis*-bicyclo[6.1.0]-nona-2,4,6-trienes is to examine their reactivity (or the lack of it) and reaction course under conditions of uniparticulate electrophilic addition. Owing to the symmetry inherent in tetracyanoethylene, however, certain points about such ionic processes remained unclear. Therefore, we next directed our attention to the more unsymmetrical reagent chlorosulfonyl isocyanate (CSI). The focus of our interest was manifold and in particular centered about: (a) establishment of the generality of the electrophilic addition-rearrangement, particularly as it relates to initial bonding at C_3 in highly stereoselective fashion from the exo direction; (b) direct modification of the *cis*-bicyclononatriene structure to determine if highly stereocontrolled behavior is a unique property of this particular ring system in such dipolar cycloadditions; and (c) utilization of substituent effects to assist in elucidating the electronic makeup of, and particularly the charge delocalization in, the cationic segment of the intermediate 1,3-bishomotropylium ions.[6]

Results

CSI Additions to *cis*-Bicyclo[6.1.0]nonatrienes. When parent hydrocarbon **1** was treated with an equimolar quantity of CSI in methylene chloride solution at 25° for 35–40 hr, conditions under which all the *cis*-bicyclo[6.1.0]nonatrienes examined are otherwise stable, a highly crystalline *N*-chlorosulfonyl β-lactam (**2**) could be isolated in 60% yield. This product, which displays an intense infrared carbonyl band ($CHCl_3$) at 1825 cm^{-1}, was reduced with thiophenol and pyridine in acetone at 0°[7] to afford quantitatively β-lactam **3**



($\nu_{max}^{CHCl_3}$ 1750 cm^{-1}). In the nmr, **3** showed resonances at δ 6.7 (br, 1, >NH), 5.4–6.3 (m, 6, olefinic), 3.6–4.05 (m, 2, ring juncture protons), and 2.3–2.9 (m, 2, methylene group). On the basis of these data, the elemental analysis, and the electronic spectrum [$\lambda_{max}^{C_2H_5OH}$ 224 nm (ε 6850)], the absence of a cyclopropane ring as well as the presence of a conjugated diene unit in an eight- or nine-membered ring was inferred.[8] By analogy to the behavior of **1** toward TCNE,[5] this β-lactam was assigned structure **3**, the trans-ring juncture which was confirmed by catalytic hydrogenation to **4**. The latter bicyclic lactam was synthesized independently by reaction of *trans*-cyclononene (**5**) with CSI and subsequent reductive dechlorosulfonylation. To guard against possible geometrical isomerization and/or lack of stereospecificity during the cycloaddition to **5**, *cis*-cyclononene (**6**) was



prepared and similarly subjected to the action of CSI. As expected,[9] only one β-lactam (**7**) was again formed, and it was readily distinguishable from **4**.

(1) Unsaturated Heterocyclic Systems. XCI. For the previous paper in this series, see L. A. Paquette and M. J. Broadhurst, *J. Org. Chem.*, **38**, 1893 (1973).

(2) Studies at The Ohio State University were supported in part by the National Science Foundation.

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

(4) Financial support for the work at Iowa State University was provided by the U. S. Atomic Energy Commission.

(5) L. A. Paquette, M. J. Broadhurst, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, **95**, 4639 (1973).

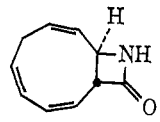
(6) Preliminary reports of these results have been made: (a) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **94**, 630 (1972); (b) L. A. Paquette and M. J. Broadhurst, *ibid.*, **94**, 632 (1972).

(7) R. Graf, *Justus Liebigs Ann. Chem.*, **661**, 111 (1963); *Org. Syn.*, **46**, 51 (1966).

(8) L. A. Paquette and R. W. Begland, *J. Amer. Chem. Soc.*, **88**, 4685 (1966); W. R. Roth, *Justus Liebigs Ann. Chem.*, **671**, 10 (1964).

(9) (a) E. J. Moriconi and J. F. Kelly, *Tetrahedron Lett.*, 1435 (1968); (b) H. Bestian, H. Biener, K. Clauss, and H. Heyn, *Justus Liebigs Ann. Chem.*, **718**, 94 (1968); (c) L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 1763 (1970).

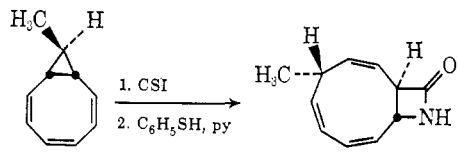
Treatment of the oily residue remaining after the initial isolation of **2** with thiophenol and pyridine gave only an additional small amount (4%) of the corresponding β-lactam **3**. Therefore, insofar as we could determine, only one nonpolymeric crystalline substance was formed during this reaction. To this point, the available data are insufficient to rule out isomeric structure **8** in which the heterocyclic ring is attached



8

end-for-end to the cyclononatriene framework. This substance would result from initial electrophilic attack at C_4 in **1** and, as indicated in the preceding paper,[5] this reaction mode is not conducive to stabilization of the initially formed cation. Convincing evidence against structure **8** is available from the detailed structural analysis of **10** and the similarity of its spectral features to those of **3**.

Similar admixture of equimolar quantities of the *anti*-9-methyl derivative **9** and CSI, followed by direct



9 **10**

reduction of the resulting adduct, afforded a single β-lactam **10**. The similarity of **10** to **3** was indicated convincingly by the infrared ($\nu_{max}^{CHCl_3}$ 1750 cm^{-1}), ultraviolet [$\lambda_{max}^{C_2H_5OH}$ 240 nm (ε 4230)], and nmr spectra (see Experimental Section). However, no definitive stereochemical information could be derived from these sources. Accordingly, a single crystal X-ray analysis was performed.

The important results of this analysis are the orientation of the β-lactam ring, the stereochemistry of the ring fusion, and the configuration of the carbon bearing the methyl group. The final X-ray model (Figure 1) clearly reveals the proximity of the nitrogen atom to the diene segment and the trans relationship of the bridgehead hydrogens. The methyl group is cis to the hydrogen on C(1). In general the bond lengths agree well with generally reported values.[10]

The C(11)–N(10) bond distance is longer than that of a normal amide (1.341 *vs.* 1.325 Å). Presumably contracting the C(11)–N(10)–C(9) bond angle from 122 to 94° gives the C(11)–N(10) bond more p character with consequential lengthening. It should be noted that the N(10)–C(9) bond is lengthened from the expected 1.46 to 1.48 Å and the C(1)–C(11) bond is the anticipated 1.51 Å. The relatively short N(10)–H bond of 0.89 Å (expected 1.02 Å) supports this analysis although the experimental uncertainty is high (0.06 Å). The β-lactam grouping is essentially planar with an average standard deviation of 0.04 Å from the best least-squares plane. The internal ring angles with vertices at atoms C(11) and N(10) are 94°, while those at C(1) and C(9) are 85°.

(10) "Molecular Structures and Dimensions," O. Kennard and D. G. Watson, Ed., Crystallographic Data Centre, Cambridge, 1970.

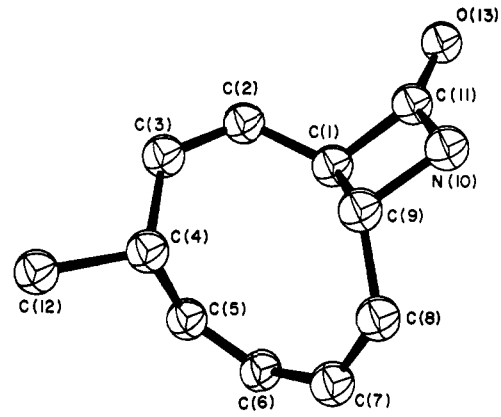
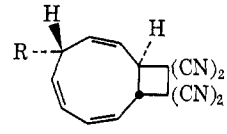


Figure 1. Final X-ray model of single crystal analysis.

The double bond lengths in the nine-membered ring are all standard and the torsional angles about them are all less than 2°. The torsional angle about the C(6)–C(7) bond of the butadiene portion is 42°.

The important intermolecular packing seems to be a N–H···O hydrogen bonding between molecules related by the twofold screw at ($^1/_2$, y, $^3/_4$). The H···O distance is 2.03(6) Å and the N–H···O angle is 168°. The N to O distance is 2.908(6) Å. No other abnormally short intermolecular contacts are present.

Thus, lactam **10** is directly relatable in structure to those adducts resulting from reaction of anti-9-substituted bicyclo[6.1.0]nonatrienes with TCNE (**11**).[5] In



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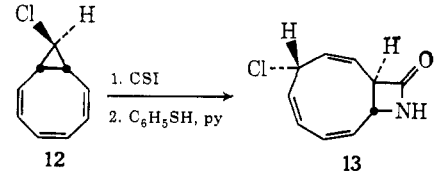
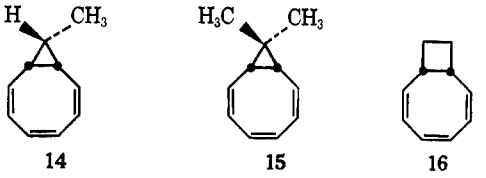
this connection, it is interesting to note that the heterocyclic ring in **10** retains planarity, presumably to achieve maximum amide resonance. However, considerations gained from examination of molecular models suggest that the attendant conformation enforced upon the cyclononatriene ring corresponds to a species having enhanced nonbonded interactions. This conclusion is supported by the geometry of **11**. In this system, the energetics of the medium ring now dominate, with the result that the tetracyanocyclobutane ring adopts a rather folded conformation.[5]

Reaction of CSI with 9-chloro derivative **12** (anti/syn = 23:5) under comparable conditions was carried only to partial completion (25 hr at 25°). There was produced β-lactam **13**, which has been assigned the in-



12 **13**

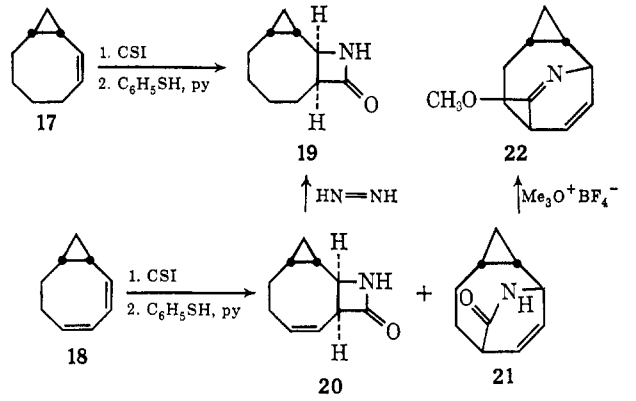
dicated structure on the strength of its spectra and by analogy. Nmr analysis of the recovered unreacted chlorocarbon showed the material to consist of anti and syn isomers in the ratio of 7:5, suggesting again[5] that the syn isomer is unreactive under these conditions. Each of the trienes **14**–**16** also failed to react with CSI



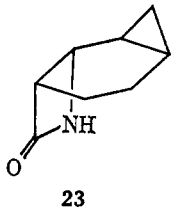
14 15 16

even at the reflux temperature of methylene chloride for 72 hr. Due to partial decomposition of these hydrocarbons at these somewhat elevated temperatures, recoveries of unreacted starting material ranged only 65–80%.

