Unsaturated Heterocyclic Systems. LII.[1]
A General Synthetic Entry to Derivatives of 1H-Azepine

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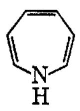
A general synthesis of 1H-azepines has been realized, which consists in the electrophilic addition of iodine isocyanate to easily accessible 1,4-dihydrobenzene derivatives. Cyclization of the resulting iodoisocyanates or their derived carbamates with various bases gives rise to unsaturated aziridines which can be brominated–dehydrobrominated to produce the desired 1H-azepines. This preparative route has been found to be versatile and to allow the ready introduction of alkyl groups on the central ring as well as a variety of substituents on nitrogen. The effect of annelation at the 2,7 positions of a 1H-azepine has been studied. The presence of a tetramethylene bridge is not sufficient to constrain the molecule into the tautomeric azanorcaradiene form; however, a trimethylene bridge serves well in this capacity. The various spectral properties of these cyclic 8π-electron heterocycles are correlated. The preparation of iron carbonyl complexes of these azepines and their fluxional nmr behavior are described.

Hückel molecular orbital calculations predict that 1H-azepine (1) will exhibit marked polyene character.[3] The absence of a driving force for delocalization in this $4n-\pi$ system suggests decreased π-electron stability relative to open-chain congeners. This antiaromaticity[4] in 1H-azepines will be of importance only if the molecule is planar. Recent X-ray studies of the N-*p*-bromobenzenesulfonyl derivative of **1** have confirmed that the molecule clearly exists in a boat conformation with substantial sp^2 character for the nitrogen atom.[5]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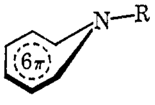
There remains the question of the precise structural makeup and conformation of 1H-azepines as the transition states demanded by their chemical reactions are approached. For example, the azahomoaromatic formulation **2** or the tautomeric azanorcaradiene form **3**[6] can be considered.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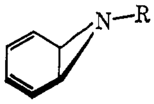
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We have explored in some detail a number of ground- and excited-state properties of these interesting molecules, and in the present paper, we describe a versatile and generally applicable synthesis of 1H-azepines.[7] Subsequent papers are concerned with their thermochemical behavior,[8] selective photoisomerization,[9] and certain cycloadditive transformations.[10]

Although 1H-azepine (**1**) remains unknown, its N-carbethoxy derivative was first prepared in the early 1960s by photolysis[11,12] or pyrolysis[13] of ethyl azidoformate in benzene solution. This ring enlargement is formulated as proceeding *via* an aziridinobenzene intermediate, and the reactive intermediate is now recognized to be singlet carbethoxynitrene.[14] Although this reaction has served well for the synthesis of unsubstituted 1H-azepines, the over-all process suffers from two serious drawbacks. With substituted aromatics such as toluene, bromobenzene, and anisole, a mixture of isomeric 1H-azepines is formed which, in general, defies preparative scale vpc separation.[15] Further, although N-carbalkoxy and N-cyano nitrenes[16] do provide useful yields of the respective azepines upon reaction with benzene, other nitrenes are not effective in this regard.[17] In view of these serious limitations and because of the need in this study for a variety of specifically substituted 1H-azepines, our efforts were concentrated on a few new synthesis of 1H-azepines which would allow for the positionally selective introduction of one or more substituents at the three different ring positions and functional groups other than carbalkoxy and cyano at the nitrogen center.

The synthetic scheme began with the monoaddition of iodine isocyanate[18-20] to 1,4-dihydrobenzene derivatives, which are readily available by means of the Birch reduction of appropriate aromatic compounds. For

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(1) For previous paper in this series, see L. A. Paquette, J. H. Barrett, and D. E. Kuhla, *J. Amer. Chem. Soc.*, **91**, 3616 (1969).

(2) (a) National Institutes of Health Predoctoral Fellow, 1965–1968; (b) National Institutes of Health Predoctoral Fellow, 1966–present.

(3) R. W. Schmid, *Helv. Chim. Acta*, **45**, 1982 (1962).

(4) R. Breslow, J. Brown, and J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(5) I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *ibid.*, **90**, 5023 (1968).

(6) Vogel and his coworkers have established that all presently known reactions of the closely related oxepin system, except photolysis, proceed by way of the arene oxide valence tautomer: E. Vogel and H. Günther, *Angew. Chem. Intern. Ed. Engl.*, **6**, 385 (1967).

(7) A preliminary account of a portion of this work has appeared: L. A. Paquette and D. E. Kuhla, *Tetrahedron Lett.*, 4517 (1967).

(8) L. A. Paquette, D. E. Kuhla, and J. H. Barrett, *J. Org. Chem.*, **34**, 2879 (1969).

(9) L. A. Paquette and D. E. Kuhla, *ibid.*, **34**, 2885 (1969).

(10) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and L. M. Leichter, *ibid.*, **34**, 2888 (1969).

(11) K. Hafner and C. König, *Angew. Chem.*, **75**, 89 (1963).

(12) (a) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **85**, 1200 (1963); (b) W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965).

(13) R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).

(14) W. Lwowski and R. L. Johnson, *Tetrahedron Lett.*, 891 (1967).

(15) (a) L. A. Paquette and J. H. Barrett, unpublished observations; (b) K. Hafner, D. Zinser, and K.-L. Moritz, *Tetrahedron Lett.*, 1733 (1964); (c) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **87**, 4819 (1965); (d) I. C. Paul, J. E. Baldwin, and R. A. Smith, *ibid.*, **88**, 3653 (1966); (e) R. A. Smith, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc.*, *B*, 112 (1967).

(16) F. D. Marsh and H. E. Simmons, *J. Amer. Chem. Soc.*, **87**, 3529 (1965).

(17) (a) R. A. Abramovitch, J. Roy, and V. Uma, *Can. J. Chem.*, **43**, 3407 (1965); (b) See, however, R. A. Abramovitch and V. Uma, *Chem. Commun.*, 797 (1968).

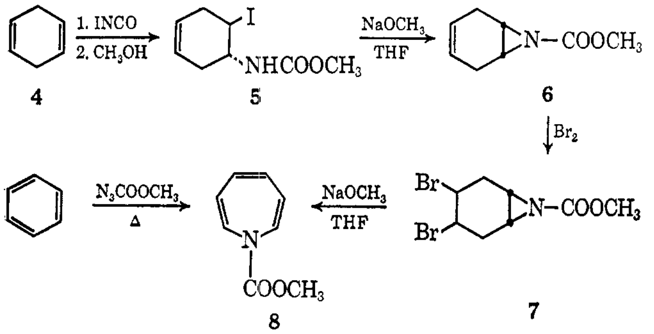
(18) A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967), and earlier papers in this series.

(19) (a) C. G. Gebelein and D. Swern, *ibid.*, **33**, 2758 (1968); (b) B. E. Grimwood and D. Swern, *ibid.*, **32**, 3665 (1967); and previous papers from this laboratory.

(20) (a) G. Drefahl and K. Ponsold, *J. Prakt. Chem.*, **23**, 136 (1964); (b) R. R. Wittekind, J. D. Rosenau, and G. I. Poos, *J. Org. Chem.*, **26**, 244 (1961); (c) G. Drefahl and K. Ponsold, *Chem. Ber.*, **93**, 519 (1960).

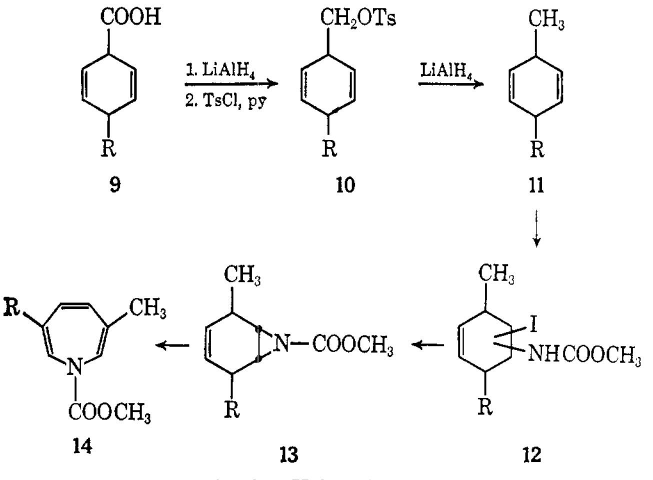
example, treatment of 1,4-dihydrobenzene (**4**) with this pseudohalogen, and finally with refluxing methanol, produced the crystalline *trans*-iodocarbamate **5** in 54% yield (Scheme I). Cyclization of **5** with powdered sodium methoxide in dry tetrahydrofuran afforded aziridine **6**. Bromination of **6** in methylene chloride solution at −70° and exposure of the crude dibromide (**7**) thus formed to powdered methoxide in refluxing tetrahydrofuran solution for 2 hr led to N-carbomethoxyazepine (**8**). The structure of **8** followed from its spectral parameters and was confirmed by independent synthesis from benzene and methyl azidoformate.

SCHEME I



1,4-Dihydrotoluene (**11a**) and 1,4-dihydro-*p*-xylene (**11b**) were accessible by virtue of the directing capability of a carboxyl group on the course of alkali metal–ammonia reductions.[21,22] Thus, 1,4-dihydrobenzoic acid (**9a**) and 1,4-dihydro-*p*-toluic acid (**9b**) were converted using the method of Nelson,[23] into the desired hydrocarbons (Scheme II). Sequential addition of iodine isocyanate and methanol to **11a** and **11b** gave rise to iodocarbamates **12a** (substitution pattern unknown) and **12b**, which, after cyclization, bromination, and dehydrobromination, were transformed into 1-carbomethoxy-3-methylazepine (**14a**) and 1-carbomethoxy-3,6-dimethylazepine (**14b**), respectively.

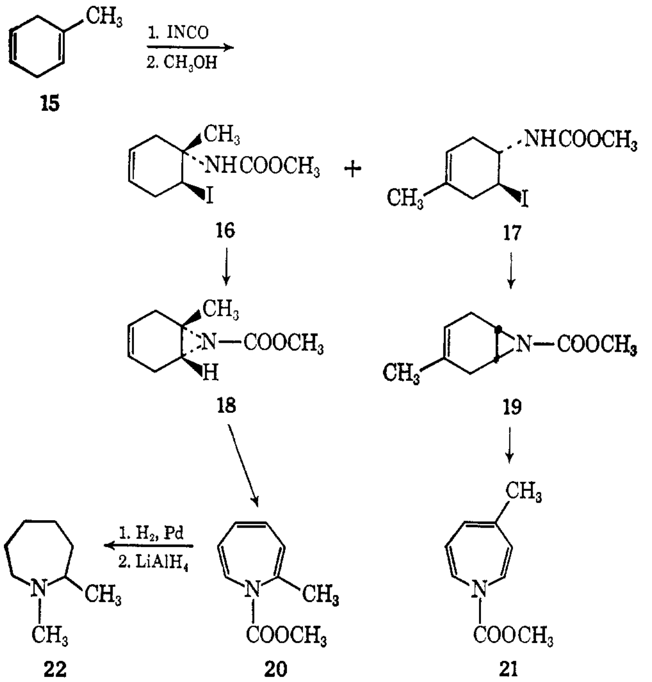
SCHEME II



a series: R = H; b series: R = CH$_3$

The effect of alkyl substitution on the vinyl carbons of the 1,4-cyclohexadiene structure was next considered. Exposure of a tetrahydrofuran solution of 2,5-dihydrotoluene (**15**) to iodine isocyanate under the standard heterogeneous conditions (silver cyanate and iodine), with subsequent methanolysis, resulted in the formation of a mixture of crystalline carbamates **16** and **17** in yields of 54% and 10%, respectively (Scheme III). The predominance of **16** over **17** was expected from the stabilities of the two possible iodonium ions. It has been shown that variously substituted olefins react with iodine isocyanate at significantly differing rates.[19,24] A typical relative reactivity order is 2,3-dimethyl-2-butene, 38; 2-methyl-1-pentene, 12.5; *trans*-3-hexene, 5.7; cyclohexene, 1.0; and 1-hexene, 0.5—in good agreement with the normal electrophilic reactivity patterns exhibited by such hydrocarbons. As will soon become evident, however, the reactivity of iodine isocyanate is markedly affected by steric influences.

SCHEME III



The iodocarbamate mixture was separated by chromatography. The availability of **16** and **17** on a preparative scale permitted independent transformation of each urethane to the 2-methyl (**20**) and 4-methyl (**21**) derivatives of 1-carbomethoxyazepine, respectively. As in the previous examples, the azepines were isolated free of contamination by positional isomers. Hydrogenation of **20** followed by reduction with lithium aluminum hydride gave 2,N-dimethylhexamethylenimine (**22**), confirming the gross structure of the substance.

