tems through more accurate X-ray and electron diffraction determinations.

Experimental Section

The nmr spectra were determined on a Varian HA-100 spectrometer. The spectra used for computer analysis were recorded either on the 50- or 100-cps sweep width. The computer analysis was performed on one representative member of several reproducible spectra. The agreement between the parameters derived from the three separate spectra of tropone indicates that a probable error of ±0.2 Hz is justified.

It was found necessary to assign the relative sign of J_{26} opposite to the remaining coupling constants in several cases to reproduce the relative sloping of the peaks labeled a, b, c in tropone or 2-cycloheptatrienylideneindanone although this feature is less recognizable in the 100-Mc spectra of tropone. The opposite sign of J_{26} was also necessary to reproduce other more subtle features in the spectra. Conversely, satisfactory agreement between the computer and experimental spectra for azulene and indenyltropenium ion necessitated that all the coupling constants have the same relative sign. The nmr spectrum of 3,3-dimethylcycloheptatrienylideneindanone was highly solvent dependent; however, by trial and error, a DMAC–hexafluorobenzene solvent mixture was found to give sufficient resolution of the various multiplets to allow solution of the nmr. The proton assignments were accomplished as follows: the position of H_2 was obvious due to the carbonyl anisotropy;[19] by spin decoupling $\Delta\nu_{23}$ could be determined thereby allowing assignment of the position of H_3; the nmr spectrum at elevated temperatures[19] showed a coalescence for H_2 and H_7 making an unequivocal assignment for H_7 possible; and the relative chemical shifts for H_{4-6} were determined by trial and error.

The compounds analyzed in this work, 3,3-dimethylcycloheptatrienylideneindanone,[19] 6,7-benzotropolone,[38] tropone,[39] 2-chlorotropone,[40] tropolone,[41] tropolone 2-methyl ether,[42] 8,8-dicyanoheptafulvene,[43] cyclohepta-2,4-dienone,[44] α-methylstyrene,[41] 6-dichloromethyl-6-methylcyclohexa-2,4-dienone,[45] troponehydroxonium perchlorate,[46] troponemethoxonium fluoroborate,[47] and 2-indenyltropenium-d_1 fluoroborate,[19] were prepared by literature methods. Azulene, commercially available from Fluka A. G. Chemische Fabrik, was deuterated in the 1 and 3 positions by dissolving it in a solution of acetic acid-d_1 containing a trace of perchloric acid. After $\sim$2 hr the solution was poured into water and the 1,3-dideuterioazulene recovered by extraction with benzene and purified by chromatography and sublimation.

Acknowledgment. The authors wish to express their indebtedness to the National Science Foundation for Research Grant GP-8168 which supported this work. Thanks are also extended to the UCSB computer center for its generous grant of computer time.

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Azabullvalenes and Benzazabullvalenes. Unsaturated Heterocyclic Systems. LX[1,2]

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Abstract: Submission of 7-azabicyclo[4.2.2]deca-2,4,9-trien-8-one (**4**) and 8-methoxy-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraene (**6**) to ultraviolet irradiation, preferentially under conditions of acetone sensitization, results in photoisomerization to the azabullvalene system. The rearrangement appears to be general and has been applied to a number of congeners of **4** and **6**. The variable-temperature nmr spectra of several azabullvalenes have been carefully examined. The observation has been made that although the vinyl and cyclopropyl protons do coalesce at the more elevated temperatures, the bridgehead proton maintains its identity throughout the averaging process. The unique rotational operations that can maintain the integrity of this proton are discussed in detail. The ground-state structures of the azabullvalenes are those in which the nitrogen atom is bonded to the bridgehead carbon atom. If the molecule possesses an additional methyl or methoxyl group, these substituents prefer to be bonded to a vinyl carbon. In contrast to the earlier examples, benzazabullvalene **18** undergoes an irreversible reaction at 125–150° with the formation of a different benzazabullvalene (**23**). A mechanism which accommodates the observed double migration is presented. Attempts to prepare a complete unsubstituted azabullvalene have not yet been successful. Interestingly, however, lithium aluminum hydride treatment of amide **5** or methylthioazabullvalene (**10**) causes overreduction to bicyclic amine **25**. A scheme is presented which accommodates the observed reactions and which is congruent with deuterium-labeling studies. Finally, the preparation of a 1:1 complex of methoxyazabullvalene and silver fluoroborate is described.

The discovery of Doering and Roth[4] of the rapidly reversible [3.3] sigmatropic rearrangement of bicyclo[5.1.0]octa-2,5-diene (**1**), along with their prediction (subsequently realized[5]) of the spectacular properties of bullvalene (**2**), has engendered considerable interest in degenerate or "no-reaction" reactions.[6] The character-

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

(2) The authors are grateful to the National Institutes of Health, the Alfred P. Sloan Foundation, and the Lilly Research Laboratories for grants which contributed to the financial support of this research.

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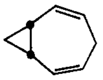

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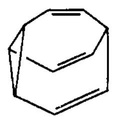
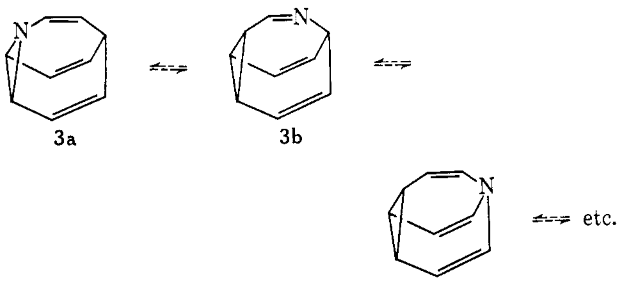


2

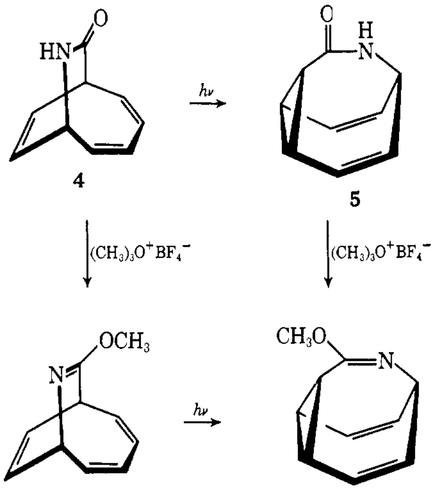
ization of molecules with such fluctuating bonds has made significant strides in recent years due chiefly to the capability of nmr spectroscopy to provide quantitative evidence on fast reactions which produce no net chemical change. As a consequence of the dynamic nature of bullvalene (**2**), all ten carbon atoms find themselves in an ever changing relationship to each other with the result that at 120° the nmr spectrum of **2** shows a single band.[5] This observation requires further that the carbon atoms undergo rapid mutual interconversion at this temperature to each 10 !/3 or 1,209,600 possible arrangements.[7] *A priori*, azabullvalene (**3**) can be expected to display the same remarkable features (1,209,600 interconvertible forms) as **2**,[8] but only if the nitrogen atom is not protected by sufficiently high-energy barriers from entering into the various bond reorganizations. In this connection, we wish to describe a remarkably simple synthetic entry into the azabullvalene (azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene) system and to make comment on the intriguing temperature-dependent nmr spectra and selected chemical reactions of a number of derivatives.



3a 3b 3c

Synthetic Aspects. Irradiation of **4** in methanol solution at 25° with an unfiltered Hanovia Type L 450-W mercury arc for 4.5 hr afforded in 54% yield the isomeric lactam **5**, $\nu_{\max}^{\text{KBr}}$ 1655 and 1640 cm^{-1}. The progress of the reaction was followed by withdrawal of small aliquots at various time intervals and examination of these for the gradual disappearance of the ultraviolet absorption band at 266 mμ which is characteristic of **4**. Although the extreme insolubility of **5** in the common organic solvents precluded obtaining a satisfactory nmr spectrum, its structure was established by conversion in 92% yield to methoxyazabullvalene (**7**) upon treatment with trimethyloxonium fluoroborate.[9]

An improved preparation of **7** was achieved by photorearrangement of imino ether **6** under conditions of acetone sensitization through Pyrex filters. In this fashion, the azabullvalene derivative was produced in 71% overall yield from **4**. In the early phases of this work, the photolysis of **6** was carried out in methanol and tetrahydrofuran solutions in the absence of a sensitizer. Consideration of the product distribution obtained in a series of irradiations *vs.* the extent of conversion (vpc analysis) showed an initial buildup of methoxyazabullvalene (**7**), followed by a decrease in the amount of **7** and the appearance of several new products. Subsequent study has established that these photoproducts are the result of further photochemical transformation of **7**.[10] Strikingly, however, when triplet sensitization is used in the conversion of **6** to **7**, no secondary photoproducts are formed.



4 5 6 7

The nmr spectrum of **7** and its variable-temperature behavior conclusively establish the structure as that of an azabullvalene.[11] At room temperature, there is discernible a sharp methoxyl singlet at δ 3.46, a three-line pattern of relative area 3 centered at δ 2.50 arising from the three cyclopropyl protons, a wider three-line pattern (with obvious additional small coupling) at δ 3.80 resulting from the proton at the bridgehead location, and a four-proton multiplet in the low-field region (δ $\sim$5.7) ascribable to the vinyl hydrogens (Figure 1). Spin-decoupling studies (Figure 1) clearly revealed that the two olefinic protons centered at δ $\sim$5.8 are strongly coupled to the cyclopropyl protons, whereas the two protons giving the more well-resolved vinyl absorption at δ $\sim$5.5 interact substantially with the bridgehead proton. The bridgehead and cyclopropyl protons do not appear to be spin coupled.