Cycloadditions to Lesser Unsaturated Analogs. To establish that the behavior of **1** and its anti-9-substituted derivatives is unique to this structural type, the addition of CSI to **17** and **18** has also been studied. Reaction with **17** proceeded smoothly at 25° with formation of **19**. The appearance of a carbonyl stretching band



($CHCl_3$) at 1745 cm^{-1} is consistent with the β-lactam formulation. The nmr spectrum (see Experimental Section) displays typical cyclopropyl proton absorptions, closely similar to those of **23**.[11] It follows that



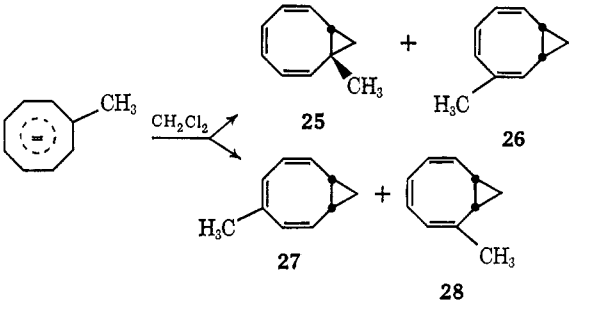
23

17 behaves as a normal cyclic vinylcyclopropane. The anti stereochemistry assigned to **19** has not been established and remains tentative at this time.

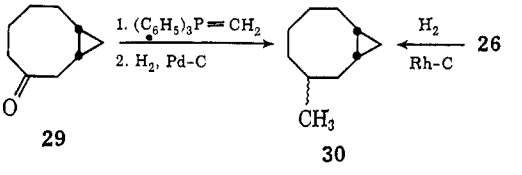
The reaction of CSI with **18** gave two products whose relative ratio varied somewhat with conditions. The first substance to elute from a Florisil column was decidedly a β-lactam ($\nu_{max}^{CHCl_3}$ 1750 cm^{-1}). The appearance of a sharp doublet of doublets at δ 4.02 in the nmr spectrum of this compound indicated that the α-carbonyl proton was allylically positioned. The presence of cyclopropyl protons was also in evidence. Diimide reduction of this substance gave rise to **19**, thereby characterizing it as **20**. From an intense carbonyl band at 1665 cm^{-1}, the second lactam was inferred to be the product of 1,4 addition (**21**). Decoupling experiments at 100 MHz confirmed the presence of the dihydropyridone unit. Any question that **21** might be a lactam of different structure was removed by conversion to imidate **22** and additional double resonance studies. These are detailed in the Experimental Section. The fact that neither **17** or **18** undergoes cyclopropyl ring opening during reaction with CSI is in accord with the proposal[5] that significant cationic stabilization attends internal strained bond cleavage in **1**, **9**, and **12**.

Substituent Effects. In an effort to understand more completely the factors which govern the intriguing reactivity of the *cis*-bicyclo[6.1.0]nonatrienes and the nature of the presumed *trans*-1,3-bishomotropylium ion intermediates,[5] we have examined the cycloaddition of CSI to several derivatives of **1** bearing substituents on the medium ring.

Addition of dichloromethane to a liquid ammonia solution of methylcyclooctatetraene dianion (**24**) proceeded to give all four possible methyl *cis*-bicyclo[6.1.0]nonatrienes (**25**–**28**). These were purified by

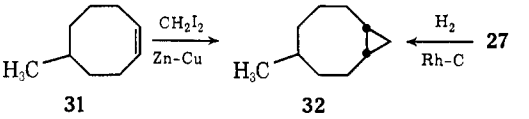


preparative scale vpc separation at 65° on a Chromosorb P column containing 15% PPGA. The component of shortest retention time was identified as **25** (14%) on the basis of its nmr spectrum, which displays the unique combination of an upfield methyl singlet at δ 1.00 and a 6 proton olefinic absorption at 5.92. That the second component was 3-methyl derivative **26** (28%) followed from its catalytic hydrogenation over 5% rhodium on carbon to a pair of hexahydro isomers (**30**) which were



synthesized independently by Wittig condensation of methylenetriphenylphosphorane with *cis*-bicyclo[6.1.0]-nonan-3-one (**29**) and subsequent reduction.

The penultimate product proved to be **27** (30.5%). Upon careful catalytic hydrogenation (5% Rh–C), this triene afforded only one isomer of 4-methyl-*cis*-bicyclo[6.1.0]nonane (**32**) which was identical with the only



hydrocarbon produced by Simmons–Smith cyclopropanation of 5-methylcyclooctene (**31**). The last component (27.5%) was assigned structure **28** in agreement with its spectral properties.

Treatment of **25** with CSI in refluxing methylene chloride solution, followed by immediate removal of the chlorosulfonyl group, afforded a homogeneous white solid in 53% yield. This β-lactam was formulated as **33** chiefly on the basis of double and triple resonance

(11) L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *J. Amer. Chem. Soc.*, 93, 4503 (1971).

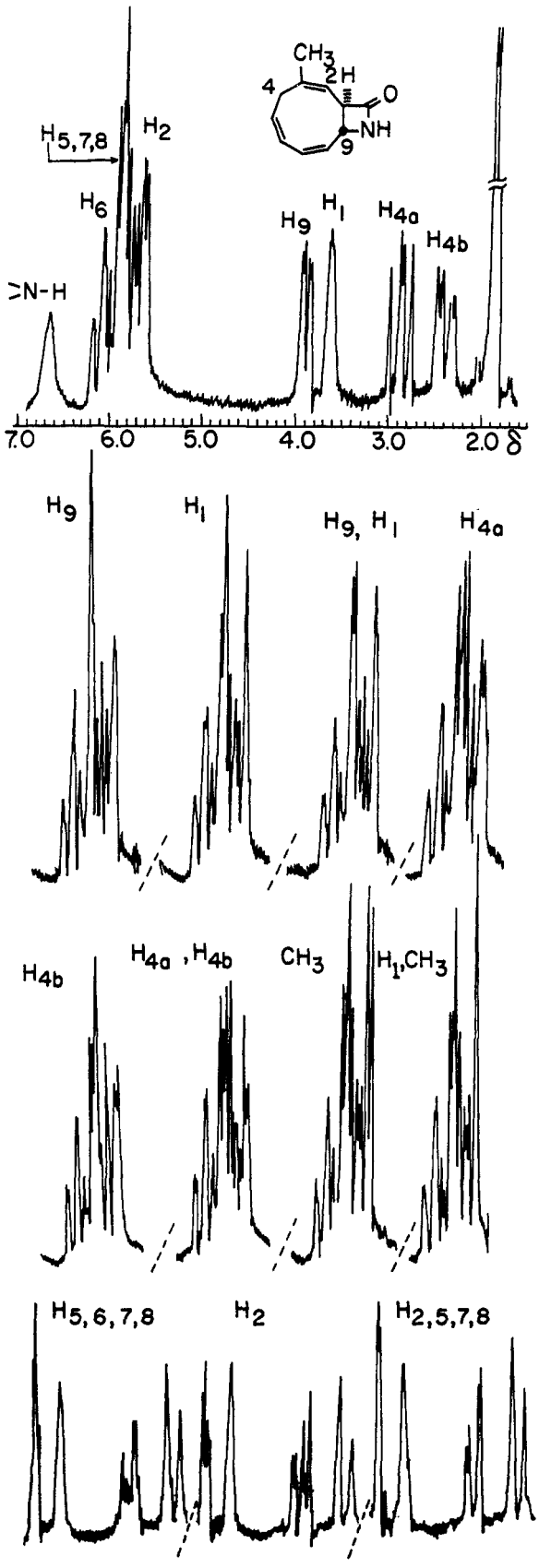
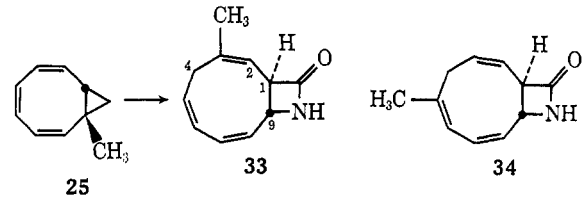


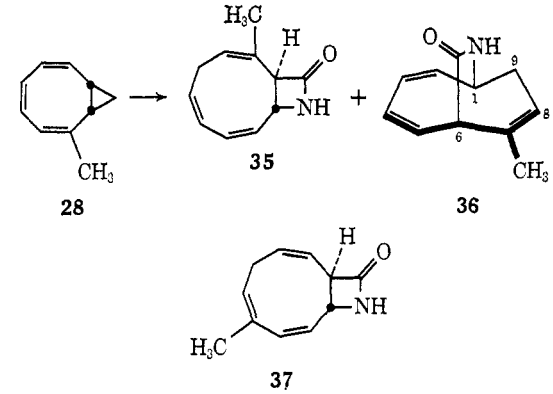
Figure 2. Row 1: 100-MHz nmr spectrum of **33**. Rows 2 and 3: Selected examples of multiplicity changes in the olefinic region upon double and triple irradiation. The superscripts refer to the proton or protons irradiated. Row 4: Selected examples of high-field multiplicity changes upon irradiation of various olefinic protons.

studies at 100 MHz. Most convincing was the observation that concomitant irradiation of H_1 (δ 3.58) and the methyl protons (δ 1.85) causes collapse of the high-field olefinic multiplet at δ 5.6 assigned to H_2 to a sharp singlet (Figure 2). Additionally, the electronic spectrum of **33** [$\lambda_{max}^{C_2H_5OH}$ 225 nm (ϵ 3590)] is essentially identical with that of **3** with no evidence of a bathochromic shift arising from methyl substitution as might be expected for **34**. In fact, no evidence was obtained for the production of other adducts such as **34**.



25 33 34

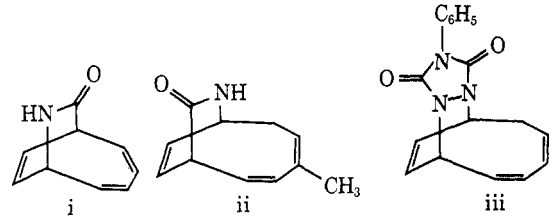
Exposure of **28** to CSI under comparable conditions



28 35 36 37

gave two lactams. The major product (53.5% yield) exhibited 1760 cm^{-1} carbonyl absorption in its infrared spectrum and a maximum at 224 nm (ϵ 4140) in the ultraviolet region. The most striking aspect of the nmr spectrum was the appearance of the α-carbonyl proton (H_1) at δ 3.75 as a relatively sharp singlet in contrast to the more extensively coupled features of this proton noted in the other compounds of the series. From these data it appeared likely that this adduct was the 2-methyl derivative **35** and this assignment was fully substantiated by spin decoupling measurements. The second product (5% yield) proved not to be a β-lactam ($\nu_{max}^{CHCl_3}$ 1660 cm^{-1}). The absence of cyclopropyl proton absorptions in the nmr revealed the adduct not to be a simple 1,4 adduct of the bicyclo[6.1.0]nonatriene system. Rather, findings derived from double and triple irradiation experiments as detailed in a later portion of this paper, coupled with the ultraviolet data [$\lambda_{max}^{C_2H_5OH}$ 215 sh nm (ϵ 4250) and 254 (3560)], support structure **36** for this substance.[12] Again, in this instance, a careful

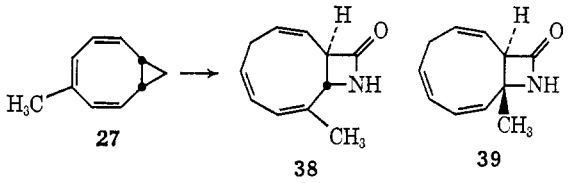
(12) In particular, the similarity of the electronic spectrum of **36** with that of i[13] [$\lambda_{max}^{CH_3CN}$ 266 nm (ϵ 3100)] suggests comparable degrees of twisting in the two diene chromophores. A possible alternative formulation for **36** is ii; molecular models of this structure suggest that far greater twisting of the diene moiety is present, a conclusion supported by the reported ultraviolet spectrum of a closely related compound (iii)[14] [$\lambda_{max}^{CH_3CN}$ shoulder at 215 nm (ϵ 15,000)].



i ii iii

search for the formation of the other possible 10-azabicyclo[7.2.0]undecan-11-one (**37**) proved negative.

