π-Equivalent Heterocyclic Congeners of Cyclooctatetraene. The Synthesis and Valence Isomerization of 2-Alkoxyazocines[1]

Leo A. Paquette,[2a] Tsuyoshi Kakihana,[2b] John F. Hansen, and J. Christopher Philips[2c]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 7, 1970*

Abstract: A general synthesis of 2-alkoxyazocines, the first monocyclic π-equivalent heterocyclic congeners of cyclooctatetraene, has been realized. The scheme consists in the electrophilic addition of chlorosulfonyl isocyanate to readily accessible 1,4-dihydrobenzene derivatives. O-Alkylation of the resulting β-lactams gives rise to 2-alkoxyazetines that can be brominated allylically (*N*-bromosuccinimide) or dibrominated (molecular bromine) and then dehydrobrominated (usually sodium methoxide or potassium *tert*-butoxide) to afford the desired heterocyclic polyenes. This preparative route is seen to be general and versatile and to permit also the ready synthesis of annelated derivatives. The valence isomerization of 2-alkoxyazocines has been examined and the tautomeric 7-azabicyclo[4.2.0]octatriene forms are seen to be present only to an extent below the customary spectroscopic detection limit. The presence of tri-, tetra-, and pentamethylene bridges at the 2 and 7 positions of the azocine ring is sufficient to constrain the respective molecules into their tricyclic forms. However, a hexamethylene bridge is sufficiently strain free to permit virtually complete displacement of the equilibrium in favor of the azocine valence tautomer. The various spectral properties of these cyclic 8π-electron heterocycles are correlated. Lastly, the attempted synthesis of 12-ethoxy-11-aza[4.4.2]propella-2,4,7,9,11-pentaene is discussed.

In retrospect, the disbelief that accompanied the initial masterful synthesis of cyclooctatetraene from pseudopelletierine by Willstätter in 1911,[3] because of the totally unexpected nonaromaticity of this higher homolog of benzene, can be viewed with a large measure of understanding. It is now common knowledge that the small resonance energy of this 8π-electron hydrocarbon (2.4–4.8 kcal/mol)[4] is due to its π-electronic instability. Also, the puckered D_{2d} "tub" conformation[5] adopted by the hydrocarbon, while allowing for a strain-free structure, effectively prevents the extended conjugation of any two neighboring double bonds. Since the discovery that cyclooctatetraene (**1**) can be prepared readily in quantity by the remarkable tetramerization of acetylene in tetrahydrofuran solutions containing nickel cyanide,[6] its chemistry has been studied in considerable detail.[7] The unusually varied reactions that this monocyclic $(CH)_8$ hydrocarbon is known to undergo have caused it to be a prime target of much mechanistic and synthetic study. Not surprisingly, intense interest in **1** persists to the present day.

1

2

Despite the blatant nonaromaticity and marked propensity for unusual structural rearrangement associated with the cyclooctatetraene molecule, no eight-membered monoheterocyclic analogs of **1** have been described. This particular investigation began with two goals—first, the development of a general synthesis of azacyclooctatetraenes (azocines, **1**) and second, elucidation of the unconventional physical and chemical properties almost certainly to be associated with such monocyclic π-equivalent[8] congeners of **1**. The present paper, the first of several detailed reports on azocine chemistry,[9] describes a convenient synthetic entry to the azocine system and concerns itself additionally with the valence tautomerism of this class of heterocycles.[10]

Synthesis of Monocyclic Azocines. At the outset, two important demands were placed on the synthetic scheme to be developed: (a) the requirement of simplicity and generality in order that suitable homologs and derivatives would be readily available when needed and (b) the necessity that the resulting azocines be so constructed that they possess reasonable stability. In this latter regard, the very real possibility that **2** would be so labile as to preclude ready examination of its chemical and physical properties led us to direct our efforts to the preparation of 2-alkoxyazocines. Although the direction and magnitude of the possible dynamic valence tautomeric equilibria in 2-alkoxyazocines remained to be established (see below), a synthetic approach based on this concept appeared most reasonable.

In the parent series (Scheme I), monocycloaddition of chlorosulfonyl isocyanate (CSI)[11] to 1,4-cyclohexadiene (**3**) in benzene solution at 70°, followed by reduction of the resulting *N*-(chlorosulfonyl) β-lactam with thio-

(1) Unsaturated Heterocyclic Systems. LXXIII. For the previous paper in this series, see L. A. Paquette and R. H. Meisinger, *Tetrahedron Lett.*, 1479 (1970).

(2) To whom correspondence should be addressed; (b) Goodyear Tire and Rubber Co. Fellow, 1969–1970; (c) National Institutes of Health Predoctoral Fellow, 1966–1968.

(3) R. Willstätter and E. Waser, *Chem. Ber.*, **44**, 3423 (1911); R. Willstätter and M. Heidelberger, *ibid.*, **46**, 517 (1913).

(4) R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *J. Amer. Chem. Soc.*, **79**, 4127 (1957).

(5) W. B. Person, G. C. Pimentel, and K. S. Pitzer, *ibid.*, **74**, 3437 (1952).

(6) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).

(7) G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim/Bergstr., Germany, 1965.

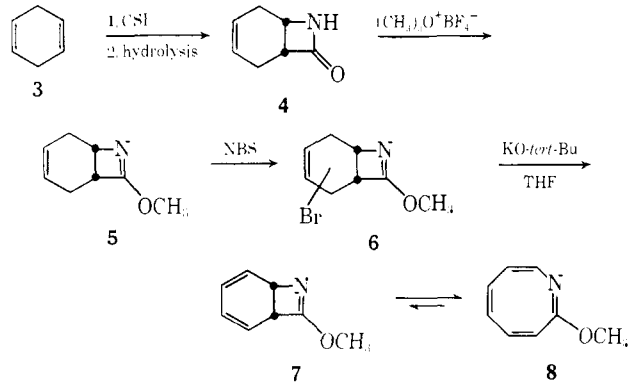
(8) A. G. Anderwon, Jr., W. F. Harrison, and R. G. Anderson, *J. Amer. Chem. Soc.*, **85**, 3448 (1963).

(9) (a) L. B. Anderson, J. F. Hansen, T. Kakihana, and L. A. Paquette, *ibid.*, **93**, 161 (1971); (b) L. A. Paquette, J. F. Hansen, and T. Kakihana, *ibid.*, **93**, 168 (1971); (c) L. A. Paquette and T. Kakihana, *ibid.*, **93**, 174 (1971); (d) L. A. Paquette, T. Kakihana, and J. F. Kelly, *J. Org. Chem.*, in press; (e) L. A. Paquette and J. F. Kelly, *ibid.*, in press, and later papers.

(10) Preliminary reports of portions of this work may be found in (a) L. A. Paquette and T. Kakihana, *J. Amer. Chem. Soc.*, **90**, 3897 (1968); (b) L. A. Paquette and J. C. Philips, *ibid.*, **90**, 3898 (1968).

(11) R. Graf, *Justus Liebigs Ann. Chem.*, **661**, 111 (1963).