As the temperature of the probe was gradually lowered, there was noted considerable alteration in the line shape of the various absorptions (Figure 2) which is presumably the result of changes in the distribution of nondegenerate isomers. Significantly, however, integration of the various absorptions at −20, −60, and −90° revealed that the ratio of peak areas was not altered with decreasing temperature. In contrast, when a sample of **7** in tetrachloroethylene solution was heated above 150° (Figure 3), the proton signals from different regions were seen to coalesce, the sole exception being the δ 3.8 signal which, apart from coupling constants, did not seem to be affected. At 194°, therefore, the

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Engl., **4**, 752 (1965); (b) G. Schröder and J. F. M. Oth, *ibid.*, **6**, 414 (1967).

(7) Because of the threefold symmetry in **2**, three sets of the possible structures are identical. Thus, the maximum statistical distribution (10!) must be divided by 3.[4]

(8) The threefold symmetry of **3** would result from the intervention of structures such as **3c**.

(9) Although unequivocal assignment of structure to **5** requires more experimental data, the thermodynamic equilibrium established by divinylcyclopropane rearrangement can be expected to favor **5** in which tautomer there exists some element of conjugation with the carbonyl group.

(10) L. A. Paquette and G. R. Krow, *J. Am. Chem. Soc.*, **90**, 7149 (1968).

(11) For preliminary communications, refer to (a) L. A. Paquette and T. J. Barton, *ibid.*, **89**, 5480 (1967); (b) L. A. Paquette, T. J. Barton, and E. B. Whipple, *ibid.*, **89**, 5481 (1967).

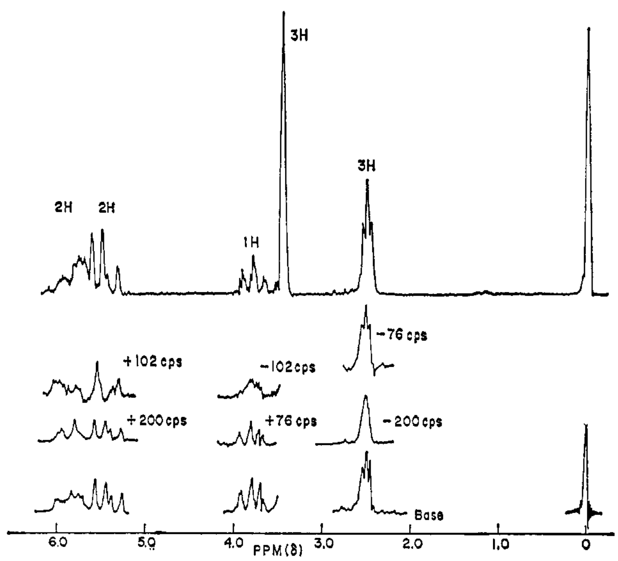


Figure 1. Upper curve: 60-MHz nmr spectrum of methoxyazabullvalene (7) in CCl_4 solution at ~38°. Lower section: spin decoupling (~38°) of 7 in CS_2 solution; values indicate the relative location of the applied stationary radiofrequency.

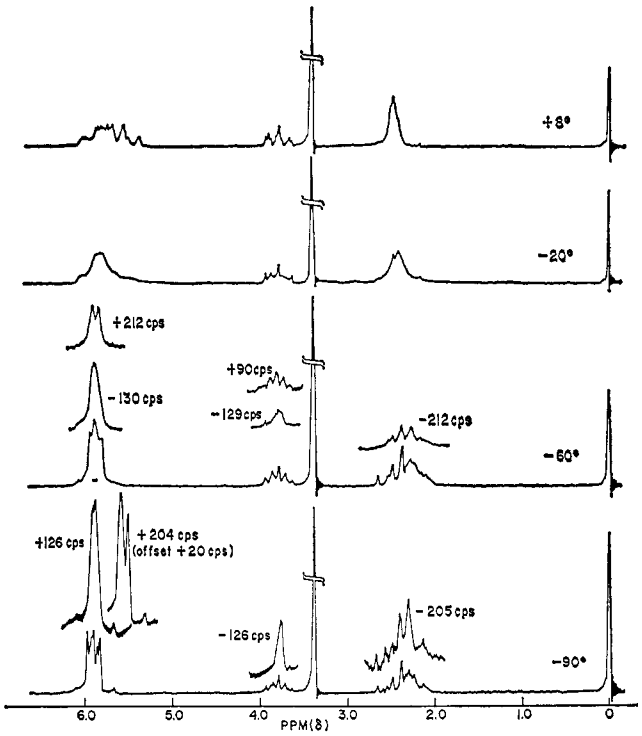


Figure 2. 60-MHz nmr spectra of 7 in CS_2 solution at 8, −20, −60, and −90°; values indicate the relative location of the applied stationary radiofrequency.

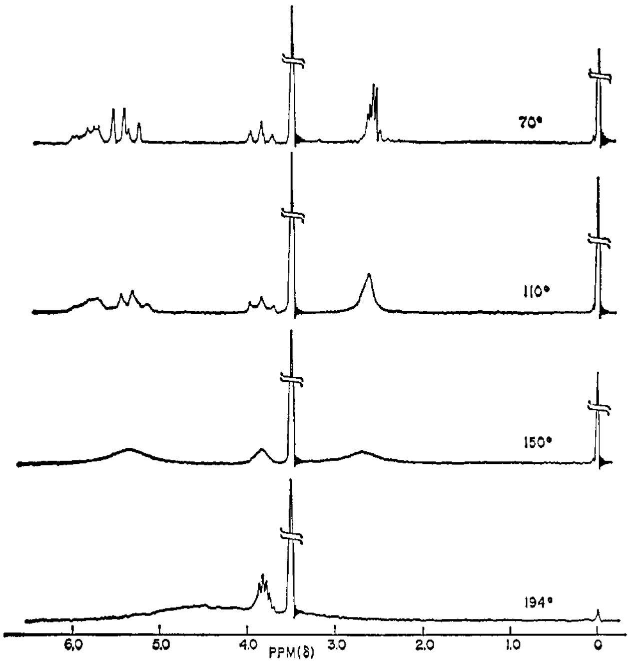
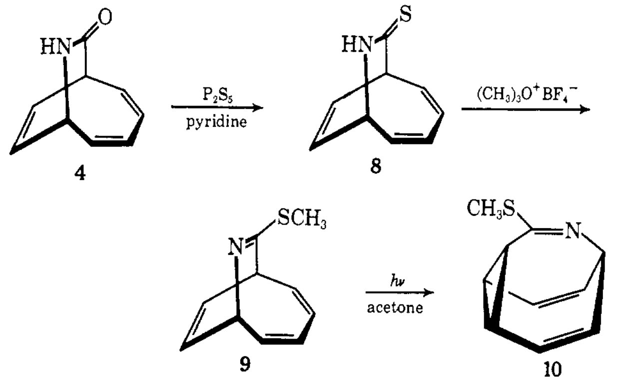


Figure 3. 60-MHz nmr spectra of 7 in $Cl_2C{=}CCl_2$ solution at 70, 110, 150, and 194°.

spectrum derives from the scrambling of the cyclopropyl and vinyl protons at a rate about equal to that of the frequency separation between the two regions. This is fast compared to any couplings to the bridgehead proton, so that in theory the latter should appear as an eight-line pattern with the same total spread as the ambient temperature triplet. In practice, however, sharply resolved components of the spectrum could not be attained in the case of 7 due to the temperature limit of the spectrometer. When the sample of 7 was subsequently cooled to room temperature, the previous spectrum reappeared without modification; the identical result was observed on returning the −90° sample to room temperature.

Leaving aside for the moment the interpretation of these spectra, it now becomes pertinent to consider the synthesis of thiomethylazabullvalene (**10**). The sequence proceeds from lactam **4** and phosphorus pentasulfide in pyridine through thioamide **8** to thiomethyl imino ether **9**. Acetone-sensitized photoisomerization of **9** (450-W Hanovia lamp, Pyrex optics, 1 hr) produced **10** in 93% yield. If the photolysis of **9** was not conducted under conditions of triplet sensitization, only dark polymeric material was produced. The nmr spectra of **10** unequivocally reveal its fluxional character (Figure 4); in particular, the high-temperature spectra were especially informative since at 169° the peak representing the coalesced vinyl and cyclopropyl protons was seen as a somewhat broadened singlet. Unfortunately, the expected sharper resolution of the bridgehead proton absorption was partially masked by this peak.[12]



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[12] The situation did not improve significantly at 100 MHz. Also, above 170°, the rate of decomposition of **10** was sufficiently rapid to prevent studies at more elevated temperatures (170–195°).