The reaction of **27** with CSI under comparable conditions was noted (periodic infrared analysis of aliquots) to give rise rapidly to an *N*-chlorosulfonyl β-lactam whose carbonyl absorption (1825 cm^{-1}) decayed rather quickly before all of the CSI was consumed with appearance of a broad ill-defined absorption at 1750 cm^{-1}. Processing of long term reactions afforded only polymeric products; consequently, recourse was made to much shortened reaction times, conditions under which **27** had undergone only partial reaction. In this way, a

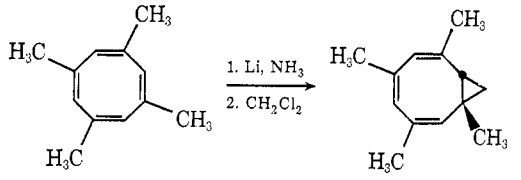


27 **38** **39**

β-lactam could be isolated, albeit in low (6%) yield. The nmr spectrum was similar to those of the other β-lactams and, in particular, featured a doublet (J = 2.5 Hz) for H_9 (>C*H*N<) at δ 3.98 and a broad unresolved absorption for H_1 at 3.65. Of the two possible adducts that could arise from "normal" attack on **27**, **39** can be ruled out since the presence of two bridgehead protons precludes the possibility of methyl substitution at one of these sites. The nmr features are entirely compatible with structure **38**; in particular, the appearance of H_9 as a narrow doublet instead of the customary doublet of doublets is consistent with methyl substitution at C_8. The electronic spectrum of **38** also reveals the requisite bathochromic shift expected from positioning of the methyl group on the diene system [$\lambda_{max}^{C_2H_5OH}$ 228 nm (ε 4670)].

In the case of **26**, it was not possible to bypass polymer formation in a satisfactory way; accordingly, β-lactams were not isolated. Competitive reaction studies with **25**–**28** revealed that **26** reacts no faster with CSI than its isomers. In fact, our results suggest a reactivity order of **27** > **25** > **26** ~ **28**. No pronounced kinetic inequalities were noted, the spread in reactivity being only a factor of <2 (1.7:1.3:1.0:1.0, respectively).

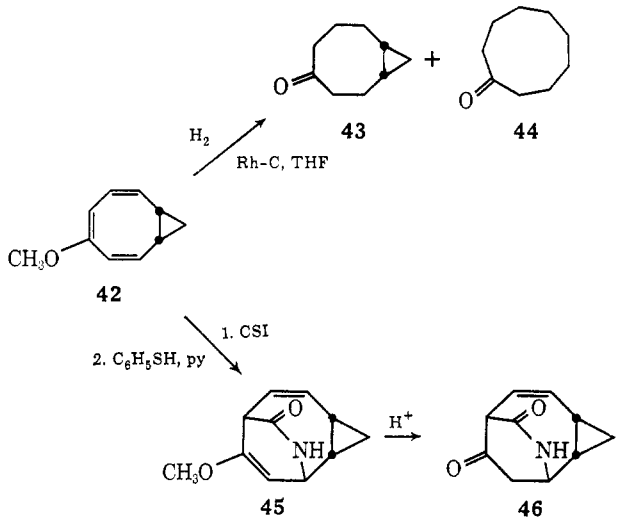
The reaction of **41** with CSI likewise met with little



40 **41**

success. Infrared analysis of numerous reactions performed under a variety of conditions indicated the consumption of CSI; however, only dark-colored polymeric substances were produced. Since **26** and **41** do share a common structural feature, their propensity for polymer formation may be traceable to this cause.

Reaction of the dianion of methoxycyclooctatetraene with methylene chloride afforded a mixture of bicyclo[6.1.0]nonatrienes from which isomer **42** could be isolated in pure form. The assignment of structure to **42** follows from its catalytic hydrogenation to a mixture of *cis*-bicyclo[6.1.0]nonan-4-one (**43**) and cyclononanone (**44**). This enol ether was quite reactive toward CSI; after 5 hr at 0–25° in dry methylene chloride solution and subsequent removal of the chlorosulfonyl group, lactam **45** could be isolated in 36% yield. Although the crude reaction mixture revealed the presence of only one methoxyl absorption (that of **45**), the lack of sufficient material precluded a search for possible minor products, if any were produced. When the cycloaddition was allowed to proceed for longer periods of time (20–30 hr) in the presence of a small excess of CSI, the only substance isolated was ketoamide **46** (30% yield). This compound could also be obtained in quantitative yield by hydrolysis of **45** with perchloric acid in methanol for several minutes. The nmr spectra of **45** and **46** are fully consistent with the proposed structures which were further substantiated by double resonance studies (see Experimental Section).



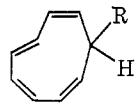
Discussion

Mechanistic Restrictions Arising from the Stereoselectivity of the Reaction. The results reported in this paper, along with the complementary observations made with tetracyanoethylene,[5] demonstrate that uniparticulate electrophilic additions to *cis*-bicyclo[6.1.0]nonatriene (**1**) are general in nature and result in the formation of [7.2.0] bicyclic products of trans stereochemistry, unless overriding stabilizing effects are present as in **42**. Whereas anti-9-substituted derivatives of this hydrocarbon system lead rapidly to bicyclic adducts, the corresponding syn congeners fail to undergo reaction. In the products formed in the first instance, the C_4 substituent is uniquely cis-oriented to H_1 and trans-disposed to H_9. It seems incontrovertible, therefore, that these impressively stereocontrolled transformations are the result of a process which is capable of generating a trans-ring juncture while simultaneously safeguarding the stereochemistry of the group positioned anti at C_9. We are forced to conclude, accordingly, that mechanistic schemes which are either stereochemically indiscriminate or irreconcilable with the wide reactivity differences of syn- and anti-9-substituted derivatives do not warrant further consideration. Mechanistic pathways such as those involving cycloaddition to *cis*[4]-cyclononatetraenes, direct ($_\pi2$ +

(13) L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, 91, 4714 (1969).

(14) A. G. Anastassiou and R. P. Cellura, *Tetrahedron Lett.*, 911 (1970).

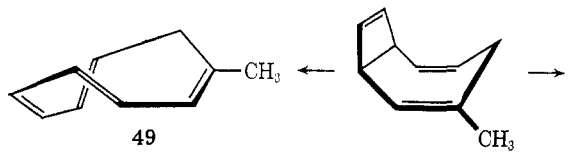
$_{\pi}8$) bonding to the *cis*-bicyclo[6.1.0]nonatriene framework and ($_{\pi}2 + _{\pi}2$) addition to *cis*[2],*trans*,*cis*-cyclononatetraenes fall into this category.[5] Although nonconcerted addition by way of the ($_{\pi}2_s + _{\pi}2_s$) mode to **47** is inherently attractive,[15] the uniqueness of positional



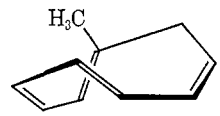
47

attack and high level of stereoselectivity encountered during formation of the β-lactam force a number of serious restrictions on this pathway. For example, if **47** were in fact the intermediate of consequence, two isomeric *trans*-β-lactams should result. Also, in those examples where R ≠ H, **47** could possibly serve as the precursor to four such adducts (albeit quite likely in varying proportions). However, in the several examples studied to date, no more than one β-lactam (or tetracyanocyclobutane[5]) has been isolated from a given anti-9-substituted *cis*-bicyclo[6.1.0]nonatriene despite a fruitless search for other isomers. There might, of course, exist some preference for that orientation which dissipates positive charge over the longest π component, but the difference between pentadienyl and allyl (assuming equivalent π overlap possibilities) does not usually generate an all-or-nothing situation. Conceivably, however, zwitterionic intermediates derivable from **47** would have differing opportunities for stabilization through charge delocation, but no information is available on this point.

Additionally, since intermediates such as **47** presumably arise by way of the [5.2.0] bicyclic isomer,[16,17] the exclusive formation of **33** from **25** necessitates highly specific conrotatory opening of the cyclobutene ring to give only **49**. Since molecular models of **49** and **50**



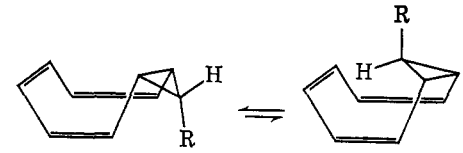
49 **48**



50

suggest that they are isoenergetic, the requirement of exclusivity in relative bond motion during conrotatory ring opening must be attributed to steric effects. However, because the methyl group resides many ångströms from the other relevant atomic centers, this argument does not inspire confidence. Nonetheless, we do expect to resolve this issue rigorously at a later date.

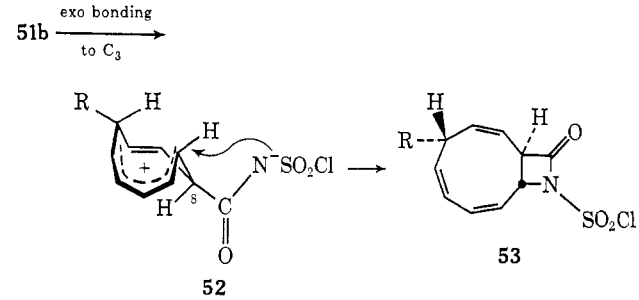
Presently, we prefer to view the capability of the bicyclo[6.1.0]nonatrienes for participation in these reactions as governed by the innate ability of the structure to attain folded conformation **51b**. As noted earlier,[5] this is because initial bonding of an electrophile to C_3



51a **51b**

of **51b** results in nearly perfect alignment of the vacant p orbital at C_2 with the internal cyclopropyl bond. Similar attack on **51a** does not result in stabilization of the developing cationic center.

Meaningfully, the lesser unsaturated analogs **17** and **18** do not undergo cyclopropane ring opening upon reaction with CSI. Furthermore, **18** is attacked by the electrophile chiefly at C_5 (with resultant 1,4 addition). We consider this to establish the existence of a significant driving force for attack at C_3 in **51b** and heterolytic rupture of the strained internal bond. This remarkable reactivity seemingly arises by virtue of the fact that addition as shown below can lead, with a small readjustment of bond angles, to *trans*-1,3-bishomotropylium ion intermediates (**52**) where delocalization



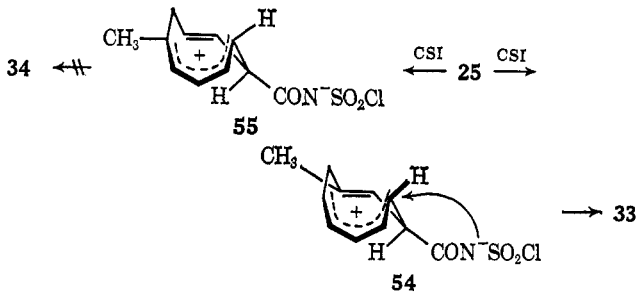
52 **53**

of the positive charge over at least five atoms can operate. Collapse of zwitterion **52** with C–N bond formation leads ultimately to trans-fused 11-azabicyclo[7.2.0]undecatrien-10-ones (**53**) of proper stereochemistry.

This pathway is the only one from among the four related mechanistic options[5] which uniquely accommodates all of the stereochemical features of the reaction. Exo bonding to C_3 operates presumably for steric reasons. Subsequent or concomitant opening of the cyclopropyl bond central to the two rings leads directly to that cationic intermediate possessing trans-disposed methylene bridges as in **52**. In other words, *trans*-1,3-bishomotropylium ions of type **52** appear to be the intermediates resulting from kinetically controlled electrophilic attack on **51b**. Under conditions of short life such as presumably relates to the present study, charge annihilation *via* cyclization occurs without competition from bridge inversion of the C_8 atom (*cf.* **52**).