Scheme I



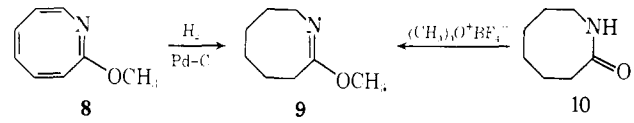
phenol and pyridine in acetone solution at 0°[11] or with 4 *N* sodium hydroxide in the same solvent, gave **4** in 55% overall yield. This β-lactam exhibited the expected intense infrared carbonyl band ($CHCl_3$) at 1760 cm^{-1} and showed in its nmr spectrum ($CDCl_3$) a two-proton multiplet at δ 5.78 (vinyl), one-proton signals at 3.93 (>C*H*NH–) and 3.33 (>C*H*CO–), and an extensively coupled four-proton absorption centered at 2.25 (allyl). O-Methylation of **4** with trimethyloxonium fluoroborate[12] led to the isolation of imino ether **5** in 50% yield. The structure of this novel 1-azetine derivative[13] followed from its spectral characteristics

Table I. Ultraviolet Spectra of 2-Methoxyazocines (Isooctane Solution)

Compd	λ_{max}, nm (ε)[a]
8	214 (8,750) and 305 (350)
14a	215 (10,600) and 307 (400)
14b	212 (12,900) and 297 (590)
14c	215 (12,400) and 285 (640)
14d	215 (10,500) and 285 (560)

[a] The 212–215 nm absorption was most often a shoulder and not a maximum.

[ν_{max}^{neat} 1618 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.58–5.75 (m, 2, vinyl), 3.68 (s, 3, $-OCH_3$), 3.62 (m, 1, >C*H*N=), 3.41 (m, 1, >C*H*C(OCH_3)=), and 1.97–2.42 (m, 4, allyl)]. This compound was found to be extremely acid and air sensitive and had to be handled with care to avoid its spontaneous exothermic decomposition. Monobromination of **5** was effected with 1 equiv of *N*-bromosuccinimide in refluxing carbon tetrachloride solution; this monobromide **6** was not characterized, and the position of entry of the halogen was not determined. Upon dehydrohalogenation of **6** with potassium *tert*-butoxide in tetrahydrofuran solution at 0°, there was obtained a yellow oil, careful gas chromatography of which revealed the presence of two main components. Preparative vpc separation of the reaction mixture permitted the purification and isolation of the desired 2-methoxy-1-azocine (**8**, 62%) and benzonitrile (26%).[14] For larger scale separations, it was found considerably more convenient to elute pentane solutions of such mixtures through a chromatographic column packed with charcoal–Celite (2:3 w/w). Azapolyene **8**, a stable yellow liquid, exhibited pertinent infrared absorptions (neat) at 1675 (s), 1640 (m), and 1620 cm^{-1} (w); its ultraviolet and nmr spectral characteristics are listed in Tables I and II (see below). The structure of **8** was established unequivocally by hydrogenation over 10% palladium on carbon at atmospheric pressure to give **9** which was prepared independently by the reaction of lactam **10** with trimethyloxonium fluoroborate.



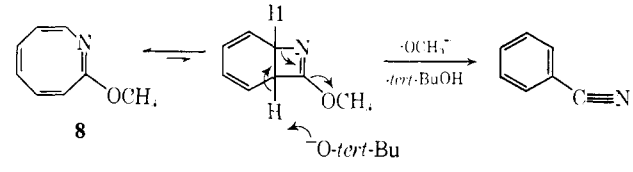
The origin of the benzonitrile was revealed when **8** was exposed to a slurry of potassium *tert*-butoxide in tetrahydrofuran at 25° for 5 hr. Under these conditions, a mixture consisting of 53% **8** and 47% benzonitrile was obtained. This result indicated that the nitrile isolated in the preparative experiment resulted from interaction of **8** with excess base, very probably by the following pathway that involves the bicyclo[4.2.0] tautomer **7**.

The desirability of expanding the generality of this synthesis (Scheme I), coupled with the need for homologs of **8** in attendant studies of the physical properties and chemical reactivity of azocines,[9] led to the preparation of variously methylated derivatives of this system (**14**). By the established sequence—Birch reduction of the appropriate benzene derivative, chlorosulfonyl isocyanate addition, O-methylation, and bromination–de-

Table II. Proton Chemical Shift Values for Various 2-Methoxyazocines ($CDCl_3$ Solution, δ Units)

Compd	$-OCH_3$	H_3	H_4	H_5	H_6	H_7	H_8
8	3.70			5.75–6.05[a]		5.12	6.54
14a	3.74			5.78–6.08[a]		5.02	(1.96)[b]
14b	3.72	(1.87)[b]		5.72[a]		4.91	(1.87)[b]
14c	3.68	5.62	(1.73)[b]	5.47	(1.73)[b]	4.94	(1.88)[b]
14d	3.71	(1.87)[b]	5.80	(1.67)[b]	(1.67)[b]	5.00	(1.87)[b]

[a] Multiplets or broad singlets. [b] Peak due to methyl group at that site; long-range coupling not included.



(12) (a) H. Meerwein, *Org. Syn.*, **46**, 120 (1966); (b) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4096 (1964), and pertinent references cited therein.

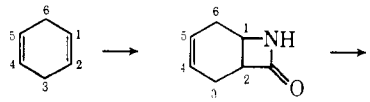
(13) At the time this work was performed, four-membered rings with an imino nitrogen were unknown. Since the completion of our synthesis, the preparation of several 1-azetines has been described: (a) G. Pifferi, P. Consonni, G. Pelizza, and E. Testa, *J. Heterocycl. Chem.*, **4**, 619 (1967); *Gazz. Chim. Ital.*, **98**, 1283 (1968); (b) D. Bormann, *Justus Liebigs Ann. Chem.*, **725**, 124 (1969); (c) L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 1763 (1970).

(14) These yields were somewhat variant with time. Minor contaminants which were present to the extent of approximately 10% were not characterized.

hydrobromination—azocines **14a–d** were obtained with no great difficulty. All of the azocines displayed medium to intense infrared absorptions at 1670–1690 cm^{-1} (imino ether) and 1625–1640 cm^{-1}. The striking similarity of their C=C bond stretching frequencies with those reported for **1**[15] and the excellent correspondence of their ultraviolet spectra (Table I) with that of **1**[16] suggest that these hetero analogs likewise exist in the strain-free puckered "tub" conformation known to be preferred by the hydrocarbon.[5,17]

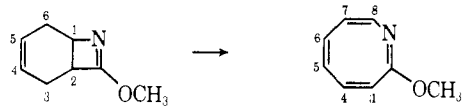
The nmr spectra of 2-methoxyazocines are characterized particularly by a low-field ($\delta \sim 6.5$) doublet due to H_8 (when present) and a high-field (δ 4.9–5.1) absorption for H_7. As is seen (Table II), increased methyl

Scheme II



11a, 1-methyl series
b, 1,2-dimethyl series
c, 1,3,5-trimethyl series
d, 1,2,4,5-tetramethyl series