A similar reaction of 2,3-dimethyl-1,4-dihydrobenzene (**23**) gave an oil, from which two compounds were isolated after column chromatography. The first product, isolated in 10% yield, was the iodocarbamate **24**. This colorless solid showed infrared absorption at 3425

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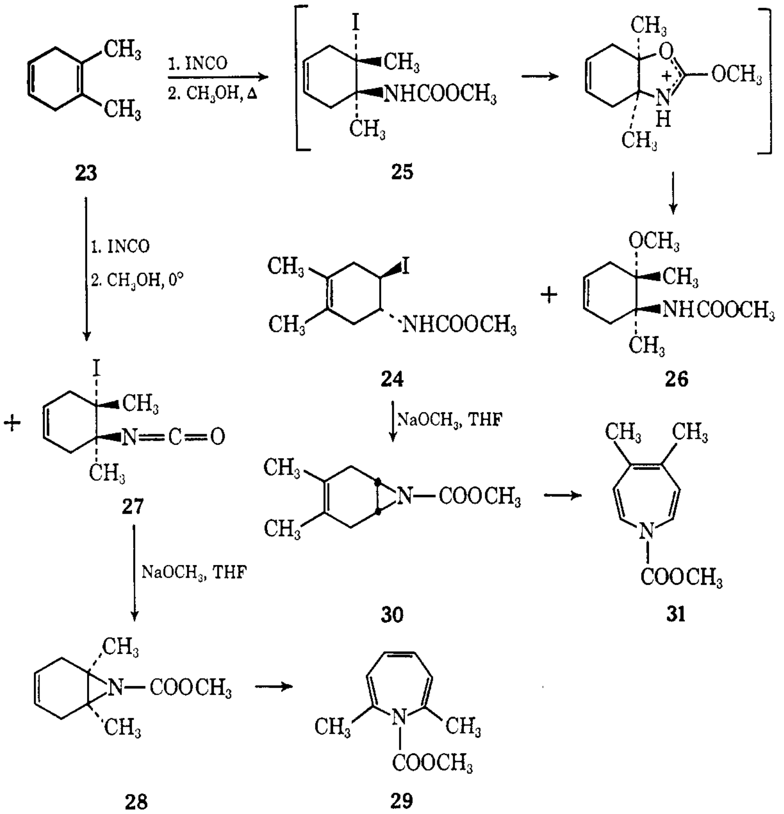
(21) Products derived from benzene derivatives bearing electron-donating substituents are 1-substituted 2,5-dihydrobenzenes, while those derived from aromatics having electron-withdrawing substituents are 1-substituted 1,4-dihydrobenzenes: (a) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 64–71; (b) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); (c) A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958).

(22) M. E. Kuehne and B. F. Lambert, *Org. Syn.*, **43**, 22 (1963).

(23) N. A. Nelson, J. H. Fassnacht, and J. U. Piper, *J. Amer. Chem. Soc.*, **83**, 206 (1961).

(24) C. G. Gebelein and D. Swern, *Chem. Ind.* (London), 1462 (1965).

Scheme IV



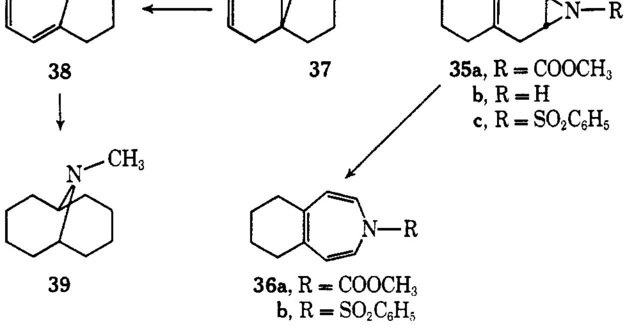
and 1725 cm^{-1} and an nmr spectrum fully compatible with the proposed structure. The major product (39% yield), a colorless oil, was shown by nmr to be **26**. The *trans* disposition of the urethan and methoxyl substituents has been assigned on the basis of the earlier observations that *trans*-2-halo-N-acylamines are converted to *cis*-oxazolines upon gentle heating[25] and that *trans*-β-halocarbamates afford *cis*-2-oxazolidones when pyrolyzed at 120–200°.[18,26] Thus, the initially produced *trans*-iodocarbamate **25** is presumably solvolyzed with anchimeric assistance from the carbamate group and subsequent backside attack of methanol at that site (Scheme IV).

The formation of **26** could be completely suppressed by treatment of the mixture of intermediate iodoisocyanates with methanol at 0°, which led to a 10% yield of **24** and a 63% yield of a pungent, waxy solid shown to be **27**. Clearly, under these reaction conditions, the less hindered isocyanate remains subject to the addition of methanol, whereas the isomeric tertiary isocyanate is virtually unreactive. Also, since the isocyanate function is a poor neighboring group, the proximate iodo substituent in **27** does not undergo assisted solvolysis.

When treated with 1 equiv of powdered sodium methoxide in tetrahydrofuran solution, **27** was converted quantitatively in a vigorously exothermic reaction to the carbomethoxy aziridine **28**. Bromination–dehydrobromination of **28** gave the 2,7-dimethyl-substituted azepine **29** in quantitative yield. The further transformation of **24** in the standard manner afforded the isomeric 4,5-dimethyl congener **31** without difficulty.

In view of these promising results, we turned our efforts to the synthesis of annelated 1H-azepine derivatives. As in the case of **23**, reaction of 1,4-dihydrotetralin (**32**) with ethereal iodine isocyanate and then methanol at −10° produced a mixture of iodoisocyanate **33** and iodocarbamate **34** (Scheme V). In contrast to the previous example, however, the two addition compounds were produced in yields of 16% and 69%, respectively. Thus, although the substitution patterns of the double bonds in **23** and **32** are virtually identical, the usual kinetically favored addition of the pseudohalogen to the more highly substituted π bond

Scheme V



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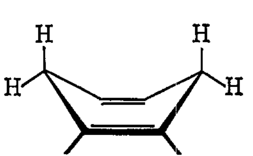
[25] S. Winstein and R. Boschan, *J. Amer. Chem. Soc.*, **72**, 4669 (1950).

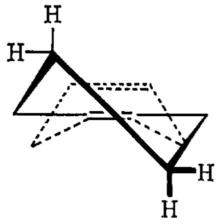
[26] E. Katchalski and D. B. Ishai, *J. Org. Chem.*, **15**, 1067 (1950).

(seen, for example, in **23**) is disfavored in **32** by a factor greater than 10.

The wide divergence in reactivity is a result of the differing steric environments of the tetrasubstituted olefin linkages. In the case of **23**, the molecule can be considered to be nearly flat[27] with some small deviation of the ring into a boat conformation (models of molecules such as **23c** suggest a very small energy barrier to boat–boat interconversion).[28] Steric inhibition to the approach of the bulky iodonium ion is expected to be minimal. By comparison, the tetramethylene bridge in **32** must adopt a half-chair conformation,[29] with the result that the π bond is effectively shielded on both sides (see **32c**). Support for these conclusions comes from a study of the reaction of 1,4-dihydroindane (**40**) with iodine isocyanate. Dreiding models of **40** indicate an almost planar conformation with little, if any, steric hindrance. Indeed, in this example the normal reactivity pattern does reemerge, with 32% iodoisocyanate **41** and 7% iodocarbamate **42** being produced (Scheme VI).

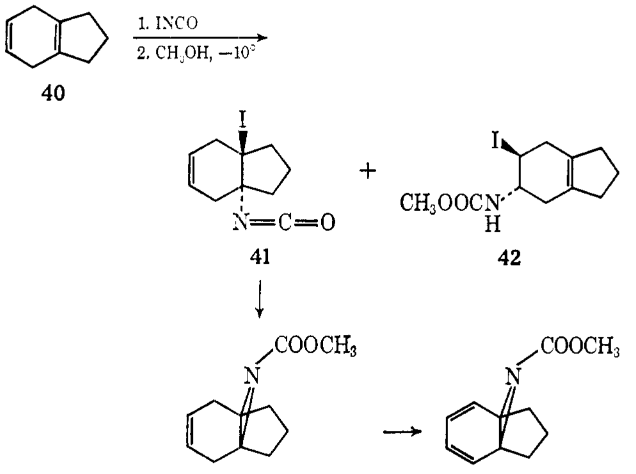


23c



32c

SCHEME VI

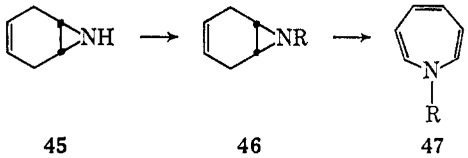


When iodoisocyanate **33** was subjected to similar methoxide treatment, aziridine **37** was isolated in excellent (92%) yield. As in the previous example, **37** was found to be uncontaminated with other possible by-products. By sequential treatment of **37** with bromine and sodium methoxide, there was produced a colorless solid (**38**) which was found to be uniform and to exist solely as the 1H-azepine tautomer. The structure of **38** was assigned on the basis of ultraviolet and nmr spectroscopy and by a three-step conversion to the known 11-methyl-11-azabicyclo-[4.4.1]undecane (**39**).[30,31]

The effect of diminishing the extent of annelation in azepine **38** from four to three methylene units was realized with the preparation of **44**, which exists as the aziridine tautomer (see above). This substance is of particular interest because it represents the only azanorcaradiene known to the present time, and for the fact that **44** displays a chemistry which differs appreciably from that of the closely related 1H-azepines.[8b,10] The result of bridging the azepine ring at the 2 and 7 positions with a methylene chain having a sufficiently small number of members is therefore to force the formation of an iminobenzene (**44**). This result parallels the earlier observations recorded for the corresponding bridged norcaradiene,[32] benzene oxide,[33] and 7-azabicyclo[4.2.0]octa-2,4,7-triene congeners.[34] In contrast, although azepine **38** is appreciably strained, the azanorcaradiene tautomer cannot be detected spectroscopically (nmr) over a wide temperature range.[35] This property is shared by the related cycloheptatriene analog,[32] but is at variance with the characteristics of the oxygen[33] and –N=C(OR)– bridged compounds.[34]

The azepine obtained from iodocarbamate **34** proved to be a heavy viscous oil which was not satisfactorily purified by distillation and chromatography (column and vapor phase). Saponification and decarboxylation of **35a** did, however, give rise to aziridine **35b**, which was conveniently transformed to the crystalline N-benzenesulfonylazepine **36b**.

The method of nitrogen functionalization has proven to be quite versatile and has permitted the synthesis of such 1H-azepines as **47a–47d**. With the successful preparation of these compounds, it becomes clear that ready access to a large number of nitrogen-substituted azepines is now available without concern for the reactivity, or unreactivity, of the derived nitrene.



a, R = SO_2CH_3; b, R = $SO_2C_6H_5$
c, R = p-$SO_2C_6H_4Br$; d, R = $PO(C_6H_5)_2$

Ultraviolet Spectra.—In general, the ultraviolet spectra of 1H-azepine derivatives consist of three major bands comprising a low-intensity maximum of variable position in the 285–330-mμ region, a medium-

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[27] From an investigation of the Raman and infrared spectra of 1,4-cyclohexadiene, Gerding and Haak [*Rec. Trav. Chim.*, **68**, 293 (1949)] concluded that the molecule is nearly flat. See also the recent nmr studies of E. W. Garbisch, Jr., and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1968).

[28] (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 125; (b) W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 3126 (1964).

[29] Reference 28a, p 109.

[30] A. C. Cope, R. J. Cotter, and G. G. Roller, *J. Amer. Chem. Soc.*, **77**, 3590 (1955).

[31] It is important to emphasize that chemical transformations of a molecule such as **38** will not necessarily differentiate between azepine and aziridine valence tautomers, but merely provide confirmation of the gross structure.

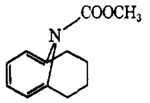
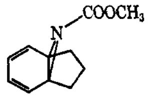
[32] E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).

[33] E. Vogel and H. Günther, *Angew. Chem. Intern. Ed. Engl.*, **6**, 385 (1967).

[34] L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **90**, 3898 (1968).

[35] As discussed in a later paper,[8b] **38** is subject to an irreversible thermal reaction above 150°.

TABLE I
ULTRAVIOLET MAXIMA OF 1H-AZEPINES

Compd	Color	N substituent	Ring substituent(s)	λ_{max}, mμ (ε)	
				n-Hexane	95% ethanol
8	Dark orange	$-COOCH_3$		210.5 (23,075), 238 sh (3,145), 330 (570)	207.5 (22,000), 242 sh (2,740), 318 (675)
14a	Yellow-orange	$-COOCH_3$	3-CH_3	212 (23,560), 238 sh (3,030), 321 (640)	212 (23,780), 238 sh (2,425), 309 (745)
14b	Pale yellow	$-COOCH_3$	3,6-$(CH_3)_2$	214.5 (22,780), 242 sh (2,695), 316 (525)	214.5 (22,820), 244 sh (2,240), 301 (674)
20	Very pale yellow	$-COOCH_3$	2-CH_3	211.5 (21,870), 302 (1,015)	209.5 (23,900), 291 (1,615)
21	Dark orange	$-COOCH_3$	4-CH_3	210.5 (22,740), 239 sh (3,210), 323 (675)	207 (24,980), 241 sh (4,720), 309 (975)
29	White	$-COOCH_3$	2,7-$(CH_3)_2$	215 (19,600), 230 sh (3,830), 285 (2,110)	208 (21,00), 275.5 (2,510)
31	Very pale yellow	$-COOCH_3$	4,5-$(CH_3)_2$	247 (5,480), 313 (1,120)	208 (22,600), 251 (4,980) 306 (1,180)
36b	Pale yellow	$-SO_2C_6H_5$	4,5-$(CH_2)_4$	*a*	205 (20,000), 274 (3,265) 350 (350)
47a	Yellow	$-SO_2CH_3$		*a*	205 (17,200), 307 (760)
47b	Pale yellow	$-SO_2C_6H_5$		*a*	205 (22,200), 266 (3,000)
47c	Yellow	*p*-$SO_2C_6H_4Br$		*a*	233 (13,200), 268 sh (3,800)
47d	Yellow	$-PO(C_6H_5)_2$		*a*	238 (9,860), 261 (2,130), 267 (2,220), 273 (1,750), 310 sh (590)
38	White			213 (18,965), 258 (2,690)	209 (20,650), 252 (3,130)
44	White			246 (2,980), 255 (2,870)	242 (2,410) 258 (2,850)

[a] Not soluble.

intensity band at 240–247 mμ, and strong end absorption (Table I). The medium-intensity band is customarily seen as a shoulder, although in certain examples it is not discernible above the intense base absorption. The long-wavelength band is solvent dependent and undergoes an hypsochromic shift when the polarity of the solvent is increased. Not unexpectedly, the position of the various bands is quite subject to the nature of the substituent on nitrogen. Somewhat less anticipated was the observation that the location of the long-wavelength band is notably dependent upon substitution of the ring with alkyl groups, particularly at the 2 and 7 positions. When this band is seen to reach a maximum at 305–330 mμ, the absorption extends to about 400–430 mμ and gives such azepines their yellow to orange color. In contrast, no tailing into the visible region is seen when this band is blue shifted to below 300 mμ, and such azepines, *e.g.*, **29**, are colorless in appearance. The blue shift is even more marked in the annelated azepine **38**, which is also a white solid. It may be concluded, therefore, that the electronic transition energy of this azepine chromophore is quite sensitive to distortions in molecular geometry and is probably associated with the interaction of the nitrogen electron pair with the carbocyclic π system. The greater the steric hindrance about the substituted nitrogen atom, the more the particular 1H-azepine is constrained into the boat conformation, and the less favorable is the electronic interaction. The bridged azepine **38** is, of course, markedly constrained in this fashion.

