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

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

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

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

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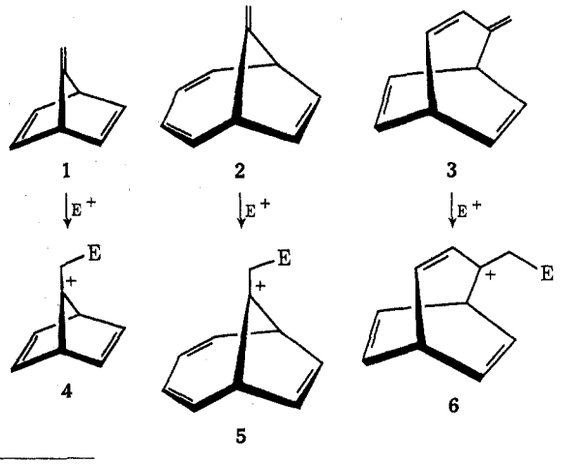
Synthesis of the methylene polyolefins 9-methylenebarbaralane (**10**), 2-methylenebicyclo[3.2.2]nona-3,6,8-triene (**3**), 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (**2**), and their benzologs, as well as 7-methylenenorbornadiene (**1**) and 7-methylenequadricyclane (**8**), has been achieved and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

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

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

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



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

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

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

(4) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(5) S. Winstein, *Chem. Soc., Spec. Publ.*, **No. 21**, 5 (1967).

(6) (a) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967); (b) A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, 3383 (1967); (c) J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); (d) J. C. Barborak and P. v. R. Schleyer, *ibid.*, **92**, 3184 (1970); (e) J. B. Grutzner and S. Winstein, *ibid.*, **92**, 3186 (1970); (f) D. Cook, A. Diaz, J. P. Dirlam, D. L. Harris, M. Sakai, S. Winstein, J. C. Barborak, and P. v. R. Schleyer, *Tetrahedron Lett.*, 1405 (1971); (g) J. S. Blair, J. Clark, and G. V. Meehan, *ibid.*, 3097 (1972); (h) J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2200 (1972).

(7) (a) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 2146 (1970); (b) P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *ibid.*, **92**, 3478 (1970); (c) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **93**, 4454 (1970); (d) P. Ahlberg, D. L. Harris, M. Roberts, P. Warner, P. Seidl, M. Sakai, D. Cook, A. Diaz, J. P. Dirlam, H. Hameberger, and S. Winstein, *ibid.*, **94**, 7063 (1972).

(8) J. B. Grutzner and S. Winstein, *ibid.*, **90**, 6562 (1968).

(9) S. W. Staley and D. W. Reichard, *ibid.*, **91**, 3998 (1969).

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

methylene center in each case, one bicycloaromatic (**4**) and two antibicycloaromatic cations (**5** and **6**) would be formed.[3] In the latter examples, the resulting long-range destabilization of the carbonium ion center could serve to substantially reduce the kinetic preference for electrophilic bonding to the $=CH_2$ group with the result that attack at a different olefinic site could become dominant.[11] Alternatively, **5** and **6** could exhibit a high propensity (relative to **4**) for structural rearrangement. Seemingly, if bicycloaromaticity does provide a source of stabilization to certain three-dimensional π-electronic arrays but not to others, then widely differing chemical reactivity toward uniparticulate electrophiles would be expected for **1–3** and related molecules.

Preparation of the Methylene Derivatives.—Synthetic entry to **1** was gained by Wittig reaction of quadricyclanone (**7**) with methylenetriphenylphosphorane and subsequent valence isomerization of the resulting methylenequadricyclane (**8**) with $[Rh(NOR)Cl]_2$.[12] The structural assignment to **1** follows from the directed synthesis and spectral evidence. Of particular interest was the finding that **1** exhibits a methylene proton signal at δ 3.63, approximately 0.9 ppm to higher field than that found in the other compounds studied herein. The excessive shielding of these two protons points to strong polarization of the exocyclic double bond in **1** with the negative terminus of the dipole oriented away from the bicyclic framework. The importance of ground-state contributions from structure **9** is revealed by the substantial dipole moment of the hydrocarbon (0.71 D) and its ^{13}C nmr and photoelectron spectra.[12]

The methylene hydrocarbons **2** and **3**, as well as 9-methylenebarbaralane (**10**) and methylenehomosemibullvalene (**11**), were synthesized by treatment of the derived ketones under Wittig conditions with methylenetriphenylphosphorane. The possibility was considered that benzo derivatives of certain of these polyenes might provide added mechanistic information. Goldschmidt and Kende, while studying the photochemical interrelationships of a number of polyolefinic hydrocarbons, have previously described the the preparation of **12–14**.[13] In contrast, because ketone **19** had been previously isolated only in low yield from benzyne addition to tropone,[14] an improved synthesis of this molecule was sought. The present scheme depends on the dienophilic character of the etheno bridge in bicyclo[4.2.1]nona-2,4,7-trien-9-one (**15**)[15,16] and subsequent adjustment of the

(11) In this regard, CSI does not differ from the common biparticulate electrophilic reagents which exhibit a kinetic preference for attack at a terminal methylene group in the presence of otherwise disubstituted double bonds: R. Graf, *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968).

(12) Subsequent to the completion of this work, we learned of a similar synthesis of **1** in Professor R. W. Hoffmann's laboratory: R. W. Hoffmann, R. Schuttler, W. Schafer, and A. Schweig, *Angew. Chem.*, **84**, 533 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 512 (1972).

(13) Z. Goldschmidt and A. S. Kende, *Tetrahedron Lett.*, 4625 (1971).

(14) T. Miwa, M. Kato, and T. Tamano, *ibid.*, 1761 (1969); H. Tanida and T. Irie, *J. Org. Chem.*, **36**, 2777 (1971).

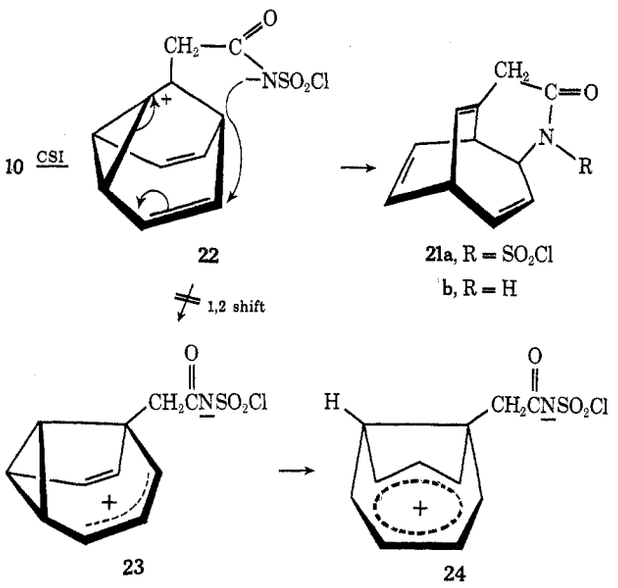
(15) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 2155 (1972).

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

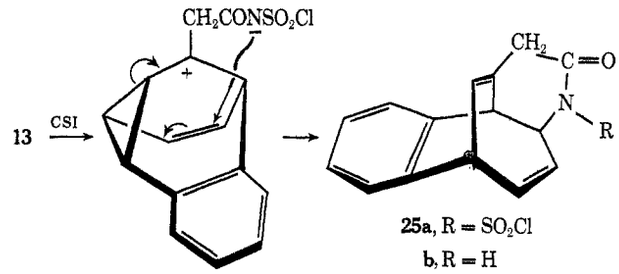
oxidation level by such controlled means which would aromatize a new six-membered ring fused to that position without engendering loss of carbon monoxide. To this end, reaction of **15** at 120–130° with an excess of α-pyrone (**16**) in xylene solution containing hydroquinone afforded, after purification by chromatography, a 34% yield of the desired adduct (**17**). A sharp-melting material was isolated, but it was not possible to determine from the available nmr data which isomer (**17a** or **17b**) was in hand. Thermal decarboxylation of **17** at 230° (0.3 mm) resulted in the formation of **18** in 80% yield. Surprisingly, ketone **18** proved to be somewhat resistant to dehydrogenation. Only when solutions of **18** in benzene containing relatively large quantities of 10% palladium on carbon were heated at reflux for 24 hr was a reasonable (54%) yield of **19** obtained. Treatment of **19** as before with methylenetriphenylphosphorane led readily to **20**.