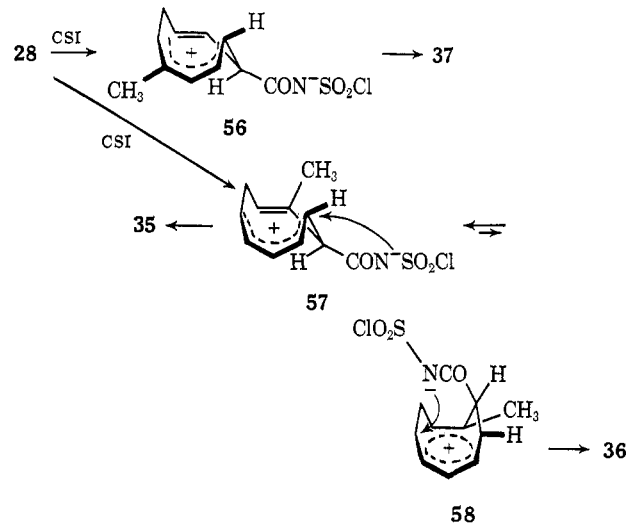
Influence of Ring Substituents. Because of the unsymmetrical nature of hydrocarbons **25**–**28**, the stage was set for the operation of a pair of competitive processes which could give rise to different zwitterionic intermediates in each instance. Notwithstanding, 1-methyl isomer **25** reacted with CSI to produce a single characterizable adduct (**33**) in good yield. This β-lactam presumably arose from zwitterion **54**, that intermediate in which the methyl group is bonded to the ethylene segment of the "5 + 2" cation (see below). Since the formation of **34** was not detected, no direct evidence for the formation of **55** is at hand. However,

(15) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971).
(16) L. A. Paquette and M. J. Epstein, *ibid.*, **93**, 5936 (1971).
(17) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *ibid.*, **94**, 5845 (1972).



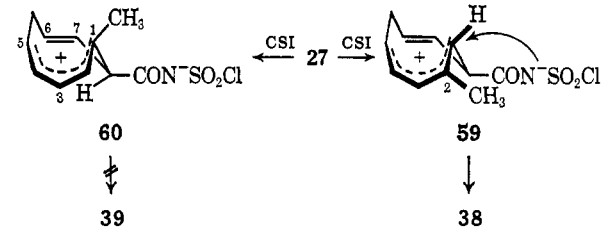
it is highly improbable that electrophilic attack on **25** is positionally selective in favor of **54**. Rather, it is likely that **55** is consumed in some reaction that does not lead to a characterizable product. As will be seen, this feature is shared by those zwitterions which have the common parameter of methyl substitution on the pentadienyl segment of the cation.

The behavior of **28** is quite comparable. When proper attention is given to the two ionic intermediates (**56** and **57**) realizable in this instance, it is seen that **57**



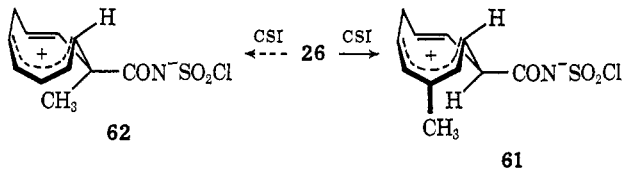
leads to the observed β-lactam (**35**). Isomeric adduct **37** was not found and its precursor ion **56** is likewise substituted on the pentadienyl part structure. Although **36** may arise in one of several ways, its genesis is most satisfactorily rationalized in terms of ion **58**. In particular, C–N bond formation in **58** follows the established precedent of preferred inside bonding to the carbon atom at the base of the methylene bridge.[18] The somewhat unique capability of **57** to undergo detectable inversion of that bridge which bears the $-CON^{-}SO_2Cl$ group would appear to be related to the enhanced ground-state strain of this ion which is engendered by the proximity of the methyl substituent.

In either of the ions derivable from **27** (*i.e.*, **59** and **60**), the longest linearly conjugated carbon segment is necessarily alkyl substituted. This may underlie the difficulties encountered in obtaining a β-lactam product in this case. It will be recalled that under controlled conditions adduct **38** derivable from **59** is obtained in low yield. This result seemingly points out the fact that methyl groups positioned at C_1, C_3, or C_5 in 1,3-bishomotropylium ions are required to interact hyperconjugatively with the adjacent ring carbons to a substantially greater extent than at C_2 or C_4 or at the



extreme C_6 and C_7 (*cf.* **60**). A distinct parallelism with the expected charge localization in this type of cation exists.[19,20] Consequently, proton loss from the methyl groups in **55**, **56**, and **60** is very likely to become competitive with cyclization (the latter process is apparently reversible, at least in certain cases), with the result that the substituted polyenes so formed undergo polymerization. With **27**, the successful isolation of **38** and not **39** after partial reaction is assumedly possible because of the charge dispersal characteristics of the cation which localizes less positive charge at C_2 than at C_1.

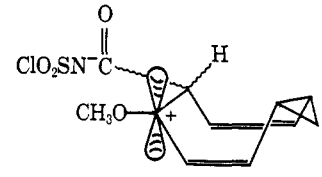
The behavior of trienes **26** and **41** is likewise accommodated by this interpretation. Our inability to isolate an adduct from **26** may follow from the facile deprotonation of **61**. The question of possible electro-



philic attack at the substituent bearing carbon in **26** (to give **62**) is left open at this time.[21]

In summary, it has been demonstrated that ring-methylated derivatives of **1** do behave as if the charge distribution in the intermediate zwitterions is that expected for a species possessing considerable capacity for charge delocalization. Complicating factors in the form of polymer formation do intervene, but these observations are in line with the assumption that maximal charge delocalization resides in the pentadienyl segment (see below).

Substitution of the *cis*-bicyclo[6.1.0]nonatriene ring with a highly activating substituent such as methoxyl does, however, override the normal reactivity of this polyene system toward electrophilic reagents. With **42**, for example, the major driving force is provided by initial formation of classical zwitterion **63**. Under such



circumstances, there exists no need for attainment by **42** of the folded conformation and it may be argued that reaction from its extended form can be expected. Subsequent minor readjustment of the bond angles

(18) R. Huisgen, G. Boche, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 3345 (1967).

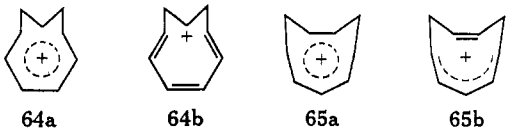
(19) P. Warner and S. Winstein, *ibid.*, **93**, 1284 (1971).

(20) L. A. Paquette, M. J. Broadhurst, P. Warner, G. Olah, and G. Liang, *ibid.*, **95**, 3386 (1973).

(21) The presence of added alkyl substituents on the site of attack by CSI in normal olefins is recognized to lower dramatically the reaction rate: R. Graf, *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968).

in **63** is then necessary to attain the proper geometry for 1,4-cyclization. The behavior of **42** approximates closely the reactivity of methoxycyclooctatetraene under comparable conditions.[13]

Nature of the Ionic Intermediate. Three different types of six-electron bishomotropylium ions (**64–66**), distinguished by the relative positioning of the two bridges,[22] were conceived by Winstein at the outset of his early research in this field.[24] Without recourse to homoconjugative interaction, the 1,2-bishomotropylium ion (**64b**) is seen to be composed formally of a secondary alkyl cation and a triene segment. In these terms, the 1,3 isomer (**65b**) is a pentadienyl cation and **66b**, the 1,4 species, is an allylic cation. Once homoconjugative interaction is effected, **64b** should be most stabilized because of resultant charge distribution over six additional carbon atoms. On the other hand, the **65b** → **65a** electronic readjustment will result in the least amount of added stabilization since only two additional carbon centers now partake in the delocalization. If equal strain is assumed for the three homoaromatic structures, then the order of predicted thermodynamic stabilization is **65a** > **66a** > **64a**.[25] As a direct consequence, the



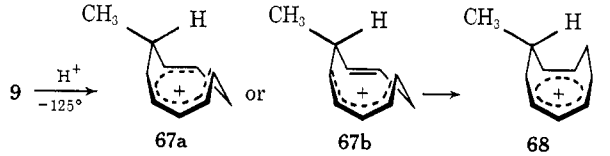
64a **64b** **65a** **65b**

66a **66b**

extent of homoaromatic delocalization is expected to increase as the stability of the cation diminishes (**65a** < **66a** < **64a**).

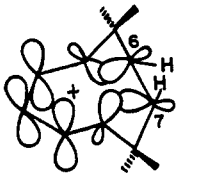
Despite the fact that bishomotropylium ions of type **66a** have already received considerable attention,[23,25] and **59a** has been generated under conditions of long life,[19,20,23] only recently has any consideration been given to the possibility of geometric isomerism in these systems.[5,6,26] In their protonation studies of *cis*- and *trans*-4,5-benzo-2,3:6,7-bishomotropones, Corver and Childs have concluded that cyclic delocalization operates only in the *cis*-1,4-bishomotropylium ion.[26]

The protonation of *cis*-bicyclo[6.1.0]nonatrienes (*e.g.*, **9**) under long life conditions is currently viewed as involving initial formation of a *trans*-1,3-bishomotropylium ion (**67**) which subsequently undergoes con-



67a **67b** **68**

formational inversion of the less substituted methylene bridge to produce the cis ion (**68**).[20] Although **68** is more thermodynamically stable than **67**, the difference in ground state energy between the two systems is apparently not excessive.[27,28] The formulation of **67** can be viewed as a fully delocalized system or as one consisting of a simple pentadienyl cation with perhaps some stabilizing homo overlap with the lone double bond (**67b**). In either case, the p orbitals at C_6 and C_7 reside in a quasi-orthogonal relationship (*cf.* **69**). The unusual three-dimensional orbital con-



69

struction of the trans ion could possibly allow for homoaromatic delocalization, but definitive information on this point is difficult to acquire. The current study suggests merely that less positive charge density is conveyed to C_6 and C_7, but this would be true for whichever geometry the cation adopted. The minimum interpretation available at this time would be that the cis ion is more stable than the trans, with the latter being produced initially. The activation energy associated with the bridge flipping process remains to be measured.

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 *cis*-Bicyclo[6.1.0]nona-2,4,6-triene (1) with CSI. A 3.54-g (0.03 mol) sample of **1**[29] in 90 ml of dry methylene chloride was treated with 4.24 g (0.03 mol) of CSI in 90 ml of the same solvent with stirring at 0° under an atmosphere of nitrogen. The solution was allowed to warm to 25° and stirring was continued for an additional 42 hr at this temperature. Progress of the reaction was followed by periodic removal of aliquots and infrared analysis of these samples. The solvent was evaporated under reduced pressure at 25° and the pale yellow solid was triturated with dry ether (*ca.* 10 ml). After filtration, *N*-chlorosulfonyl β-lactam **2** was obtained as colorless crystals (4.65 g, 60%): mp 117–118°; $\nu_{max}^{CHCl_3}$ 1825 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.4–6.6 (m, 6, olefinic), 4.4–4.7 (m, 1, >CHN<), 3.95–4.25 (m, 1, >CHCO–), and 2.68 (br, t, 2, –CH_2–).

Evaporation of the mother liquors gave a brown gum which, after treatment with thiophenol and pyridine and chromatography on Florisil as described below, gave an additional 200 mg (4%) of β-lactam **3**.

***trans*-10-Azabicyclo[7.2.0]undeca-2,5,7-trien-11-one (3).** To an ice-cooled, magnetically stirred solution of **2** (3.9 g, 0.015 mol) and thiophenol (3.3 g, 0.03 mol) in 30 mol of acetone was added dropwise 2.0 g (0.025 mol) of pyridine dissolved in 15 ml of acetone. The solution was stirred for a further 15 min and 100 ml of water

(22) Although the sizes of the interrupting links were not originally specified, they so far have not consisted of more than one methylene group.[23] For simplicity and because of the direct relevance to the present study, the bridges are denoted herein as single tetrahedral carbon atoms.

(23) 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).