Significantly, the ultraviolet spectra of **44** differ substantially from those of 1H-azepines. The substance exhibits spectra which are solvent independent and which are characteristic of the 1,3-cyclohexadiene chromophore. Perhaps the most suitable reference substance for **44** is 8,9-indanoxide, which in isooctane displays λ_{max} 258 mμ (ε 4900).[33,36]

Nmr Spectra.—The nmr spectra of a representative number of 1H-azepines are illustrated in Figure 1. In azepines substituted only on nitrogen, it is to be expected that the differing electron density at the three types of ring carbon atoms will profoundly affect the ring proton chemical shifts. Schmid's molecular orbital calculations[3] have indicated that the β carbon bears the highest charge density; on this basis, the β protons are expected to be more shielded than the remaining vinyl protons.[37] That such is the actual situation is clearly demonstrated in Figure 1A. The protons α to the nitrogen atom are located in the center of the multiplet; the over-all pattern is seen to be a doublet which is skewed in the direction of the β-proton absorption. The slight broadening observed is most likely caused by long range coupling effects with the γ protons which appear at lowest field.

Symmetrical dialkyl substitution of the ring results in simplification of the nmr spectrum. As can be seen

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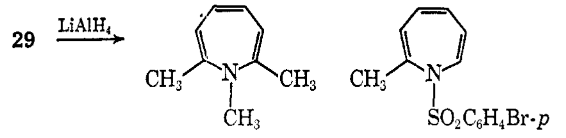
(36) For a survey of additional bridged cyclohexadienes, see G. Maier *Angew. Chem. Intern. Ed. Engl.*, **6**, 402 (1967).

(37) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 256.

in Figure 1B, methyl substituents in the 4,5 positions reduce the spectrum to a doublet of doublets (J = 7.5 Hz). Replacement of hydrogen by methyl groups at the 3 and 6 positions causes the most dramatic spectral alteration, the α- and γ-proton pairs appearing as singlet absorptions. The greater line broadening apparent in the singlet due to the α protons is congruent with allylic coupling to the methyl groups not available to the γ positions because of the fixed nature of the π bonds.

In the 2,7-dimethyl isomer, the β protons appear as a broadened multiplet. The situation is much the same in the annelated azepine **38**. Perhaps the most remarkable feature of these spectra (Figures 1D and 1E) is the marked downfield shift of the β protons. Since the nitrogen atom in ring-unsubstituted 1H-azepines is sp^2 hybridized, there is substantial interaction of the nonbonded nitrogen electrons with the carbonyl group and with the triene π system. For maximum overlap with the carbonyl function, the carbon and oxygen atoms must lie in the plane defined by C_2, C_7, and N. The steric effect of substituents at C_2 and C_7 reduces this overlap, leading to a change in hybridization of the nitrogen atom from sp^2 toward sp^3 and therefore a downfield shift of the β protons.

The strong dependence of the chemical shifts of the vinyl protons, and in particular the β protons, upon the nature of the nitrogen substituent is further seen when comparing the spectrum of **8** (Figure 1A) with those of N-methylazepine ($\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.5–5.0),[38] 1,2,7-trimethylazepine (**48**) [$\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.05 (β protons) and 5.70 (γ protons)], **47c** ($\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.74–5.87), **49** ($\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.75–6.15), and **36b** doublets, J = 7.5 Hz, centered at [$\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.62 (β) and 5.95 (γ)].



48 49

Especially noteworthy is the fact that all of the nmr spectra of these 1H-azepines proved to be invariant over a substantial temperature range (−90° to 130°). This lack of change with temperature points to the absence of valence tautomerism of the 1H-azepine–benzenimine type.

The nmr spectrum of **44** (Figure 1F) clearly differs from those of the azepines, and those of a number of 1,3-cyclohexadienes.[39]

Mass Spectra.—The overwhelmingly favored electron impact fragmentation of ring unsubstituted 1H-azepines occurs between the ring nitrogen atom and the 1 substituent to give the corresponding azatropylium cation **51** (base peak, m/e 92).[40] Although the azepinium molecular ion **50** is always seen, its intensity is variable within the series, presumably because of a propensity for conversion to cation **51** in certain derivatives (see Table II). Another feature of the spectra is due mainly to loss of the elements of HCN from **51**; the particle thus formed, which is presumably the cyclopentadienyl cation, decomposes further by the loss of acetylene to yield the cyclopropenium cation. Alternate bond reorganization in **51** can also lead to **52**, from which the elements of acetylene can be expelled to pro-

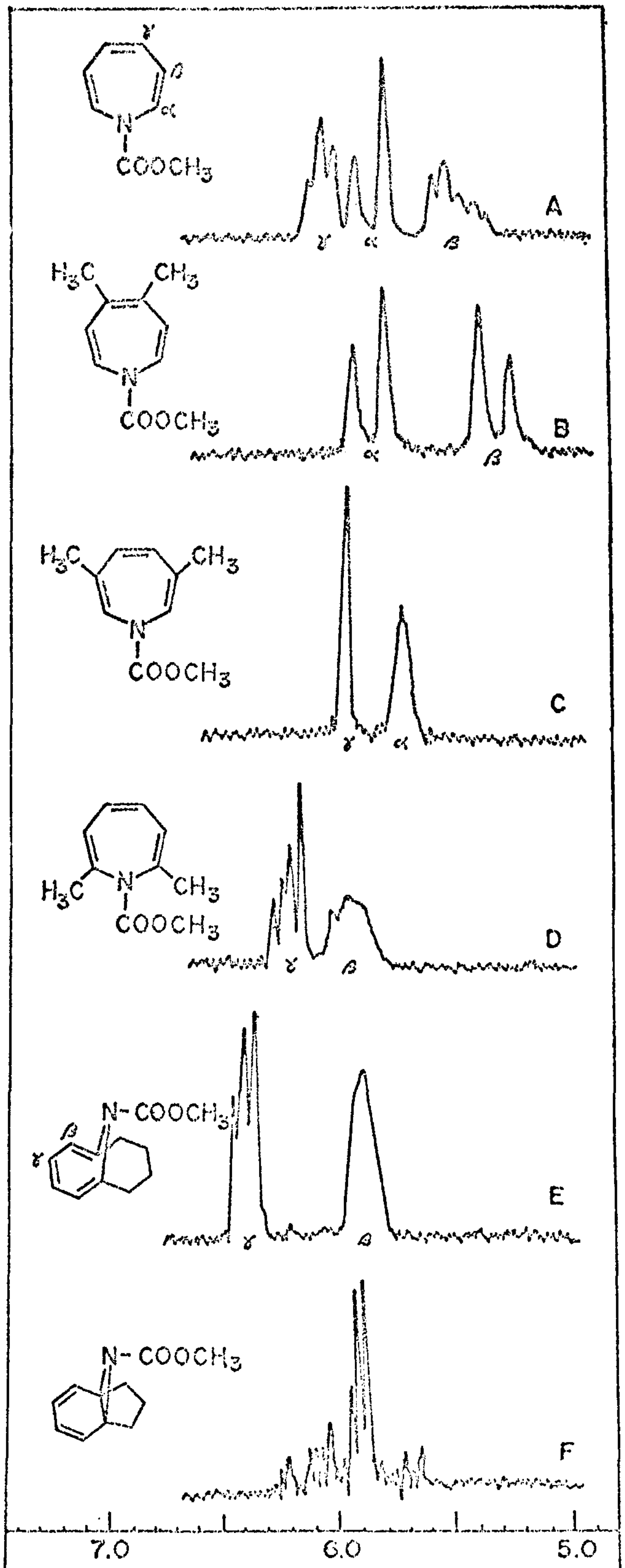


Figure 1.—60-MHz nmr spectra of representative 1H-azepines in deuteriochloroform (δ units).

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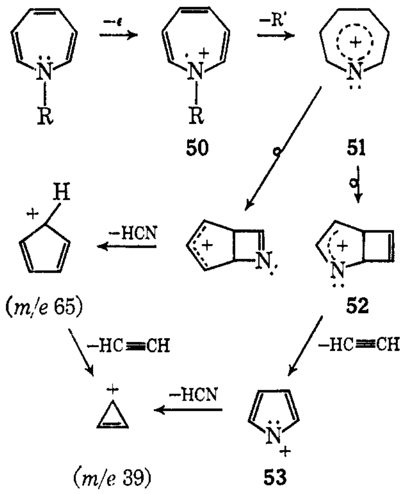
[38] K. Hafner and J. Mondt, *Angew. Chem.*, **78**, 822 (1966).

[39] H. Günther and H.-H. Hinrichs, *Ann.*, **706**, 1 (1967); *Tetrahedron Lett.*, 787 (1965).

[40] The lone exception to this generalization noted in this study is found in the case of **47d**, where the diphenylphosphinoxy group appears to control the course of the fragmentation.



duce **53**. However, this mode of cleavage does not seem to be of general importance. The mass spectral fragmentation of 1H-azepines parallels the behavior of anilines under such conditions, since the latter compound fragment by way of intermediate azepinium ions.[41]

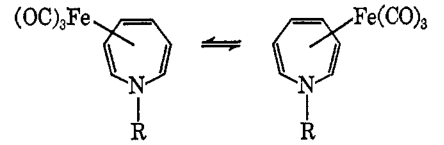
TABLE II

MASS SPECTRAL DATA FOR VARIOUS FRAGMENT IONS OF SELECTED 1H-AZEPINES

Compd	m/e (% relative abundance)
8	39 (25), 59 (11), 65 (73), 92 (100), 93 (10), 119 (15), 151 (63)
14a	39 (15), 44 (28), 51 (18), 77 (17), 78 (30), 91 (18), 104 (44), 105 (23), 106 (38), 132 (30), 133 (100), 165 (41)
14b	39 (23), 77 (38), 91 (41), 93 (33), 105 (20), 118 (32), 119 (25), 120 (100), 132 (41), 146 (25), 147 (84), 179 (93)
20	39 (15), 51 (14), 65 (14), 77 (18), 78 (30), 91 (15), 104 (50), 105 (25), 106 (55), 132 (30), 133 (100), 165 (140)
21	40 (45), 44 (70), 51 (20), 77 (25), 78 (20), 104 (20), 106 (30), 132 (40), 133 (100), 165 (50)
29	51 (11), 56 (12), 77 (30), 78 (11), 79 (36), 91 (10), 120 (100), 179 (35)
31	39 (20), 41 (13), 51 (15), 76 (29), 91 (27), 93 (23), 118 (16), 120 (100), 132 (57), 147 (72), 179 (96)
36a	39 (36), 41 (30), 43 (50), 44 (72), 51 (20), 55 (21), 57 (23), 65 (25), 67 (32), 77 (29), 78 (30), 79 (26), 91 (82), 93 (100), 94 (35), 104 (80), 128 (25), 132 (70), 150 (19), 205 (25)
36b	77 (19), 91 (19), 146 (100), 287 (58)
38	91 (19), 117 (15), 132 (48), 146 (100), 173 (34), 205 (44)
44	117 (68), 130 (21), 132 (100), 159 (42), 191 (42)
47a	39 (20), 65 (70), 78 (15), 92 (100), 93 (18), 171 (15)
47b	39 (15), 65 (38), 92 (100), 233 (15)
47d	51 (14), 65 (17), 77 (26), 92 (25), 201 (100), 243 (48)
49	39 (25), 65 (37), 77 (35), 106 (100), 327 (5)

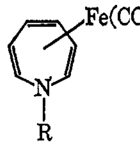
The mass spectra of 1-carbomethoxy-1H-azepines bearing the one or more alkyl groups at the 2, 3, or 4 positions show that loss of methanol is also a very significant process. Although of considerable mechanistic interest, these observations have not been studied to an extent sufficient to warrant mechanistic speculation.