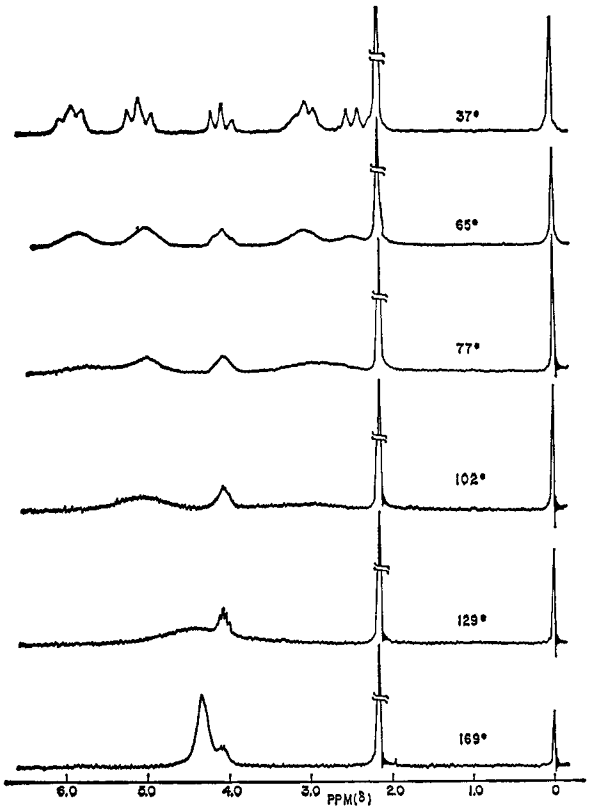


Figure 4. 60-MHz nmr spectra of **10** in $Cl_2C{=}CCl_2$ solution as the probe temperature was gradually increased.

Nevertheless, the lower coalescence temperature displayed by **10** denotes that the replacement of methoxyl by methylthio as an azabullvalene substituent occasions a somewhat faster averaging of the cyclopropyl and vinyl protons.

Spectral Analysis. Although the lower temperature effects only scramble signals within each separate region, the more elevated temperatures cause coalescence of the various proton signals with the exception of the 3.8–4.1-ppm absorption (1 H) in **7** and **10**. The downfield location of this nonexchanging proton requires that it be positioned on the carbon atom adjacent to nitrogen. Furthermore, since the spectra reveal the presence of three cyclopropyl and four vinyl protons, the proton which is adjacent to nitrogen must necessarily occupy the bridgehead position and there must be only one such proton. The ground-state structures of the molecules in question must therefore be **7** and **10**. The nmr spectra impose the added stringent condition that the favored interconversion routes must preserve the positional integrity of the bridgehead proton and thereby insulate it from the scrambling that occurs among the other protons.

The only averaging process that can give rise to the observed behavior is the combination of the two Cope rearrangements illustrated in A–E.[13] The two-step conversion of B to the equivalent D amounts formally to a rotation of the inner triatomic "spoke" on the outer "rim" by $2\pi/7$ radians, it being evident that continued repetition of such a process would average the rim positions and exclude the spoke. Each of the seven equivalent structures (B, D, etc.) thus generated is connected by a second Cope rearrangement of the type A $\leftrightarrows$ B to a more stable isomer (*e.g.*, E) whose structure corresponds to A. The entire rotational operation is shown in Figure 5. Particularly significant is the realization that such a succession of rotational operations results in retention of the structural integrity of the three-atom system $(-\mathrm{C(XCH_3)}{=}\mathrm{NCH}<)$ about which the rotation occurs.

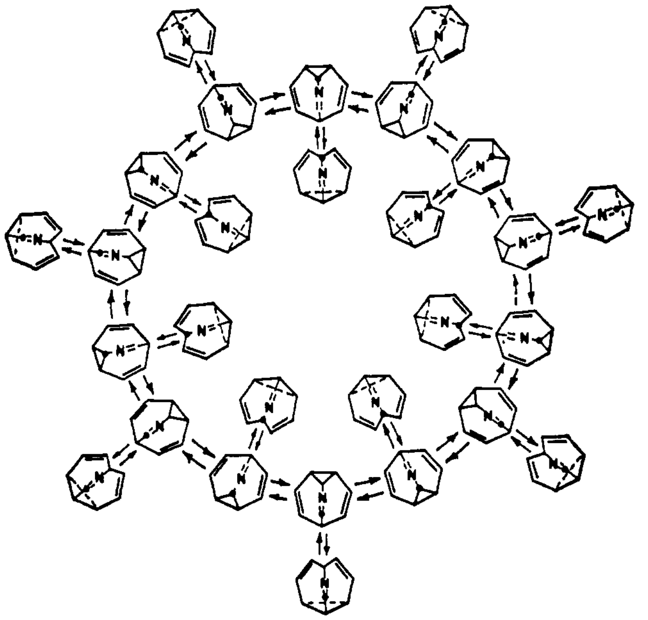
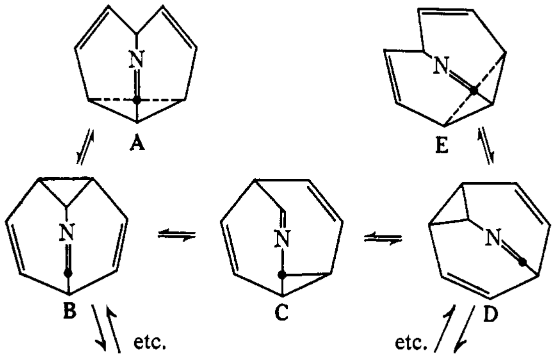


Figure 5. The sequential Cope rearrangements in **7** and **10** showing the averaging of the seven peripheral hydrogens coupled with retention of the structural integrity of the triatomic "spoke."



The reason that such a relatively simple averaging process occurs is apparently the strong preference of the nitrogen atom for participation in a double bond. By precluding any rearrangement path that places the heteroatom in the three-membered ring or at the bridgehead position, the integrity of the skeletal atoms constituting the "spoke" is maintained and the number of accessible structural arrangements is limited to 28: seven each of type A (outermost periphery of Figure 5), B and C (wheel of the same figure), and seven apparently incidental ones related to C as A is to B (inner periphery of wheel). Since the passage from B to C necessitates placement of the methoxyl or methylthio substituent at one of the cyclopropyl positions with simultaneous disruption of the imino ether functionality, this particular step is very likely rate determining. The lower coalescence temperature exhibited by **10** (relative

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[13] The heavy dots in these formulas denote the location of the methoxyl and methylthio functions.

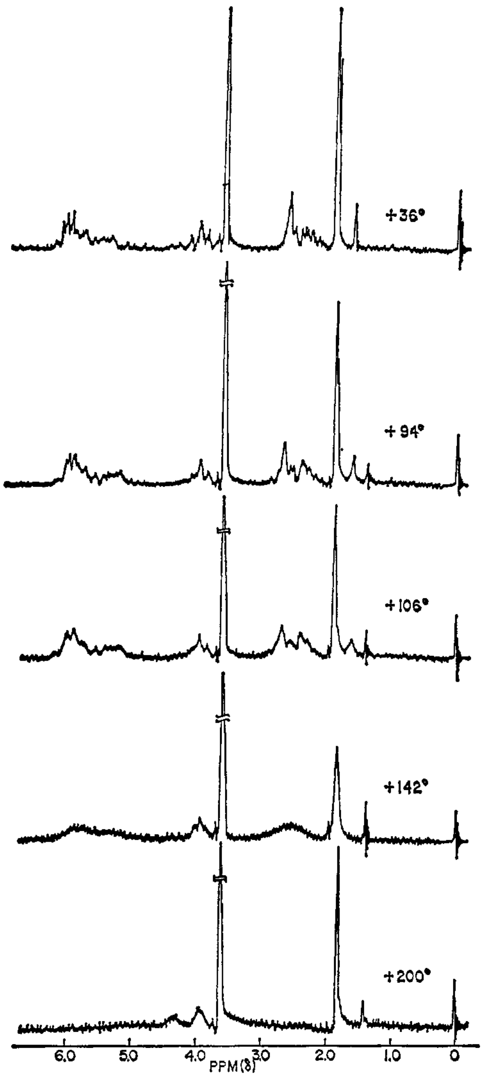
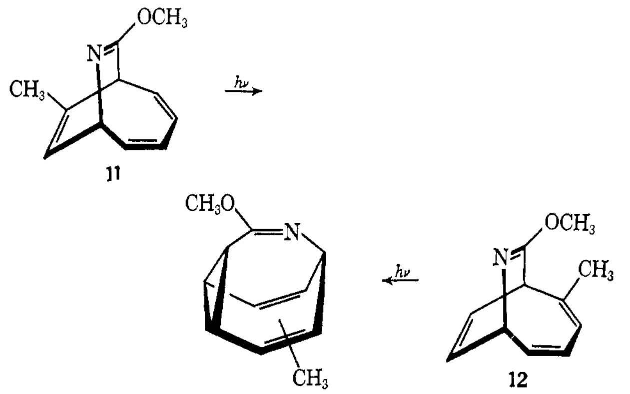


Figure 6. 60-MHz nmr spectra of **13** in $Cl_2C{=}CCl_2$ solution at 36, 94, 106, 142, and 200°. The sharp peak at δ 1.39 is due to an impurity that could only be removed with great difficulty.

to 7) denotes that it is somewhat less energetically demanding to achieve this Cope rearrangement with $-(CH_3S)C{=}N-$ than with $-(CH_3O)C{=}N-$, in agreement with the greater stability of the latter group.[14] In neither example, however, is the rotational scrambling of the seven "rim" protons sufficiently rapid at the temperatures examined to cause their absorption to appear as a doublet arising from coupling identical with the bridgehead hydrogen.