12

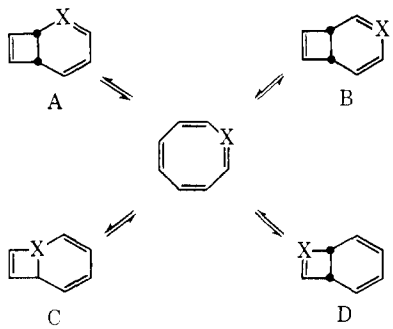


13

14a, 8-methyl derivative
b, 3,8-dimethyl derivative
c, 4,6,8-trimethyl derivative
d, 3,5,6,8-tetramethyl derivative

substitution serves to simplify the spectra. Clearly, the placement of methyl groups on the azocine nucleus does not exert an influence which significantly favors one or more of the possible bicyclic valence tautomeric forms.[18] In actuality, all five azocines exhibit temperature-invariant (−75 to 185°) nmr spectra which fail to provide any suggestion of the presence of isomeric imidates.[19]

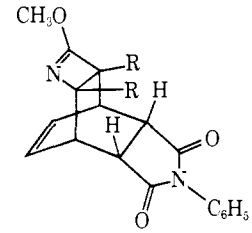
According to generalized theory, π-equivalent heterocyclic congeners of cyclooctatetraene may theoretically be characterized by dynamic equilibria with four structurally distinct valence tautomers (A–D). One of the



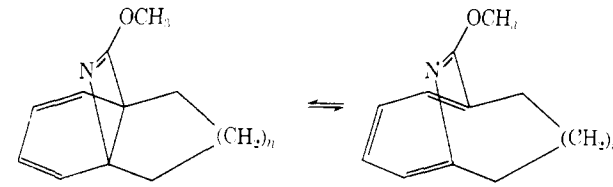
A B C D

heteroatomic bicyclo[4.2.0]octatrienes is likely to be preferred, however, for reasons such as more advantageous electronic interactions, more favorable conformational environments, and the like. Evidently, the 2-methoxyazocines are sufficiently stabilized that the proportion of valence tautomer in equilibrium is below the spectroscopic detection limit.

In **8** and **14a**, azetine tautomer D appears to be the reacting species in their base-induced conversion to benzonitriles. Further support for the existence of this reversible equilibrium was provided by the Diels–Alder reaction of **8** and **14b** with *N*-phenylmaleimide in refluxing toluene. The resulting colorless crystalline (4 + 2) π adducts exhibited spectral properties in unique agreement with structures **15a** and **15b**, respectively. The products are formulated with the imide moiety syn to the double bond in accordance with established precedence.[7,20]



15a, R = H
b, R = CH_3



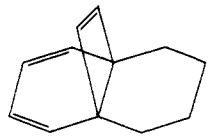
16a 16b

Synthesis of Unsaturated Azapropellanes. Because the constitution and diene characteristics of the 2-methoxyazocines parallel closely those of cyclooctatetraene in which the concentration of bicyclic tautomer at 100° is only 0.01%,[21] the opportunity of relating substituent effects to the position of equilibrium did not present itself. Due to considerable interest in the effect of steric influences on the course of such electrocyclic reactions,[18] attention was turned to the preparation of a number of annelated 7-azabicyclo[4.2.0]-octatrienes (**16**).

In 1963, Vogel reported that the result of bridging a cycloheptatriene ring by a trimethylene chain at the 2 and 7 positions was to impose a strain sufficiently large that the molecule was restricted to its valence-tautomeric norcaradiene form.[22] Complete reversal of the equilibrium was noted when the chain was lengthened to four methylene groups. Later, Paquette demonstrated that this same propensity for formation of the triene tautomer was shared by the *N*-carbalkoxyazepine system.[23] In contrast, the arene oxide–oxepin equilibrium is much more closely balanced, as revealed by the fact that the relatively unstrained $(CH_2)_3$ bridged derivative consists of approximately equal concentrations of the two tautomers.[18a] Related molecules with a diatomic cen-

(15) E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Amer. Chem. Soc.*, 73, 3370 (1951).
(16) A. C. Cope and C. G. Overberger, *ibid.*, 70, 1433 (1948).
(17) I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952).
(18) (a) E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967); (b) G. Maier, *ibid.*, **6**, 402 (1967).
(19) L. A. Paquette, T. Kakihana, J. F. Kelly, and J. R. Malpass, *Tetrahedron Lett.*, 1455 (1968).
(20) J. G. Martin and R. K. Hill, *Chem. Rev.*, 61, 537 (1961).
(21) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, **No. 19**, 3 (1965).
(22) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).
(23) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969).

tral bridge have been virtually neglected, perhaps because of misconceived synthetic inaccessibility. In this regard, Paquette and Philips have recently established that **17** is a stable bicyclo[4.2.0]octatriene that exhibits no spectroscopically detectable tendency to undergo valence tautomerism to an annelated cyclo-

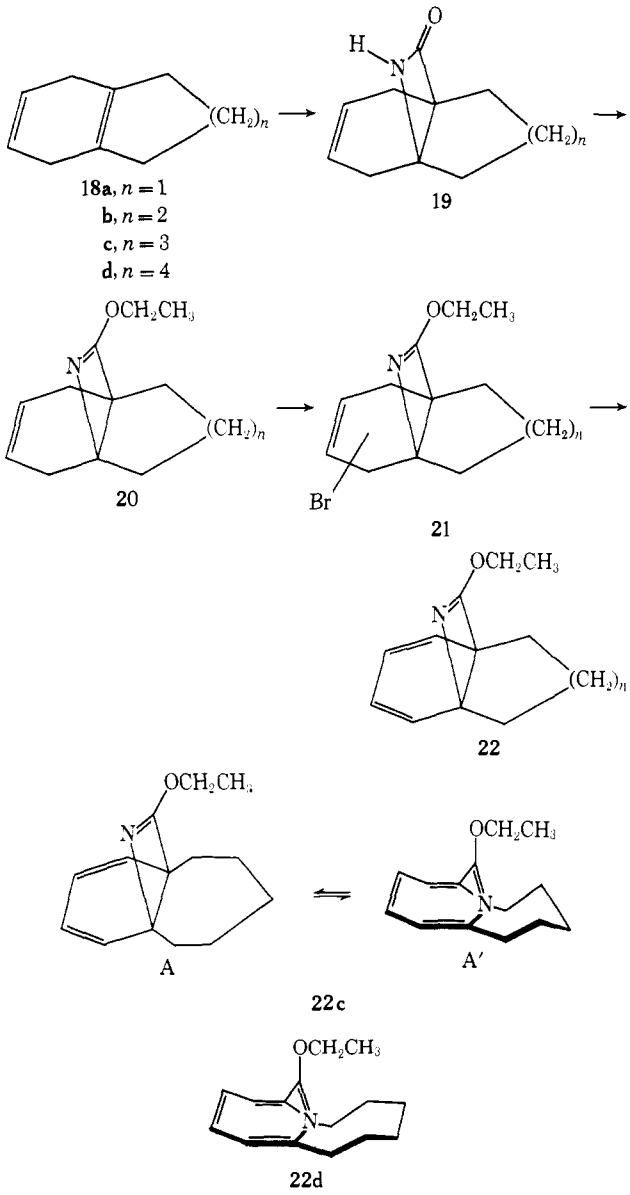


17

octatetraene over an appreciable temperature range.[24]

Taking into account the different equilibrium positions in the above molecules, it was expected that the annelated 7-azabicyclo[4.2.0]octatriene–azocine systems would be essentially completely tricyclic at $n = 1$ and 2 (*cf.* **16a**). A detailed investigation of the spectral and chemical properties of such azetines would therefore be possible. Also at issue was the question concerning the relationship of chain length to the capability of such

Scheme III



(24) L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969).