Chlorosulfonyl Isocyanate Additions. 9-Methylenebarbaralane and Its Benzolog.—Reaction of **10** with CSI in dry methylene chloride solution at 25° for 2.5 hr and subsequent dechlorosulfonylation with alkaline sodium sulfite[17] resulted in the formation of lactam **21b**. Its infrared carbonyl absorption (1660 cm^{-1}) is typical of a δ-lactam. The absence of ultraviolet absorption apart from end absorption attests to the lack of extended conjugation. The nmr spectrum shows five olefinic protons as a series of three unevenly weighted multiplets at δ 6.8 (area 1), 6.18 (area 3), and 5.0 (area 1), an allylically disposed >CHN< hydrogen at 3.6 (m), a sharp methylene singlet (2 H) at 3.3, and a broad methine multiplet (2 H) centered at 3.2. These data signify in particular that (a) electrophilic attack has occurred at the methylene carbon in **10** with ultimate attachment of the $-CH_2CO-$ functionality to a trigonal carbon (note downfield position of the methylene singlet); (b) structural rearrangement accompanied by opening of the cyclopropane ring did operate (note lack of cyclopropyl protons); and (c) closure of the intermediate zwitterion occurred with C–N bond formation at an allylic center to produce a six-ring lactam. Double-resonance studies, which are detailed in the Experimental Section, confirmed the structural assignment to **21**.

A reasonable mechanism for the formation of **21a** involves initial generation of zwitterion **22**, followed by direct trapping of this barbaralyl cation according to the indicated series of electron shifts. Interestingly, **22** has given no evidence for rearrangement *via* **23** to **24**, despite the bishomoaromatic nature of this species.[18] This is in contrast to the 9-methylbarbaralyl cation, which under long-life conditions rearranges at −116° exclusively to the methyl 1,4-bishomotropylium ion corresponding to **24**.[7a,18] We attribute this difference to the rapid intramolecular capture of **22** which, because it is simply an exothermic bond-forming charge annihilation process, can compete favorably with the apparently more energetically demanding 1,2 carbon shift required for passage to **24**.



When benzo derivative **13** was similarly treated with CSI, a lactam of comparable structure (**25b**)

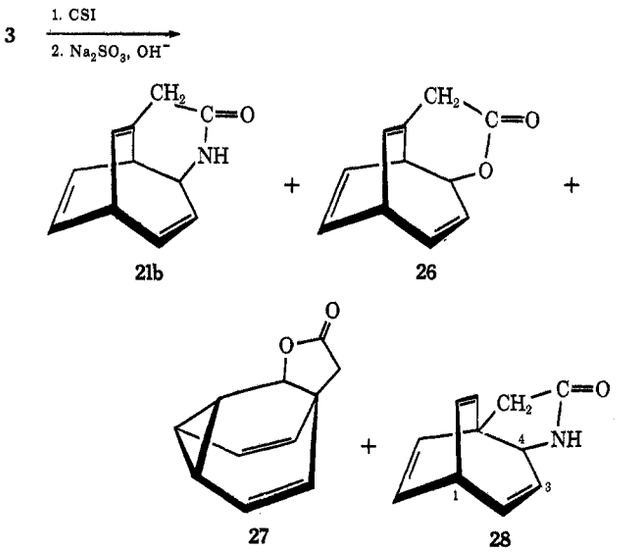


was isolated. Since one of the double bonds in **22** remains essentially isolated from the requisite electronic shifts, the formation of **25** was not unexpected.[6g] Structure **25b** was assigned chiefly on the basis of the following nmr observations. In addition to the four aromatic protons seen as a multiplet centered at δ 7.2, two olefinic proton absorptions were evident at 6.1–6.5 (m, area 2) and 4.85–5.2 (m, area 1). The bridgehead protons were deshielded relative to those in **21b** and appeared at 3.75 superimposed upon the >CHN< hydrogen. The chemical shift of the methylene group (3.35) was again in accord with expectations based upon its allylic nature.

2-Methylenebicyclo[3.2.2]nona-3,6,8-triene and Its Benzolog.—CSI addition to **3** was carried out under conditions which matched those used for **10** and **13**. A number of products, all resulting from initial electrophilic attack at the methylene group, was formed. Direct crystallization of the reaction mixture permitted isolation of the major product (52%), which was identified as lactam **21b**. Subsequent column chromatography served to separate a two-component lactone mixture from residual **21b** and a second lactam. Preparative-scale vpc permitted isolation of **26** (2%) and a second lactone tentatively characterized as **27** (4%). The first of these substances exhibited an intense carbonyl stretching frequency at 1780 cm^{-1} and showed resonances in the nmr at δ 6.18–7.05 (m, 4), 5.75 (d with fine splitting, J = 8 Hz, 1), 5.3 (dd, J = 10.5 and 2.5 Hz, 1), 4.5 (m, 1), 3.45 (m, 1), and 2.83 (narrow AB pattern, 2). Of particular significance are the chemical shifts of the methylene (2.83) and >CHO–

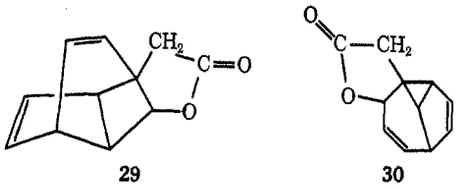
(17) T. Durst and M. J. O'Sullivan, *J. Org. Chem.*, **35**, 2043 (1970).

(18) (a) S. Yonida, S. Winstein, and Z. Yoshida, *Bull. Chem. Soc. Jap.*, **45**, 2510 (1972); (b) R. Hoffmann, W.-D. Stohrer, and M. J. Goldstein, *ibid.*, **45**, 2513 (1972); (c) R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).



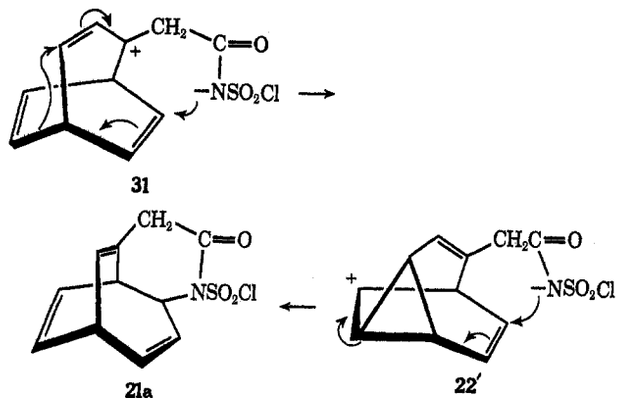
protons, which reveal their nonallylic and allylic features, respectively, the presence of six olefinic hydrogens, and the unique triply allylic nature of the *lone* methine proton. Spin-decoupling studies confirmed the spatial orientation of the various protons (see Experimental Section).

The second lactone (ν_{max} 1780 cm^{-1}) has proven more difficult to characterize unambiguously. The presence in **27** of an additional ring is revealed by the appearance in the nmr of only four olefinic protons at δ 5.45–6.05 (m, 3), and 5.12 (d, 1). The upfield positions of the >CHO– (3.9) and methylene protons (2.57) seemingly attests to their attachment to nonallylic tetrahedral carbon. Insufficient material precluded examination of the possible fluxional nature of **27**. Accordingly, we point out that other structural formulations such as **29** and **30** cannot be excluded on the basis of the available data.

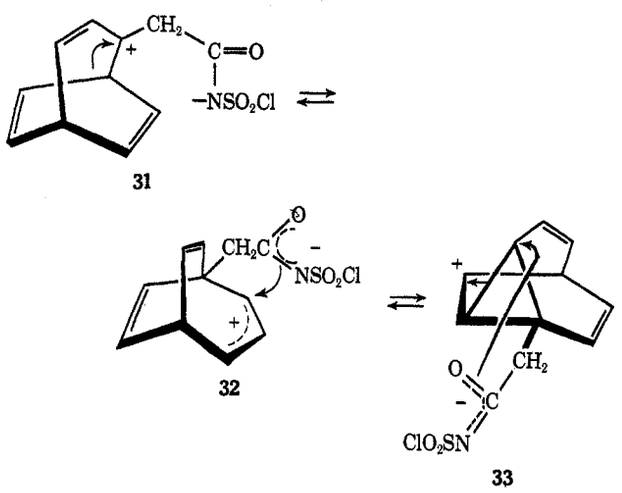


The minor lactam (**28**) was characterized by an nmr spectrum exceedingly similar to that of **26**, thus showing that these products were of comparable structure.