Iron Tricarbonyl Complexes.—A number of π-bonded olefin complexes of transition metals are known in which the free ligand has π electrons to offer in excess of the electronic requirements of the metal.[42] Several of these π-type complexes are now recognized to be subject to degenerate valence tautomerism by virtue of the capability of the metal atom to move from one diene or triene unit to the next. The best known species of this type are the cyclooctatetraene-derived metal carbonyls. Iron tricarbonyl complexes of 1H-azepines were considered by us to be possible new examples of such fluxional molecules, since the metal could take up two alternative coordination positions on the seven-membered heterocyclic ring as shown in **54a** and **54b**.



54a **54b**

Brief treatment of N-carbomethoxyazepine (**8**) with iron enneacarbonyl in warm hexane produced in 69% yield the air stable, highly crystalline iron tricarbonyl complex **55a**. Similar reaction of the N-carbophenoxy and N-methanesulfonyl (**47a**) analogs gave rise to **55b** and **55c**, respectively. Fischer and Rühle[43] have found that irradiation of N-carbethoxyazepine and iron pentacarbonyl in tetrahydrofuran solution gave the derived $Fe(CO)_3$ complex. We have applied their procedure to the synthesis of **55a**, **55d**, and **55e**, and conclude that the iron enneacarbonyl method is simpler and leads to cleaner products. Both procedures failed in attempts to prepare iron tricarbonyl derivatives of alkyl-substituted azepines. Intractable black gums or highly colored green solutions (from which a quantity of azepine could generally be recovered) were obtained.



55a, R = $COOCH_3$
b, R = $COOC_6H_5$
c, R = SO_2CH_3
d, R = $COOC(CH_3)_3$
e, R = $COOCH_2C_6H_5$

The proton nmr spectra of the various iron tricarbonyl complexes were dramatically temperature dependent. This characteristic was also recognized independently by Günther and Wenzl,[44] who have reported the details of an equally thorough study with N-carbethoxyazepineiron tricarbonyl. Since our results and conclusions do not differ from those of the above

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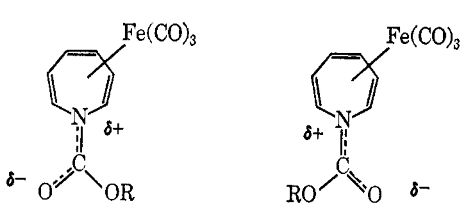
[41] K. L. Rinehart, Jr., A. C. Buchholz, and G. E. VanLear, *J. Amer. Chem. Soc.*, **90**, 1073 (1968); A. V. Robertson, M. Marx, and C. Djerassi, *Chem. Commun.*, 414 (1968).

[42] For leading references, see (a) J. E. Mahler, D. A. K. Jones, and R. Pettit, *ibid.*, **86**, 3589 (1964); (b) G. F. Emerson, J. E. Mahler, R. Pettit, and R. Collins, *ibid.*, **86**, 3590 (1964); (c) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965); (d) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *ibid.*, **88**, 3444 (1966); (e) F. A. Cotton, J. W. Faller, and A. Musco, *ibid.*, **88**, 4506 (1966); (f) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966); (g) F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *ibid.*, **89**, 2489 (1967); (h) F. A. L. Anet, *ibid.*, **89**, 2491 (1967); (i) R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, *ibid.*, **89**, 6864 (1967); (j) F. A. Cotton and A. Musco, *ibid.*, **90**, 1444 (1968); (k) R. B. King, *J. Organometal. Chem.*, **8**, 129 (1967).

[43] E. O. Fischer and H. Rühle, *Z. Anorg. Allg. Chem.*, **341**, 137 (1965).

[44] H. Günther and R. Wenzl, *Tetrahedron Lett.*, 4155 (1967).

workers, we will only summarize the pertinent points of our study.[45] At room temperature, the onset of the equilibrium **54a** $\leftrightarrows$ **54b** has already begun, as seen by the broad coalesced peaks which characterize the spectra. In the vicinity of 65–85°, the movement of the iron tricarbonyl residue about the two possible positions becomes sufficiently rapid that a symmetrical spectrum of the AA'XX'YY' type results. At 0°, there is a well-defined spectrum indicative of the fixed structure **54a** (or alternatively **54b**). In the N-carbalkoxy derivatives, further lowering of the probe temperature (to −30° and −60°) is seen to cause new line broadening, coalescence, and finally the appearance of additional signals. Such observations can be best attributed to the "freezing out" of the normally rapid rotation of the carbalkoxy function about the C–N bond (see **56a** and **56b**); when this rotational process is sufficiently retarded, the chemical shifts of the α, α', β, β', γ, and γ' protons will understandably be different and unique and will give rise to the observed spectra. As anticipated, this last consideration does not apply to the N-methanesulfonyl derivative **55c**.



56a **56b**

Thus, the 1H-azepineiron tricarbonyls represent new examples in the rapidly expanding number of fluxional π-bonded organometallic molecules.

Experimental Section[46]

Methyl N-(*trans*-2-Iodo-4-cyclohexene)carbamate (5).—To a cooled (−20°) stirred slurry consisting of 25.0 g (0.312 mol) of 1,4-dihydrobenzene (**4**), 60.0 g (0.40 mol) of freshly prepared silver cyanate,[47] and 600 ml of anhydrous tetrahydrofuran was added 76.0 g (0.30 mol) of iodine. The reaction mixture became dark brown, but developed a canary-yellow hue after stirring for 4 hr at this temperature. The reaction mixture was allowed to warm to room temperature, at which point the inorganic salts were removed by filtration and the filtrate was concentrated to about 75–100 ml *in vacuo*. Anhydrous methanol (600 ml) was added and the orange solution was refluxed for 1.5 hr. The methanol was evaporated under reduced pressure and the residue was dissolved in 400 ml of ether and washed with a water solution (200 ml) of sodium sulfite (5 g). The layers were separated and the aqueous phase was extracted with two additional 100-ml portions of ether. The combined organic layers were dried and evaporated and the resulting yellow gummy solid was recrystallized from methylene chloride–hexane. There was obtained 45.2 g (53.6%) of **5** as a fluffy white solid, mp 99.5–100.5° (lit. mp 93–95°,[18] 100–101°[19b]); ir $\nu_{\max}^{\mathrm{CCl_4}}$ 3365, 3268 (N–H), and 1733 cm^{-1} (C═O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.28–5.85 (br m, 2 H, vinyl protons), *ca.* 5.3 (br, 1 H, N-H), 3.73–4.58 (m, 2 H, CHI and CHN), 3.66 (s, 3 H, —OCH$_3$), 1.81–3.05 (m, 4 H, allylic protons).

Anal. Calcd for $C_8H_{12}INO_2$: C, 34.18; H, 4.30; N, 4.98. Found: C, 34.11; H, 4.36; N, 4.78.

N-Methylcarbamoyl-1,2-iminocyclohex-4-ene (6).—A mixture of 18.2 g (0.065 mol) of **5** and 3.52 g (0.065 mol) of freshly prepared powdered sodium methoxide in 100 ml of anhydrous tetrahydrofuran was refluxed with rapid stirring for 1 hr. The solvent was removed *in vacuo*, and the residue was dissolved in 300 ml of ether. The ether solution was washed carefully with water, dried, and evaporated. Distillation of the residue afforded 7.85 g (79.1%) of **6** as a colorless liquid, bp 63–65° (0.1–0.2 mm), $n^{25}\mathrm{D}$ 1.4902; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1720 cm^{-1} (>C═O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.08–5.30 (br s, 2 H, vinyl protons), 3.59 (s, 3 H, —OCH$_3$), 2.39–2.71 (m, 2 H, CHN), 2.11–2.43 (br d, 4 H, allylic protons).

Anal. Calcd for $C_8H_{11}NO_2$: C, 62.72; H, 7.24; N, 9.14. Found: C, 63.09; H, 7.47; N, 9.08.

N-Carbomethoxyazepine (8). A. Bromination–Dehydrobromination of 6.—Bromine (3.2 g, 0.02 mol) in methylene chloride (15 ml) was added dropwise to a solution of 3.34 g (0.02 mol) of **6** in 20 ml of the same solvent cooled to −78°. After completion of the addition, the solution was allowed to warm to room temperature and the solvent was removed *in vacuo*. Recrystallization of the remaining solid from ether–pentane gave 3.12 g (76.4%) of **7** as white crystals, mp 69–70.5°; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1727 cm^{-1} (C═O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.79–4.34 (m, 2 H, CHBr), 3.59 (s, 3 H, —OCH$_3$), 2.03–3.06 (complex series of bands, 6 H, CHN and methylene protons).

Anal. Calcd for $C_8H_{11}Br_2NO_2$: C, 30.70; H, 3.54; N, 4.48. Found: C, 30.70; H, 3.68; N, 4.30.

A solution of 3.0 g (9.6 mmol) of **7** in 100 ml of anhydrous tetrahydrofuran was treated with 1.04 g (0.0192 mol) of powdered sodium methoxide and the mixture was refluxed for 2 hr. Workup in a manner paralleling that employed for **6** gave 970 mg (66.9%) of **8** (99% purity) as an orange liquid, bp 59–61° (0.2 mm), $n^{25}\mathrm{D}$ 1.5379; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1735 cm^{-1} (C═O); identical in all respects with the sample prepared by method B.

B. Carbomethoxynitrene–Benzene Method.—A solution of 15.0 g (0.14 mol) of methyl azidoformate in 400 ml of benzene was placed in a sealed tube which was heated at 135° for 5 hr. The benzene was subsequently evaporated under reduced pressure. From seven such reactions, there was obtained 173 g of crude product. Chromatography of this material on 250 g of Florisil and elution with ether until the yellow eluate no longer appeared, followed by fractional distillation of this eluate, afforded 52 g (33%) of **8**, bp 62–63° (0.05 mm), $n^{25}\mathrm{D}$ 1.5367.

Anal. Calcd for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.23; H, 5.79; N, 9.13.

1,4-Dihydrotoluene (11a).—To a rapidly stirred slurry of 3.94 g (0.103 mol) of lithium aluminum hydride in 300 ml of anhydrous ether was added dropwise a solution of 53.5 g (0.203 mol) of **10a**[23] in 150 ml of ether. The mixture was refluxed overnight, cooled in an ice bath, treated sequentially with 4 ml of water, 4 ml of 30% sodium hydroxide solution, and 12 ml of water, and filtered. The residue was washed well with ether, and the combined filtrate and washings were fractionally distilled through a vacuum-jacketed, 100-cm glass helix packed column and a fraction boiling at 95–105° was collected. Redistillation of this material through a spinning-band column yielded 11.76 g (61.2%) of **11a**, bp 102.5–103.0°.

Anal. Calcd for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.16; H, 10.64.

Methyl (*trans*-2-Iodo-6-methyl-4-cyclohexene)carbamate (12a and Isomers).—From 4.08 g (0.0435 mol) of **11a**, 15.0 g (0.1 mol) of freshly prepared silver cyanate, and 11.0 g (0.0435 mol) of iodine in 150 ml of tetrahydrofuran (0°, 4 hr), there was obtained 11.2 g (87.4%) of **12a** as a viscous pale brown oil that was used without further purification.

N-Methylcarbamoyl-1,2-imino-3-methylcyclohex-4-ene (13a).—A stirred solution of 12.8 g (0.0435 mol) of **12a** in 150 ml of anhydrous tetrahydrofuran was treated with 2.35 g (0.0435 mol) of freshly prepared sodium methoxide in one portion. The mixture was refluxed for 1 hr and worked up as above to give 4.13 g (56.5%) of a colorless liquid, bp 61–68° (0.2 mm). Because the liquid consists of two isomers, both of which will lead to **14a**, no further purification was undertaken.

3-Methyl-N-carbomethoxyazepine (14a).—Bromination of 4.06 g (0.0242 mol) of **13a** produced 7.93 g (100%) of a viscous yellow oil which was dehydrobrominated with 2.62 g (0.0484 mol) of fresh sodium methoxide in 200 ml of anhydrous tetrahydrofuran as described earlier. Distillation afforded 1.61 g (40.2%) of orange liquid, bp 62–65° (0.15–0.25 mm), of 90% purity. Pre-

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[45] Much of this variable temperature nmr study was done in cooperation with Professor F. A. L. Anet of UCLA to whom we are indebted.

[46] Melting points are corrected and boiling points are uncorrected. The microanalyses were performed by the Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer fitted with a sodium chloride prism. Ultraviolet spectra were recorded with a Cary Model 14 spectrometer. The nmr spectra were determined with Varian A-60 or A-60A spectrometers purchased with funds made available through the National Science Foundation. The mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV.

[47] L. Birkenbach and M. Lindhard, *Chem. Ber.*, **62B**, 2261 (1929); **63B**, 2528, 2544 (1930); **64B**, 961, 1076 (1931).

parative scale gas chromatography[48] (121°) provided the analytical sample; ir $\nu_{max}^{CCl_4}$ 1725 (C=O), 1665, and 1630 cm^{-1} (C=C); nmr $\delta_{TMS}^{CCl_4}$ 5.81–6.15 (m, 3 H, β and γ protons), 5.33–5.77 (m, 2 H, α protons), 3.69 (s, 3 H, —OCH$_3$), and 1.67 (d, J = 1.5 Hz, 3 H, —CH$_3$).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.50; H, 6.66; N, 8.46.