(24) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(25) G. Schröder, U. Prange, and J. F. M. Oth, *Chem. Ber.*, **105**, 1854 (1972), and references therein.

(26) H. A. Corver and R. F. Childs, *J. Amer. Chem. Soc.*, **94**, 6201 (1972).

(27) Preliminary calculations have suggested that there exists no strong dependence between ground state stability and molecular geometry in such 1,3-bishomo cations (R. Gleiter and J. Clardy, personal communications). Consequently, in the absence of precise information concerning the spatial orientation of atoms in *cis*- and *trans*-1,3-bishomotropylium ions, an accurate assessment of relative energy content is not possible at this time. The isolation of crystalline salts of these cations, coupled with X-ray structural data, would clearly go far in resolving this issue.

(28) Molecular models reveal that the *trans*-1,4-bishomotropylium ion is significantly more sterically demanding than its 1,3 counterpart.

(29) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).

was added. The precipitated solid was extracted into methylene chloride and the aqueous layer was extracted twice more. The combined organic extracts were washed with water, dried, and evaporated. Chromatography of the crystalline residue on Florisil (3 × 30 cm) permitted the ready separation of diphenyl disulfide (pentane elution) from β-lactam **3** (chloroform elution). There was obtained 2.24 g (93%) of white crystals, mp 103–103.5°, after recrystallization from methylene chloride and pentane: $\nu_{max}^{CHCl_3}$ 1750 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 224 nm (ε 6850); $\delta_{TMS}^{CDCl_3}$ 6.7 (br s, 1, >NH), 5.4–6.3 (m, 6, olefinic), 3.7 (AB pattern, J_{AB} = 3 Hz, 1 >CHN<), 3.95 (m, 1, >CHCO–), and 2.3–2.9 (m, 2, –CH_2–).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.46; H, 6.96; N, 8.67.

***trans*-10-Azabicyclo[7.2.0]undecan-11-one (4). A. Hydrogenation of 3.** A solution of 180 mg (0.011 mol) of **3** in 20 ml of ethanol containing 40 mg of 10% palladium on charcoal was hydrogenated in a Parr apparatus at 40 psi. The catalyst was separated by filtration, the filtrate evaporated, and the residue passed down a small column (1 × 10 cm) of Florisil (elution with chloroform). The saturated lactam was obtained as colorless crystals (134 mg, 72%), mp 62–64°, after recrystallization from ether–pentane: $\nu_{max}^{CHCl_3}$ 1750 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.9 (br, s, 1, >NH), 3.52 (m, 1, >CHN<), 2.88 (m, 1, >CHCO–), and 0.85–2.4 (br m, 14, –CH_2–).

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.80; H, 10.24; N, 8.38. Found: C, 71.90; H, 10.24; N, 8.31.

B. Cycloaddition to *trans*-Cyclononene (5). To a solution of 1.0 g (0.0081 mol) of *trans*-cyclononene (**5**)[30] in 20 ml of dry methylene chloride cooled to −78° under an atmosphere of nitrogen was added dropwise during 15 min with stirring 1.41 g (0.01 mol) of CSI in 10 ml of the same solvent. The solution was allowed to warm to 25°, stirred at that temperature for 24 hr, and processed as above. There was obtained 1.16 g (86%) of colorless crystals, mp 62.5–64°, which were identical (melting point, mixture melting point, tlc, ir, nmr) with the substance isolated above.

***cis*-10-Azabicyclo[7.2.0]undecan-11-one (7).** *cis*-Cyclononene (**6**) was prepared by the sodium–liquid ammonia reduction of 1,2-cyclononadiene[31a] as previously described.[31b] Like reaction of 0.83 g (6.7 mmol) of **6** with 1.0 g (7.1 mmol) of CSI initially at −78° and then at 25° for 48 hr furnished 661 mg (59%) of **7** as colorless needles, mp 85–85.5°, from methylene chloride–pentane: $\nu_{max}^{CHCl_3}$ 1750 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.6 (br s, 1, >NH), 3.55–3.95 (m, 1, >CHN<), 2.95–3.35 (m, 1, >CHCO–), and 0.85–2.3 (br m, 14, –CH_2–).

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.80; H, 10.26; N, 8.38. Found: C, 71.95; H, 10.17; N, 8.41.

Reaction of *anti*-9-Methyl-*cis*-bicyclo[6.1.0]nona-2,4-6-triene (9) with CSI. The hydrocarbon was prepared from the *anti*-9-hydroxymethyl derivative[32] by conversion to the tosylate and subsequent lithium aluminum hydride reduction.[33] A solution of 1.42 g (0.01 mol) of CSI in 10 ml of dry methylene chloride was heated to reflux with stirring under nitrogen and treated dropwise with 1.32 g (0.01 mol) of **9** in 40 ml of the same solvent during 30 min. The solution was stirred at reflux for 19 hr, cooled, evaporated, and processed in the usual manner. There was obtained 988 mg (56%) of **10** as colorless needles, mp 123.5–124.5°, from methylene chloride–pentane: $\nu_{max}^{CHCl_3}$ 1750 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 240 nm (ε 4230); $\delta_{TMS}^{CDCl_3}$ 6.85 (br s, 1, >NH), 4.90–6.05 (m, 6, olefinic), 4.05–4.4 (m, 2, >CHN< and >CHCO–), 2.9–3.6 (m, 1, >CH–), and 1.17 (d, J = 7 Hz, 3, –CH_3).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.41; H, 7.48; N, 8.00. Found: C, 75.47; H, 7.49; N, 8.05.

Single crystals of **10** were grown by slow evaporation of methylene chloride–hexane solutions. Preliminary Weissenberg and precession photographs displayed the 2/*m* Laue symmetry appropriate for monoclinic crystals. Systematic extinctions of the type *h*0*l* (extinct for $l = 2n + 1$) and 0*k*0 (extinct for $k = 2n + 1$) uniquely indicated the common monoclinic space group $P2_1/c$ (C_{2h}^5). A 0.2-mm cubic crystal, mounted along *b*, was then transferred to a fully automated Hilger–Watts four-circle diffractometer. The lattice parameters and associated errors were determined by a least-squares fit to 12 independent reflection angles whose centers were determined by a left–right, top–bottom beam splitting technique.[34] The cell constants are a = 11.535 (2), b = 5.706, c = 16.980 (2) Å, and β = 116.55 (3)°. A calculated density of 1.16 g/cm^3 for Z = 4 was taken to mean that there was one molecule of $C_{11}H_{13}NO$ per asymmetric unit. All reflections in the *hkl* octants within a 2θ sphere of 60° were observed with a (θ–2θ) scan technique using Mo K_α radiation (λ 0.7107 Å). Periodically monitored check reflections showed a gradual (~10%) decline in intensities. No corrections were made for this sample deterioration or absorption (μ = 0.8 cm^{-1}). A total of 3333 reflections were measured. The intensity data were corrected for Lorentz and polarization effects. The estimated error in the observed intensity was calculated from $\sigma(I)^2 = C_T + C_B + (0.05)C_T^2 + (0.05)C_B^2$, where C_T and C_B are the total count and background count, respectively. The reflection was considered unobserved if $I < 3\sigma(I)$. The error in the observed magnitude of the structure factor was calculated using

$$\sigma(F) = \sqrt{(I + \sigma(I))/L_p - F_o}$$

Weights for observed reflections were set by $1/\sigma(F)$. A total of 1335 reflections (40%) were judged to be observed.

The intensity data were made to yield normalized structure factors by use of the Wilson plot.[35] The 358 normalized structure factors with magnitudes greater than 1.5 were assigned signs by an iterative application of Sayre's equation.[36] The 13 unique nonhydrogen atoms were clearly visible in the three-dimensional E synthesis.[37] Full-matrix least-squares refinements (minimizing $\Sigma w(|F_o| - |F_o|)^2$) converged to a conventional discrepancy index of 0.15 (wR = 0.17).[38] Eleven hydrogen atoms were found at this stage in the difference electron density synthesis. Final least-squares refinements with anisotropic carbon, oxygen, and nitrogen and isotropic hydrogens converged to R = 0.10. The final difference electron density map showed no peaks greater than 0.3 e/Å^3. The final positional and thermal parameters are given in Table I, along with their standard deviations as derived from the variance–covariance matrix of the final least-squares cycle.

A computer drawing of the final X-ray model is given in Figure 1.[39] Tables II and III contain selected bond distances and angles along with the derived standard deviations.[40] Table IV contains the magnitudes (×10) of the observed and calculated structure factors.[41]

Reaction of *anti*-9-Chloro-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (12) with CSI. To a solution of freshly distilled **12** (contaminated with syn isomer in a ratio of 23:5; 1.52 g, 0.01 mol)[42] in 15 ml of dry methylene chloride under nitrogen was added 1.41 g (0.01 mol) of CSI in 10 ml of the same solvent and the solution was stirred at room temperature for 25 hr (incomplete reaction). After reductive dechlorosulfonylation with thiophenol and pyridine, the product was chromatographed on Florisil. Elution with pentane served to separate unreacted chlorocarbon (anti/syn ratio 7:5 by nmr analysis) and diphenyl disulfide. Elution with chloroform gave a pale yellow solid, recrystallization of which from methylene chloride–ether–pentane gave 293 mg (15%) of **13** as colorless crystals: mp

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(31) (a) L. Skattebøl and S. Solomon, *Org. Syn.*, **49**, 35 (1969); (b) P. D. Gardner and M. Narayara, *J. Org. Chem.*, **26**, 2518 (1961).

(32) D. Phillips, *J. Amer. Chem. Soc.*, **77**, 5179 (1955).

(33) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969).

(34) D. E. Williams, "LCR-2, A Fortran Lattice Constant Refinement Program," U. S. Atomic Energy Commission Report IS-1052, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1964.

(35) A. J. C. Wilson, *Nature* (*London*), **150**, 151 (1942); H. Hauptman and J. Karle, *Acta Crystallogr.*, **6**, 136 (1953).

(36) R. E. Long, Ph.D. Thesis, Department of Chemistry, University of California, Los Angeles, Calif., 1965.

(37) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT, and FRIEDEL," Ames Laboratory, USAEC, Iowa State University, Ames, Iowa, 1971.

(38) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(39) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," USAEC Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(40) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE: A Fortran Crystallographic Function and Error Program," USAEC Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(41) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4647. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(42) E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965).