The formation of **21b** formally requires the 1,2 shift of a vinyl bridge. Although this reaction course can be depicted by means of the electronic reorganization shown in zwitterion **31**, it is perhaps more reasonable in the light of ancillary data to formulate the genesis of **21a** on the basis of barbaralyl cation **22′**. For example, Winstein,[7c,d] Schleyer,[6c,d] and Goldstein[6a] have provided evidence that suitable precursors of the destabilized $3^+2^02^0$ cation lead instead to generation of the barbaralyl cation. Also, the nearly exclusive production of **21a** from 9-methylenebarbaralane, which must necessarily involve **22**, serves to support additionally the likely involvement of **22′** in the present situation.

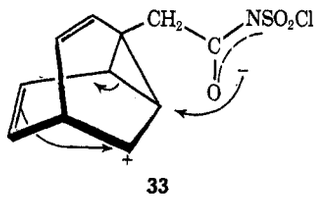


The isolation of lesser amounts of **26** and **28** serves to reveal, however, the less marked capability of the bicyclo[3.2.2]nona-3,6,8-trien-2-yl cation for degenerate rearrangement.[6d,6e,18] Whether **31** transmutes



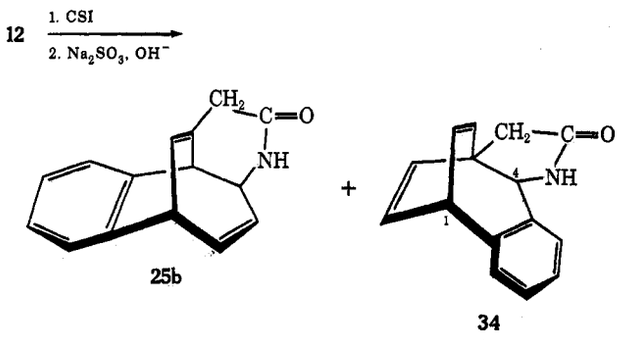
to **32** through a 1,2-vinyl shift mechanism (as illustrated), the equivalent homoallylic barbaralyl cation (**33**), or a combination of these processes is not known (see Discussion). Once access is gained to **33**, C–N and C–O bond formation can now operate to furnish **28** and **26**, respectively.

It can be immediately seen that alternative intramolecular bonding in **33** adapts itself nicely to the



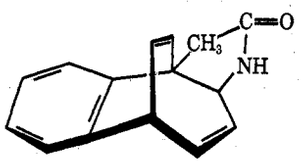
ultimate formation of **27**. In this connection, it is noteworthy that traces of a lactam corresponding in structure to **27** were also encountered in the very minor fractions obtained from the chromatographic separation.

When treated similarly with CSI, the benzo analog **12** was found to give rise to **25b** (68%) and **34** (2.4%). Lactone formation was not observed. The identity of **34** is apparent on the basis of its physical and spec-



25b 34

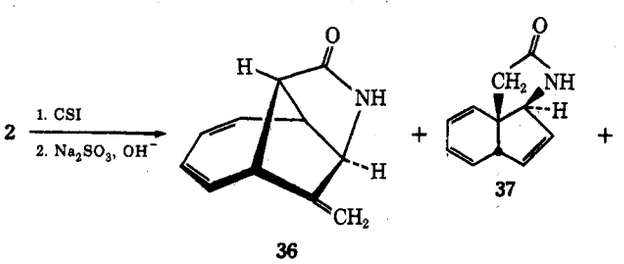
tral properties, which match those recorded above for this lactam. The assignment of structure to **34** was supported by comparison of its nmr spectrum with that of **28**. In particular, alternative formulation **35**



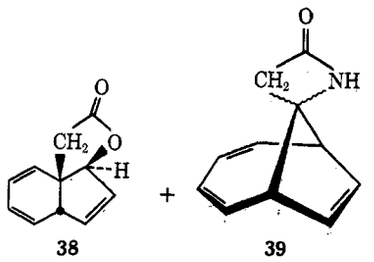
35

which would result from 1,2-benzo migration can be convincingly ruled out on the following grounds. Firstly, the high-field olefinic doublet of doublets due to H_3 in **28** is absent in **34**. Secondly, H_4 in **34** appears as a relatively sharp singlet, indicating lack of sizable spin–spin interaction with adjacent protons; H_4 is a higher order multiplet in **28** and appears at significantly higher field in the latter spectrum. Lastly, H_1 in **34** is seen to experience a 0.6-ppm downfield shift relative to **28** as a result of its benzylic environment. The results with **12** are most economically explained in terms of an intermediate benzobicyclo[3.2.2]nonatrienyl zwitterion[19] and its subsequent rearrangement *via* 1,2-benzo migration.

9-Methylenebicyclo[4.2.1]nona-2,4,7-triene and Its Benzolog.—When **2** was treated with CSI in analogous fashion, a complex mixture of products resulted. The four major components of this mixture have been isolated in a pure state, but those substances present in trace quantities have not been characterized. The principal cycloadduct was obtained in 26% isolated yield and assigned structure **36**. The absorption



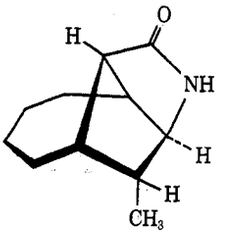
36 37



38 39

(19) J. S. Blair, J. Clark, and G. V. Meehan, *Tetrahedron Lett.*, 3097 (1972).

maximum at 1705 cm^{-1} in chloroform was appropriate for a γ-lactam, as was the ultraviolet maximum in ethanol at 254 nm for the conjugated diene moiety. In the nmr spectrum, there were the expected absorptions for the olefinic protons of the diene (δ 5.5–6.45, m, 4) and exocyclic methylene groups (5.15, d, J = 2.5 Hz, 2) in addition to the allylic >CHN< proton (4.25, m, 1), doubly allylic (3.38, m, 1) and allylic bridgehead hydrogen (2.88, m, 1), and α-carbonyl proton (2.33, br s, 1) peaks. Double-resonance studies supported these assignments. Confirmatory evidence for the presence of the exocyclic methylene functionality was obtained by catalytic hydrogenation of **36** to the hexahydro lactam **40**, the nmr spectrum

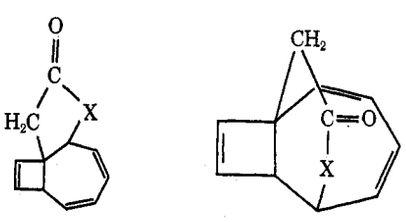


40

of which now revealed the presence of a sharp doublet at δ 0.98 (J = 7 Hz) typical for a methyl group attached to a saturated carbon atom and coupled to a lone methine hydrogen.

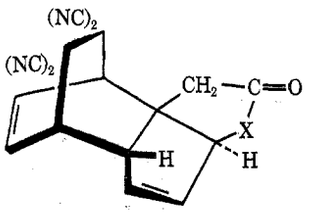
β-Lactam **39** (1%) was readily identified as a product of CSI addition to the terminal methylene group of **2** without structural reorganization of the [4.2.1]-bicyclic skeleton. This colorless solid showed the expected 1760 cm^{-1} carbonyl stretching frequency and an ultraviolet spectrum characteristic of bicyclo[4.2.1]nona-2,4,7-trienes. Additional support for the assignment comes from comparison of the nmr of **39** with that of hydrocarbon **2**. The observed chemical shift of the methylene protons (δ 3.77) does not, however, allow an unequivocal decision to be made between the two possible stereoisomers of this β-lactam.