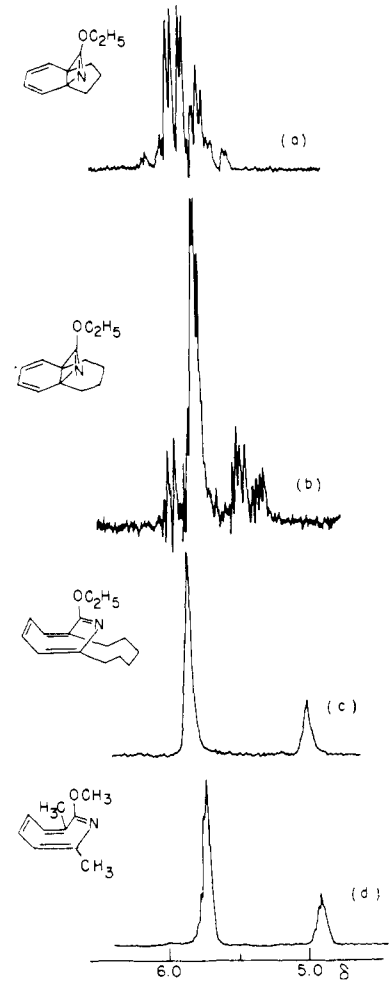


Figure 1. Partial 60-MHz nmr spectra of some azocines and 7-azabicyclo[4.2.0]octatrienes.

molecules to establish their apparent ground-state preference for the azocine tautomeric forms.

The synthetic method described earlier was employed as the means of entry into the annelated 7-azabicyclo[4.2.0]octatrienes (Scheme III). Stable azetine **22a** (prepared from 4,7-dihydroindan) revealed in its nmr spectrum a multiple line pattern at δ 5.55–6.20 (Figure 1) expected[25] for the four vinyl protons of the "locked in" cyclohexadiene tautomer and an ultraviolet spectrum differing considerably from that of the azocines (Table III). On being subjected to the same sequence of reactions, 5,8-dihydrotetralin (**18b**) was transformed sequentially into β-lactam **19b**, imino ether **20b**, and ultimately **22b**. The *temperature-independent* nmr spec-

Table III. Ultraviolet Spectra of Annelated 7-Azabicyclo[4.2.0]octatrienes (Isooctane Solution)

Compd	λ_{max}, nm (ϵ)[a]
22a	220 (1650) and 267 (2200)
22b	230 (1250) and 272 (2100)
22c	230 (1800) and 268 (2000)
22d	270 (560), 278 (570), and 292 (580)

[a] The 220–230 nm absorptions are not maxima.

(25) H. Günther and H.-H. Hinrichs, *Justus Liebigs Ann. Chem.*, **706**, 1 (1967).

trum of **22b** likewise displayed a pattern assignable to the vinyl protons of a 1,3-cyclohexadiene system (Figure 1). On the basis of the spectral properties of **22a** and **22b** (see also Table IV), it is apparent that for

Table IV. Mass Spectral Data for Various Fragment Ions of the 2-Methoxyazocines and Their Annelated Derivatives (70 meV)

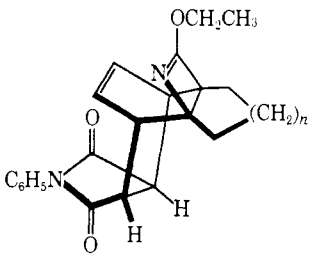
Compd	*m/e* (% relative abundance)
8	135 (35), 120 (100), 103 (14), 91 (59), 77 (67), 76 (28), 65 (55), 52 (21), 51 (33), 50 (20), 39 (47), and 38 (14)
14a	149 (61), 134 (100), 108 (34), 106 (66), 93 (28), 92 (73), 91 (100), 79 (22), 78 (36), 77 (23), 65 (91), 64 (10), 63 (19), 52 (10), 51 (24), 50 (12), 41 (13), 40 (10), and 39 (56)
14b	163 (74), 148 (100), 132 (11), 122 (26), 121 (14), 120 (41), 107 (28), 106 (30), 105 (26), 103 (12), 93 (15), 92 (14), 91 (61), 80 (10), 79 (44), 78 (15), 77 (31), 65 (19), 63 (13), 53 (18), 52 (14), 51 (27), 50 (10), 42 (13), 41 (17), and 39 (36)
14c	177 (7), 162 (28), 147 (10), 134 (10), 121 (12), 120 (43), 119 (20), 106 (13), 105 (100), 103 (12), 93 (19), 91 (40), 79 (15), 78 (14), 77 (40), 65 (17), 63 (15), 57 (11), 41 (19), and 39 (43)
14d	191 (14), 176 (38), 161 (21), 135 (17), 134 (50), 133 (15), 120 (12), 119 (100), 107 (12), 91 (24), 77 (12), 65 (11), 57 (11), 51 (10), 41 (13), and 39 (13)
22a	119 (10), 118 (100), 117 (84), 115 (18), 91 (21), and 39 (14)
22b	178 (10), 174 (14), 136 (27), 134 (13), 133 (11), 132 (80), 131 (38), 130 (12), 129 (15), 128 (22), 117 (18), 115 (18), 105 (14), 104 (100), 92 (10), 91 (60), 79 (12), 78 (10), 77 (17), 65 (16), 51 (15), 43 (12), 41 (16), and 39 (17)

steric reasons the tri- and tetramethylene bridges achieve complete displacement of the 2-alkoxyazocine equilibrium in favor of the azabicyclooctatriene tautomer.

The imino ether obtained from **18c** was also found to be uniform at room temperature; the spectral properties of this compound, particularly its ultraviolet (Table III) and nmr spectra (complex four-proton multiplet at δ 5.22–6.22), provide clear evidence for the 1-azetine formulation **22cA**. However, contrary to the behavior of **22a** and **22b**, the pentamethylene-bridged heterocycle exhibits a temperature-dependent nmr spectrum ($Cl_2C{=}CCl_2$ solution). As 100° is approached, the broad-resonance line of the methylene proton signal (δ 1.3–1.7) and the vinyl proton region begin to exhibit pronounced changes; interestingly, although a progressive series of changes is evidenced in the 100–150° region, no further alterations are spectroscopically detectable above this latter temperature. At 150° and above, the saturated protons appear as a 4 H low-field and a 6 H high-field pattern with a chemical-shift difference of approximately 0.35 ppm. Such changes (which are totally reversible) denote substantial displacement of the azabicyclooctatriene–azocine equilibrium in favor of bridged azocine **22cA′** at the elevated temperatures.