1,4-Dihydro-*p*-toluic Acid (9b).—To a stirred solution consisting of 75.0 g (0.55 mol) of *p*-toluic acid, 750 ml of absolute methanol, and approximately 2.5 l. of liquid ammonia was added in small pieces 68.0 g (2.96 g-atoms) of sodium metal, allowing the blue color to disappear before further addition. After consumption of the sodium, ammonium chloride (322.5 g, 5.92 mol) was cautiously added. Stirring was continued for 3 hr and the ammonia was then allowed to evaporate overnight. Water (1500 ml) was carefully added to the residue under a stream of nitrogen. The aqueous solution was poured onto 1 kg of ice and acidified with 10% hydrochloric acid. The product was extracted into ether (four 400-ml portions); the combined organic layers were dried and evaporated. The resulting light brown solid was distilled in a Claisen flask and recrystallized from ether–petroleum ether to give 66.1 g (87.0%) of white crystalline solid, mp 105–107°; ir $\nu_{max}^{CCl_4}$ 1710 cm^{-1} (—COOH).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.75; H, 7.34.

1,4-Dihydro-*p*-xylene (11b).—A 4.8-g sample of 9b was reduced with lithium aluminum hydride according to the procedure of Nelson[23] to give 3.92 g (91.0%) of 4-methyl-1,4-dihydrobenzyl alcohol as a colorless liquid, bp 70–72° (0.3 mm), ir $\nu_{max}^{CCl_4}$ 3310 cm^{-1} (—OH).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.50; H, 9.94.

A 54.04-g (0.194-mol) sample of the derived tosylate was reduced with 3.80 g (0.10 mol) of lithium aluminum hydride as described earlier. Careful work-up and distillation afforded 10.32 g (49.2%) of 11b as a colorless liquid, bp 119–122°.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.62; H, 11.37.

Methyl (*trans*-2-Iodo-3,6-dimethyl-4-cyclohexene)carbamate (12b).—From 3.5 g (0.0324 mol) of 11b, there was obtained 4.13 g (40.5%) of 12b as a white solid, mp 146–147.5° (from ether); ir $\nu_{max}^{CCl_4}$ 3360 (NH) and 1735 cm^{-1}; nmr $\delta_{TMS}^{CDCl_3}$ 5.29–5.71 (m, 2 H, vinyl protons), *ca.* 5.2 (br, 1 H, NH), 4.47–4.83 (m, 1 H, CHI), 3.40–4.29 (m, 1 H, CHN), 3.70 (s, 3 H, OCH$_3$), 1.98–3.01 (m, 2 H, CHCH$_3$), and 0.99–1.37 (m, 6 H, methyl groups).

Anal. Calcd for $C_{10}H_{16}INO_2$: C, 38.84; H, 5.22; N, 4.53. Found: C, 38.42; H, 5.33; N, 4.49.

N-Methylcarbamoyl-1,2-imino-3,6-dimethylcyclohex-4-ene (13b).—From 5.70 g of 12b, there was produced 2.68 g (79.7%) of a colorless liquid, bp 63–65° (0.05–0.1 mm), shown by vpc to consist of a mixture of two isomers present in approximately equal amounts. A center cut from a redistillation, bp 64° (0.07 mm), was submitted for analysis; ir $\nu_{max}^{CCl_4}$ 1729 cm^{-1}; nmr $\delta_{TMS}^{CCl_4}$ 5.09–5.41 (m, 2 H, vinyl protons), 3.64 (s, 3 H, —OCH$_3$), 0.95–2.79 (m, 10 H, CHN and aliphatic protons).

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.45; H, 8.44; N, 7.52.

3,6-Dimethyl-N-carbomethoxyazepine (14b).—Bromination of 13b was readily achieved by means of the generalized procedure. The resulting viscous yellow oil (26.0 g, 0.0762 mol) was dehydrobrominated as before to give 6.71 g (49.1%) of 14b as a light yellow liquid, bp 80–85° (0.1 mm). Vpc analysis indicated the material to be of 90% purity. Preparative scale vpc[48] (130°) yielded pure 14b as a pale yellow solid, mp 29–31°; ir $\nu_{max}^{CCl_4}$ 1710 cm^{-1} (C=O).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.07; H, 6.94; N, 7.83.

Methyl (*trans*-1-Methyl-2-iodo-4-cyclohexene)carbamate (16) and Methyl (*trans*-2-Iodo-4-methyl-4-cyclohexene)carbamate (17).—From 40.0 g (0.44 mol) of 2,5-dihydrotoluene (15),[49] 60.0 g (0.40 mol) of freshly prepared silver cyanate, and 101.6 g (0.40 mol) of iodine in 800 ml of anhydrous ether (−10°, 2 hr; 25°, 1 hr), there was obtained 30.6 g of white solid, mp 109–113°, and 32.4 g of residual brown oil after one recrystallization from ether–hexane. Chromatography of the oil on Florisil afforded an additional 1.2 g of solid, mp 108–112°, and 11.5 g of a second product, mp 80–83°.

Recrystallization of the first solid (27% yield) from ether gave white crystals of 16, mp 115–116°; ir ν_{max} 3320 (N-H) and 1705 cm^{-1} (C=O); nmr $\delta_{TMS}^{CDCl_3}$ 4.77–5.83 (m, 4 H, vinyl protons, CHI and CHN), 3.65 (s, 3 H, —OCH$_3$), 2.34–3.18 (m, 4 H, allylic protons), and 1.37 (s, 3 H, —CH$_3$).

Anal. Calcd for $C_9H_{14}INO_2$: C, 36.63; H, 4.78; N, 4.75. Found: C, 36.76; H, 4.76; N, 4.68.

Recrystallization of the second solid (9.8% yield) from hexane gave fluffy white crystals of 17, mp 82–84°; ir $\nu_{max}^{CCl_4}$ 3320 (N-H) and 1715 cm^{-1} (C=O); nmr $\delta_{TMS}^{CDCl_3}$ 4.77–5.45 (m, 2 H, vinyl proton and N-H), 3.68–4.59 (m, 2 H, CHI and CHN), 3.65 (s, 3 H, —OCH$_3$), 1.77–3.07 (m, 4 H, allylic protons), and 1.54–1.73 (s, 3 H, —CH$_3$).

Anal. Calcd for $C_9H_{14}INO_2$: C, 36.63; H, 4.78; N, 4.75. Found: C, 36.83; H, 4.97; N, 4.86.

N-Methylcarbamoyl-1,2-imino-1-methylcyclohex-4-ene (18).—From 6.0 g (0.0204 mol) of 16, there was obtained 3.02 g (88.9%) of 18 as a colorless liquid, bp 52–55° (0.15 mm); ir ν_{max} 1718 cm^{-1} (C=O); nmr $\delta_{TMS}^{CCl_4}$ 5.26–5.42 (d, J = 3.0 Hz, vinyl protons), 3.59 (s, 3 H, —OCH$_3$), 1.88–2.85 (m, 5 H, allylic protons and CHN), and 1.28 (s, 3 H, —CH$_3$).

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.68; H, 8.00; N, 8.21.

2-Methyl-N-carbomethoxyazepine (20).—Bromination of 18 in the predescribed manner led to the formation of a pale yellow oil in quantitative yield. Dehydrobromination of 11.38 g (0.0348 mol) of this crude dibromide in the predescribed fashion afforded 2.81 g (48.7%) of 20 as a light yellow liquid, bp 62–64° (0.10 mm), n^{25}D 1.5264; ir $\nu_{max}^{CCl_4}$ 1720 cm^{-1} (C=O); nmr $\delta_{TMS}^{CCl_4}$ 5.62–6.27 (m, 5 H, vinyl protons), 3.65 (s, 3 H, —OCH$_3$), and 2.05 (s, 3 H, —CH$_3$).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.22; H, 6.70; N, 8.42.

2,N-Dimethylhexamethylenimine (22).—A solution containing 1.0 g (6.05 mmol) of 10 in 50 ml of methanol was hydrogenated over 10% palladium on carbon at 50 psig. Reduction of the resulting colorless liquid (1.02 g) with 1.0 g of lithium aluminum hydride in 25 ml of tetrahydrofuran and customary alkaline work-up gave an amine which was treated directly with ethanolic picric acid. Recrystallization of the derived picrate from 95% ethanol afforded flat, light yellow prisms, mp 232–233°, identical with a known sample of 22 picrate (lit.[50] mp 233°).

N-Methylcarbamoyl-1,2-imino-4-methylcyclohex-4-ene (19).—When the generalized procedure was applied to 9.0 g (0.0306 mol) of 17, there was isolated 4.49 g (87.8%) of 19 as a colorless liquid, bp 53–54° (0.05–0.1 mm), n^{25}D 1.4867; ir $\nu_{max}^{CCl_4}$ 1725 cm^{-1} (C=O); $\delta_{TMS}^{CCl_4}$ 4.91–5.22 (m, 1 H, vinyl proton), 3.60 (s, 3 H, —OCH$_3$), 2.61 (br s, 2 H, CHN), 1.98–2.60 (m, 4 H, allylic protons), and 1.50 (d, J = <1.0 Hz, —CH$_3$).

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.65; H, 7.90; N, 8.43.

4-Methyl-N-carbomethoxyazepine (21).—Bromination–dehydrobromination of 19 (3.6 g, 0.0216 mol) led to the isolation of 1.97 g (55.6%) of 21 as an orange liquid, bp 62–65° (0.20 mm), n^{25}D 1.5338; ir $\nu_{max}^{CCl_4}$ 1730 cm^{-1} (C=O); nmr $\delta_{TMS}^{CCl_4}$ 5.13–5.92 (m, 5 H, vinyl protons), 3.72 (s, 3 H, —OCH$_3$), 1.77 (s, 3 H, —CH$_3$).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.68; H, 7.00; N, 8.30.

Reaction of 2,3-Dimethyl-1,4-dihydrobenzene (23) with Iodine Isocyanate. A. Standard Conditions.—A mixture of 11.0 g (0.10 mol) of 23,[49] 30.0 g (0.20 mol) of silver cyanate, and 25.4 g (0.10 mol) of iodine in 300 ml of anhydrous tetrahydrofuran was stirred vigorously for 2 hr at −20°. The reaction mixture was filtered and the solids were washed well with 100 ml of the same solvent. To the combined filtrate and washings was added 300 ml of absolute methanol and 3 drops of a dilute lithium methoxide solution (25 mg of lithium in 50 ml of methanol). After standing at room temperature in the dark for 24 hr, the solution was evaporated under reduced pressure and the resulting oil was chromatographed on 60 g of Florisil. Elution with hexane gave an oil which after distillation afforded 8.3 g (39%) of colorless oil identified as 26, bp 110° (0.10 mm); ir $\nu_{max}^{CCl_4}$ 3390 (N-H) and 1710 cm^{-1} (C=O); nmr $\delta_{TMS}^{CDCl_3}$ 5.60 (m, 2 H, vinyl protons), 5.38 (br, 1 H, N-H), 3.60 and 3.26 (s, 6 H, —OCH$_3$), 2.17–2.86 (m, 4 H, allylic protons), and 1.30 and 1.18 (s, 6 H, —CH$_3$).

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(48) A 5 ft × 0.25 in aluminum column packed with 20% SF96 on Chromosorb W was employed.

(49) (a) W. Hückel and V. Wörffel, *Chem. Ber.*, **88**, 338 (1955); (b) L. A. Paquette and J. H. Barrett, *Org. Syn.*, in press.

(50) G. R. Clemo, R. Raper, and H. J. Vipond, *J. Chem. Soc.*, 2095 (1949).

Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.94; H, 8.98; N, 6.57. Found: C, 61.45; H, 8.87; N, 6.33.

Elution with ether–hexane (1:9) afforded 2.1 g (7%) of **24**, white crystals, mp 78–79°; ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 3425 (N–H) and 1725 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.5 (br, 1 H, N–H), 4.3–5.6 (m, 2 H, CHI and CHN), 3.62 (s, 3 H, —OCH$_3$), 2.2–3.0 (m, 4 H, allylic protons), and 1.58 (s, 6 H, —CH$_3$).

Anal. Calcd for $C_{10}H_{16}INO_2$: C, 38.85; H, 5.22; N, 4.53. Found: C, 38.68; H, 5.28; N, 4.50.

B. Controlled Conditions.—A mixture of 26.4 g (0.20 mol) of **23** (82% purity, contaminant being *o*-xylene), 60 g (0.40 mol) of silver cyanate, and 50.7 g (0.20 mol) of iodine in 600 ml of tetrahydrofuran was allowed to react in the above manner. The clear filtrate was concentrated to *ca.* 20% of its original volume and to this solution (precooled to 0°) was added 800 ml of cold absolute methanol. After being stored at 0° for 24 hr, the solution was concentrated under reduced pressure below 10°. Chromatography of the residue on 100 g of Florisil gave, upon elution with hexane, 22.3 g (40.3%) of iodoisocyanate **27**, mp 84–86° [after sublimation at 60° (0.4 mm)]; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 2250 cm^{-1} (N=C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.58 (m, 2 H, vinyl protons), 2.52–2.84 (m, 4 H, allylic protons), 2.05 and 1.60 (s, 6 H, —CH$_3$).

Anal. Calcd for $C_9H_{12}INO_2$: C, 39.01; H, 4.37; N, 5.05. Found: C, 39.46; H, 4.42; N, 5.06.

Continued elution with hexane–ether (7:3) gave 5.88 g (9.9%) of **24**, mp 78–79°.