The ultraviolet spectra of **37** and **38** are consistent with a conjugated diene system in a six-membered ring and inconsistent with isomeric 1,3-cycloheptadiene structures such as **41** and **42**, particularly owing



41 42

to the twisted diene chromophore structurally enforced in the latter pair of molecules. Spin-decoupling experiments were of little confirmatory value in these cases. In confirmation of the structural assignments, however, **37** and **38** underwent ready [4 + 2] cycloaddition to TCNE at room temperature to give adducts **43a** and **43b**, respectively. Of particular relevance was the finding that the chemical shifts of the proton α to the heteroatom in **43a** and **43b** remained essentially unchanged from their positions in the spectra of the parent compounds. This observation

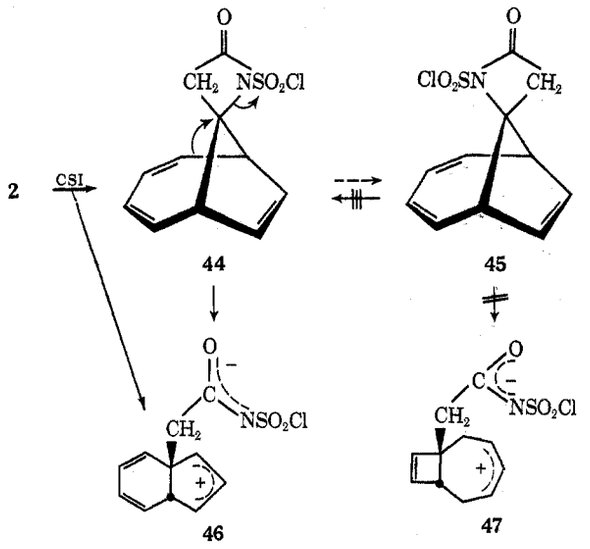


43a, X = NH
b, X = O

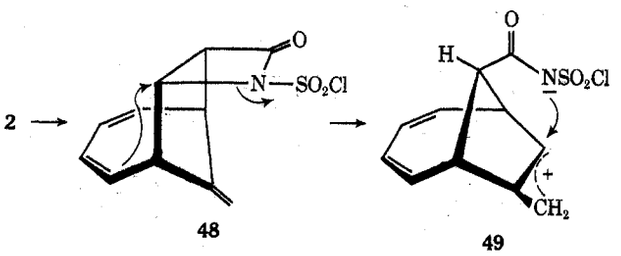
signifies that no gross structural reorganization has occurred in the vicinity of the particular carbon atom in question and is in keeping with **37** and **38** and not **41** and **42**.

A mechanistic rationalization of the formation of **37**, **38**, and **39** involves the assumption that **2** is first attacked by CSI at the exocyclic double bond from the less sterically hindered direction[16] to give **44**. Monitoring of the progress of the reaction by ir spectroscopy did provide evidence of *N*-(chlorosulfonyl) β-lactam intervention. Interestingly, however, there invariably remained a weak carbonyl absorption due to this functionality which no longer decayed with time. We reason that this band corresponds to the precursor to **39**. The questions arise as to why any β-lactam remains at all and why only a single isomer was isolated. A possible explanation is that **45** is formed in the reaction. Whether this adduct arises from ring opening of **44** and closure from the opposite direction or from direct [2 + 2] condensation is not known. It does appear, however, that **45** is not reconvertible to **44**.[20]

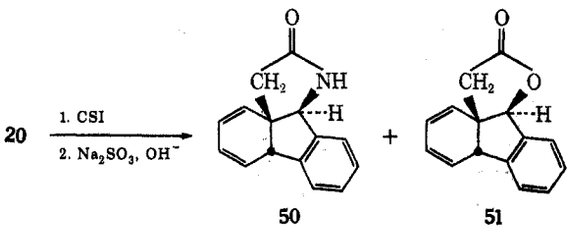
What there is to say about the mechanism of conversion of **44** to **37** and **38** is based in part upon the earlier observations of Kende and Bogard,[6b] who observed that treatment of 9-phenylbicyclo[4.2.1]-nona-2,4,7-trien-9-ol with 2 equiv of thionyl chloride and 1 equiv of pyridine gave a high yield of 1-chloro-9-phenyl-*cis*-8,9-dihydroindene. Thus, C–N bond heterolysis in **44** and essentially synchronous 1,2-diene migration from the rear side direction could lead to **46**. Alternatively, **46** could arise by bond reorganization in the electrophilic process proper. A similar driving force does not appear to underlie the conversion of **45** to **47**, where a 1,2-vinyl shift is necessary. However, this possibility cannot be entirely excluded, since it remains possible that **47** could cyclize exclusively by bonding of nitrogen to the proximate trigonal cyclobutene carbon with electronic readjustment to regenerate the [4.2.1] bicyclic unit.[18]



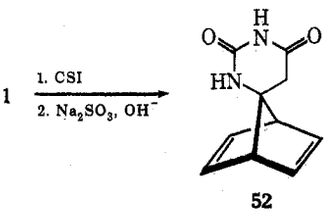
Competitive attack by the CSI reagent at the etheno bridge in **2** is revealed by the isolation of **36**. Indeed, it appears that **2** may resemble to an extent the closely related bicyclo[4.2.2]deca-2,4,7,9-tetraene system[1] and lead *via* **48** to zwitterion **49**. Stereoselective approach from the exo direction is required, followed by preferential 1,2-migration of the butadiene bridge. Charge annihilation in **49** understandably is regioselective because of strain considerations.



Benzo derivative **20** also undergoes the interesting conversion to lactam **50** (51.5%) and lactone **51** (~10%) resulting from exclusive initial bonding to its terminal methylene group. Examination of the nmr spectra of both products discloses an unmistakable similarity with those of **37** and **38**. The ultraviolet spectra of these compounds likewise show significant common features.



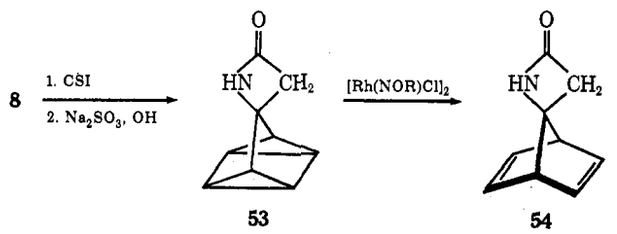
7-Methylenenorbornadiene and 7-Methylenequadricyclane.—When **1** was allowed to react with CSI at room temperature, there resulted rapid consumption of the reagents. Aqueous sodium bisulfite treatment followed after 10 min and the highly insoluble uracil derivative **52** was obtained in good yield. The nmr, ir, and mass spectra, as well as the low solubility in organic solvents and high melting point, befit this structure well.



The β-lactam originally expected from this reaction (**54**) was then prepared by treatment of **8** with CSI and subsequent isomerization of the novel β-lactam **53**

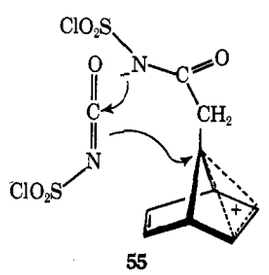
(20) Implicit in this conclusion is the requirement that **39** be related configurationally to **45**. This is consistent with the spectral data.

with Rh(I). In contrast to the behavior of **8** toward the rhodium catalyst, **53** reacted rapidly and exothermically in $CDCl_3$ to afford **54**. Not unexpectedly, the spectral and physical properties of **54** differ markedly from those of **52**.



53 54

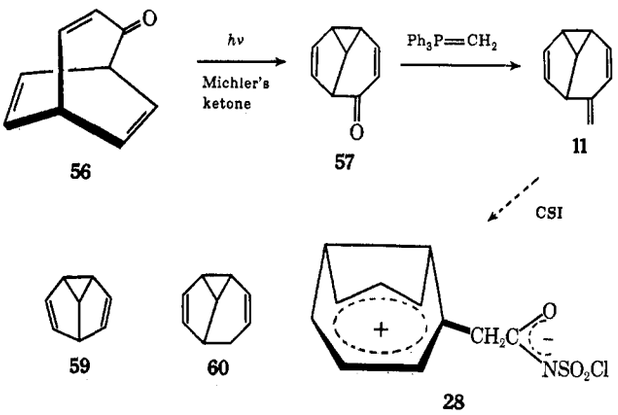
The unique nature of **52** appears to be a consequence of an inordinately long lifetime for the stabilized zwitterionic intermediate **55**,[21] such that sufficient



55

time is available for reaction with a seond molecule of CSI.[22] Alternatively, it can be argued that cyclization to the β-lactam is particularly slow in this instance because of strain factors. However, the ready formation of **53** does not lend support to the latter proposal.