The imidate **22d** obtained from **18d** differed substantially from **22a–22c** in its spectral characteristics. For example, the infrared spectrum does not show the intense single absorption at 1603 cm^{-1} characteristic of the other unsaturated azapropellanes, but rather intense bands at 1672 and 1650 cm^{-1} which are characteristic of the azocines. Also, in isooctane three relatively weak ultraviolet maxima are seen at 270, 278, and 293 nm (Table III). The nmr spectrum, which is virtually identical with that of **14b** in the vinyl region (Figure 1), permitted definitive assignment of the azocine formulation (**22d**) to this substance. Not unexpectedly, the nmr spectrum of **22d** was temperature invariant. Thus, it would seem that, when the central bridge of a propellane derivative is a small diatomic sp^2-hybridized unit, a chain of six methylene units is required to arrive at a strain-free, uniform substance.

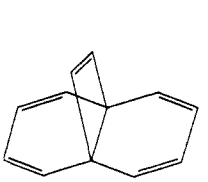
In refluxing toluene, **22a** and **22b** condensed readily with *N*-phenylmaleimide to afford the colorless (4 + 2) π adducts **23a** and **23b**, respectively. The stereochemistry of these products has been assigned on the basis of vicinal proton coupling constants (see Experimental Section) and analysis of nonbonded interactions oper-



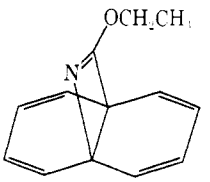
23a, $n = 1$
b, $n = 2$

ating in the various possible transition states.[26]

Attempted Synthesis of 11-Aza-12-ethoxy[4.4.2]propella-2,4,7,9,11-pentaene (25). In a somewhat related study, we have shown that [4.4.2]propella-2,4,7,9,11-pentaene (**24**) derives little or no enhancement of thermodynamic stabilization from overlap interaction of 10π electrons in the unusual fashion (orthogonal in part and uniquely along the top surface of the molecule) enforced by the inflexibility of the ring system.[27] Concurrently, we have examined the synthesis of **25** for a



24



25

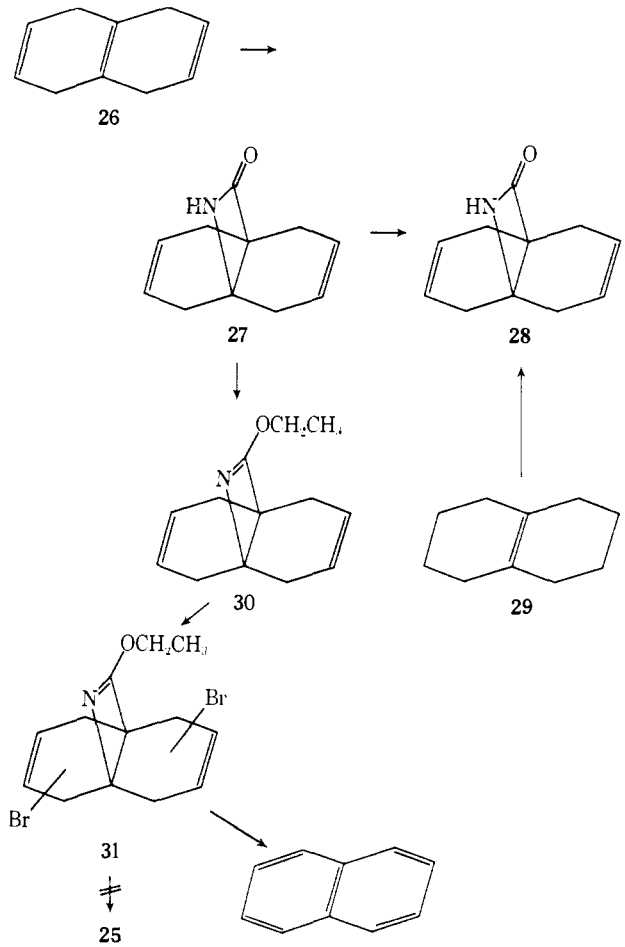
similar evaluation of possible homoconjugative stabilization. In particular, the question was raised concerning the possible effect of the imino nitrogen on the reactivity of a molecule possessing such an arrangement of π-atomic orbitals.

The cycloaddition of chlorosulfonyl isocyanate to 1,4,5,8-tetrahydronaphthalene (**26**) was carried out in the predescribed fashion and resulted in a 39% yield of β-lactam **27** (Scheme IV). The infrared carbonyl absorption (1748 cm^{-1}) and the four-proton multiplet in the vinyl region of the nmr spectrum of **27** were indicative of cycloaddition at the tetrasubstituted double bond. Further confirmatory evidence was derived from hydrogenation to β-lactam **28** which was prepared in unequivocal fashion from $\Delta^{9,10}$-octalin (**29**). O-Alkylation of **27** with triethyloxonium fluoroborate gave the expected imino ether **30** in 53% yield. Allylic bro-

(26) In particular, G. L. Thompson in these laboratories (unpublished results) has established that a hydrocarbon analog of **22b** is attacked by electrophilic reagents exclusively from the endo direction.

(27) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969).

Scheme IV



mination of **30** was achieved with 2 equiv of *N*-bromosuccinimide. No attempt was made at isolation or characterization of the resulting dibromide **31**. The dehydrobromination was accomplished with potassium *tert*-butoxide in tetrahydrofuran. Nmr analysis of the crude dehydrobromination product revealed, however, that **25** was not present. Rather, the formation of naphthalene was indicated. This was confirmed by vpc, and the hydrocarbon was isolated in 22% yield by column chromatography. Under no set of conditions examined could the formation of naphthalene be bypassed in favor of **25**.

Experimental Section[28]

7-Azabicyclo[4.2.0]oct-3-en-8-one (4). Into a 1-l. three-necked flask fitted with a mechanical stirrer, pressure-equalizing addition funnel, and reflux condenser (protected from the atmosphere with a drying tube) was placed a solution of 87.5 g (1.15 mol) of 1,4-dihydrobenzene in 70 ml of anhydrous benzene. The stirred solution was heated to 72–74° and chlorosulfonyl isocyanate (141.5 g, 1.0 mol) was added dropwise during 4 hr. Upon completion of the addition, the mixture was stirred for an additional 7 hr at the same temperature. After cooling, the mixture was poured onto *ca.* 500 g of ice contained in a 3-l. beaker, 250 ml of acetone was added, and hydrolysis was achieved by the dropwise addition of 4 *N* sodium hydroxide solution. The pH of the solution was maintained at 6–7 during the titration, and the temperature was maintained near 35° by the occasional addition of ice. The product was extracted with three 500-ml portions of methylene chloride. The combined organic layers were dried, filtered, and evaporated to give a yellow solid. Recrystallization of this material from tetrahydrofuran afforded 63.3 g (52%) of colorless crystals of **4**: mp 121.5–122.5°; $\nu_{max}^{CHCl_3}$ 3430, 1760, and 1670 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.78 (br s, 1, >NH), 5.78 (m, 2, vinyl), 3.93 (m, 1, >C*H*–N<), 3.33 (m, 1, >C*H*–CO–), and 2.25 (m, 4, allyl).