A final important aspect concerns the decided preference of **7** and **10** to exist as A and not as B in the equilibrium mixture. In A, the nitrogen atom is bonded to the bridgehead carbon, whereas in B nitrogen is attached to a cyclopropyl carbon; because the remainders of the two structures are identical (except for scrambling), they need not be considered. We have concluded that the heteroatom prefers bonding to the bridgehead carbon atom because the nitrogen center requires maximum satisfaction of its electronegativity requirements and because the bond to bridgehead carbon (sp^3) is endowed with less s character and is therefore less electronegative than that to cyclopropyl carbon ($sp^{2.27}$). In actuality, similar electronegativity considerations have been used to explain such phenomena as (a) the strong partiality shown by the fluorine substituent in fluorobullvalene to occupy the bridgehead position, while all other substituents preferentially occupy one of the vinyl sites;[6b] (b) the planarity of $\cdot CH_3$ in contrast to the nonplanarity of $\cdot SiH_3$ and related radicals;[15] and (c) the marked propensity of fluorine atoms to occupy apical positions in alkylfluorophosphoranes, whereas the less electronegative alkyl groups preferentially occupy equatorial positions.[16]

Higher Substituted Azabullvalenes. With the establishment of the ground-state structure of methoxyazabullvalene (**7**) and the mechanism of its averaging process, attention was directed to an analysis of the effect which additional substituents may have on the two different Cope rearrangements which are operational in **7**. To this end, an acetone solution of a mixture of **11** and **12** (65:35) was irradiated as above in Pyrex vessels for 4 hr to give a single photoproduct (**13**) in 89% yield.[17] Independent photorearrangement of pure samples of **11** and **12** likewise yielded only **13**. Identification of **13** as a methyl-substituted methoxyazabullvalene was again achieved by nmr spectroscopy which revealed complex olefinic absorption (3 H) at δ 5.0–6.0, a multiplet at δ 3.8 ascribable to the bridgehead proton, a methoxyl singlet at δ 3.54, a complex multiplet (3 H) at δ 2.1–2.7 resulting from the cyclopropyl protons, and methyl absorptions at δ 1.89 (doublet, $J = 1.5$ Hz) and 1.58 (singlet). The ratio of the last two signals was approximately 9:1 (Figure 6). These features revealed that the methyl substituent resides largely on the vinyl carbons, as seen also in methylbullvalene.[6b] Double resonance studies of **13** at 100 MHz established that the splitting of the δ 1.89 methyl signal was the result of spin–spin coupling to the neighboring vinyl proton. As the temperature of a solution of **13** in tetrachloroethylene was gradually raised above 100°, mutual coalescence of the cyclopropyl and vinyl protons was seen to occur in a manner paralleling the behavior of **7** (Figure 6). The two methyl absorptions also coalesced. All observations were completely reversible.



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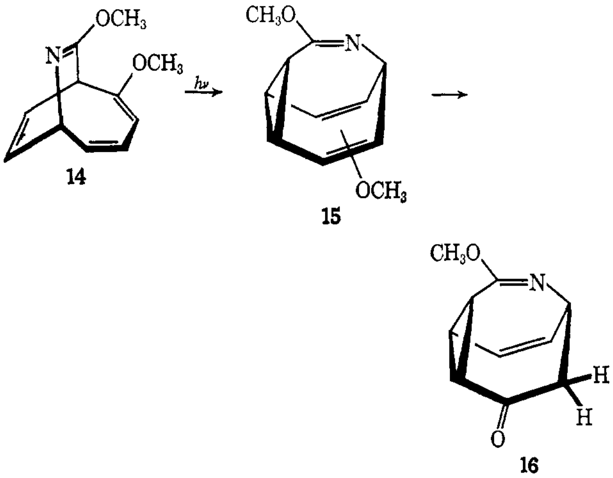
[14] (a) P. Beak, J. Bonham, and J. T. Lee, Jr., *J. Am. Chem. Soc.*, **90**, 1569 (1968); (b) P. Beak, private communication.

[15] A result of the fact that hydrogen is less electronegative than carbon, but more electronegative than silicon: R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966).

[16] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963). For a recent review, see F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

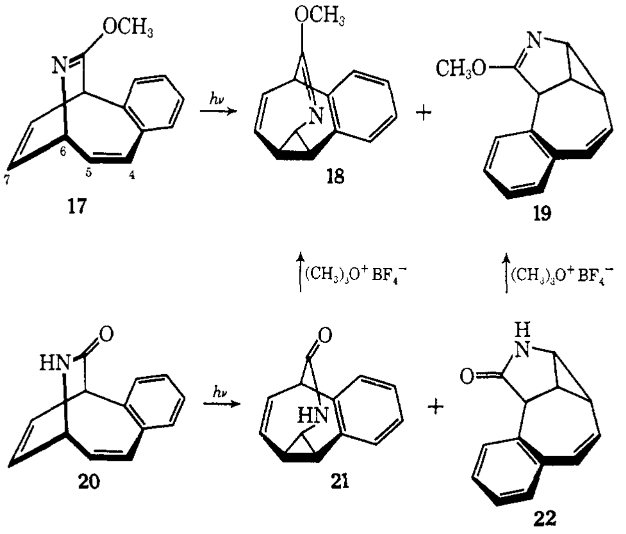
[17] This photolysis was also performed in dilute (1%) methanol solution for 1 hr in quartz vessels. There was obtained the same chief photoproduct (**13**) together with a trace of starting material and three minor photoproducts (~11%). The sensitized irradiation of **11** and **12**, as before, yielded a much purer sample of **13**.

Irradiation of **14** in acetone solution in the predescribed manner proceeded smoothly to give an almost colorless oil whose spectra were in accord with structure **15**. In its 38° nmr spectrum, there were displayed two vinyl protons as a complex pattern at δ 5.7–6.05, a vinyl ether proton as a peak centered at δ 4.75, a bridgehead proton as a multiplet at δ 4.0, and three cyclopropyl protons as a complex pattern in the δ 2.0–2.7 region, all of these absorptions being rather broad. In addition, two methoxyl peaks were seen, one as a sharp singlet at δ 3.49 and the other as a slightly split singlet at δ 3.44. As before, azabullvalene **15** exhibited highly temperature-dependent spectra, the room temperature features of which were completely restored on returning the sample to that condition. Again in this example, therefore, the additional substituent prefers to occupy an olefinic position.



Treatment of **15** with perchloric acid in methanol resulted in hydrolysis of the vinyl ether function and formation of the crystalline perchlorate of **16**. This structure was assigned on the basis of its nmr spectrum (see Experimental Section), the position of the carbonyl group being decided by the fact that the bridgehead proton adjacent to nitrogen appeared as a complex multiplet rather than the doublet expected if the carbonyl group were adjacent. The nmr spectrum of **16** was unchanged over the range 35–195°.

Photolysis of **17** with acetone sensitization afforded in 93% yield primarily benzazabullvalene **18** (>95%), plus benzisobullvalene **19** (<5%).[18] The structures of **18** and **19** follow unequivocally from their derived spectral properties (see Experimental Section). Direct irradiation of **17** in ether (quartz optics) led to much polymerization; the characterizable portion of the product mixture consisted of **18** (20%) and at least 18 minor products (total yield of 10%). In contrast, it was found that photosensitized irradiation of lactam **20** in acetone solution produced in quantitative yield a mixture of amides which without purification was treated directly with trimethyloxonium fluoroborate. Vpc analysis and preparative-scale isolation of the two major imino ethers indicated that these products were **18** (17%) and **19** (50%). This provided clear evidence that lactum **22** (which could also be isolated in pure form) predominated in the sensitized irradiation. Direct photolysis of **20** (THF, quartz optics) afforded **21** and **22** in yields of 21 and 33%, respectively.



These strikingly different product ratios show that the primary photoisomerization pathway is highly dependent upon the nature of the heteroatomic bridge. In **17**, "topside" migration of the nitrogen atom from C$_6$ to C$_5$ with concurrent rebonding of the "underside" p orbital at C$_4$ to the backside of C$_6$ is preferred. Rebonding of the nitrogen atom again occurs in **20**, but migration to C$_7$ predominates. Remarkably, shift of the carbonyl group in **20** (or of the methoxyl-bearing carbon in **17**) is not detected despite the fact that the majority of the known $(2\sigma + 2\pi)$ cycloadditions are in the area of ketone photochemistry.[19] The causative factors behind the contrasting photochemical behavior of **17** and **20** appear to be subtle and are presently under study.

Because of the benzo fusion in **18**, this azabullvalene was not expected to exhibit a propensity for Cope rearrangement,[20] and such was the case. However, when a solution of **18** in tetrachloroethylene was heated to 125–150°, an irreversible reaction occurred in high yield. The rate of rearrangement could be conveniently followed by nmr spectroscopy and the following first-order rate constants and thermodynamic parameters were determined: $k_{125} = 1.68 \times 10^{-4}$ sec^{-1}; $k_{133} = 3.08 \times 10^{-4}$ sec^{-1}; $k_{143} = 7.53 \times 10^{-4}$ sec^{-1}; $\Delta H^{\ddagger} = 26.6$ kcal/mole; $\Delta S^{\ddagger} = -9.6$ eu. The nmr spectrum of the thermal product is uniquely adaptable to benzazabullvalene structure **23**.[21] Mechanistic passage from **18** to **23** requires a double migration; two possible reaction pathways are outlined below. More careful analysis of the thermal behavior of **18** reveals that the operation of a similar rearrangement in the case of benzobullvalene would pass undetected because of the obvious degeneracy of the process in this latter instance. At question, therefore, is whether there may be available to bullvalene and its congeners additional degenerate pathways which would compete with the Cope rearrangement at moderate to elevated temperatures.