N-Methylcarbamoyl-1,2-imino-1,2-dimethylcyclohex-4-ene (28).—To a rapidly stirred slurry of 6.0 g (0.11 mol) of sodium methoxide in 100 ml of anhydrous tetrahydrofuran was added 27.7 g (0.10 mol) of solid **27** in portions over a 2-min period. The reaction was exothermic and the mixture began to reflux spontaneously. Heating was continued for 30 min, after which time the mixture was filtered and the filtrate was concentrated. The crude aziridine was extracted from the remaining salts with hot hexane. Distillation gave 17.2 g (95%) of **28**, bp 60° (0.7 mm), $n^{24.5}\mathrm{D}$ 1.4794; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1725 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.35 (m, 2 H, vinyl protons), 3.56 (s, 3 H, —OCH$_3$), 2.45 (m, 4 H, allylic protons), and 1.31 (s, 6 H, —CH$_3$).

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.74. Found: C, 66.49; H, 8.43; N, 7.75.

2,7-Dimethyl-N-carbomethoxyazepine (29).—Bromination of 1.81 g (0.01 mol) of **28** led to the formation of 3.4 g (100%) of the corresponding dibromide, mp 109–111° (from ether); ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1720 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.16 (m, 2 H, CHBr), 3.68 (s, 3 H, —OCH$_3$), 1.85–3.13 (m, 4 H, —CH$_2$), and 1.29 and 1.32 (s, 6 H, —CH$_3$).

Anal. Calcd for $C_{10}H_{15}Br_2NO_2$: C, 35.21; H, 4.43; N, 4.11. Found: C, 35.25; H, 4.49; N, 4.03.

Dehydrobromination of 11.9 g (0.035 mol) of this dibromide gave 6.25 g (100%) of **29**, white solid, mp 53–54° (from hexane); ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1725 (C=O) and 1650 cm^{-1} (C=C).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.10; H, 7.38; N, 7.78.

N-Methylcarbamoyl-1,2-imino-3,4-dimethylcyclohex-4-ene (30).—To a slurry of 1.20 g (0.03 mol) of sodium hydride (60% mineral oil dispersion) in 20 ml of anhydrous tetrahydrofuran was added at 0° with rapid stirring a solution of 9.27 g (0.03 mol) of **24** in 20 ml of the same solvent. The mixture came rapidly to reflux, and after 30 min, water (50 ml) was added. The solution was extracted with ether and the combined ether extracts were dried, filtered, and evaporated. Distillation of the residue yielded 5.0 g (92%) of **30**, bp 62° (0.04 mm), $n^{24}\mathrm{D}$ 1.4957; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1715 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.55 (s, 3 H, —OCH$_3$), 2.65 (s, 2 H, CHN), 2.33 (br s, 4 H, allylic protons), and 1.53 (s, 6 H, —CH$_3$).

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.30; H, 8.43; N, 7.56.

4,5-Dimethyl-N-carbomethoxyazepine (31).—Bromination of 4.1 g (22.6 mmol) of **30** gave 7.7 g (100%) of the derived dibromide, mp 100–102° (from ether); ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1725 (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.62 (s, 3 H, —OCH$_3$), 3.45–3.85 (m, 6 H, aziridine and methylene protons), 1.95 (s, 6 H, —CH$_3$).

Anal. Calcd for $C_{10}H_{15}Br_2NO_2$: C, 35.21; H, 4.43; N, 4.10. Found: C, 35.49; H, 4.51; N, 4.05.

Dehydrobromination of this dibromide (6.6 g, 27.4 mmol) in the predescribed manner afforded 2.85 g (63%) of **31**, mp 60–61° (from hexane at 0°); ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1727 cm^{-1} (C=O).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.70; H, 7.34; N, 7.90.

Reaction of 5,8-Dihydrotetralin (32) with Iodine Isocyanate.—A mixture of 53.68 g (0.40 mol) of **32**,[49a] 112.5 g (0.75 mol) of silver cyanate, and 101.6 g (0.40 mol) of iodine in 600 ml of anhydrous tetrahydrofuran was stirred at −20° for 5 hr. The inorganic salts were separated by filtration and the tetrahydrofuran was removed *in vacuo* at room temperature. The light brown residue was taken up in 600 ml of cold anhydrous methanol and the solution was stored at 0° for 48 hr. The pale yellow solid precipitate of **34** (49.0 g) was filtered and the filtrate was concentrated at <25°. The residue was dissolved in methylene chloride, washed with cold aqueous sodium sulfite solution, dried, and evaporated. The semicrystalline mass was filtered to afford an additional 21.5 g of **34**. The remaining oil (41.0 g) was chromatographed on 250 g of Florisil; elution with hexane gave 7.6 g of recovered **32** and 16.8 g (16.2%) of iodoisocyanate **33**. Elution with hexane–ether (9:1) yielded an additional 8.2 g of **34**. The combined fractions of iodocarbamate **34** (78.7 g, 68.6%) were recrystallized from methylene chloride–ether to give a fluffy white solid, mp 148–149°; ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 3345 (N–H) and 1740 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.0 (br, 1 H, N–H), 3.75–4.38 (m, 2 H, CHI and CHN), 3.65 (s, 3 H, —OCH$_3$), 1.39–2.82 (m, 12 H, methylene protons).

Anal. Calcd for $C_{12}H_{18}INO_2$: C, 43.00; H, 5.42; N, 4.17. Found: C, 42.89; H, 5.40; N, 4.38.

Iodoisocyanate **33** ($\nu_{\max}^{\mathrm{CHCl_3}}$ 2260 cm^{-1}) was not further purified and was used directly in the ensuing step.

N-Methylcarbamyl-2,3-imino-1,2,3,4-tetrahydrotetralin (35a).—Cyclization of 16.75 g (0.05 mol) of **34** with sodium methoxide in tetrahydrofuran according to the predescribed conditions yielded 9.13 g (88.3%) of **35a** as a colorless solid [after distillation at 101–105° (0.3 mm)], mp 38–40° from ether–hexane; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1720 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.55 (s, 3 H, —OCH$_3$), 2.60, 2.28, and 1.31–1.95 (complex m, 2 H, 4 H, and 8 H, respectively, due to CHN, allylic protons, and methylene groups).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.70; H, 8.42; N, 6.64.

4,5-Butylene-N-carbomethoxyazepine (36a).—The generalized bromination procedure was applied to 2.0 g (9.7 mmol) of **35a** and yielded 2.96 g (83.6%) of dibromide, white solid, mp 102–104° (from ether–hexane); ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1727 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.74 (s, 3 H, —OCH$_3$), 2.51–2.96 (m, 6 H, —CH$_2$CHN), and 1.46–2.24 (m, 8 H, remaining methylene groups).

Anal. Calcd for $C_{12}H_{17}Br_2NO_2$: C, 39.26; H, 4.67; N, 3.82. Found: C, 39.35; H, 4.74; N, 3.73.

Dehydrobromination of 10.0 g (0.027 mol) of the above dibromide gave rise to 2.39 g (42.9%) of a viscous orange oil after elution of the crude product through a column of Florisil. This oil could not be distilled without decomposition. Thin layer chromatography indicated the presence of two minor impurities which were not removed on repeated column chromatography.

2,3-Imino-1,2,3,4-tetrahydrotetralin (35b).—A solution of 10.0 g (0.03 mol) of **34** in a mixture of 150 ml of methanol and aqueous potassium hydroxide (15 g in 30 ml of H$_2$O) was refluxed with stirring for 5 hr. The solvent was removed *in vacuo* and the residue was treated with 300 ml of ether and 300 ml of water. The layers were separated and the aqueous layer was further extracted with ether. The combined organic layers were dried, filtered, and evaporated to give 2.38 g (53.4%) of an unstable waxy, white solid, mp 120–124.5° (from ether–hexane).

N-Benzenesulfonyl-2,3-imino-1,2,3,4-tetrahydrotetralin (35c).—A stirred solution of 1.10 g (7.4 mmol) of **35b** and 0.78 g (7.4 mmol) of triethylamine in 35 ml of benzene was cooled in ice while 1.31 g (7.4 mmol) of benzenesulfonyl chloride in 20 ml of benzene was added dropwise. Removal of the solvent and crystallization of the oil from ether–hexane gave 1.91 g (89.6%) of white, colorless plates, mp 102.5–104°; ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1330 and 1165 cm^{-1} (SO$_2$N).

Anal. Calcd for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62; N, 4.84. Found: C, 66.28; H, 6.62; N, 4.87.

4,5-Butylene-N-benzenesulfonylazepine (36b).—Bromination of 2.15 g of **35c** afforded 2.35 g (70.5%) of white crystalline dibromide, mp 135.5–136°.

Anal. Calcd for $C_{16}H_{19}Br_2NO_2S$: C, 42.78; H, 4.26; N, 3.12. Found: C, 42.82; H, 4.28; N, 3.18.

To a cold (0°) stirred slurry of 0.96 g (8.5 mmol) of potassium *t*-butoxide in 75 ml of anhydrous tetrahydrofuran was added dropwise a solution of 1.90 g (4.2 mmol) of the dibromide in 75 ml of the same solvent. Stirring was continued for 2 hr at this temperature and the solvent was evaporated *in vacuo*. The residue was treated with ether (400 ml) and water (300 ml) and the organic phase was worked up in the usual manner. There was obtained 790 mg of **36b** as light yellow plates, mp 105–107° (from ether–pentane); ir $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1355 and 1175 $\mathrm{cm^{-1}}$ (SO_2N).

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; S, 11.16. Found: C, 66.99; H, 5.99; S, 11.09.

11-Carbomethoxy-11-azatricyclo[4.4.1.0^{1,6}]undec-3-ene (37).—A solution of 16.8 g (0.056 mol) of **33** in 150 ml of anhydrous tetrahydrofuran was treated with 3.0 g (0.056 mol) of powdered sodium methoxide in one portion. The reaction mixture was seen to reflux gently. After stirring for 30 min, the solvent was evaporated, water and ether were added, and the customary work-up was followed. Distillation afforded 10.6 g (92.2%) of **37** as a colorless liquid, bp 75–77° (0.03–0.05 mm); ir $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 1712 $\mathrm{cm^{-1}}$ (C═O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.25–5.39 (m, 2 H, vinyl protons), 3.49 (s, 3 H, —OCH_3), 1.13–2.69 (m, 12 H, methylene protons).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.67; H, 8.37; N, 6.63.

11-Carbomethoxy-11-azabicyclo[4.4.1]undeca-1,3,5-triene (38).—Bromination of 4.3 g (0.021 mol) of **37** yielded 5.26 g (69.1%) of colorless crystalline dibromide, mp 85.5–87° (from ether–pentane); ir $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 1712 $\mathrm{cm^{-1}}$ (C═O).

Anal. Calcd for $C_{12}H_{17}Br_2NO_2$: C, 39.26; H, 4.67; N, 3.82. Found: C, 39.30; H, 4.68; N, 3.77.

Reaction of 6.60 g (0.018 mol) of this dibromide with an equivalent quantity of sodium methoxide in tetrahydrofuran in the above manner gave 3.07 g (83.3%) of **38** as large colorless plates from ether–pentane, mp 57.5–59°; ir $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 1705 $\mathrm{cm^{-1}}$ (C═O).

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 70.33; H, 7.45; N, 6.82.

11-Methyl-11-azabicyclo[4.4.1]undecane (39).—A solution of 500 mg (2.46 mmol) of **38** in 50 ml of dry tetrahydrofuran was hydrogenated over 10% palladium on charcoal at 60 psig. The incompletely hydrogenated product was added dropwise to a stirred slurry of 500 mg (13.2 mmol) of lithium aluminum hydride in 35 ml of the same solvent, and the reaction mixture was refluxed for 18 hr. After the standard alkaline work-up, the resulting light yellow oil was rehydrogenated under the same conditions. Vpc analysis of hydrogenated product indicated the material to be 90% pure. A sample was purified by preparative scale vpc and converted to its picrate in the usual manner, mp 250–252° (sample introduced at 246°), identical with an authentic sample.[51]

Reaction of 4,7-Dihydroindan (40) with Iodine Isocyanate.—Reaction of 40.0 g (0.33 mol) of **40**[52] with 90.0 g (0.60 mol) of silver cyanate and 84.5 g (0.30 mol) of iodine in 500 ml of dry tetrahydrofuran at −20° for 5 hr and subsequent reaction with methanol in the cold as described for **32** gave a mobile, light orange oil which was chromatographed directly on 300 g of Florisil. Elution with hexane gave 34.0 g of a light yellow oil which proved to be a mixture of unreacted **40** and iodoisocyanate **41**. This oil was employed directly without further purification.

Elution with hexane–ether (9:1) yielded 5.80 g (7.0%) of iodocarbamate **42** as white crystals from ether–hexane, mp 120–121°; ir $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 3345 (N-H) and 1730 $\mathrm{cm^{-1}}$ (C═O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.18 (br, 1 H, NH), 3.86–4.63 (m, 2 H, CHI and CHN), 3.66 (s, 3 H, —OCH_3), 1.50–2.97 (m, 10 H, allylic and methylene protons).

Anal. Calcd for $C_{11}H_{16}INO_2$: C, 41.14; H, 5.02; N, 4.36. Found: C, 41.20; H, 4.98; N, 4.33.