Anal. Calcd for C_7H_9NO: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.33; H, 7.46; N, 11.26.

8-Methoxy-7-azabicyclo[4.2.0]octa-3,7-diene (5). To a solution of 19.0 g (0.154 mol) of **4** in 150 ml of dry methylene chloride was added 23.6 g (0.194 mol) of trimethyloxonium fluoroborate[29] and the resulting suspension was stirred at 0° for 7 hr. To this mixture was added 400 ml of cold 5% aqueous potassium carbonate solution and the layers were thoroughly mixed. The organic layer was separated, washed rapidly with three 400-ml portions of ice water, and dried. The dried solution was evaporated and the residual oil was rapidly distilled under reduced pressure with the receiver cooled to −78°. There was obtained 11.4 g (54%) of **5** as a colorless, mobile liquid with a penetrating odor: bp 43–44° (0.3 mm); ν_{max}^{film} 1618 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.58–5.75 (m, 2, vinyl), 3.60–3.80 (m, 1, >C*H*—N=), 3.68 (s, 3, –OCH_3), 3.27–3.54 (m, 1, >C*H*—C(OCH_3)=), and 1.97–2.42 (m, 4, allyl).

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.44; H, 8.13; N, 10.59.

2-Methoxyazocine (8). To a suspension of 15.45 g (0.087 mol) of *N*-bromosuccinimide in 150 ml of carbon tetrachloride was added 11.36 g (0.083 mol) of **5** followed by 0.3 g of benzoyl peroxide. The mixture was heated at reflux with stirring and concomitant irradiation with a sunlamp under a nitrogen atomsphere. After 10 min, the mixture was cooled to room temperature, filtered to remove succinimide, and evaporated. The viscous slightly brown oil was employed without further purification.

To a suspension of 18.6 g (0.166 mol) of potassium *tert*-butoxide in 150 ml of anhydrous ether cooled to 0° was added dropwise a solution of the crude bromide in 30 ml of anhydrous tetrahydrofuran during 10 min under a nitrogen atmosphere. The rate of addition was adjusted to maintain gentle reflux. After stirring for an additional 9 hr at 0°, the dark reaction mixture was shaken with 20 ml of water. This aqueous layer was extracted with two 150-ml portions of ether and the combined organic layers were dried, filtered, and evaporated. Distillation under reduced pressure gave 5.16 g of a yellow, mobile liquid, bp 80–84° (14 mm). Vpc analysis (10 ft × 0.25 in. column packed with 10% XF-1150 on 60–80 Chromosorb G, 120°) indicated the presence of **8** (55%, 6.8 min) and benzonitrile (45%, 15 min). Preparative scale separation gave pure **8** as a yellow liquid: ν_{max}^{film} 1675, 1640, and 1620 cm^{-1}.

Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.87; H, 6.54; N, 10.21.

The peak of longer retention time was identified as benzonitrile by comparison of various spectra with those of an authentic sample.

The azocine can also be purified by column chromatographic means. For example, elution of 5.16 g of a similar mixture through charcoal–Celite (2:3) (50 g) using petroleum ether (30–60°) gave the following results: fr 1, 90 ml, no material; fr 2, 100 ml, 1.14 g of pure **8**; fr 3, 30 ml, 86% of **8** and 14% nitrile (1.07 g); fr 4, 30 ml, 77% of **8** and 23% nitrile (0.22 g); fr 5, 30 ml, 5% of **8** and 95% nitrile (0.49 g).

Treatment of 8 with Potassium *tert*-Butoxide. To a suspension of 59.5 mg (0.53 mmol) of potassium *tert*-butoxide in 10 ml of anhydrous tetrahydrofuran was added 36.4 mg (0.27 mmol) of **8** and the mixture was stirred at room temperature for 5 hr. Work-up in the predescribed fashion gave a mobile yellow oil, vpc analysis of which indicated the presence of 53% **8** and 47% benzonitrile.

Hydrogenation of 8. Hydrogenation of **8** over 10% palladium-on-charcoal catalyst in methanol solution afforded **9** as a colorless oil after the uptake of 3 equiv of hydrogen: ν_{max}^{film} 1680 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 3.52 (s, 3, –OCH_3), 3.20–3.45 (m, 2, >C*H*—N=), 2.08–2.40 (m, 2, >C*H*—C(OCH_3)=), and 1.15–1.90 (m, 8, methylene).[30]

An authentic sample of **9** was prepared by adding 2.0 g (15.8 mmol) of **10** to a suspension of 2.86 g (23.7 mmol) of trimethyloxonium fluoroborate in 25 ml of dry methylene chloride. The mixture was stirred at 0° under anhydrous conditions for 7 hr, rendered alkaline by the addition of saturated aqueous sodium bicarbonate solution, and separated into two layers. The organic layer was dried, filtered, and evaporated to give 2.07 g (94%) of **9**, bp 78° (20 mm).

6-Methyl-7-azabicyclo[4.2.0]oct-3-en-8-one (12a). To a solution of 37.6 g (0.4 mol) of 3,6-dihydrotoluene (**11a**)[31] in 100 ml of an-

(28) All melting points were taken in open capillaries and are corrected, while boiling points are uncorrected.

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

(30) Compare W. Z. Heldt, *J. Amer. Chem. Soc.*, 80, 5880 (1958).

(31) W. Hückel, B. Graf, and D. Münker, *Justus Liebigs Ann. Chem.*, 614, 47 (1958).

hydrous ether was added a solution of 40 ml of chlorosulfonyl isocyanate in 50 ml of ether in one portion. The solution refluxed gently as the reaction proceeded. After 90 min, the solvent was removed *in vacuo* and the residue was dissolved in 50 ml of acetone. This solution was poured onto 100 g of ice and titrated at pH 8 with 4 *N* sodium hydroxide solution with occasional addition of ice to keep the temperature below 30°. The solution was extracted with methylene chloride (four 250-ml portions) and the combined extracts were washed with water (50 ml), dried, and evaporated to yield 49.5 g (90%) of **12a**. An analytical sample melted at 89–91° after recrystallization from benzene–petroleum ether and sublimation at 85° (0.5 mm): ν_{max}^{Nujol} 3100 and 1750 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.60 (br s, 1, >NH), 5.75–5.90 (m, 2, vinyl), 2.90 (m, 1, >C*H*CO–), 1.80–2.60 (m, 4, allyl), and 1.36 (s, 3, –CH$_3$).

Anal. Calcd for $C_8H_{11}NO$: C, 70.01; H, 8.08; N, 10.21. Found: C, 70.13; H, 8.28; N, 10.59.