5-Methylenetricyclo[6.1.0.0^{4,9}]nona-2,6-diene and Related Compounds.—Although not of direct relevance to the bicycloaromaticity question, the reaction of CSI with **11** and **14** was studied to determine if exocyclic methylene derivatives of this general structure could serve as synthetically useful precursors to zwitterionic 1,4-bishomotropylium ions such as **58**.[23] Triene **11** was most readily accessible from triplet-sensitized photoisomerization[24,25] of **56**[6a] and subsequent reaction of homosemibullvalenone **57** with methylenetriphenylphosphorane. When **11** and **14** were allowed to react with CSI, rapid formation of insoluble yellow polymeric substances were observed. No characterizable lactam or lactone products could be isolated. The causative factors underlying the ill-defined nature of these processes are not known. However, it is worthy of note that similar results have been obtained with the somewhat related divinylcyclopropanes semibullvalene (**59**) and homosemibullvalene (**60**).[26]



56 57 11 59 60 28

Discussion

The fact that lactam **21b** is the product of CSI addition to 9-methylenebarbaralane (**10**) is in consort with the assumption that this reaction is proceeding through barbaralyl cation **22**. In view of the stabilized nature of the $3^+3^-1^+$ construct inherent in **22**,[4] high preference for attack by the uniparticulate electrophile at the methylene carbon should be exhibited, and such is observed. Our inability to isolate β-lactam product which would result from direct collapse of **22** is perhaps a consequence of kinetic control, which would presumably lead to more rapid six-center cyclization. Transient formation of β-lactam products in all of the described reactions must, however, be considered to be a possible initial event.[27]

The experimental results show that exclusive attack at the methylene carbon of 2-methylenebicyclo[3.2.2]-nona-3,6,8-triene (**3**) also occurs. However, the absence of unrearranged products in the mixture, **21b** and **26–28**, introduces the possibility that [3.2.2] zwitterion **31** may never be truly formed during the addition. In actuality, the seemingly overwhelming preference for initial bonding to the methylene carbon of **3** might be construed to mean either that the [3.2.2] cation is not really destabilized so that its intervention can compete favorably with the several other possibilities or that this positional selectivity is the result of direct passage to the barbaralyl system, the stabilization in which is reflected in the transition state. An unequivocal answer to this dichotomy is not presently available. However, it is clear from the relative yields of products that a preference for the intermediacy of **22** does exist. No obvious guideline is available to assess why the intervention of isomeric skeletal modification **33** is not fully competitive.

The less discriminatory reactivity of **2** toward CSI has been discussed above in mechanistic terms. Electrophilic attack at the etheno bridge is followed by structural bond reorganization to a [3.2.1] bicyclic framework in a manner reminiscent of the behavior of bicyclo[4.2.2]decatetraenes.[1] Interestingly, attack at the methylene center also occurs, this reaction mode operating exclusively in **20** where benzo fusion denies access to the first process. In this instance, consideration must be accorded to the stereoselectivity of CSI attack. Analysis of the product data reveals

(21) (a) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6350 (1967); (b) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352, 6354 (1967); (c) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **90**, 7364 (1968).

(22) Analogous behavior of CSI, albeit, under quite different circumstances, has been encountered previously: E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **33**, 3036 (1968); E. J. Moriconi and Y. Shimakawa, *ibid.*, **37**, 196 (1972).

(23) M. Sakai, D. L. Harris, and S. Winstein, *ibid.*, **37**, 2631 (1972).

(24) A. S. Kende and Z. Goldschmidt, *Tetrahedron Lett.*, 783 (1970).

(25) The singlet excited state behavior of such ketones has been examined: (a) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *J. Amer. Chem. Soc.*, **91**, 6856 (1969); (b) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *ibid.*, **91**, 6858 (1969).

(26) M. Sakai, D. L. Harris, and S. Winstein, *J. Chem. Soc., Chem. Commun.*, 861 (1972).

(27) J. R. Malpass and N. J. Tweddle, *ibid.*, 1244, 1247 (1972); T. J. Barton and R. J. Rogido, *Tetrahedron Lett.*, 3901 (1972).

that approximately 1% of unrearranged adduct in the form of **39** is isolable. Lactam **37** and lactone **38**, on the other hand, denote the transient formation of dihydroindenyl zwitterion **46**. It is not possible at this time to distinguish between the direct intervention of **46** or its genesis as a result of a 1,2-butadienyl shift in **44**. Transient *N*-(chlorosulfonyl) β-lactam formation is observed, but the number of reaction pathways which give rise to this functionality is unknown. Since CSI additions have been claimed to be "quasiconcerted" in certain cases, it is not unreasonable that the formation of **44** could operate without build-up of excessive cationic character at C_9. Notwithstanding, the incursion of competitive electrophilic addition elsewhere in the molecule serves to provide convincing evidence that the bicyclo[4.2.1]-nona-2,4,7-trien-9-yl cation is not particularly stabilized.

The high reactivity of 7-methylenequadricyclane (**8**) toward CSI agrees well with the remarkably rapid solvolytic behavior of 7-nortricyclyl chloride and tosylate.[28,29] The absence of structural rearrangement in **53** also compares favorably with the earlier results of Story and Fahrenholtz,[30] who demonstrated that sodium borohydride reduction of nortricyclyl brosylate is capable of almost completely trapping the derived cation prior to isomerization.

The rapidity with which 7-methylenenorbornadiene (**1**) reacts with CSI can be attributed to the highly polarized ground state of this hydrocarbon and the exceptional stability of the 7-norbornadienyl cation.[31] The extent of interaction between the two vinyl bridges and the cationic center cannot be derived from the CSI reaction. However, the previous demonstration by Winstein[21a] of the unsymmetrical nature of this carbonium ion[32] is probably applicable here with little modification. Exclusive formation of uracil **52** phenomenologically distinguishes zwitterion **55** from the other dipolar species evaluated herein. Apart from the question of whether the stability of the 7-norbornadienyl cation has its origin in homaromatic or bicycloaromatic interaction,[6g,31] it must once again be concluded that it represents a particularly fascinating example of long-range longicyclic carbonium ion stabilization.

Experimental Section

Nmr spectra were obtained with Varian A-60A and HA-100 instruments; ir spectra with a Perkin-Elmer Infracord; mass spectra with the AEI-MS9. The elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

7-Methylenequadricyclane (8).—To a stirred suspension of methyltriphenylphosphonium bromide (16.8 g, 0.047 mol) in dry ether (125 ml) under a nitrogen atmosphere was added *n*-butyllithium (24 ml of 2 *M* solution in hexane). The mixture was stirred for 1 hr at room temperature and then a solution of quadricyclanone (**7**, 5.0 g, 0.047 mol)[33] in ether (25 ml) was added over a period of 5 min. A thick, white precipitate formed immediately. The reaction mixture was stirred and heated under reflux for 4 hr, cooled, and poured into ice water (200 ml). The ether layer was separated and the aqueous layer was extracted twice with pentane (50 ml). The combined organic extracts were washed five times with water, dried, and carefully evaporated through a short (1 cm) Vigreux column. The residue was distilled under reduced pressure to give 2.0 g (40%) of **8** as a colorless oil, bp 80–85° (25 mm). An analytical sample was obtained by preparative vpc isolation (5 ft × 0.25 in. column packed with 20% SE-30 at 55°): $\delta_{TMS}^{CDCl_3}$ 5.08 (s, 2, methylenes), 1.85 (d, J = 3.5 Hz, 2), and 1.52 (t, J = 3.5 Hz, 2).

Anal. Calcd for C_8H_8: C, 91.25; H, 8.75. Found: C, 91.38; H, 8.85.

7-Methylenenorbornadiene (1).—To a solution of 1.0 g of **8** in 15 ml of carbon tetrachloride was added 90 mg of $[Rh(NOR)Cl]_2$ and the mixture was refluxed under nitrogen for 20 min. At this point, vpc analysis indicated that no starting material remained. The solvent was carefully evaporated and the residue was distilled to furnish 850 mg (85%) of **1** as a colorless liquid, bp 70° (40 mm). An analytical sample was obtained by preparative-scale vpc isolation as above: $\lambda_{max}^{cyclohexane}$ 242 nm (ε 200); $\delta_{TMS}^{CDCl_3}$ 6.8 (t, J = 2.5 Hz, 4, olefinic), 3.84 (m, 2, methine), and 3.63 (s, 2, methylene).

Anal. Calcd for C_8H_8: C, 91.25; H, 8.75. Found: C, 91.42; H, 8.81.

9-Methylenebicyclo[4.2.1]nona-2,4,7-triene (2).—This hydrocarbon was prepared from the corresponding ketone[15,16] by a method identical with that utilized above. From 9.6 g of the ketone, there was isolated 3.6 g (38%) of **2** as a colorless liquid: bp 40–42° (0.5 mm); $\delta_{TMS}^{CDCl_3}$ 5.7–6.4 (m, 4, diene protons), 5.4 (s, 2, ethano protons), 4.79 (s, 2, methylene), 3.44 (broadened d, J = 6.5 Hz, 2, methine); $\lambda_{max}^{cyclohexane}$ 270 nm (ε 3400) and 261 nm (3400) with shoulders at 280 (2150) and 254 (2850).

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: 92.39; H, 7.73.