10-Carbomethoxy-10-azatricyclo[4.3.1.0^{1,6}]dec-3-ene (43).—The crude sample of **41** which was isolated above was treated with 5.4 g (0.1 mol) of powdered sodium methoxide in 200 ml of dry tetrahydrofuran. The customary work-up gave 8.8 g of recovered **40**, bp 30–35° (0.1 mm) and 14.07 g of **43** as a colorless liquid, bp 85–86° (0.05 mm); ir $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 1718 $\mathrm{cm^{-1}}$ (C═O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.30–5.44 (m, 2 H, vinyl protons), 3.51 (s, 3 H, —OCH_3), and 1.08–3.05 (m, 10 H, methylene groups). The quantity of **43** isolated indicates that iodoisocyanate **41** was produced in the previous reaction in at least 32% yield.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.70; H, 7.96; N, 7.22.

10-Carbomethoxy-10-azatricyclo[4.3.1.0^{1,6}]deca-2,4-diene (44).—The generalized bromination procedure was employed to convert 2.30 g (0.012 mol) of **43** into its dibromide (3.48 g, 83.0%), mp 101.5–103° (from ether–pentane); ir $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 1727 $\mathrm{cm^{-1}}$.

Anal. Calcd for $C_{11}H_{15}Br_2NO_2$: C, 37.42; H, 4.28; N, 3.97. Found: C, 37.41; H, 4.29; N, 3.93.

Dehydrobromination of 3.30 g (9.35 mmol) of this dibromide afforded 1.21 g (67.6%) of a yellowish liquid, bp 68–69° (0.03–0.06 mm). Vpc analysis indicated two products to be present. Preparative scale separation[53] of the two components at 135° gave **44** (major product) as a white waxy solid, mp 42–44°; ir $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 1665 $\mathrm{cm^{-1}}$ (C═O).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.86; H, 6.77; N, 7.25.

The second component was obtained as a light yellow solid, mp 61–63°, shown to be 2,3-propylene-N-carbomethoxyazepine.[8b]

1,2-Iminocyclohex-4-ene (45). A. Saponification of 5.—To a stirred refluxing solution of 40 g of 85% potassium hydroxide in 200 ml of water was added 20.0 g (0.071 mol) of **5**. Reflux was maintained for 1 hr, during which time the insoluble iodocarbamate dissolved. After cooling, the organic material was extracted into ether and the combined ether layers were dried, filtered, and evaporated. Distillation of the residue gave 5.91 g (87.5%) of **45** as a clear colorless liquid, bp 60.5–61° (14 mm), $n^{24}\mathrm{D}$ 1.5024; ir $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 3260 (NH) and 1645 $\mathrm{cm^{-1}}$ (C═O). This amine formed a picrate, mp 146–147° dec (from ethanol).

Anal. Calcd for $C_{12}H_{12}N_4O_4$: C, 44.45; H, 3.73; N, 17.28. Found: C, 44.32; H, 3.84; N, 17.38.

The N-methanesulfonyl derivative (**46a**) was obtained in 91.7% yield as a clear, colorless, viscous liquid, bp 107–113° (0.3 mm); ir $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1660 (C═C), 1310, and 1150 $\mathrm{cm^{-1}}$ (SO_2N); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.47 (br s, 2 H, vinyl protons), 2.97 (s, 5 H, overlapping —CH_3 and CHN), and 2.42 (br s, 4 H, allylic protons).

Anal. Calcd for $C_7H_{11}NO_2S$: C, 48.53; H, 6.40; S, 18.51. Found: C, 48.34; H, 6.63; S, 18.57.

The N-benzenesulfonyl derivative (**46b**) was obtained in 96.4% yield as lustrous white plates, mp 86–87° (from tetrahydrofuran–pentane); ir $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1670, 1590 (C═C), 1325, and 1165 $\mathrm{cm^{-1}}$ (SO_2N).

Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; S, 13.63. Found: C, 60.98; H, 5.80; S, 13.51.

The N-(*p*-bromobenzenesulfonyl) derivative (**46c**) was obtained in 73% yield as lustrous white plates, mp 106.5–107.5° (from tetrahydrofuran–hexane); ir $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1660, 1580 (C═C), 1330, and 1165 $\mathrm{cm^{-1}}$ (SO_2N).

Anal. Calcd for $C_{12}H_{12}BrNO_2S$: C, 45.85; H, 3.81; S, 10.21. Found: C, 45.99; H, 3.81; S, 10.24.

The N-diphenylphosphinoxy derivative (**46d**) was obtained in quantitative yield[54] as lustrous white plates, mp 119–120.5° (from ether); ir $\nu_{\mathrm{max}}^{\mathrm{CS_2}}$ 1655, 1590 (C═C), 1205 $\mathrm{cm^{-1}}$ (P═O).

Anal. Calcd for $C_{18}H_{18}NOP$: C, 73.21; H, 6.14; N, 4.74. Found: C, 73.20; H, 6.37; N, 4.64.

B. Direct from Iodoisocyanate.—A mixture of 4.64 g (0.058 mol) of 1,4-dihydrobenzene (**4**), 17.2 g (0.115 mol) of silver cyanate, and 14.5 g (0.057 mol) of iodine in 200 ml of tetrahydrofuran was stirred at 0° for 1 hr. The precipitated silver salts were removed by filtration and the filtrate was stirred for 9 hr with a solution of 20 g of potassium hydroxide in 100 ml of water. The same work-up as above afforded 2.76 g (51% over-all) of **45**.

N-Methanesulfonylazepine (47a).—The dibromide of **46a** was obtained in 83.8% yield as small yellow needles, mp 126.5–127.5° (from tetrahydrofuran–pentane); ir $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1330 and 1155 $\mathrm{cm^{-1}}$ (SO_2N).

Anal. Calcd for $C_7H_{11}Br_2NO_2S$: C, 25.24; H, 3.33; N, 9.63. Found: C, 25.59; H, 3.55; N, 9.85.

Dehydrobromination (KO-*t*-Bu) of 9.8 g (0.0294 mol) of this dibromide gave **47a** in 47.4% yield as lustrous yellow needles, mp 91.5–92.5° (from ether–hexane); ir $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1640, 1620 (C═C), 1350, and 1165 $\mathrm{cm^{-1}}$ (SO_2N); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.20 (m, 2 H), 5.76 (m, 4 H), and 2.89 (s, 3 H).

Anal. Calcd for $C_7H_9NO_2S$: C, 49.10; H, 5.30; N, 8.18. Found: C, 49.06; H, 5.50; N, 8.08.

N-Benzenesulfonylazepine (47b).—The dibromide of **46b** was obtained in 71.2% yield as small yellow needles, mp 123–124° (from tetrahydrofuran–pentane); ir $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1325 and 1170 $\mathrm{cm^{-1}}$ (SO_2N).

Anal. Calcd for $C_{12}H_{13}Br_2NO_2S$: C, 36.47; H, 3.32; S, 8.12. Found: C, 36.62; H, 3.35; S, 8.16.

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(53) A 3 ft × 0.25 in. aluminum column packed with 20% SF-96 on Chromosorb W was employed.

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Dehydrobromination (KO-*t*-Bu) of 6.8 g (0.0172 mol) of this dibromide gave **47b** in 52.4% yield as yellow plates, mp 132–133° (from tetrahydrofuran–pentane); ir $\nu_{max}^{CHCl_3}$ 1645, 1625 (C=C), 1360, and 1175 cm^{-1} (SO_2N); nmr $\delta_{TMS}^{CDCl_3}$ 7.62 (m, 5 H, aromatic protons) and 5.76 (m, 6 H, vinyl protons).

Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00. Found: C, 61.82; H, 4.65; N, 6.08.

N-(*p*-Bromobenzenesulfonyl)azepine (**47c**).—The dibromide of **46c** was obtained in quantitative yield as lustrous yellow crystals, mp 165–167° (from tetrahydrofuran–hexane); ir $\nu_{max}^{CHCl_3}$ 1330 and 1165 cm^{-1} (SO_2N).

Anal. Calcd for $C_{12}H_{12}Br_3NO_2S$: C, 30.40; H, 2.55; S, 6.76. Found: C, 30.67; H, 2.64; S, 6.90.

Dehydrobromination (KO-*t*-Bu) of 20 g (0.042 mol) of this dibromide gave **47c** in 67.9% yield as large yellow crystals, mp 132.5–134° (from tetrahydrofuran); ir $\nu_{max}^{CHCl_3}$ 1645, 1625 (C=C), 1365, and 1170 cm^{-1} (SO_2N); nmr $\delta_{max}^{CDCl_3}$ 7.59 (m, 4 H, aromatic protons), 5.74 (d, 2 H), and 5.87 (m, 4 H, vinyl protons).

Anal. Calcd for $C_{12}H_{10}BrNO_2S$: C, 46.16; H, 3.23; N, 4.49. Found: C, 46.30; H, 3.33; N, 4.55.

N-Diphenylphosphinoxyazepine (**47d**).—The dibromide of **46d** was obtained in 99.2% yield as yellow needles, mp 192–192.5° (from tetrahydrofuran); ir $\nu_{max}^{CS_2}$ 1205 cm^{-1} (P=O).

Anal. Calcd for $C_8H_{18}Br_2NOP$: C, 47.50; H, 3.99; N, 3.08. Found: C, 47.62; H, 4.13; N, 3.11.

To a stirred refluxing solution of 3.49 g (8.66 mmol) of this dibromide in 150 ml of anhydrous tetrahydrofuran was added dropwise a solution of 3.26 g (26.3 mmol) of 1,5-diazabicyclo[4.3.0]non-5-ene in 10 ml of the same solvent. The reaction mixture was refluxed for 4 hr, cooled in ice, and hydrolyzed by addition of 150 ml of water and stirring at room temperature for 30 min. Careful extraction with ether and subsequent processing of the combined organic layers in the usual fashion gave 2.16 g (85%) of **47d** as large yellow crystals, mp 151.5–153° (from tetrahydrofuran–ether, 1:4); ir $\nu_{max}^{CS_2}$ 1640, 1610 (C=O), and 1220 cm^{-1} (P=O); nmr $\delta_{TMS}^{CDCl_3}$ 8.13–7.64 (m, 4 H, aromatic protons), 7.37 (m, 6 H, aromatic protons), 6.20 (m, 2 H, vinyl protons), and 5.48 (m, 4 H, vinyl protons).

Anal. Calcd for $C_{18}H_{16}NOP$: C, 73.71; H, 5.50; N, 4.78. Found: C, 73.64; H, 5.46; N, 4.82.

1,2,7-Trimethylazepine (**48**).—A solution of 1.79 g (0.01 mol) of **29** in 10 ml of anhydrous tetrahydrofuran was added dropwise during 10 min to a stirred slurry of 0.38 g (0.01 mol) of lithium aluminum hydride in 25 ml of the same solvent. The reaction mixture was refluxed for 15 hr under nitrogen and was cooled to 0°. To the cold mixture was added carefully 0.4 g of water, 0.4 g of 30% sodium hydroxide solution, and 1.2 g of water in that order. Anhydrous magnesium sulfate (2.0 g) was added and the solids were filtered and rinsed thoroughly. The combined filtrate and washings were evaporated and the residual liquid was subjected to bulb-to-bulb distillation at 20°. A dilute solution of **48** in tetrahydrofuran could be stored for several weeks at 0°; however, pure **48** was seen to decompose rapidly; ir $\nu_{max}^{CCl_4}$ 1655 cm^{-1} (C=C—N); uv $\lambda_{max}^{isooctane}$ 215 (ϵ 15,400) and 257 mμ (ϵ 1650); nmr $\delta_{TMS}^{CS_2}$ 5.72 (m, 2 H, γ ring protons), 5.07 (m, 2 H, β ring protons), 2.58 (s, 3 H, NCH_3), and 1.73 (s, 6 H, C—CH_3).

2-Methyl-N-(*p*-bromobenzenesulfonyl)azepine (**49**).—To a refluxing solution of 40 g of potassium hydroxide in 200 ml of water was added 20.0 g (0.068 mol) of iodocarbamate **16**. Heating was continued for 30 min, during which time the solid dissolved. After cooling, the organic product was extracted with ether and the oil thus obtained was transferred under high vacuum to give 5.32 g (72%) of colorless 1-methyl-1,2-iminocyclohex-4-ene, ir ν_{max}^{neat} 3300 cm^{-1} (N—H).

The N-(*p*-bromobenzenesulfonyl) derivative was obtained in quantitative yield as colorless crystals, mp 128–129.5° (from tetrahydrofuran); ir $\nu_{max}^{CHCl_3}$ 1320 and 1165 cm^{-1} (SO_2N); nmr $\delta_{TMS}^{CDCl_3}$ 7.68 (q, 4 H, aromatic protons), 5.37 (br d, 2 H, vinyl protons), 3.19 (br, 1 H, CHN), 2.2–2.5 (m, 4 H, allylic protons), and 1.79 (s, 3 H, —CH_3).

Anal. Calcd for $C_{13}H_{14}BrNO_2S$: C, 47.57; H, 4.30; N, 4.27; S, 9.77. Found: C, 47.81; H, 4.38; N, 4.26; S, 9.75.

The derived dibromide was obtained in 61% yield as a powdery white solid, mp 125.5–127.5° (from tetrahydrofuran); ir $\nu_{max}^{CHCl_3}$ 1325 and 1165 cm^{-1} (SO_2N).

Anal. Calcd for $C_{13}H_{14}Br_3NO_2S$: C, 31.99; H, 2.89; S, 6.57. Found: C, 32.49; H, 3.01; S, 6.65.