Table I. Final Atomic Positional and Thermal Parameters with Their Standard Deviations for β-Lactam **10**[a]

Atom	x/a	y/b	z/c	β_{11} (×10⁴)	β_{22} (×10⁴)	β_{33} (×10⁴)	β_{12} (×10⁴)	β_{13} (×10⁴)	β_{23} (×10⁴)
C(1)	0.6987 (5)	−0.2004 (6)	−0.0281 (3)	180 (6)	216 (12)	40 (2)	9 (7)	42 (3)	0 (4)
C(2)	0.6541 (5)	−0.2854 (8)	0.0365 (3)	174 (6)	307 (16)	58 (3)	−33 (8)	47 (3)	15 (5)
C(3)	0.6788 (5)	−0.1836 (8)	0.1121 (3)	181 (6)	384 (17)	52 (3)	−25 (9)	51 (3)	15 (5)
C(4)	0.7630 (5)	0.0337 (9)	0.1455 (3)	160 (6)	503 (21)	48 (2)	15 (9)	50 (3)	13 (5)
C(5)	0.8973 (5)	−0.0194 (9)	0.1593 (3)	158 (6)	479 (20)	44 (2)	25 (9)	39 (3)	18 (5)
C(6)	0.9579 (5)	0.0587 (8)	0.1121 (3)	156 (6)	439 (19)	53 (2)	26 (9)	45 (3)	−0 (6)
C(7)	0.9109 (5)	0.2097 (8)	0.0345 (3)	162 (6)	349 (17)	68 (3)	−3 (8)	62 (4)	−4 (6)
C(8)	0.7991 (5)	0.2130 (8)	−0.0362 (3)	179 (7)	274 (15)	56 (2)	26 (8)	59 (3)	19 (5)
C(9)	0.6809 (4)	0.0641 (7)	−0.0566 (2)	163 (6)	265 (14)	43 (2)	32 (7)	44 (3)	12 (4)
N(10)	0.6132 (4)	−0.0238 (8)	−0.1481 (2)	209 (6)	362 (15)	38 (2)	33 (7)	32 (2)	17 (4)
C(11)	0.6124 (5)	−0.2478 (8)	−0.1244 (3)	189 (6)	319 (17)	41 (2)	42 (8)	37 (3)	−10 (5)
C(12)	0.7678 (7)	0.1155 (14)	0.2354 (3)	211 (8)	967 (39)	68 (3)	−35 (15)	75 (4)	−104 (9)
O(13)	0.5596 (3)	−0.4234 (5)	−0.1685 (2)	246 (13)	387 (13)	51 (2)	13 (6)	33 (2)	−48 (4)
H(14)	0.7941 (56)	−0.2291 (103)	−0.0071 (35)						
H(15)	0.5958 (58)	−0.3894 (117)	0.0190 (38)						
H(16)	0.6446 (50)	−0.2899 (107)	0.1483 (34)						
H(17)	0.7252 (51)	0.1712 (107)	0.0902 (36)						
H(18)	0.9487 (53)	−0.0934 (102)	0.2124 (38)						
H(19)	1.0573 (59)	0.0416 (98)	0.1395 (35)						
H(20)	0.9827 (54)	0.3181 (106)	0.0404 (35)						
H(21)	0.7819 (52)	0.3242 (109)	−0.0845 (36)						
H(22)	0.6087 (53)	0.1304 (109)	−0.0488 (34)						
H(23)	0.5647 (55)	0.0292 (108)	−0.2026 (40)						
H(24)	0.6724 (58)	0.1086 (110)	0.2231 (34)						

[a] The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. Estimated standard deviations are given in parentheses for the least significant figure.

Table II. Selected Bond Distances[a] (Å)

C(1)–C(2)	1.485 (6)	C(7)–C(8)	1.319 (6)
C(2)–C(3)	1.320 (6)	C(8)–C(9)	1.500 (6)
C(3)–C(4)	1.519 (6)	C(9)–C(10)	1.479 (5)
C(4)–C(5)	1.491 (6)	C(11)–O(13)	1.236 (5)
C(4)–C(12)	1.573 (6)	C(11)–N(10)	1.341 (5)
C(5)–C(6)	1.353 (6)	C(1)–C(9)	1.570 (5)
C(6)–C(7)	1.461 (6)	C(1)–C(11)	1.511 (5)

[a] Estimated standard deviations are given in parentheses for the least significant figure.

Table III. Table of Selected Bond Angles[a]

Atom	Angle, deg	Atom	Angle, deg
C(5)–C(4)–C(3)	109.8 (4)	C(9)–N(10)–C(11)	94.6 (3)
C(5)–C(4)–C(12)	108.9 (4)	N(10)–C(11)–O(13)	131.2 (4)
C(3)–C(4)–C(12)	110.1 (4)	N(10)–C(11)–C(1)	93.7 (3)
C(4)–C(5)–C(6)	128.0 (4)	O(13)–C(11)–C(1)	135.1 (4)
C(5)–C(6)–C(7)	130.3 (5)	C(9)–C(1)–C(11)	84.6 (3)
C(6)–C(7)–C(8)	130.4 (5)	C(11)–C(1)–C(2)	117.6 (4)
C(7)–C(8)–C(9)	128.5 (4)	C(9)–C(1)–C(2)	120.1 (3)
C(8)–C(4)–N(10)	115.7 (3)	C(1)–C(2)–C(3)	125.4 (4)
C(8)–C(9)–C(1)	119.6 (4)	C(2)–C(3)–C(4)	123.1 (4)
N(10)–C(9)–C(1)	86.1 (3)		

[a] Estimated standard deviations are given in parentheses for the least significant figure.

127.5–128°; $\nu_{max}^{CHCl_3}$ 1760 cm⁻¹; $\lambda_{max}^{C_2H_5OH}$ 239 nm (ε 4345); $\delta_{TMS}^{CDCl_3}$ 6.95 (br s, 1, >NH), 5.51–6.1 (m, 5, olefinic), 5.15–5.51 (m, 2, olefinic and >CHCl), 4.09 and 4.3 (AB pattern, J_{AB} = 3 Hz, 2, >CHN< and >CHCO–). This spectrum exhibits a remarkable lack of olefinic proton coupling, particularly with the >CHN< proton (conformationally related?).

Anal. Calcd for $C_{10}H_{10}ClNO$: C, 61.39; H, 5.15; N, 7.16. Found: C, 61.46; H, 5.15; N, 7.09.

11-Azatricyclo[7.2.0.0^{2,4}]undecan-10-one (19). To a stirred solution of 1.22 g (0.01 mol) of **17**[43] in 25 ml of dry methylene chloride cooled to −78° in an atmosphere of nitrogen was added 1.42 g (0.01 mol) of CSI in 25 ml of the same solvent. The solution was kept at 25° for 42 hr and processed in the customary fashion. Chloroform elution of the Florisil column gave 724 mg (44%) of **19** as colorless crystals, mp 106–107°, on recrystallization from methylene chloride–pentane: $\nu_{max}^{CHCl_3}$ 1745 cm⁻¹; $\delta_{TMS}^{CDCl_3}$ 6.8 (br s, 1, >NH), 4.15–4.45 (m, 1, >CHN<), 3.35–3.8 (m, 1, >CHCO–), 0.5–2.6 (m, 11, $-CH_2-$ and 3 cyclopropyl), and 0.2 (m, 1, cyclopropyl).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.79; H, 9.08; N, 8.55.

Continued elution of the column afforded no additional characterizable material.

Reaction of *cis*-Bicyclo[6.1.0]nona-2,4-diene (18) with CSI. To a stirred solution of 1.2 g (0.01 mol) of **18**[43] in 20 ml of dry methylene chloride cooled to 0° under nitrogen was added dropwise during 0.5 hr 1.42 g (0.01 mol) of CSI. The solution was allowed to stand at 25° for 35 hr and worked up in the above manner. Pentane was employed to elute the diphenyl disulfide (Florisil column). Pentane–chloroform (1:1) eluted 132 mg (8%) of **20**: mp 137–138°; $\nu_{max}^{CHCl_3}$ 1750 cm⁻¹; $\delta_{TMS}^{CDCl_3}$ 7.0 (br s, 1, >NH), 5.25–6.3 (m, 2, olefinic), 4.3–5.65 (m, 1, >CHN<), 4.02 (dd, J = 9.5 and 5.5 Hz, 1, >CHCO–), and 0.15–2.65 (m, 8, $-CH_2-$ and cyclopropyl).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.58; H, 8.02; N, 8.58. Found: C, 73.53; H, 8.05; N, 8.54.

Continued elution of the column with chloroform afforded 175 mg (11%) of a white crystalline solid, mp 142.5–143°, identified as **21**: $\nu_{max}^{CHCl_3}$ 1665 cm⁻¹; $\delta_{TMS}^{CDCl_3}$ 8.4 (br s, 1, >NH), 5.75–6.6 (m, 2, olefinic), 4.2–4.6 (m, 1, >CHN<), 3.0–3.45 (m, 1, >CHCO–), and 0.25–2.8 (m, 8, $-CH_2-$ and cyclopropyl).

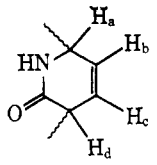
Anal. Calcd for $C_{10}H_{13}NO$: C, 73.58; H, 8.03; N, 8.58. Found: C, 73.50; H, 8.15; N, 8.63.

Using the above conditions but stirring for 85 hr gave 3% of **20** and 21% of **21**. When the methylene chloride solution was stirred at reflux for 43 hr, there was produced 1% of **20** and 40% of **21**.

At 100 MHz, the olefinic protons of **21** appear as two distinct dd patterns, J = 9 and 6 Hz in both cases; additionally, the low-field set is split by a further coupling of *ca.* 2 Hz. Irradiation of H_a caused no change in the pattern for H_c but collapsed H_b to a simple dd with J = 9 and 2 Hz. Irradiation of H_d did not affect H_b while H_c now appeared as a sharp doublet (J = 9 Hz). Simultaneous irradiation of H_a and H_d reduced H_b to a dd (J = 9 and 2 Hz) and H_c to a doublet (J = 9 Hz). Upon irradiation of H_b, H_a appeared as a triplet with fine splitting (apparent coupling constant of *ca.* 4 Hz). Finally, when H_c was irradiated, H_d was seen as a broad poorly resolved doublet ($J \approx$ 8–9 Hz) with additional splitting.

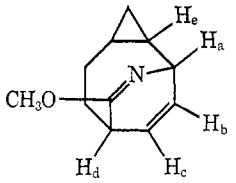
Diimide Reduction of 20. β-Lactam **20** (80 mg, 5.0 mmol) was dissolved in methanol (6 ml) and dipotassium azodicarboxylate

(43) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. K. Krause, H. V. Cortez, and P. D. Gardner, *J. Amer. Chem. Soc.*, 87, 3158 (1965).



(2.0 g) was added. The suspension was stirred during the slow addition of acetic acid (2.0 g) over a period of *ca.* 30 min. After a further 4 hr the methanol was evaporated and the residue was treated with 25 ml of water. Extraction of the product with methylene chloride, followed by drying and evaporation of this solution, gave 50 mg (62%) of a colorless crystalline residue, mp 103–104.5°. Two recrystallizations from ether–pentane raised the melting point to 105–106°. The nmr spectrum of this product was identical with that of **19**.

O-Methylation of Lactam 21. A solution of 326 mg (0.02 mol) of **21** in 15 ml of dry methylene chloride was treated under nitrogen with 450 mg (0.03 mol) of trimethyloxonium fluoroborate. The mixture was stirred at 25° for 15 hr and treated with excess 50% potassium carbonate solution. After separation of the organic layer, the aqueous phase was extracted twice again with methylene chloride. Molecular distillation of the resulting pale yellow oil (360 mg) at 45° and 0.1 mm afforded 250 mg (65%) of **22** as a colorless liquid which solidified on cooling to 0°: ν_{max}^{neat} 1680 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.14 (dd, J = 9.5 and 5 Hz, 1, olefinic), 5.72 (dd, J = 9.5 and 6 Hz, 1, olefinic), 4.56 (t, J = 5 Hz, 1, >CHN<), 3.74 (s, 3, $-OCH_3$), 2.97 (m, 1, >CHC=), 1.16–2.2 (m, 5, $-CH_2-$ and 1 cyclopropyl), 0.18–1.0 (m, 3, cyclopropyl).



At 100 MHz the following coupling constants were established: $J_{b,c}$ = 9.5 Hz; $J_{a,b}$ = 5 Hz; $J_{c,d}$ = 6 Hz. Irradiation of H_a resulted in collapse of the low-field olefinic absorption to a doublet (J = 9.5 Hz) and slight modification of part of the cyclopropyl region, while similar action on H_d modified H_c to a doublet (J = 9.5 Hz) and produced alterations in the methylene region. Furthermore, irradiation of H_c resulted in simplification of the H_d absorption which was collapsed still further to a broad "singlet" (additional fine splitting remained) upon simultaneous irradiation of the methylene region. Spin decoupling of H_b reduced H_a to a dd (J = 4.5 and *ca.* 2.5 Hz); clearly H_a is coupled long range to a second cyclopropyl proton. Triple irradiation involving H_b and H_e revealed a triplet pattern ($J \approx$ 2.5 Hz) for H_a in confirmation of this conclusion.