2-Methylenebicyclo[3.2.2]nona-3,6,8-triene (3).—Reaction of 2.01 g of bicyclo[3.2.2]nona-3,6,8-trien-2-one[6a] with an equimolar amount of methylenetriphenylphosphorane in the predescribed manner furnished 1.35 g (68%) of **3** as a colorless liquid: bp 70° (5 mm); $\lambda_{max}^{cyclohexane}$ 255 nm (sh, ε 5500) and 232 (9050); $\delta_{TMS}^{CDCl_3}$ 5.90–6.75 (m, 5, olefinic), 5.48 (d with fine splitting, J = 10 Hz), 5.05 (s with fine splitting, 1, methylene proton), 4.7 (s with fine splitting, 1, methylene proton), and 3.20–3.87 (m, 2, methines).

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.98; H, 7.92.

9-Methylenetricyclo[3.3.1.0^{2,8}]nona-3,6-diene (9-Methylenebarbaralane, 10).—Treatment of 9.1 g of barbaralone[15,16,34] with an equimolar quantity of methylenetriphenylphosphorane as described above afforded 5.7 g (63.5%) of **10** as a colorless liquid: bp 71–73° (5 mm); $\delta_{TMS}^{CDCl_3}$ 5.65 (m, 2, olefinic), 4.7 (s, 2, methylene protons), 4.12 (m, 4), and 2.82 (m, 2).

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.76.

Reaction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one (15) with α-Pyrone (16).—A solution of 18.6 g (0.14 mol) of **15**,[15,16] 20 g (0.21 mol) of α-pyrone,[35] and 100 mg of hydroquinone in 30 ml of xylene was heated at 120–130° under nitrogen for 20 hr. After cooling, the product was chromatographed on Florisil. Elution with chloroform afforded 11.06 g (34%) of **17** as colorless needles, mp 204–205° dec, from methylene chloride–ether: $\nu_{max}^{CHCl_3}$ 1765 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 310 nm (ε 400), 274 (3000), 264 (3580), and 258 (sh, 2830); $\delta_{TMS}^{CDCl_3}$ 6.5 (m, 2, olefinic), 5.85 (m, 4, diene protons), 5.26 (m, >CHO–), 3.72 (m, 1, methine), 3.25 (br m, 2, methine), and 2.6 (m, 2, methine).

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.46; H, 5.17.

Decarboxylation of 17.—A 1.5-g sample of **17** was heated to 230° in a small, short path distillation column under 0.3 mm pressure. Carbon dioxide evolution was observed and a distillate which solidified in the cold portion of the apparatus was obtained. Upon completion of the gas evolution, the product was washed out with ether. Evaporation of the solvent yielded 830 mg (70%) of **18** as colorless crystals: mp 74–77° (sublimation at 80° (0.5 mm) raised the melting point to 81–83°); $\nu_{max}^{CHCl_3}$ 1745

(28) H. G. Richey, Jr., and N. C. Buckley, *J. Amer. Chem. Soc.*, **85**, 3057 (1963).
(29) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964).
(30) P. R. Story and S. R. Fahrenholtz, *ibid.*, **88**, 374 (1966).
(31) S. Yoneda, Z. Yoshida, and S. Winstein, *Tetrahedron*, **28**, 2395 (1972).
(32) S. Winstein and C. Ordronnean, *J. Amer. Chem. Soc.*, **82**, 2084 (1960); P. R. Story and M. Saunders, *ibid.*, **84**, 4876 (1962).
(33) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2347 (1972).
(34) W. von E. Doering, B. M. Ferrier, E. D. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).
(35) H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler, *Org. Syn.*, **46**, 101 (1966).

cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 310 nm (sh, ϵ 930), 258 (6500), and 240 (5150); $\delta_{TMS}^{CHCl_3}$ 5.4–5.9 (m, 8, olefinic), 3.45 (m, 2, methine), and 2.65 (m, 2, >CHCO–).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.59. Found: C, 84.71; H, 6.56.

7,8-Benzobicyclo[4.2.1]nona-2,4,7-trien-9-one (19).—A solution of 1.2 g of **18** in 20 ml of benzene containing 2.0 g of 10% palladium on charcoal was heated at reflux for 24 hr. The catalyst was separated by filtration, the solvent was evaporated, and the pale yellow oil was chromatographed on Florisil. Elution with benzene–pentane (1:1) furnished 650 mg (54%) of **19** as colorless crystals, mp 80–82° (lit.[14] mp 82–82.5°).

9-Methylene-7,8-benzobicyclo[4.2.1]nona-2,4,7-triene (20).—Ketone **19** (800 mg) was treated with 1 equiv of methylenetriphenylphosphorane as described earlier. After the usual work-up, the crude reaction mixture was chromatographed on Florisil. Elution with pentane gave 450 mg (56%) of **20** as a colorless oil which slowly crystallized on cooling to 0°: $\lambda_{max}^{cyclohexane}$ 284 nm (ϵ 2920), 273 (4700), 262 (4400), 254 (3260), and 242 (sh, 2960); $\delta_{TMS}^{CDCl_3}$ 7.15 (s, 4, aromatic), 6.0–6.4 (m, 2, olefinic), 5.5–5.85 (m, 2, olefinic), 4.98 (s, 2, methylene), and 4.1 (d, J = 7.5 Hz, 2, methine).

Anal. Calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.46; H, 6.75.

Reaction of 10 with CSI.—To a magnetically stirred solution of 4.55 g (35.5 mmol) of **10** in 50 ml of dry dichloromethane was added under nitrogen 3.1 ml (37 mmol) of CSI dissolved in 20 ml of the same solvent over a period of 20 min. The solution was stirred at room temperature for 2.5 hr and the solvent was evaporated. The residue was dissolved in 40 ml of ether containing 10 ml of acetone and this solution was added dropwise to a rapidly stirred suspension of sodium sulfite (30 g) in 80 ml of water. The pH of the aqueous layer was kept at *ca.* 8–9 by the addition of 20% aqueous potassium hydroxide solution as required. After the addition was complete, stirring was continued for a further 45 min and the product was then extracted into methylene chloride (6 × 50 ml). The combined organic layers were dried and evaporated to give a colorless, crystalline product which was triturated with ether, filtered, and dried (4.7 g, 77.5%). Recrystallization from dichloromethane gave pure **21b**: mp 207.5–208.5°; $\nu_{max}^{CHCl_3}$ 1660 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ end absorption only; $\delta_{TMS}^{CDCl_3}$ 7.4 (br, 1, >NH), 6.8 (m, 1, olefinic), 6.18 (m, 3, olefinic), 5.0 (m, 1, >CHN<), 3.3 (s, 2, methylene), and 3.2 (m, 2, methine).

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.08. Found: C, 76.13; H, 6.40; N, 7.96.

When the >NH proton was saturated, the absorption at δ 3.6 collapsed to a triplet with no other observable changes. Double irradiation of the δ 3.6 multiplet resulted in the appearance of the high-field olefinic proton (dd, J = 10.5 and 2.0 Hz); clearly, this proton must be the adjoining vinyl hydrogen, the small coupling constant arising from allylic coupling to the bridgehead proton. This last conclusion was supported by the finding that spin decoupling of the δ 3.2 multiplet caused simplification of this olefinic proton (dd, J = 10.5 and 4 Hz). Expectedly, additional simplification of all the remaining olefinic signals was also seen.

Evaporation of the mother liquors resulting from the cycloaddition yielded an oily residue that was chromatographed on Florisil. Elution with chloroform gave a crystalline lactam fraction (400 mg, 6.5%), the nmr spectrum of which indicated it to consist mainly of **21b**. However, a small amount of a second component was also present. Attempts to obtain a pure sample of this very minor component were not successful.

Reaction of 13 with CSI.—Treatment of 470 mg (2.6 mmol) of **13**[13] with 360 mg of CSI in 10 ml of methylene chloride (25°, 40 min) and subsequent dechlorosulfonylation as above afforded 370 mg (64%) of **25b** as colorless crystals, mp 224–224.5°, from methylene chloride–ether: $\nu_{max}^{CHCl_3}$ 1660 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 265 nm (ϵ 150); $\delta_{TMS}^{CDCl_3}$ 7.2 (m, 4, aromatic),6.1–6.5 (m, 2, olefinic), 4.85–5.2 (m, 1, olefinic), 3.75 (m, 3, methine), and 3.35 (m, 2, $-CH_2CO-$).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.43; H, 5.87; N, 6.23.