Dehydrobromination of the dibromide (5.46 g, 11.2 mmol) was achieved by the use of 1,5-diazabicyclo[4.3.0]non-5-ene (4.18 g, 33.7 mmol) in 150 ml of tetrahydrofuran as described above. There was produced 1.73 g (47.4%) of **49** as a white powder, mp 94.5–95.5° (from ether–hexane); ir $\nu_{max}^{CHCl_3}$ 1645, 1625 (C=C), 1385, 1165, and 1150 cm^{-1} (SO_2N); nmr $\delta_{max}^{CDCl_3}$ 7.80 (d, 4 H, aromatic protons), 5.75–6.35 (m, 5 H, vinyl protons), and 2.29 (s, 3 H, —CH_3); uv λ_{max}^{EtOH} 234 (ϵ 13,000) and 269 sh mμ (ϵ 3580).

Anal. Calcd for $C_{13}H_{12}BrNO_2S$: C, 47.86; H, 3.71; N, 4.29. Found: C, 48.00; H, 3.83; N, 4.18.

N-Carbomethoxyazepineiron Tricarbonyl (**55a**). **A. Irradiation with Iron Pentacarbonyl.**—A solution of 4.53 g (0.03 mol) of **8** and 7.84 g (0.04 mol) of iron pentacarbonyl in 300 ml of anhydrous tetrahydrofuran was irradiated with a 200-W Hanovia lamp in a quartz immersion well for 36 hr. The solvent was evaporated and the residual solid was dissolved in hexane and filtered through a 1.5-in. pad of Woelm grade II neutral alumina (30 g). The filtrate was evaporated and the resulting solid was crystallized from hexane to give 5.84 g (70.5%) of **55a** as yellow prisms, mp 115–115.5° (from hexane); ir ν_{max}^{Nujol} 2070, 1190 (Fe-CO) 1750, 1730 (C=O), and 1655 cm^{-1} (C=C); uv λ_{max}^{EtOH} 250 (ϵ 17,670) and 297 sh mμ (ϵ 5390); nmr $\delta_{TMS}^{CDCl_3}$ 6.3, 5.0, 4.6 (broad peaks, temperature dependent, 6 H, vinyl protons) and 3.85 (s, 3 H, —OCH_3).

Anal. Calcd for $C_{11}H_9FeNO_5$: C, 45.39; H, 3.12; N, 4.81. Found: C, 45.44; H, 3.22; N, 4.82.

B. Heating with Iron Enneacarbonyl.—A mixture of 750 mg (5.0 mmol) of **8** and 1.82 g (5.0 mmol) of iron enneacarbonyl[55] in 30 ml of hexane was refluxed with stirring under nitrogen for 20 min. After cooling, the solution was filtered through Celite to remove a small amount of insoluble dark residue. The solvent was evaporated and the resulting solid was recrystallized from hexane to give 1.0 g (69%) of **55a**, mp 116–116.5°.

N-Carbophenoxyazepineiron Tricarbonyl (**55b**).—A solution of 81.5 g (0.5 mol) of phenyl azidoformate in 2800 ml of benzene was heated in a 6-l. autoclave at 130° for 2 hr. The benzene was removed *in vacuo* and the residual oil was chromatographed on 200 g of Florisil. Elution with ether–hexane (1:1) and ether gave 30.1 g (27.1%) of N-carbophenoxyazepine as pale yellow crystals, mp 67–68° (from hexane–ether); ir $\nu_{max}^{CCl_4}$ 1730 (C=O), 1653, and 1621 cm^{-1} (C=C); nmr $\delta_{TMS}^{CDCl_3}$ 7.2–8.5 (m, 5 H, aromatic protons), and 5.35–6.2 (m, 6 H, vinyl protons).

A 1.05-g (5.0 mmol) sample of 1-carbophenoxyazepine was treated with 1.82 g (5.0 mmol) of iron enneacarbonyl in the manner described above. There was obtained 850 mg (48.2%) of **55b** as yellow prisms, mp 108–109° dec (from hexane); ir $\nu_{max}^{CCl_4}$ 2060, 2000 (FeCO), and 1740 cm^{-1} (C=O); nmr $\delta_{TMS}^{CDCl_3}$ 7.2 (m, 5 H, phenyl protons), 6.6, 6.1, 5.1, 4.6, and 3.5 (broad peaks, temperature dependent, 6 H, vinyl protons).

Anal. Calcd for $C_{16}H_{11}FeNO_5$: C, 54.42; H, 3.14; N, 3.96. Found: C, 54.37; H, 3.20; N, 3.93.

N-Methanesulfonylazepineiron Tricarbonyl (**55c**).—To a stirred solution of 967 mg (5.65 mmol) of **47a** in 40 ml of tetrahydrofuran at room temperature was added 2.04 g (5.61 mmol) of iron enneacarbonyl. After stirring for 75 min, all of the metal carbonyl had dissolved and the dark reaction mixture was filtered through Celite. The filtrate was evaporated and the residue was crystallized from hexane to give 1.20 g (69%) of **55c** as lustrous orange-yellow prisms, mp 94.5–96° (from hexane); ir $\nu_{max}^{CHCl_3}$ 2070, 1990 (Fe-CO), 1635 (C=C), 1350, and 1170 cm^{-1} (SO_2N); uv λ_{max}^{EtOH} 232 mμ (ϵ 14,600); nmr $\delta_{TMS}^{CDCl_3}$ 3.5–6.5 (broad humps, temperature dependent, 6 H, vinyl protons), and 2.92 (s, 3 H, —CH_3).

Anal. Calcd for $C_{10}H_9FeNO_5S$: C, 38.61; H, 2.92. Found: C, 38.74; H, 3.01.

N-Carbo-*t*-butoxyazepineiron Tricarbonyl (**55d**).—A solution of 14 g (0.1 mol) of *t*-butylazidoformate[56] in 400 ml of benzene was heated in a sealed tube at 145° for 4.5 hr. The solvent was evaporated and the residues from four such runs (65.1 g) were combined. Addition of ether to the crude product resulted in the crystallization of 29.0 g of 5,5-dimethyl-2-oxazolidone, mp 80.5–81.5°.[57] The remaining oil was chromatographed on Florisil. Elution with ether and distillation gave 9.4 g (12.5%) of N-carbo-*t*-butoxyazepine as a red-orange liquid, bp 72–73° (0.05 mm), n^{25}D 1.5073; uv λ_{max}^{EtOH} 209 (ϵ 22,500), 240 sh (ϵ 3270), and 317 mμ (ϵ 638); $\lambda_{max}^{isooctane}$ 206 (ϵ 22,900) 238 sh (ϵ 3520), and 330 mμ (ϵ 520); ir $\nu_{max}^{CCl_4}$ 1665, 1625 (C=C), and 1712 cm^{-1}

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(C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.2–6.1 (m, 6 H, vinyl protons) and 1.49 [s, 9 H, —$C(CH_3)_3$].

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.19; H, 7.85; N, 6.96.

This azepine was also prepared in the following manner. The iodoisocyanate resulting from the reaction of 8.0 g (1.10 mol) of 1,4-dihydrobenzene with 40 g (0.20 mol) of silver cyanate and 25.4 g (0.10 mol) of iodine in 30 ml of tetrahydrofuran was treated with 11.2 g (0.10 mol) of powdered potassium *t*-butoxide. The mixture was shaken vigorously for 5 min, filtered, and evaporated. Distillation of the residue gave 16.95 g (87%) of N-*t*-butylcarbamoyl-1,2-iminocyclohex-4-ene, bp 81° (0.6 mm); ir $\nu_{\max}^{\mathrm{CCl_4}}$ 1725 cm^{-1} (C=O); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.40 (br m, 2 H, vinyl protons), 2.61 (br m, 2 H, CHN), 2.44 (m, 4 H, allylic protons), and 1.44 [s, 9 H, —$C(CH_3)_3$].

Anal. Calcd for $C_{11}H_{18}N_2O$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.67; H, 8.81; N, 7.01.

An 8.65-g (0.044 mol) sample of this aziridine was brominated in the customary fashion to give 15.1 g (100%) of crude dibromide as a yellow oil. Dehydrobromination of this material gave 7.93 g (93%) of N-carbo-*t*-butoxyazepine, bp 71–73° (0.05 mm), identical with the material prepared above.

A solution of 4.60 g (0.0238 mol) of this azepine and 5.5 g (0.028 mol) of iron pentacarbonyl in 350 ml of tetrahydrofuran was irradiated as above for 24 hr. Evaporation of the solvent gave a black oil which was filtered through 50 g of Woelm basic alumina. Crystallization of the resulting orange oil from hexane gave 3.12 g (39.4%) of **55d** as yellow prisms, mp 70–70.5°; ir $\nu_{\max}^{\mathrm{Nujol}}$ 2070, 1990 (FeCO), 1750 (C=O), and 1650 cm^{-1} (C=C); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 249.5 (ϵ 18,770) and 298 sh mμ (ϵ 5825); nmr $\delta_{\max}^{\mathrm{CCl_4}}$ 4.5–6.4 (broad humps, temperature dependent, 6 H, vinyl protons) and 1.48 [s, 9 H, —$C(CH_3)_3$].

Anal. Calcd for $C_{14}H_{15}FeNO_5$: C, 50.47; H, 4.54; N, 4.21. Found: C, 50.57; H, 4.68; N, 4.24.

N-Carbobenzyloxyazepineiron Tricarbonyl (55e).—A solution of 5.5 g (0.031 mol) of benzyl azidoformate in 400 ml of benzene was heated at 135–140° for 6 hr in a sealed vessel.[58] The solvent was removed *in vacuo* and the residue was chromatographed on 130 g of Florisil. Elution with ether–hexane (1:19) gave 1.7 g (24%) of N-carbobenzyloxyazepine as an orange oil, $n^{29}\mathrm{D}$ 1.5762.

Irradiation of a solution containing 10.9 g (0.048 mol) of this azepine and 9.8 g (0.050 mol) of iron pentacarbonyl in 300 ml of tetrahydrofuran gave 17.45 g (99%) of crude crystalline product mp 112–116°. Three recrystallizations from hexane gave pure **55e** as yellow-orange needles, mp 127–128°; ir $\nu_{\max}^{\mathrm{Nujol}}$ 2065, 2000 (FeCO), 1750 (C=O), and 1650 cm^{-1} (C=C); nmr $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.35 (s, 5 H, aromatic protons), 6.0–6.5 and 4.2–4.8 (broad absorption, temperature dependent, 6 H, vinyl protons), and 5.17 (s, 2 H, $ArCH_2$—).

Anal. Calcd for $C_{17}H_{13}FeNO_5$: C, 55.61; H, 3.57; N, 3.82. Found: C, 55.23; H, 3.57; N, 3.81.

Registry No.—**5,** 20646-79-1; **6,** 20646-80-4; **7,** 20646-81-5; **8,** 17870-94-9; **9b,** 20646-36-0; **11a,** 2050-31-9; 1,4-dihydro-*p*-xylene **11b,** 20646-38-2; **13a,** 20646-82-6; **13b,** 20646-83-7; **14a,** 14194-60-6; **14b,** 20646-39-3; **16,** 20646-84-8; **17,** 20646-85-9; **18,** 20646-86-0; **19,** 20646-87-1; **20,** 14194-59-3; **21,** 20646-42-8; **24,** 20647-01-2; **26,** 20646-88-2; **27,** 20646-89-3; **28,** 20646-90-6; **28** (dibromide), 20646-91-7; **29,** 20646-43-9; **30,** 20646-92-8; **30** (dibromide), 20646-93-9; **31,** 20646-44-0; **34,** 20646-94-0; **35a,** 20646-95-1; **35a,** (dibromide), 20646-96-2; **35b,** 20646-97-3; **35c,** 20646-98-4; **35c** (dibromide), 20646-99-5; **36b,** 20646-45-1; **37,** 20646-51-9; **37** (dibromide), 20708-16-1; **38,** 20646-46-2; **42,** 20647-00-1; **43,** 20646-47-3; **43** (dibromide), 20646-48-4; **44,** 20646-52-0; **45,** 20647-02-3; **45** (picrate), 20647-03-4; **46a,** 20647-04-5; **46a** (dibromide), 20647-05-6; **46b,** 20647-06-7; **46b** (dibromide), 20647-07-8; **46c,** 20647-08-9; **46c** (dibromide), 20647-09-0; **46d,** 20647-10-3; **46d** (dibromide), 20674-11-4; **47a,** 20646-53-1; **47b,** 20646-54-2; **47c,** 20646-55-3; **47d,** 20646-56-4; **48,** 20646-57-5; **49,** 20646-58-6; **55a,** 12359-60-3; **55b,** 12359-62-5; **55c,** 12359-59-0; **55d,** 12359-61-4; **55e,** 12359-63-6; 1-methyl-1,2-iminocyclohex-4-ene, 20647-15-8; 1-methyl-1,2-iminocyclohex-4-ene [N-(*p*-bromobenzenesulfonyl) derivative], 20647-12-5; 1-methyl-1,2-iminocyclohex-4-ene [N-(*p*-bromobenzenesulfonyl) derivative, dibromide], 20647-13-6; N-carbophenoxyazepine, 18697-60-4; N-carbo-*t*-butoxyazepine, 20646-60-0; N-*t*-butylcarbamoyl-1,2-iminocyclohex-4-ene, 20647-14-7; 4-methyl-1,4-dihydrobenzyl alcohol, 20646-50-8.

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[58] This experiment was performed by Mr. Tedd Dawson.