The perchlorate salt of **22** was obtained as colorless prisms, mp 155–157°, from methylene chloride–ether.

Anal. Calcd for $C_{11}H_{16}ClNO_5$: C, 47.56; H, 5.81; N, 5.04. Found: C, 47.38; H, 5.85; N, 5.04.

Preparation of the Isomeric Methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-trienes 25–28. To a solution of 5.9 g (0.05 mol) of methylcyclooctatetraene in 200 ml of anhydrous liquid ammonia under nitrogen was added 0.7 g (0.1 g-atom) of lithium wire in small pieces. The solution was stirred at *ca.* −33° for 1.5 hr and a solution of 10 g of dry methylene chloride in anhydrous ether (50 ml) was added dropwise. After 3 hr, the ammonia was evaporated under a nitrogen stream and 200 ml of saturated ammonium chloride solution was introduced. The product was extracted into ether and the ether layer washed with water and saturated brine. Evaporation of the dried solution and distillation of the residue afforded 4.43 g (67%) of a colorless oil, bp 54–57° (3.8 mm). Vpc analysis (15% PPGA on Chromosorb P, 6 ft × 0.25 in. column at 65°) indicated the presence of four major components plus small amounts of impurities. Repeated preparative vpc isolation ultimately gave 200–400-mg samples of the pure isomeric hydrocarbons.

The first component to elute was shown to be **25**: $\lambda_{max}^{cyclohexane}$ 243.5 nm (ϵ 3240); $\delta_{TMS}^{CDCl_3}$ 5.92 (s, 6, olefinic), 1.29 (dd, J = 9.5 and 6 Hz, 1, cyclopropyl), 1.0 (s, 3, $-CH_3$), 0.74 (dd, J = 9.5 and 3.5 Hz, 1, cyclopropyl), and 0.31 (dd, J = 6 and 3.5 Hz, 1, cyclopropyl).

Anal. Calcd for $C_{10}H_{12}$: C, 90.84; H, 9.16. Found: C, 90.65; H, 9.42.

The second hydrocarbon to appear was identified as **26**: $\lambda_{max}^{cyclohexane}$ 241 nm (ϵ 2950); $\delta_{TMS}^{CDCl_3}$ 5.96 and 5.8 (br peaks, 5, olefinic), 1.75 (s broadened by long range coupling, 3, $-CH_3$), 1.4 (m, 2, cyclopropyl), and 0.9 and 0.0 (m, 1 each, cyclopropyl).

Anal. Calcd for $C_{10}H_{12}$: C, 90.84; H, 9.16. Found: C, 90.55; H, 9.36.

The third isomer was characterized as **27**: $\lambda_{max}^{cyclohexane}$ 245 nm (ϵ 4050); $\delta_{TMS}^{CDCl_3}$ 5.8 (br, s, 4, olefinic), 5.61 (br s, 1, olefinic), 1.83 (s, 3, $-CH_3$), 1.38 (m, 2, cyclopropyl), 0.9 and 0.15 (m, 1 each, cyclopropyl).

Anal. Calcd for $C_{10}H_{12}$: C, 90.84; H, 9.16. Found: C, 90.57; H, 9.34.

3-Methyl-*cis*-bicyclo[6.1.0]nonane (30). A. Catalytic Hydrogenation of 26. A solution of 132 mg of **26** in 10 ml of tetrahydrofuran was hydrogenated at atmospheric pressure over 5% rhodium on carbon catalyst until the uptake of hydrogen ceased. The catalyst was separated by filtration and the filtrate was carefully concentrated. Preparative vpc analysis (10% SE-30 on Chromosorb W, 12 ft × 0.25 in. column, 70°) gave evidence of two major products in addition to significant amounts of material in which the cyclopropane ring had also experienced cleavage. The isomer of **30** with the shorter retention time displayed an nmr spectrum featuring: $\delta_{TMS}^{CDCl_3}$ 1.19–2.24 (br m, 11, 10 methylene and 1 methine), 0.87 (d, J = 6 Hz, 3, $-CH_3$), 0.66 (m, 3, cyclopropyl), and −0.28 (m, 1, cyclopropyl).

Anal. Calcd for $C_{10}H_{18}$: C, 86.86; H, 13.12. Found: C, 86.80; H, 12.86.

The isomer with the longer retention time showed: $\delta_{TMS}^{CDCl_3}$ 1.17–2.3 (br m, 11, 10 methylene and 1 methine), 0.97 (d, J = 5 Hz, 3, $-CH_3$), 0.63 (m, 3, cyclopropyl), and −0.28 (m, 1, cyclopropyl).

Anal. Calcd for $C_{10}H_{18}$: C, 86.86; H, 13.12. Found: C, 86.78; H, 12.95.

B. From *cis*-Bicyclo[6.1.0]nonan-3-one (29). A solution of *n*-butyllithium (15.5 ml of a 1.3 *M* solution in pentane) was added to 7.14 g (0.028 mol) of methyltriphenylphosphonium bromide suspended in 100 ml of dry ether under nitrogen. The yellow solution was stirred for 4 hr at 25° and 2.7 g (0.02 mol) of **29**[44] dissolved in 5 ml of ether was added. The mixture was refluxed overnight with stirring, cooled, and filtered to remove the precipitated solids. This material was dissolved in water and the aqueous solution was extracted with ether. The combined filtrate and extracts were washed repeatedly with water, dried, and carefully evaporated. The methylene derivative was obtained as a colorless liquid: bp 97–99° (44 mm); 1.73 g, 64%. An analytical sample was collected by vpc: ν_{max}^{neat} 1640 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 4.65 (s, 2, vinyl), 1.12–3.87 (m, 10, $-CH_2-$), 0.8 (m, 3, cyclopropyl), and −0.24 (m, 1, cyclopropyl).

Anal. Calcd for $C_{10}H_{16}$: C, 88.20; H, 11.79. Found: C, 87.80; H, 11.67.

Hydrogenation of the methylene derivative over 5% rhodium on carbon as before also gave two isomers of **30** which were separated in analogous fashion and shown to be identical (ir, nmr, vpc) with the substances isolated previously.

4-Methyl-*cis*-bicyclo[6.1.0]nonane (32). A. Catalytic Hydrogenation of 27. A sample of **27** was hydrogenated as described above. After preparative vpc, a single isomer of **32** was isolated: $\delta_{TMS}^{CDCl_3}$ 1.0–2.28 (m, 11, ten methylene and one methine), 0.93 (d, J = 6 Hz, 3, methyl), 0.6 (br s, 3, cyclopropyl), and −0.3 (m, 1, cyclopropyl).

Anal. Calcd for $C_{10}H_{18}$: C, 86.86; H, 13.12. Found: C, 86.85; H, 13.03.

B. Cyclopropanation of 5-Methylcyclooctene (31). A mixture of methylene iodide (20.1 g, 0.075 mol), iodine (0.03 g), zinc–copper couple (6.6 g),[45] and ether (40 ml) was heated under reflux for 30 min. Heating was stopped and 5.5 g (0.045 mol) of **31**[46] in 2.5 ml of ether was added. The mixture was maintained at reflux for 4 days, cooled, and filtered. The ethereal filtrate was washed with 3% hydrochloric acid, 10% sodium bicarbonate solution, and saturated brine. After drying and removal of the solvent, the residue was distilled and the fraction boiling at 94–98° (56 mm) was collected. This colorless liquid (4.8 g) was found to be 95% pure by vpc analysis (5% residual **31**). A pure sample was collected and shown to be identical (ir, nmr, vpc) with the sample of **32** isolated in A.

Reaction of 25 with CSI. To a solution of 51 mg (0.36 mmol)

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of CSI in 5 ml of dry methylene chloride at 42° under nitrogen was added 41 mg (0.31 mmol) of **25** dissolved in 10 ml of the same solvent. This solution was heated at 42° for 20 hr, cooled, and evaporated. The residue was worked up as previously described. Pentane was employed to elute the disulfide. β-Lactam **33** eluted with chloroform–pentane (1:1) as a crystalline white solid (29.5 mg, 53%), mp 145.5–146.5° (from methylene chloride–hexane): $\nu_{max}^{CHCl_3}$ 1760 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 225 nm (ε 3590); $\delta_{TMS}^{CDCl_3}$ 6.64 (br s, 1, >NH), 5.6–6.2 (m, 5, olefinic), 3.85 (dd, J = 10 and 3 Hz, 1, >CHN<), 3.58 (br s with fine splitting, 1, >CHCO–), 2.83 (dd, J = 13.5 and 11 Hz, 1 methylene proton), 2.37 (dd, J = 13.5 and 4 Hz, 1, other methylene proton), and 1.85 (d, J = 2 Hz, 3, –CH_3).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.41; H, 7.48; N, 8.00. Found: C, 75.23; H, 7.55; N, 7.80.

Irradiation of H_9 resulted in some simplification of the vinyl region and no change for H_{4a}, H_{4b}, and the methyl group. Irradiation of H_1 reduced the highest field portion of the vinyl region to a fairly sharp singlet; also, while H_{4a} and H_{4b} were unchanged, the methyl group now appeared as a singlet. Conversely, when the methyl absorption was saturated, H_1 was distinctly simplified and H_9 was unchanged. The highest field olefinic region assigned to H_2 was also affected, appearing now as a sharp doublet ($J \approx 4.5$ Hz). Triple resonance studies involving both H_1 and the methyl group resulted in change of the H_2 absorption to a sharp singlet. Concomitant saturation of H_2 and the methyl absorption caused H_1 to reduce to a doublet (J = 3 Hz), indicating only relatively weak coupling to the adjacent trans-positioned bridgehead proton.

Careful examination (chiefly by nmr methods) of the mother liquors and noncrystalline fractions eluted from the column failed to disclose the presence of other lactams.

Reaction of 28 with CSI. Treatment of 553 mg (4.2 mmol) of **28** with 610 mg (4.3 mmol) of CSI in 30 ml of dry methylene chloride at 42° for 20.5 hr gave a crude product which, after dechlorosulfonylation, was chromatographed on Florisil. After elution of the sulfides with pentane, β-lactam **35** was eluted with pentane–chloroform (1:1) as a white crystalline solid (394 mg, 53%), mp 145.5–146° (from methylene chloride–hexane): $\nu_{max}^{CHCl_3}$ 1760 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 224 nm (ε 4140); $\delta_{TMS}^{CDCl_3}$ 6.96 (br s, 1, >NH), 5.3–6.2 (m, 5, olefinic), 3.75 (s superimposed on dd, 2, >CHN< and >CHCO–), 2.09 (m, 2, –CH_2–), and 1.88 (s, 3, –CH_3).

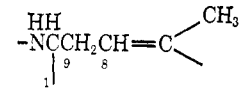
Anal. Calcd for $C_{11}H_{13}NO$: C, 75.41; H, 7.48; N, 8.00. Found: C, 75.57; H, 7.57; N, 7.95.

Irradiation of H_1 and H_2 caused major modification of only the "central" olefinic region (δ 5.62–5.92); H_{4a} and H_{4b} were unaffected. When this area of olefinic absorption was saturated, H_1 and H_9 appeared as an AB quartet ($J_{1,9} \approx 2$ Hz). Double resonance studies involving H_{4a} and H_{4b} resulted in modification of the remaining olefinic proton pattern (5.3–5.67). Also, the proton seen at *ca.* δ 5.4 is weakly spin-coupled to the methyl group, as revealed by saturation at 1.88 and attendant collapse of the downfield multiplet to a doublet of doublets (J = 9.5 and 2.5 Hz). The high-field olefinic proton is assigned as H_3 since it appears as a singlet upon irradiation of H_{4a} and H_{4b}. The lowest field proton at δ 6.1 appears as a doublet of doublets (J = 11 and 2.5 Hz) and remains unchanged upon saturation of H_{4a}, H_1, H_9, and the methyl group. On this basis, this absorption is assigned to H_6 or H_7.