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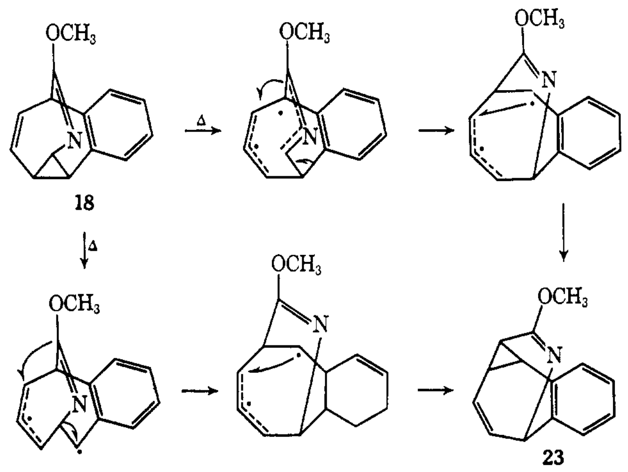
(18) The name isobullvalene has been proposed earlier for the derived hydrocarbon: L. A. Paquette and J. R. Malpass, *J. Am. Chem. Soc.*, **90**, 7151 (1968).

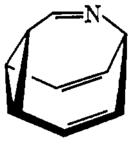
(19) For a partial listing of references to this work see footnote 11 of ref 18.

(20) The preclusion of degenerate Cope rearrangements upon introduction of a fused benzene ring in bullvalene[6b] and semibullvalene derivatives [I. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5081 (1967)] has already been noted.

(21) The nmr spectra of both **18** and **23** have been illustrated in our preliminary communication of this work.[18]



Attempted Preparation of the Parent System. A structural consequence of the fluxional character of azabullvalenes **7** and **10** is the disruption of the rather stable $-(CH_3O)C{=}N-$ and $-(CH_3S)C{=}N-$ functions, respectively (Figure 5). If the methoxyl and methylthio groups were replaced by hydrogen, the resulting parent compound (**24**) would exhibit rotational operations the extent and rate of which would surely be substantially altered from those of **7** and **10**. Because of the desirability of comparing the properties of **24** with those of its substituted derivatives, considerable effort has been expended in attempts to prepare **24**. Although the synthesis of **24** has not yet been achieved,[22] an interesting reduction of the azabullvalene system has been observed, the details of which follow.

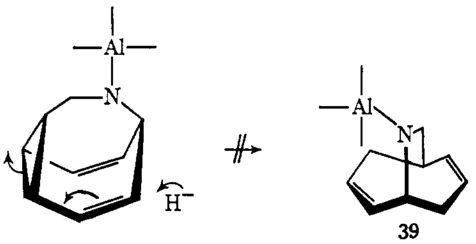


24

Exposure of **10** to a refluxing ether solution of lithium aluminum hydride led in 95% yield to the formation of an amine of molecular formula $C_9H_{13}N$ (**25**) which was characterized as its picrate, benzenesulfonamide (**26a**), and methylurethan (**27**). Interestingly, this amine was also produced in the lithium aluminum hydride reduction of amide **5**, albeit in substantially lower yield (33%). Confirmatory evidence that amine **25** was the result of overreduction and consequently bicyclic in nature was obtained from deuterium-labeling studies. Reduction of **10** with $LiAlH_4$ as before and hydrolysis with deuterium oxide gave **26b** containing one deuterium atom; the nmr spectrum of **26b** revealed that an allylic proton had been replaced by the label. The results with $LiAlD_4$ and D_2O established that **26c** had been produced; significantly, the three additional deuteriums were located on the two carbon atoms adjacent to the nitrogen center (nmr analysis). The mass spectra of the three benzenesulfonamides which fully confirm these assignments are tabulated in the Experimental Section. Also relevant is the fact that exhaustive hydrogenation of **26a** over a rhodium catalyst resulted in the uptake of 2 mol of hydrogen to give **28**.

The structure assigned to **25** was confirmed by exhaustive Hofmann degradation to 1,4-dimethylcycloheptane (**33**) as shown in the accompanying scheme. An authentic sample of **33** prepared by diazomethane ring expansion of 4-methylcyclohexanone with subsequent methylene transfer and catalytic hydrogenation was found to be identical with the product of degradation.

A mechanism capable of rationalizing the formation of **25** from both **10** and **5** is advanced below. Of special interest is the fact that the 3-azabicyclo[3.3.2]decadiene system is most likely produced by rupture of a cyclopropyl bond in **37b**. Whether this occurs by 1,3 migration of aluminum from nitrogen to carbon as shown by path a or by a 1,5-homodienyl shift of aluminum (path b) cannot be established with the present data. However, it is of more than minor concern that a number of plausible alternative processes do not appear to be operative. For example, isomerization of **37a** by means of a 1,5-homodienyl proton transfer analogous to the thermal behavior exhibited by dihydrobullvalene,[23] dihydrosemibullvalene,[24] and bicyclo[5.1.0]octa-2,4-diene[25] does not seem to be favored. Nor does direct attack at vinyl carbon with concomitant cleavage of a cyclopropane bond take place.[26]



39

Silver Cation Complex Formation. Treatment of a solution of methoxyazabullvalene (**7**) in 1,2-dichloroethane with a solution of anhydrous silver fluoroborate in the same solvent resulted in the immediate formation of a white precipitate. Although this solid proved to be quite insoluble, it could be recrystallized from isopropyl alcohol as white needles which blackened rapidly on exposure to light. The stoichiometric ratio of the complex was 1 : 1, and no other complexes were isolated. These results contrast with the behavior of bullvalene which has been observed to form several complexes with $AgBF_4$ under these conditions.[27,28] Because of the in-

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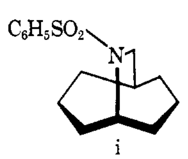
(22) In particular, imino ethers **6** and **7** were quite resistant to reduction with either lithium aluminum hydride or sodium borohydride. Reductive desulfurization of **9** and **10** under a variety of conditions (Raney nickel, Raney cobalt, triethyl phosphite, aluminum amalgam, etc.) also did not lead to the desired imines. Sodium borohydride reduction of the fluoroborate salts of **6** and **7** likewise did not result in formation of the corresponding secondary amines [R. F. Borch, *Tetrahedron Letters*, 61 (1968)].

(23) J. N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schröder, *J. Am. Chem. Soc.*, **89**, 612 (1967).

(24) W. Roth, *Angew. Chem. Intern. Ed. Engl.*, **3**, 440 (1964).

(25) W. Roth, *Ann.*, **671**, 10 (1964); D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963).

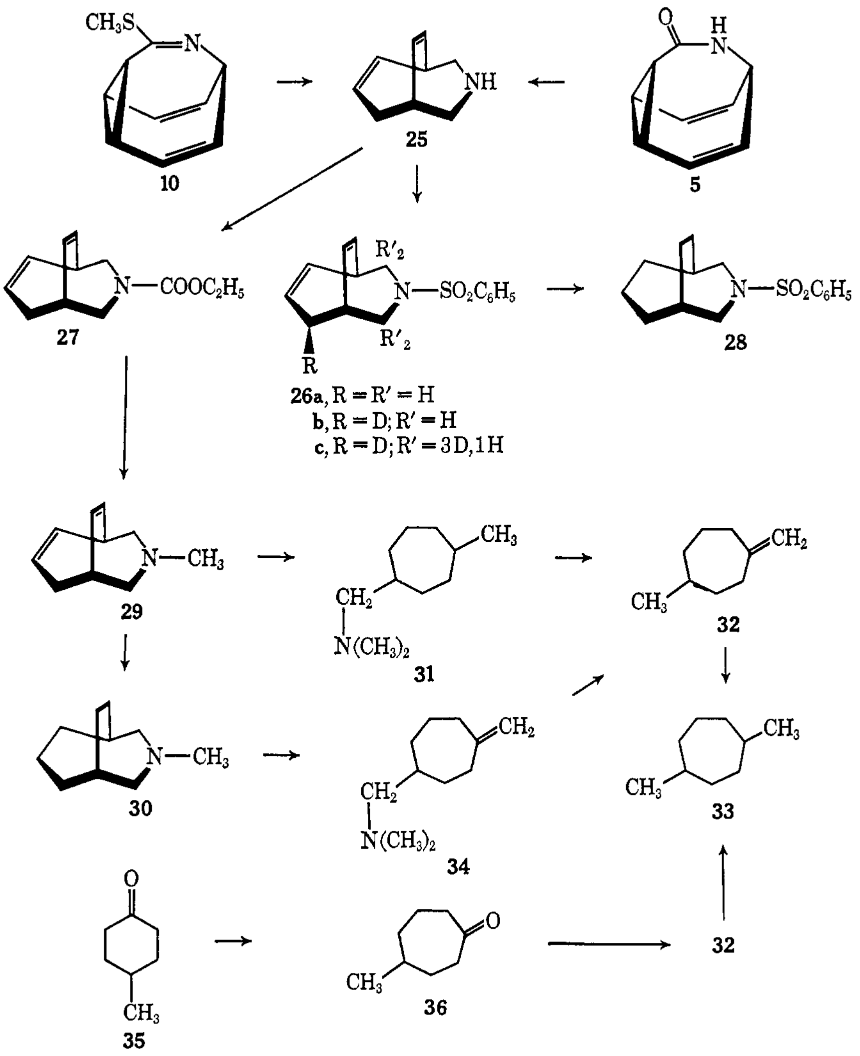
(26) To be quite sure that **39** was not produced, its tetrahydrobenzenesulfonamide (i) was prepared in unequivocal fashion and compared to **28**. The sequence proceeded from bicyclo[3.3.1]nonan-9-one through its oxime to the ring-expanded lactam (Beckmann rearrangement), followed by lithium aluminum hydride reduction and benzenesulfonylation. The two sulfonamides were not at all comparable.