6-Methyl-8-methoxy-7-azabicyclo[4.2.0]octa-3,7-diene (13a). A solution of 34.3 g (0.25 mol) of **12a** in 100 ml of methylene chloride was added dropwise to a stirred mixture of 44.5 g (0.30 mol) of trimethyloxonium fluoroborate in 100 ml of the same solvent at 0° under nitrogen. The addition required 90 min. The mixture was stirred for 2 hr at 0° and then filtered. The filtrate was swirled in ice while an iced solution of 35 g of potassium carbonate in 100 ml of water was added. The organic phase was decanted from the aqueous paste which was reextracted with 100 ml of methylene chloride. The combined organic layers were processed in the usual manner. Since the product was essentially pure but decomposed on heating, it was generally employed without distillation. A reference sample was subjected to molecular distillation at 26° (0.07 mm): ν_{max}^{film} 1625 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 5.67–5.83 (m, 2, vinyl), 3.72 (s, 3, –OCH$_3$), 2.89 (br t, J = 4.5 Hz, 1, >C*H*—C(OCH$_3$)=), 1.70–2.60 (m, 4, allyl), and 1.31 (s, 3, –CH$_3$).

2-Methoxy-8-methylazocine (14a). A solution of 7.51 g (0.05 mol) of **13a** in 75 ml of methylene chloride and 0.5 ml of pyridine was stirred at −65° to −70° under nitrogen while a solution of 9.6 g (0.06 mol) of bromine in 25 ml of methylene chloride was added dropwise. When the addition was completed, the solvent was evaporated *in vacuo* at <0°. The residue was dissolved in 75 ml of anhydrous tetrahydrofuran and an excess of sodium methoxide was added to the stirred solution under nitrogen during 10 min. The mixture was stirred for 5 hr at 0° and filtered. The filtrate was evaporated without heating at reduced pressure, and the residual oil was extracted with 150 ml of ether. This extract was washed with water (two 50-ml portions), dried and evaporated. The residue was dissolved in 200 ml of petroleum ether (30–60°)–benzene (3:1) and passed through a 3 × 10-cm column of alumina (neutral, activity III), and the column was eluted with an additional 200 ml of the same solvent combination. On evaporation, 2.7 g of a 5:1 mixture of azocine and *o*-toluonitrile was obtained; this represents a 28% yield of azocine. Separation was effected by preparative scale vpc at 100° on a 6 ft × 0.25 in. column packed with 10% XF-1150 on Chromosorb W. Under these conditions, **14a** had a retention time of 4.1 min while the nitrile appeared after 10 min; ν_{max}^{film} 1685, 1640, and 1280 cm^{-1}.

Anal. Calcd for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.30; H, 7.63; N, 9.36.

1,6-Dimethyl-7-azabicyclo[4.2.0]oct-3-en-8-one (12b). To a solution of 53 g (0.5 mol) of 1,2-dimethyl-1,4-cyclohexadiene (**11b**)[32] in 50 ml of anhydrous benzene cooled to 0° was added dropwise 70.8 g (0.5 mol) of chlorosulfonyl isocyanate during 80 min. The reaction mixture was stirred at this temperature for 4 hr and was worked up according to the generalized procedure. There was obtained a colorless solid, recrystallization of which from hexane gave 54.3 g (72%) of **12b**: mp 91–92°; $\nu_{max}^{CHCl_3}$ 3360, 3200, and 1760 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.89 (br s, 1, >NH), 5.58–5.68 (m, 2, vinyl), 1.51–2.55 (m, 4, allyl), 1.43 and 1.21 (s, 3 each, –CH$_3$).

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.49; H, 8.77; N, 9.23.

1,6-Dimethyl-8-methoxy-7-azabicyclo[4.2.0]octa-3,7-diene (13b). Treatment of 22.97 g (0.15 mol) of **12b** with 20.2 g (0.165 mol) of trimethyloxonium fluoroborate in 150 ml of methylene chloride for 8 hr at 0° and processing in the predescribed fashion afforded 19.91 g (80%) of **13b** as a colorless mobile liquid: bp 46–47 (0.3 mm); $n^{25}D$ 1.5329; ν_{max}^{film} 1635 and 1600 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 5.66–5.88 (m, 2, vinyl), 3.77 (s, 3, –OCH$_3$), 1.73–2.38 (m, 4, allyl), 1.29 and 1.18 (s, 3 H, each, –OCH$_3$).

The perchlorate salt of **13b** was obtained as colorless crystals: mp 139–140° (from methanol–ether); $\nu_{max}^{CHCl_3}$ 3100 and 1690 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}ClNO_5$: C, 45.20; H, 6.07; N, 5.27. Found: C, 45.23; H, 6.07; N, 5.19.

3,8-Dimethyl-2-methoxyazocine (14b). A mixture of 19.91 g (0.12 mol) of **13b**, 22.4 g (0.126 mol) of *N*-bromosuccinimide, 0.3 g of benzoyl peroxide, and 200 ml of carbon tetrachloride was refluxed with stirring under a nitrogen atmosphere. The mixture was simultaneously irradiated with a sunlamp. After 20 min, the contents were cooled to room temperature and filtered. Evaporation of the filtrate under reduced pressure at 25° afforded a somewhat viscous orange oil.

A solution of this oil in 50 ml of anhydrous tetrahydrofuran was added dropwise to a rapidly stirred refluxing suspension of freshly prepared sodium methoxide (from 5.52 g of sodium metal) in 200 ml of the same solvent. Upon completion of the addition, the mixture was refluxed for 23 hr, cooled, filtered, and evaporated. The residual dark oil was mixed with 300 ml of water and extracted with ether (three 150-ml portions). The combined extracts were washed with water, dried, and evaporated to give 13.13 g of a yellow oil, bp 45–50° (0.15 mm). Vpc analysis (10 ft × 0.25 in. column packed with 10% XF-1150 on Chromosorb W) at 130° showed two peaks at 6.5 (95%) and 7.0 min (5%). For purification, this oil was stirred at room temperature with methyl iodide (1.13 g, 0.08 mol) for 1 hr. Removal of the excess methyl iodide, followed by distillation, afforded 11.35 g of yellow oil containing only 1% of impurity. An analytical sample was obtained by preparative scale vpc: ν_{max}^{film} 1670, 1640, and 1630 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.11; H, 8.10; N, 8.41.

2,4,6-Trimethyl-7-azabicyclo[4.2.0]oct-3-en-8-one (12c). A solution of 130 g of 65% pure 3,6-dihydromesitylene (**11c**)[31] (containing 35% mesitylene) in 100 ml of acetonitrile was cooled in ice and treated dropwise with 100 g of chlorosulfonyl isocyanate during 60 min. One hour after completion of the addition, the mixture was poured into 500 ml of iced acetone and titrated at pH 7–8 with 4 *N* sodium hydroxide solution. After the hydrolysis, 1500 ml of water was added and the mixture was extracted with methylene chloride. The product was isolated in the usual manner; there was obtained 97.8 g (83%) of white needles: mp 89–91° (from petroleum ether–ether); ν_{max}^{Nujol} 3250 and 1750 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 7.13 (br s, 1, >NH), 5.50 (br d, J = 7.0 Hz, 1, vinyl), 2.51 (m, 2, >C*H*CO– and 3° allylic), 2.12 (m, 2, allylic), 1.69 (d, J = 1.0 Hz, 3, 4-methyl), 1.47 (s, 3, 6-methyl), and 0.96 (d, J = 7.0 Hz, 3, 2-methyl).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.76; H, 9.22; N, 8.39.