Reaction of 3 with CSI.—From 1.2 g (9.25 mmol) of **3** and 0.84 ml (9.5 mmol) of CSI in 40 ml of dichloromethane (25°, 2 hr) and subsequent hydrolysis with alkaline sodium sulfite solution, there resulted a slightly sticky, colorless solid, trituration of which with ether gave 810 mg (50.5%) of **21b** identical in all respects with the lactam isolated above.

Evaporation of the filtrate yielded *ca.* 1 g of a pale yellow, oily residue which was chromatographed on Florisil. Pentane–chloroform (4:1) eluted a colorless oil which crystallized from ether at −78° to give 120 mg (7.5%) of colorless crystals, mp 67–76°. The nmr spectrum clearly indicated a mixture of two components and the ir spectrum suggested that these were lactones (ν_{max} 1780 cm^{-1}). These were separated by preparative scale vpc (5 ft × 0.25 in. column packed with 5% SE-30, 130°).

The major component has been tentatively assigned structure **27**: $\nu_{max}^{CHCl_3}$ 1780 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ shoulder on end absorption, 222 nm (ϵ 3600); $\delta_{TMS}^{CDCl_3}$ 5.45–6.05 (m, 3, olefinic), 5.12 (d, 1, olefinic), 3.9 (br s, 1 >CHO–), 2.7 (m, 3, methine), and 2.57 (s, 2, methylene); mass spectrum, 174.0682 (calcd for $C_{11}H_{10}O_2$, 174.0681).

The minor component was identified as lactone **26**: $\nu_{max}^{CHCl_3}$ 1780 cm^{-1}; uv showed only end absorption; $\delta_{TMS}^{CDCl_3}$ 6.18–7.05 (m, 4, olefinic), 5.75 (d with fine splitting, J = 8 Hz, 1, olefinic), 5.3 (dd, J = 10.5 and 2.5 Hz, 1, olefinic), 4.5 (m, 1, >CHO–), 3.45 (m, 1, methine), and 2.83 (s, 2, methylene) [the latter absorption was shown to be a distorted AB system (J = 16 Hz) at 100 MHz]; mass spectrum, 174.0678 (calcd for $C_{11}H_{10}O_2$, 174.0681).

Continued elution of the chomatography column with chloroform gave a solid mixture of three lactams (nmr analysis) weighing 105 mg (6.5%). Rechromatography of this mixture on Florisil using pentane–chloroform (1:1) as eluent gave 52 mg (3.2%) of pure lactam **28** as the first compound from the column: colorless crystals; mp 145–147°; $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}; uv showed only end absorption; $\delta_{TMS}^{CDCl_3}$ 6.0–6.96 (m, 5, olefinic and >NH), 5.73 (d with fine splitting, J = 8 Hz, 1, olefinic), 5.1 (dd, J = 10.5 and 2.5 Hz, 1, olefinic), 3.92 (m, 1, >CHN<), 3.25 (m, 1, methine), and 2.61 (distorted AB pattern, J = 15 Hz, 2, methylene).

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.08. Found: C, 76.01; H, 6.40; N, 8.14.

Continued elution of the column with chloroform yielded an additional 45 mg (2.8%) of **21b**. Only traces of the third lactam were eluted and these were insufficient for characterization.

Reaction of 12 with CSI.—The cycloaddition was carried out essentially as described above with 7.3 g (40.5 mmol) of **12**.[13] After the usual work-up and solvent removal, trituration of the solid residue with ether gave 5.63 g (62.5%) of **25b**, mp 224–224.5°, identical in all its spectral properties with the lactam isolated above.

Chromatography of the noncrystalline residue on Florisil using pentane–chloroform (1:1) as eluent led to the isolation of **34** (220 mg, 2.4%) as fine, colorless needles, mp 204.5–205.5°, from methylene chloride–ether: $\nu_{max}^{CHCl_3}$ 1695 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 268 nm (ϵ 300); $\delta_{TMS}^{CDCl_3}$ 8.0 (br, 1, >NH), 7.18 (m, 4, aromatic), 6.23–7.0 (m, 3, olefinic), 5.8 (d, J = 8 Hz, 1, olefinic), 4.54 (s, 1, >CHN<), 3.86 (m, 1, methine), and 2.73 (part of distorted AB pattern, J = 16 Hz, 2, methylene).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.32; H, 5.81; N, 6.27.

After the appearance of **34**, an additional 503 mg (5.5%) of **25b** was obtained upon continued elution.

Reaction of 2 with CSI.—A 5.5-g (43 mmol) sample of **2** was treated with 3.7 ml (44 mmol) of CSI in 60 ml of methylene chloride as outlined above. After dechlorosulfonylation and solvent removal, a sticky white solid was obtained which on trituration with ether afforded 2.23 g (30.5%) of white solid. Nmr analysis of this material showed it to be a mixture of **36** and **37** in a ratio of *ca.* 3:1. These lactams were readily separated by chromatography on Florisil, lactam **36** eluting with chloroform–pentane (1:1) and **37** eluting with chloroform.

36 was a colorless solid: mp 168.5–169.5°; $\nu_{max}^{CHCl_3}$ 1705 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 254 nm (ϵ 4950); $\delta_{TMS}^{CDCl_3}$ 7.3 (br, 1, >NH), 5.5–6.45 (m, 4, diene protons), 5.15 (d, J = 2.5 Hz, 1, exocyclic methylene), 4.85 (d, J = 2.0 Hz, 1, exocyclic methylene), 4.25 (m, 1, >CHN<), 3.38 (m, 1, doubly allylic methine), 2.88 (m, 1, methine), and 2.33 (br s, 1, >CHCO–).

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 640; N, 8.08. Found: C, 75.99; H, 6.35; N, 7.99.

37 was a colorless solid: mp 120–122°; $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 276 nm (sh, ϵ 2250), 267 (3990), 259 (3930), and 250 (sh, 2900); $\delta_{TMS}^{CDCl_3}$ 7.4 (br, 1, >NH), 5.45–6.02 (m, 6, olefinic), 4.4 (m, 1, >CHN<), 3.48 (m, 1, methine), and 2.41 (distorted AB pattern, J_{AB} = 17 Hz, 2, methylene).

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.08. Found: C, 76.21; H, 6.38; N, 8.08.

Evaporation of the above filtrate gave a pale yellow, viscous residue which was chromatographed on Florisil. Elution with pentane–chloroform (4:1) gave 433 mg (5.9%) of lactone **38** as colorless crystals, mp 54.5–55.5°, from pentane–ether: $\nu_{max}^{CHCl_3}$ 1770 cm^{-1}; $\lambda_{max}^{cyclohexane}$ 276 nm (sh, ϵ 1965), 269 (3795), 256 (3795), and 248 (sh, 2887); $\delta_{TMS}^{CDCl_3}$ 5.47–6.15 (m, 6, olefinic), 5.2 (m, 1, >CHO–), 3.5 (m, 1, methine), and 2.6 (distorted AB pattern, J_{AB} = 18 Hz, 2, methylene).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.06; H, 5.80.

Continued elution of the column with pentane–chloroform (1:1) gave 77 mg (1%) of β-lactam **38** as colorless crystals: mp 158–159°; $\nu_{max}^{CHCl_3}$ 1760 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 285 nm (ϵ 1350), 271 (sh, 2380), and 265 (2450); $\delta_{TMS}^{CDCl_3}$ 6.4 (br, 1, >NH), 5.95 (m, 4, diene protons), 5.42 (d, J = 1 Hz, 2, olefinic), 4.1 (m, 2, methine), and 3.77 (d, J = 1.5 Hz, methylene).

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.08. Found: C, 75.97; H, 6.41; N, 8.03.

Further elution yielded fractions rich in lactam **36** contaminated with small amounts of unidentified products. Crystallization yielded an additional 320 mg (4.4%) of pure **36**. Attempts to obtain pure samples of the minor components were not successful because of a lack of material and their apparent ready polymerization.

Finally, elution with chloroform afforded a further 410 mg (5.6%) of **37** after crystallization from methylene chloride–ether.

Hydrogenation of 36.—A solution of 200 mg of **36** in 25 ml of ethyl acetate containing 100 mg of 10% palladium on charcoal was hydrogenated at 25 psig and 25° in a Parr apparatus for 25 hr. The catalyst was removed by filtration and the filtrate was evaporated to give 178 mg of **40** as a colorless solid, mp 138.5–141.5°, $\delta_{TMS}^{CDCl_3}$ 1.03 (d, J = 6.5 Hz, 3, methyl).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.47; H, 9.39; N, 7.76.