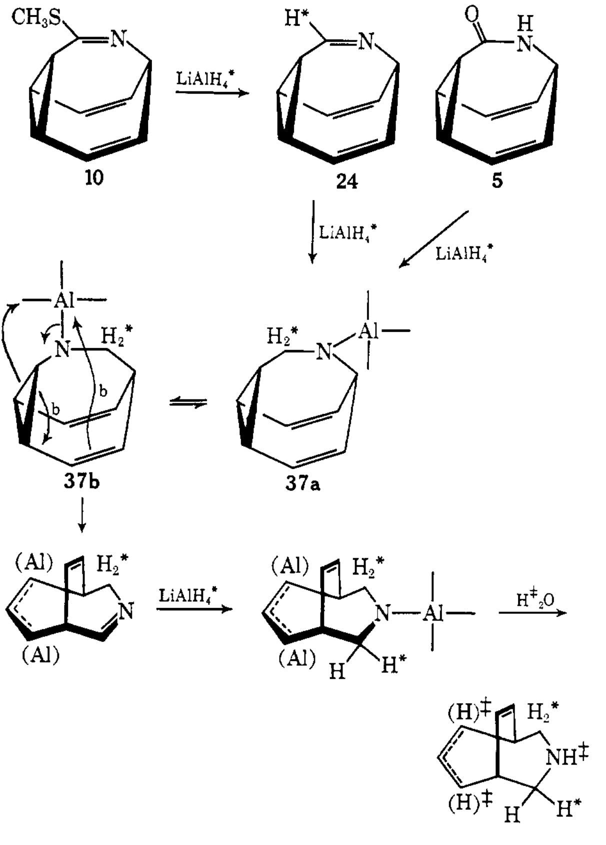


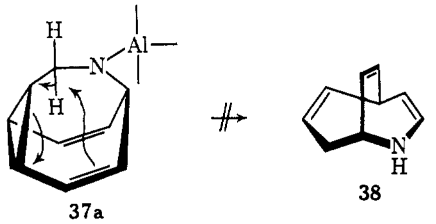
i

(27) A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.*, **87**, 4092 (1965).

(28) M. G. Newton and I. C. Paul, *ibid.*, **88**, 3161 (1966); J. S. McKechnie, M. G. Newton, and I. C. Paul, *ibid.*, **89**, 4819 (1967).







solubility and light sensitivity of 7·AgBF₄, no nmr or X-ray studies have been performed on this material.

Experimental Section[29]

4-Azatricyclo[3.3.2.0^{2,8}]deca-6,9-dien-3-one (5). Irradiation of a solution of 3.79 g (0.026 mol) of amide 4[1] in 450 ml of methanol with an unfiltered 450-W Hanovia lamp under nitrogen (quartz vessel) afforded, after removal of the solvent *in vacuo*, a reddish solid. Digestion of this solid in hot benzene, followed by cooling and filtration, yielded 2.00 g (54%) of **5**. Digestion in hot methanol, followed by recrystallization from chloroform-ether, gave pure **5**, mp >300°. Interestingly, when a sample of **5** was inserted into the oil bath preheated to 250°, immediate melting occurred; $\nu_{\max}^{\mathrm{KBr}}$ 1655 and 1640 cm^{-1}.

Anal. Calcd for C_9H_9NO: C, 73.41; H, 6.16; N, 9.56. Found: C, 73.44; H, 6.24; N, 9.48.

3-Methoxy-4-azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (7). A. From Lactam 5. To a magnetically stirred slurry of 1.91 g (0.013

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(29) Melting points are corrected and boiling points are uncorrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV.

mol) of **5** in 25 ml of dry methylene chloride was added 2.00 g (0.014 mol) of trimethyloxonium fluoroborate in one portion. During 8 hr at room temperature, a homogeneous solution was obtained. This was carefully treated with 5.6 g of 50% aqueous potassium carbonate solution; the organic portion was filtered through alumina (elution with pentane). Removal of the solvent *in vacuo* afforded 1.92 g (92%) of **7** as a clear, colorless oil which slowly crystallized. Recrystallization from pentane afforded white needles: mp 49.5–50.5°; $\nu_{\max}^{\text{film}}$ 1667 cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 271 mμ (ϵ 2000).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.31; H, 7.01; N, 8.73.

Treatment of an ether solution of **7** with ethanolic perchloric acid deposited crystals of the perchlorate salt, mp 185.5–186° dec (white needles from acetonitrile–ether).

Anal. Calcd for $C_{10}H_{12}ClNO_5$: C, 45.90; H, 4.62; N, 5.35. Found: C, 45.67; H, 4.70; N, 5.24.

B. Photorearrangement of 6. A 2.4-g (0.015 mol) sample of imino ether **6**[1] was dissolved in 500 ml of reagent grade acetone and this solution was irradiated through a Pyrex filter sleeve as above. After 8 hr, the solvent was evaporated *in vacuo*, and the resulting yellowish oil was dissolved in 50–75 ml of hexane and clarified by filtration through neutral alumina. Concentration afforded a colorless oil which was crystallized from pentane to give 2.1 g (88%) of white crystals, mp 49.5–50.5°, identical in all respects with the sample prepared in A.

7-Azabicyclo[4.2.2]deca-2,4,9-triene-8-thione (8). A solution of 11.5 g (0.078 mol) of **4** and 14.1 g (0.063 mol) of phosphorus pentasulfide in 120 ml of pyridine was refluxed for 3 hr. The solution was cooled and poured into 450 ml of water. After cooling overnight at 5°, there was deposited 10.4 g of brown solid. Extraction of this solid with several 100-ml portions of hot acetone, decolorization of the combined extracts by filtration through neutral alumina, and concentration of the eluate yielded 8.7 g (68%) of **8** as white crystals: mp 190.5–191.5°; $\nu_{\max}^{\text{Nujol}}$ 1120 cm^{-1} (>C=S); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 216 mμ (ϵ 8120) and 278 (12,950).

Anal. Calcd for C_9H_9NS: C, 66.22; H, 5.56; N, 8.56. Found: C, 66.44; H, 5.87; N, 8.39.

8-Methylthio-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraene (9). A solution of 2.0 g (0.012 mol) of **8** and 2.0 g (0.014 mol) of trimethyloxonium fluoroborate in 25 ml of dry methylene chloride was stirred at room temperature and worked up as above. There was obtained 1.55 g (71%) of **9** as white crystals: mp 53.5–54.5°, from hexane; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 214 mμ (ϵ 7230) and 282 (1710); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.51–6.58 (multiplet, 6 H vinyl protons), 4.60 (multiplet, 1 H, >NC*H*<), 3.50 (multiplet, 1 H, >C(SCH_3)C*H*<), and 2.31 (singlet, 3 H, –SCH_3).

Anal. Calcd for $C_{10}H_{11}NS$: C, 67.76; H, 6.26; N, 7.90. Found: C, 67.73; H, 6.32; N, 7.82.

3-Methylthio-4-azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (10). A solution of 1.5 g of **9** in 500 ml of acetone was irradiated through Pyrex as above for 1 hr. The solvent was evaporated *in vacuo* and the residue was dissolved in hexane, filtered through neutral alumina, and concentrated. There was obtained 1.4 g (93%) of **10** as a fluffy white solid: mp 47.5–48° (from hexane); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 235 mμ (ϵ 7250).

Anal. Calcd for $C_{10}H_{11}NS$: C, 67.76; H, 6.26; N, 7.90. Found: C, 67.84; H, 6.31; N, 7.62.

3-Methoxy-*x*-methyl-4-azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (13). A solution of 1.48 g of a mixture of **11** and **12** (ratio 65:35) in 320 ml of acetone was irradiated through Pyrex for 4 hr at which point vpc analysis indicated reaction to be complete. The solvent was evaporated and the residue was dissolved in ether. This solution was passed through neutral alumina to remove color and evaporated to give 1.33 g (89%) of **13** as a colorless oil, $\nu_{\max}^{\text{neat}}$ 1660 cm^{-1}. This material was converted to its perchlorate salt in the usual fashion to give colorless crystals, mp 134–136°, from methanol.

Anal. Calcd for $C_{11}H_{14}ClNO_5$: C, 47.92; H, 5.12; N, 5.08. Found: C, 47.82; H, 5.28; N, 4.86.

Independent photolysis of smaller samples of pure **11** and **12** gave identical results.

3,*x*-Dimethoxy-4-azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (15). A solution of 103 mg of **14**[1] in 30 ml of acetone was irradiated through Pyrex in the usual way for 2 hr. The resulting oil was characterized as **15** on the basis of its nmr spectrum. Preparative vpc could not be used for the purpose of purification because decomposition occurred.

A solution of **15** in ether was treated with methanolic perchloric acid; upon cooling to −20° with scratching, a crystalline precipitate formed which was filtered and recrystallized from methanol, white crystals, mp 177–178° dec. Elemental and infrared analysis revealed that vinyl ether hydrolysis had taken place to give the perchlorate salt of **16**, $\nu_{\max}^{\text{Nujol}}$ 1700 and 1665 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}ClNO_6$: C, 43.26; H, 4.30; N, 5.04. Found: C, 42.87; H, 4.30; N, 4.87.