Continued elution of the column with chloroform–pentane (1:1) led to the ultimate isolation of **36** (38 mg, 5%) as colorless prisms, mp 135.5–137.5° (from methylene chloride–hexane): $\nu_{max}^{CHCl_3}$ 1660 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 254 nm (ε 3560) and shoulder at 215 nm (ε 4250); $\delta_{TMS}^{CDCl_3}$ 7.27 (br s, 1, >NH), 5.37–6.16 (m, 5, olefinic), 3.70–4.10 (m, 2, >CHN< and >CHCO–), 2.76 (d with fine splitting, J = 17.5 Hz, 1, H_{9a} or H_{9b}), 2.30 (ddd, J = 17.5, 8, and 4.5 Hz, 1, H_{9a} or H_{9b}), and 1.72 (s, 3, –CH_3).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.41; H, 7.48; N, 8.00. Found: C, 75.09; H, 7.51; N, 8.02.

Irradiation of H_1 (and partial irradiation of H_5 because of its proximity) resulted in simplification of the high-field methylene proton (δ 2.3) to a doublet of doublets (J = 17.5 and 8 Hz) but only slight sharpening of the low-field methylene proton (δ 2.76). Some modification of the vinyl region was also noted. Saturation of the low-field methylene proton did not noticeably affect the olefinic absorption; however, some simplification of H_1 occurred and H_6 was slightly sharpened. Simultaneous irradiation of both methylene protons caused the olefinic proton at δ 5.5 to appear as a moderately sharp singlet, H_1 to collapse to a doublet of doublets (J = 8 and 6 Hz), and H_6 to become slightly modified. Evidence was likewise obtained for a substantial interaction between H_1 and the >NH proton (J = 6 Hz). These data reveal the following part structure



in which H_1 is spin-coupled to both methylene protons and one of these H_9 protons interacts strongly (J = 8 Hz) with H_8 (the latter is not significantly coupled to any other proton).

Examination of the noncrystalline fractions from the later stages of the chromatographic process by nmr methods failed to give evidence for the presence of other nonpolymeric products.

Reaction of 27 with CSI. A solution of CSI (384 mg, 2.8 mmol) and **27** (362 mg, 2.8 mmol) in 20 ml of dry methylene chloride was heated with stirring at 42° under nitrogen for 3 hr. After this time, a moderately intense infrared band at 1830 cm^{-1} had peaked and was beginning to decay; much unreacted CSI remained. Workup in the predescribed fashion led to the isolation of 28 mg (6%) of **38** as a colorless solid: mp 123.5–124°; $\nu_{max}^{CHCl_3}$ 1760 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 228 nm (ε 4670); $\delta_{TMS}^{CDCl_3}$ 6.75 (br s, 1, >NH), 5.2–6.1 (m, 5, olefinic), 3.98 (d, J = 2.5 Hz, 1, >CHN<), 3.65 (br s, 1, >CHCO–), 2.54 (br t, $J \approx 7$ Hz, 2, –CH_2–), and 1.76 (br s, 3, –CH_3).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.41; H, 7.48; N, 8.00. Found: C, 75.24; H, 7.54; N, 7.95.

1,3,5,7-Tetramethyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (41). To a solution of 2.78 g (0.0175 mol) of 1,3,5,7-tetramethylcyclooctatetraene (**40**) in 200 ml of anhydrous liquid ammonia was added under nitrogen small pieces of lithium wire (244 mg, 0.035 g-atom). A dark brown color was immediately produced. After 1 hr at −33°, dry methylene chloride (10 g) dissolved in 50 ml of anhydrous ether was added slowly. The solution was stirred for an additional hour and 3 g of solid ammonium chloride was introduced. Most of the ammonia was evaporated. Distillation of the residue afforded 2.5 g (83%) of **41** as a colorless liquid: bp 41–41.5° (0.5 mm); $\lambda_{max}^{cyclohexane}$ 242 nm (ε 3680); $\delta_{TMS}^{CDCl_3}$ 5.64 and 5.41 (2 br s, ratio 1:2, olefinic), 1.8 (2 overlapping s slightly broadened by fine splitting, 6, –CH_3), 1.62 (s with fine splitting, 3, –CH_3), 1.25 (m, 1, cyclopropyl), 0.95 (s, 3, –CH_3), 0.54 (dd, J = 9 and 3.5 Hz, 1, cyclopropyl), and 0.23 (dd, J = 6 and 3.5 Hz, 1, cyclopropyl).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.56; H, 10.40.

4-Methoxy-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (42). To a solution of 6.7 g of methoxycyclooctatetraene in 250 ml of dry liquid ammonia was added under nitrogen 0.7 g of lithium wire in small pieces. The resulting dark brown solution was stirred at −33° for 2 hr, at which time a solution of methylene chloride (10 ml) in 50 ml of anhydrous ether was added dropwise. The cutomary processing gave an orange oil which, on distillation, afforded 5.7 g of a pale yellow liquid, bp 42–46° (0.3 mm). Vpc analysis of this mixture on a variety of columns generally showed poor separative quality. Utilization of a 0.25 in. × 24 ft column packed with 5% QF-1 on Chromosorb W did provide sufficient resolution to permit isolation of pure **42** on a preparative scale: $\delta_{TMS}^{CDCl_3}$ 5.9 (m, 4, olefinic), 5.0 (br d with fine splitting, 1 olefinic), 3.58 (s, 3, –OCH_3), 1.45 (m, 2, cyclopropyl), 0.88 (m, 1, cyclopropyl), and 0.3 (m, 1, cyclopropyl); mass spectrum 148.08856 (calcd for $C_{10}H_{12}O$, 148.08881).

Samples of this vinyl ether soon became viscous even upon storage at 0° or below and satisfactory analytical data were not obtained.

Hydrogenation of 42. A 100-mg sample of **42** was dissolved in tetrahydrofuran and hydrogenated over 10 mg of 5% rhodium on carbon catalyst at atmospheric pressure until the uptake of hydrogen ceased. Vpc analysis of the product on an OV-11 (5% on Chromosorb W) column showed three major and one minor component. The first material to elute (~25%) was an ether which was not further characterized. The second product was identified as bicyclo[6.1.0]nonan-4-one (**43**) by comparison of its infrared and nmr spectra with those of an analytical sample.[44] Similarly identified was cyclononanone (**44**), the third component. The minor product (<15% of total ketones) was not identified.

Reaction of 42 with CSI. A. Short Term. A solution of 100 mg (0.675 mmol) of **42** in 10 ml of dry methylene chloride, cooled to 0° under nitrogen, was treated with 0.08 ml (0.95 mmol) of CSI. The solution was allowed to warm slowly to room temperature and after 5 hr the solvent was evaporated and the usual dechlorosulfonylation was performed. Chromatography on Florisil with chloroform elution afforded 46 mg (35.5%) of **45** as colorless needles, mp 195–195.5°, from ether: $\nu_{max}^{CHCl_3}$ 1675 and 1690 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ end absorption only; $\delta_{TMS}^{CDCl_3}$ 8.0 (br, 1, >NH), 5.95 (m, 2, olefinic), 4.6 (m, 2, >CH=C(OCH$_3$)– and >CHN<), 3.6 (s, 3,

$-OCH_3$), 3.3 (m, 1, >CHCO–), and 0.65–2.1 (m, 4, cyclopropyl); mass spectrum calcd, 191.09462; found, 191.09425.

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.99; H, 6.85; N, 7.39.

Irradiation of the 2-proton multiplet at δ 4.6 resulted in simplification of the lowest field cyclopropyl absorption. Also, saturation of the olefinic signal at 5.95 caused collapse of the broad doublet due to >CHN< and some sharpening of the higher field cyclopropyl region.

B. Longer Reaction Time. When the reaction was carried out as above except that the reaction mixture was left at room temperature for 22 hr prior to treatment with thiophenol and pyridine, the only product found was **46**, 35 mg (30%), in the form of colorless crystals, mp 227.5–228.5°, from methylene chloride: $\nu_{max}^{CHCl_3}$ 1680 and 1725 cm^{-1}; $\delta_{TMS}^{CDCl_3 + DMSO\text{-}d_6}$ 8.6 (br, 1, >NH), 6.15 (dd, J = 4 and 11 Hz, 1, olefinic), 5.5 (t, J = 11 Hz, 1, olefinic), 4.35 (m, 1, >CHN<), 3.5 (d, J = 11 Hz, 1, >CHCO–), and 2.7 (peak partially obscured by DMSO, $-CH_2-$); mass spectrum calcd, 177.07897; found, 177,07865.

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.28; N, 7.91. Found: C, 67.27; H, 6.31; N, 7.92.

Hydrolysis of 45. A solution of 20 mg of **45** in 0.3 ml of $CDCl_3$ was placed in an nmr tube and treated with one drop of a solution of perchloric acid in methanol. Scanning of the spectrum within minutes of the acid treatment showed only peaks due to **46**. The solution was washed with water, dried, and evaporated to afford 18 mg (97%) of colorless crystals, mp 226–228°, identical (ir) with the material isolated above.

Stereochemistry of Oxidation of Trivalent Phosphorus and Configurational Assignments in 2-Substituted 1,3,2-Dioxaphosphorinanes

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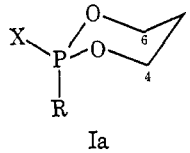
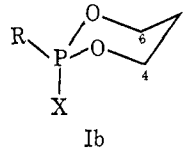
Abstract: From dipole moment and nmr measurements on the isomeric 2-oxo-2-methoxy-1,3,2-dioxaphosphorinanes VIIIa,b, it is shown that the stereospecific oxidation of the parent compounds IIa,b occurs with retention of configuration at phosphorus. With this information and additional dipole moment and nmr studies carried out on the isomeric 2-oxo-2-dimethylamino-1,3,2-dioxaphosphorinanes VIIa,b, the configurations at phosphorus in these isomers as well as those in the trivalent phosphorus parents Va,b are assigned The equilibrium ratio of Va,b (1:10) shows that in contrast to the 2-methoxy analogs IIa,b the more stable configuration is that wherein the Me_2N group is equatorial. That the same is true for the oxidized analogs VIIa,b relative to VIIIa,b is shown from hydrolysis experiments. The results for the 2-methoxy systems are rationalized on the basis of a modified gauche effect, which in the case of the 2-dimethylamino compounds is dominated by a steric problem incurred by the Me_2N group in its attempt to adopt a preferred rotameric conformation. The analogous stability relationships in the 2-substituted-2-oxo systems are also consistent with a modified gauche effect tempered by steric requirements of the dimethylamino group.

The bulk of the information regarding the preferred stereochemical disposition of phosphorus substituents in chair-form 2-R-1,3,2-dioxaphosphorinanes Ia,b (where X = lone pair and R = halogen, alkoxy,



Ia



Ib

alkyl, phenyl), while not unequivocal nor uncontested,[2] indicates rather strongly that configuration Ia is thermodynamically the more stable one. The axial preference of R has been inferred from dipole moment measurements,[3] nmr couplings and chemical shifts,[4] X-ray structural work on derivatives formed by assumed stereochemical paths,[5] and deductive reasoning concerning the stereochemical course of exchanging one R group for another.[6] Most of the structural knowledge obtained to date on the 2-oxo derivatives of Ia,b (X = O) stems from crystal structure determinations on compounds possessing various R groups (OPh, OH, Br, Ph, Me, NR_2) along with ring substituents in some cases.[5,7] With the apparent exception of R = NR_2,[7f] the phosphoryl oxygen is equatorial in the solid state. The structural behavior of 1,3,2-dioxaphosphorinane systems where X = lone pair or O is complicated in the solution state by the presence of conformational

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