TCNE Addition to Lactam 37.—A solution of 60 mg of **37** and 56 mg of TCNE in 1.5 ml of dry tetrahydrofuran was left to stand at room temperature for 24 hr. The colorless, crystalline product that formed (96 mg, 92%) was separated by filtration and recrystallized from acetone–ether. The resulting white crystals darken above 270° and decompose with melting at 290–300°: ν_{max}^{Nujol} 1695 cm^{-1}; $\delta_{TMS}^{acetone\text{-}d_6}$ 7.25 (br, 1, >NH), 6.55–7.15 (m, 2, olefinic), 5.9 (s, 2, olefinic), 4.55 (m, 2, >CHN< and and one methine proton), 4.1 (m, 1, methine), 3.48 (m, 1, methine), 3.4 and 2.56 (centers of AB doublets, J = 18 Hz, 2, methylene).

Anal. Calcd for $C_{17}H_{11}N_5O$: C, 67.77; H, 3.68; N, 23.24. Found: C, 67.55; H, 3.70; N, 23.20.

TCNE Addition to Lactone 38.—Reaction of 154 mg of **38** and 160 mg of TCNE in tetrahydrofuran as above gave 223 mg (84%) of adduct **43b** as colorless crystals, mp >270° dec, from acetone–ether: ν_{max}^{Nujol} 1760 cm^{-1}; $\delta_{TMS}^{acetone\text{-}d_6}$ 6.5–7.1 (m, 2, olefinic), 5.9–6.25 (m, 2, olefinic), 5.3 (m, 1, >CHO–), 4.55 (d with fine splitting, 1, methine), 4.15 (t of d, J = 6.0 and 1.5 Hz, 1, methine), 3.61 (m, 1, methine), 3.66 and 2.92 (centers of AB doublets, J = 19 Hz, 2, methylene).

Anal. Calcd for $C_{17}H_{10}N_4O_2$: C, 67.51; H, 3.33; N, 18.54. Found: C, 67.55; H, 3.35; N, 18.55.

Reaction of 20 with CSI.—Treatment of 150 mg (8.45 mmol) of **20** with 0.08 ml (9.5 mmol) of CSI in 7 ml of methylene chloride (25°, 14 hr), subsequent hydrolysis with sulfite ion, and chromatography on Florisil gave (pentane elution) 13 mg of a colorless oil identified as lactone **51**: $\nu_{max}^{CHCl_3}$ 1780 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.28 (s, 4, aromatic), 5.65–6.0 (m, 4, olefinic), 5.5 (s, 1, >CHO–), 3.87 (m, 1, methine), and 2.62 (s, 2, methylene).

Continued elution of the column with pentane–chloroform (1:1) furnished 96 mg (51.5%) of **50** as colorless crystals, mp 180–182°, from chloroform–ether: $\nu_{max}^{CHCl_3}$ 1685 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.7 (br s, 1, >NH), 7.2 (s, 4, aromatic), 5.55–6.0 (m, 4, olefinic), 4.72 (s, 1, >CHN<), 3.84 (m, 1, methine), and 2.42 (s, 2, methylene).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.90; H, 5.81; N, 6.28.

Reaction of 1 with CSI.—To a solution of 104 mg (1 mmol) of **1** in 7 ml of dry methylene chloride was added under nitrogen 0.084 ml (1 mmol) of CSI. After stirring for 10 min, the solvent was evaporated and the residue was hydrolyzed in the usual manner. The product was extracted into methylene chloride and this solution was dried and evaporated to give 50 mg (52%) of white, crystalline product: mp 234–235° dec; $\nu_{max}^{CHCl_3}$ 1700 cm^{-1} (sh at 1725 cm^{-1}); $\delta_{TMS}^{DMSO\text{-}d_6}$ 7.48 (br s, 1, >NH), 6.63 (t, J = 2 Hz, 4, olefinic), 3.38 (m, 2, methine), and 2.77 (s, 2, methylene); mass spectrum, 190.0744 (calcd m/e 190.0742).

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.91; H, 5.33; N, 14.64.

Reaction of 8 with CSI.—Treatment of 400 mg (3.8 mmol) of **8** with 0.33 ml (4 mmol) of CSI in 10 ml of methylene chloride for 15 min at 25° led to the ready isolation of 300 mg (53%) of **53** after dechlorosulfonylation as colorless crystals, mp 96.5–97°, from ether–pentane: $\nu_{max}^{CHCl_3}$ 1750 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.4 (br, 1, >NH), 3.2 (d, J = 1.5 Hz, 2, methylene), 1.77 (m, 4, cyclopropyl), and 1.29 (m, 2, cyclopropyl).

Anal. Calcd for C_9H_9NO: C, 73.41; H, 6.16. Found: C, 73.16; H, 6.25.

Rearrangement of 53.—To a solution of 30 mg of **53** dissolved in 0.4 ml of $CDCl_3$ in an nmr tube was added three crystals of $[Rh(NOR)Cl]_2$. The initially orange-brown solution rapidly became warm and then changed in color to a pale yellow. A small amount of yellow, insoluble precipitate formed also. The nmr spectrum of the reaction mixture showed complete conversion to **54**. The solution was filtered and evaporated to give a quantitative yield of colorless crystals, mp 123–125°, from ether–pentane: $\nu_{max}^{CHCl_3}$ 1750 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.9 (br, 1, >NH), 6.6 (m, 4, olefinic), 3.48 (m, 2, methine), and 2.53 (d, J = 1.5 Hz, 2, methylene).

Anal. Calcd for C_9H_9NO: C, 73.41; H, 6.16; N, 9.56. Found: C, 73.19; H, 6.22; N, 9.61.

Tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one (57).—A solution of 400 mg of **56**[6a] and 200 mg of Michler's ketone in 400 ml of benzene maintained under a constant nitrogen atmosphere was irradiated with a 450-W Hanovia lamp source through Pyrex for 20 min. The solvent was evaporated and the residue was extracted with pentane–ether (1:1). The combined organic layers were washed with dilute hydrochloric acid and distilled water, dried, and evaporated to give 344 mg of **57** as a colorless oil contaminated with approximately 5% of starting material. This material was utilized without further purification in the next step.

5-Methylenetricyclo[6.1.0.0^{4,9}]nona-2,6-diene (11).—To a solution of methylenetriphenylphosphorane in 50 ml of ether prepared from 1.8 g of methyltriphenylphosphonium bromide and 2.1 ml of 2 M n-butyllithium solution in hexane was added 560 mg of somewhat impure **57**. The mixture was heated at reflux for 4 hr and worked up in the customary manner. Vacuum transfer afforded 210 mg of colorless oil, vpc analysis of which indicated it to be chiefly **11**. Purification was achieved by preparative scale vpc isolation from a 0.25 in. × 5 ft column packed with 5% SE-30 on Chromosorb W at 60°: $\delta_{max}^{CDCl_3}$ 5.22–6.42 (m, 4, olefinic), 4.67–4.92 (m, 2, methylene), 3.50–3.73 (m, 1, methine), and 1.36–2.46 (m, 3, cyclopropyl).

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.23; H, 7.66.

Registry No.—**1,** 37846-63-2; **2,** 38898-39-4; **3,** 38898-40-7; **7,** 1072-92-0; **8,** 38898-42-9; **10,** 37816-60-7; **11,** 38898-44-1; **12,** 34886-92-5; **13,** 34886-93-6; **15,** 34733-74-9; **16,** 504-31-4; **17,** 38898-48-5; **18,** 38898-26-9; **19,** 22824-77-7; **20,** 38898-50-9; **21b,** 38898-51-0; **25b,** 38974-07-1; **26,** 38898-52-1; **27,** 38898-53-2; **28,** 38898-54-3; **29,** 38898-55-4; **36,** 38898-56-5; **37,** 38898-27-0; **38,** 38898-28-1; **39,** 38898-57-6; **40,** 38898-29-2; **43a,** 38898-30-5; **43b,** 38974-08-2; **50,** 38898-31-6; **51,** 38898-32-7; **52,** 38898-58-7; **53,** 38898-59-8; **54,** 38898-60-1; **56,** 17684-75-2; **57,** 38898-62-3; bicyclo[4.2.1]nona-2,4,7-trien-9-one, 34733-74-9; bicyclo[3.2.2]nona-3,6,8-trien-2-one, 17684-75-2; barbaralone, 6006-24-2; CSI, 1189-71-5; TCNE, 670-54-2; Michler's ketone, 90-94-8.

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