Treatment of the perchlorate with aqueous sodium hydroxide and isolation with ether gave a quantitative yield of **16**: $\nu_{\max}^{\text{neat}}$ 1685 cm^{-1}; $\lambda_{\max}^{\text{hexane}}$ end absorption with shoulders at 273 mμ (ϵ 125) and 280 (110); $\delta_{\mathrm{TMS}}^{\mathrm{C_2Cl_4}}$ 6.08 (multiplet, 2 H, vinyl protons), 4.14 (five-line multiplet, 1 H, bridgehead proton), 3.58 (singlet, 3 H, –OCH_3), and 2.2–2.9 (complex pattern, 5 H, cyclopropyl and –COCH_2– protons).

Sensitized Irradiation of 17. 4-Methoxy-6,7-benzo-3-azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (18). A solution of 79 mg of **17**[1] in 24 ml of dry acetone was carefully purged with dry nitrogen and was irradiated through Pyrex in the usual fashion for 1 hr. The reaction could be easily followed by intermittent tlc analysis. The resultant oil was taken up in ether and passed down a short column of alumina to afford a colorless oil which crystallized when scratched. Vpc analysis showed that this material consisted of two products in the ratio of 95:5. The minor product was later identified as **19** (see below). Recrystallization from benzene–hexane gave colorless crystals (40 mg) of **18**: mp 113–114°; $\nu_{\max}^{\text{Nujol}}$ 1672 cm^{-1}; $\lambda_{\max}^{\text{hexane}}$ end absorption in addition to weak benzenoid absorption at 270 mμ (ϵ 800) and 281 (510).[21]

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.50; H, 6.65; N, 6.57.

Sensitized Irradiation of 20. 2,3-Benzo-9-azatricyclo[5.3.0.0^{6,10}]deca-2,4-dien-8-one (22). A solution of 23 mg of **20**[1] in 12 ml of dry acetone was irradiated as above. In this instance, the course of the photolysis could not be followed by tlc due to extensive streaking; however, examination of aliquots by infrared (Nujol mulls) proved successful. After 155 min, the reaction was judged complete and the solvent was evaporated *in vacuo* to yield a colorless solid, mp 195–230° (21 mg, less infrared samples).

Treatment of this product mixture with trimethyloxonium fluoroborate in methylene chloride solution overnight, followed by the usual work-up, gave a slightly yellow oil (23 mg) which was passed down a short alumina column in ether to give a colorless oil (17 mg, 75%). Vpc analysis on a 5 ft 10% SF 96 on Chromosorb G column showed the presence of **18** (22%) and **19** (66%) in addition to two impurities (10 and 2%, respectively). Preparative tlc separation of **18** and **19** from this mixture showed them to be identical with the other samples of these imino ethers.

In a repeat experiment, a 90-mg sample of **20** in 35 ml of acetone was irradiated; removal of the solvent gave a crystalline product (90 mg) which was recrystallized several times from absolute ethanol to give colorless plates: mp 239–243° dec of **22** (24 mg); $\nu_{\max}^{\mathrm{CH_2Cl_2}}$ 3390 and 1710 cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3CN}}$ 264.5 mμ (ϵ 6500); $\delta_{\mathrm{TMS}}^{\mathrm{DMSO}\text{-}d_6}$ 8.03 (broad, 1 H, >NH), 7.22 (singlet, 4 H, aromatic protons), 6.52 (doublet, J = 11.7 Hz, H-4), 5.91 (doublet of doublets, J = 11.7 and 3.8 Hz, H-5), 3.89 (doublet, J = 7.5 Hz, >C*H*CO–), 3.05 (complex triplet, $J \sim 6.5$ Hz, >NHC*H*<), 2.11 (quartet, $J \approx 7$ Hz, H-7), and 1.58 (complex multiplet, H-6).[30]

Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.65; H, 5.53; N, 6.92.

Treatment of a 3-mg sample of pure **22** with trimethyloxonium fluoroborate gave authentic **19** as a colorless oil: $\nu_{\max}^{\text{neat}}$ 1635 cm^{-1}; $\lambda_{\max}^{\text{hexane}}$ 265 mμ; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.21 (singlet, 4 H, aromatic protons), 6.53 (doublet, J = 11.7 Hz, H-4), 5.92 (doublet of doublets, J = 11.7 and 3.8 Hz, H-5), 4.18 (doublet, J = 7.1 Hz, H-1), 3.72 (singlet, 3 H, –OCH_3), 3.45 (doublet of doublets, J = 5 and 7 Hz, H-10), and 1.5–2.2 (complex pattern, 2 H, H-6 and H-7).[30]

Thermal Rearrangement of 18. 3-Methoxy-6,7-benzo-4-azatricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (23). A solution of 31 mg of **18** in 150 ml of tetrachloroethylene was sealed in an nmr tube and placed in a probe preheated to 150°; the progress of the reaction was followed by repeated scanning of the spectrum. The solvent was evaporated *in vacuo* and the residue was dissolved in ether and passed down a short alumina column. Evaporation afforded 23 mg (74%) of a colorless crystalline solid, mp 127–128.5° (from benzene–hexane), identified as **23**: $\nu_{\max}^{\text{Nujol}}$ 1675 cm^{-1}; $\lambda_{\max}^{\text{hexane}}$ strong end absorption with weak benzenoid absorption at 265 mμ (ϵ 350) and 276 (280).[21]

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.38; H, 6.08; N, 6.31.

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(30) The assignments were made on the basis of extensive spin-decoupling studies.

For the kinetic measurements, use was made of the fact that the intensity of the olefinic peaks in the nmr spectra remained constant (2 H) throughout the course of the rearrangement; this absorption band was therefore used as an effective internal standard against which to follow the appearance of lone proton H-5 in **23**.[21] A measure of the first-order rate of disappearance of **18** was then obtained by plotting graphs of log (concentration) *vs.* time for the reaction at 125, 133, and 143°. The reactions were taken to greater than 75% completion in each instance.

Hydride Reductions of 10. To a slurry of 0.55 g (0.0145 mol) of lithium aluminum hydride in 50 ml of anhydrous ether was added 2.5 g (0.0143 mol) of **10** and the mixture was heated overnight under gentle reflux with stirring. With cooling, there was added dropwise 0.5 ml of water, 0.5 ml of 25% sodium hydroxide solution, and 1.5 ml of water in that order. The precipitated salts were separated by filtration and washed well with ether. The combined filtrates were evaporated and the residual oil was distilled to give 1.78 g (95%) of **25**, bp 65–70° (0.75 mm). Vpc analysis indicated that the colorless liquid was entirely one component. The picrate of **25** was prepared in the usual fashion to give yellow crystals, mp 215–217°, from ethanol.

Anal. Calcd for $C_{15}H_{16}N_4O_7$: C, 49.45; H, 4.43; N, 15.38. Found: C, 49.52; H, 4.51; N, 15.21.

The benzenesulfonamide **26a** was obtained as white crystals, mp 108–109°, from ethanol: $\nu_{max}^{CHCl_3}$ 1330 and 1165 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.55 (multiplet, 5 H, aromatic protons), 5.5–6.3 (multiplet, 4 H, vinyl protons), 3.65–4.15 and 2.55–2.90 (multiplets, 2 H each, $(-CH_2)_2NSO_2-$), and 2.20–2.50 (broad absorption, 4 H, allylic protons).

Table I. *m/e* Values and Per Cent Relative Abundance for Various Fragment Jons of Benzenesulfonamides **26a, b, c**

Compd	*m/e* (% relative abundance)
26a	42 (100), 77 (30), 91 (49), 92 (7), 105 (76), 106 (14), 107 (39), 133 (13), 134 (42), 135 (6), 141 (9), 275 (24)
26b	42 (100), 77 (32), 91 (21), 92 (29), 105 (29), 106 (55), 107 (14), 108 (40), 133 (5), 134 (17), 135 (42), 141 (12), 276 (25)
26c	45 (100), 77 (27), 91 (13), 92 (28), 106 (20), 107 (42), 108 (30), 109 (10), 110 (27), 111 (14), 136 (5), 137 (14), 138 (43), 139 (5), 141 (10), 279 (20)

Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.42; H, 6.22; N, 5.09. Found: C, 65.38; H, 6.22; N, 4.97.

Reaction of **25** with ethyl chloroformate and triethylamine gave ethylurethan **27**; bp 103–104° (0.6 mm); $\nu_{max}^{CHCl_3}$ 1730 cm^{-1}.

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.19; H, 8.29; N, 6.65.

The deuterium-labeled studies were carried out in an analogous fashion. When **10** was reduced with $LiAlH_4$, but hydrolysis was effected with D_2O and NaOD, benzenesulfonamide **26b**, mp 108–109°, was obtained; nmr spectrum very similar to that of **26a**, but with one less allylic proton in the δ 2.20–2.50 region.

Similar treatment with $LiAlD_4$ and D_2O gave benzenesulfonamide **26c** (mp 105–106°, nmr comparable to that of **26b**), but with three additional protons absent in the δ 2.55–3.65 region.

Hydride Reduction of 5. A mixture of 2.5 g (0.017 mol) of **5** and 500 mg (0.013 mol) of lithium aluminum hydride in 125 ml of anhydrous tetrahydrofuran was refluxed with stirring for 48 hr. Hydrolysis was performed in the previously employed manner. There was obtained 745 mg (33%) of **25**, bp 65–70° (0.75 mm), identical in all respects with the previously prepared sample.

Hydrogenation of 26a. A 400-mg sample of **26a** was hydrogenated in ethanol solution over a 10% rhodium on carbon catalyst at 50 psig for 48 hr. Work-up afforded a white solid, mp 114–115°, from ethanol, $\nu_{max}^{CHCl_3}$ 1325 and 1155 cm^{-1}.

Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.44; H, 7.58; N, 4.76.

3-Methyl-3-azabicyclo[3.3.2]deca-6,9-diene (29). A mixture of 4.5 g (0.0217 mol) of **27** and 830 mg (0.0217 mol) of lithium aluminum hydride in 150 ml of ether was refluxed with stirring overnight and worked up in the usual way. Distillation afforded 2.9 g (90%) of **29**, bp 74–75° (4.5 mm). This amine was customarily converted directly to its methiodide by stirring with excess methyl iodide in ether at 45° for 16 hr. Yields from the amine averaged 97%. The methiodide was obtained as white crystals, mp 246–247°, from ethanol–ether.

Anal. Calcd for $C_{11}H_{18}IN$: C, 45.37; H, 6.23; N, 4.81. Found: C, 45.31; H, 6.26; N, 4.72.

3-Methyl-3-azabicyclo[3.3.2]decane (30). A solution of 1.15 g of **29** in 50 ml of methanol was catalytically hydrogenated over Adams catalyst. After removal of the catalyst and solvent, the residue was distilled to give 780 mg (68%) of **30**, bp 62–63° (1.5 mm). The picrate of **30**, mp 248–250° dec, was purified by recrystallization from ethanol.

Anal. Calcd for $C_{16}H_{22}N_4O_7$: C, 50.26; H, 5.80; N, 14.65. Found: C, 50.08; H, 5.94; N, 14.24.

1-Dimethylaminomethyl-4-methylcycloheptane (31). The methiodide of **29** (2.95 g, 0.01 mol) and 2.3 g (0.01 mol) of freshly prepared silver oxide were placed in 30 ml of 1:1 methanol–water and stirred for 2 hr. The mixture was filtered, the filtrate was concentrated *in vacuo*, and the residue was pyrolyzed at 145°. The resulting distillate was redistilled to afford 1.1 g (65%) of an unstable tertiary amine: bp 47–48° (0.3 mm); $\lambda_{max}^{CH_3OH}$ 244 mμ (ϵ 11,500). Vpc analysis indicated the substance to be of high purity.[31]

Catalytic hydrogenation of this material over Adams catalyst in methanol solution yielded **31** as a colorless liquid: bp 79–80° (1.5 mm); $\delta_{TMS}^{CDCl_3}$ 2.20 (singlet, 6 H, dimethylamino group), 0.9–2.2 (broad absorption, 14 H, methylene and methine protons), and 0.88 (doublet, J = 6 Hz, 3 H, methyl group).

Anal. Calcd for $C_{17}H_{26}N_4O_7$: C, 51.25; H, 6.58; N, 14.06. Found: C, 51.50; H, 6.74; N, 14.20.

Hofmann Degradation of 31. The methiodide of **31** was prepared by heating the free base with excess methyl iodide in acetone (average yield, 97%). Because of difficulties in the crystallization of this salt, the crude material was used directly. A 2.07-g (6.84 mmol) sample of the methiodide of **31** and 1.59 g (6.84 mmol) of freshly prepared silver oxide were placed in 30 ml of 1:1 methanol–water and stirred for 2 hr. The mixture was filtered, the filtrate was carefully concentrated, and the residue was pyrolyzed (receiver cooled in a Dry Ice–acetone trap). The distillate was partitioned between ether and water, and the organic layer was washed with dilute hydrochloric acid and water, and dried.

The ether solution containing **32** was hydrogenated directly over Adams catalyst at atmospheric pressure. Processing of the filtrate after catalyst removal gave a small amount of liquid which was purified by molecular distillation at 94–95° (90 mm), 20 mg. This hydrocarbon proved to be identical in all respects with authentic 1,4-dimethylcycloheptane (**33**).

A very similar Hofmann degradation of **30** likewise produced a small amount of liquid hydrocarbon which was identified as **33**.

4-Methylcycloheptanone (36). A mixture of 250 ml of ether and 75 ml of 40% potassium hydroxide solution was cooled to 5°. With cooling and shaking, 21 g (0.20 mol) of N-nitroso-N-methylurea was added in small portions. The resulting yellow layer was decanted and to this solution was added dropwise a solution of 15.0 g (0.134 mol) of 4-methylcyclohexanone in 100 ml of ethanol. The reaction mixture was stirred at room temperature for 6 days and then a few drops of acetic acid were added to decompose the excess diazomethane. The solvent was evaporated *in vacuo* and the residue was distilled through a spinning band column to give 5.0 g (34%) of **36**, bp 83–85° (19 mm); semicarbazone, mp 156–157° (lit.[32] mp 157.5–158°).

1-Methylene-4-methylcycloheptane (32). To a suspension of methyltriphenylphosphonium bromide (14.3 g, 0.04 mol) in 250 ml of anhydrous ether was added dropwise under nitrogen 29.4 ml of 1.7 *M* *n*-butyllithium in hexane (0.0396 mol). The mixture was stirred for 2 hr at which point a solution of 5.0 g (0.0396 mol) of **36** in 100 ml of anhydrous tetrahydrofuran was added dropwise and the suspension was refluxed for 70 hr. The reaction mixture was filtered and partitioned between water and ether, and the ether solution was dried. The solvent was carefully evaporated and the residue was extracted with pentane. The pentane was carefully

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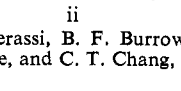
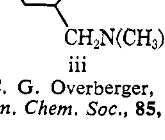
[31] It remained unclear whether this amine was ii or iii.



ii



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[32] C. Djerassi, B. F. Burrows, C. G. Overberger, T. Takekoshi, C. D. Gutsche, and C. T. Chang, *J. Am. Chem. Soc.*, **85**, 949 (1963).

removed and the residual hydrocarbon was distilled to give 3.2 g (65%) of **32** as a colorless liquid, bp 78–80° (57 mm). A small sample of the olefin was further purified by preparative vpc on a 12 ft × 0.25 in. 10% SF96 on Chromosorb G column at 125°.

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.72; H, 13.08.

1,4-Dimethylcycloheptane (33). A 1.1-g (8.9 mmol) sample of **32** was hydrogenated over Adams catalyst at 3 atm. Filtration of the catalyst and evaporation of the ether afforded a liquid which was rigidly purified by preparative scale vpc on the above column at 120°.[33] The infrared and nmr spectra of **33**, as well as its vpc retention time on several columns, were identical with those from the Hofmann degradations.

9-Azabicyclo[3.3.2]decane. A solution of 900 mg (6.5 mmol) of bicyclo[3.3.1]nonan-9-one,[34] 560 mg (8.0 mmol) of hydroxylamine hydrochloride, 3 ml of pyridine, and 10 ml of absolute ethanol was refluxed for 12 hr. The ethanol was evaporated, 10 ml of water was added to the cooled residue, and the organic material was extracted with methylene chloride. Removal of solvent from the dried solution left a solid which when recrystallized from ethanol was obtained as white crystals (500 mg, 50%), mp 156–157°.

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.59; H, 9.98; N, 9.05.

To 1.53 g (0.01 mol) of this oxime in 15 ml of 5 *N* sodium hydroxide solution was added 1.76 g (0.01 mol) of benzenesulfonyl chloride during 15 min. After 30 min, the solution was extracted with chloroform, and the combined organic layers were dried and evaporated. The nitrile which distilled at 110° (0.3 mm) was the product of a second-order Beckmann rearrangement,[35] and was not further examined. The residue was recrystallized from ether (charcoal decolorization) to give 600 mg (34%) of 9-azabicyclo[3.3.2]decan-10-one as white crystals: mp 181–182°; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1650 cm^{-1}.

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.46; H, 9.87; N, 9.02.

A solution of this lactam (600 mg, 6.54 mmol) in 60 ml of dry tetrahydrofuran was refluxed with 270 mg (7.1 mmol) of lithium aluminum hydride for 3 days. The usual work-up yielded 400 mg (73%) of 9-azabicyclo[3.3.2]decane which was converted directly to its benzenesulfonamide: white crystals; mp 80–81° (from ethanol); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1330 and 1165 cm^{-1}.

Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.51; H, 7.53; N, 4.81.

The various spectra of this substance were at wide variance to those exhibited by **28**.

Methoxyazabullvalene–Silver Fluoroborate Complex. A solution of 480 mg (0.30 mmol) of **7** in 20 ml of 1,2-dichloroethane was slowly added to a stirred solution of 580 mg (0.30 mmol) of silver fluoroborate in 20 ml of the same solvent. The white precipitate which formed immediately was separated by filtration and recrystallized three times from isopropyl alcohol. The complex was obtained as white crystals, mp 168° dec (with prior sintering at 115°). The material turned black rapidly on exposure to light.

Anal. Calcd for $C_{10}H_{11}NO \cdot AgBF_4$: C, 33.74; H, 3.12; N, 3.94. Found: C, 33.43; H, 3.26; N, 3.84.

Acknowledgments. We are grateful to Dr. Earl Whipple for several particularly informative discussions. We wish especially to thank the Badische Anilin und Soda Fabrik for the generous gift of cyclooctatetraene which made this work possible.

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[33] As this work was being completed, G. Mann, M. Mühlstädt, R. Müller, E. Kern, and W. Habedall [*Tetrahedron*, **24**, 6941 (1968)] reported an alternate synthesis of the *cis*- and *trans*-1,4-dimethylcycloheptanes.

[34] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

[35] H. K. Hall, *J. Am. Chem. Soc.*, **82**, 1209 (1960).