2,4,6-Trimethyl-8-methoxy-7-azabicyclo[4.2.0]octa-3,7-diene (13c). A 25.0-g sample (0.15 mol) of **12c** in 50 ml of methylene chloride was added dropwise to 30 g (0.20 mol) of trimethyloxonium fluoroborate in 150 ml of the same solvent at 0° under nitrogen. After an additional 6 hr at 0°, the cooled mixture was treated slowly with a solution of 13.8 g of potassium carbonate in 75 ml of water and worked up in the predescribed fashion. Distillation afforded 9.5 g (35.3%) of colorless oil: bp 52–54° (0.3 mm); ν_{max}^{film} 1630 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 5.34 (br d, J = 6.5 Hz, 1, vinyl), 3.62 (s, 3, –OCH$_3$), 2.1–2.6 (m, 2, methine protons), 2.08 (br s, 2, allyl), 1.65 (s, 3, 4-methyl), 1.30 (s, 3, 6-methyl), and 0.94 (d, J = 7.0 Hz, 3, 2-methyl).

2-Methoxy-4,6,8-trimethylazocine (14c). A solution of 4.08 g (23 mmol) of **13c** in 50 ml of methylene chloride was stirred at −70° under nitrogen while a solution of 3.7 g (23 mmol) of bromine in 25 ml of the same solvent was added dropwise during 1 hr. The solution was stirred for 15 min and then warmed to 0° while the solvent was removed *in vacuo*. To the residue was added 50 ml of anhydrous tetrahydrofuran and this cold solution was treated with an excess of sodium methoxide and allowed to warm to room temperature. After 3 hr, the mixture was processed as above. Rapid chromatography of the crude product on alumina (basic, activity I) gave 2.99 g (73%) of yellow oil, bp 37° (0.25 mm); ν_{max}^{film} 1675 and 1625 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.79; H, 8.56; N, 7.83.

1,2,4,5-Tetramethyl-1,4-cyclohexadiene (11d). To a solution of 134 g (1 mol) of durene in 1200 ml of anhydrous tetrahydrofuran was added 1500 ml of liquid ammonia. The resulting suspension was stirred while 49 g (7 g-atom) of lithium wire cut into short lengths was added during 15 min. The mixture was stirred vigorously for 4 hr under reflux (Dry Ice–acetone condensers). Ethanol (500 ml) was added dropwise (45 min), the ammonia was allowed to evaporate, and the residue was treated with 2000 ml of water and extracted with ether (500 ml). The ether solution was washed successively with water (two 1000-ml portions), 10% hydrochloric acid (500 ml), and water (1000 ml). This solution was dried and

(32) L. A. Paquette and J. H. Barrett, *Org. Syn.*, **49**, 62 (1969).

evaporated, and the residue was recrystallized from ethanol to give 115 g (85%) of pure **11d**, mp 62–63° (lit.[33] mp 61.9–62.2°).

1,3,4,6-Tetramethyl-7-azabicyclo[4.2.0]oct-3-en-8-one (12d). A solution of 17 g (0.12 mol) of chlorosulfonyl isocyanate in 20 ml of dry ether was added in one portion to a solution of 13.6 g (0.1 mol) of **11d** in 25 ml of ether. After approximately 10 min, the solution began to reflux gently. After 45 min, the solution was evaporated and the residue was hydrolyzed in the usual manner. The β-lactam was obtained as white needles: mp 114–116°, from benzene–petroleum ether; 14.0 g (78%); ν_{max}^{Nujol} 1745 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.90 (br s, 1, >NH), 1.8–2.1 (m, 4, allyl), 1.70 (s, 6, allylic methyl groups), 1.34 and 1.20 (s, 3 H each, bridgehead methyls).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.74; H, 9.45; N, 7.73.

1,3,4,6-Tetramethyl-8-methoxy-7-azabicyclo[4.2.0]octa-3,7-diene (13d). A solution of 36.0 g (0.20 mol) of **12d** in 100 ml of methylene chloride was treated with 45 g (0.3 mol) of trimethyloxonium fluoroborate as outlined above. Vacuum distillation of the crude product gave 28.1 g (73%) of **13d**: bp 71–75° (0.8 mm); ν_{max}^{film} 1630 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 3.80 (s, 3, $-OCH_3$), 2.08 and 1.89 (br s, 2 H each, allyl), 1.66 (s, 6, allylic methyls), 1.25 and 1.13 (s, 3 H each, bridgehead methyls).

Treatment of **13d** with ethanolic perchloric acid yielded a colorless crystalline perchlorate, mp 155–157° (from ethanol).

Anal. Calcd for $C_{12}H_{20}ClNO_5$: C, 49.06; H, 6.88; N, 4.77. Found: C, 49.06; H, 6.98; N, 4.67.

The pot residue from the above distillation was recrystallized from petroleum ether (30–60°) to give 2.8 g (7.3%) of colorless prisms: mp 93–94°; identified as 1,3,4,6,7-pentamethyl-7-azabicyclo[4.2.0]oct-3-en-8-one; ν_{max}^{Nujol} 1750 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 2.58 (s, 3, N–CH_3), 1.9–2.2 (m, 4, allyl), 1.68 (s, 6, allylic methyls), 1.25 and 1.18 (s, 3 H each, bridgehead methyls).

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.87; H, 10.00; N, 7.30.

2-Methoxy-3,5,6,8-tetramethylazocine (14d). A 3.00-g (15.5 mmol) sample of **13d** was brominated (Br_2, CH_2Cl_2, −70°) and dehydrobrominated (excess sodium methoxide in dry tetrahydrofuran, 25°, 5 hr) as before. The crude product was passed through a 1 × 15 cm column of alumina (basic, activity I) and vacuum distilled to give 1.28 g (43%) of **14d** as a yellow oil: bp 46–47° (0.8 mm); ν_{max}^{film} 1690, 1245, and 1130 cm^{-1}.

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.64; H, 9.03; H, 7.25.

***N*-Phenylmaleimide Adduct of 8.** A solution of 320 mg (18.5 mmol) of *N*-phenylmaleimide and 0.48 g of a mixture of **8** (52%, 18.5 mmol) and benzonitrile (48%) in 8 ml of toluene was heated at reflux for 5 hr. Evaporation of the solvent and recrystallization of the residue from benzene–hexane gave 348 mg (61%) of **15a**, mp 205–207°; $\nu_{max}^{CHCl_3}$ 1730 and 1625 cm^{-1}; $\delta_{TMS}^{CD_3CN}$ 7.07–7.68 (m, 5, aryl), 6.00–6.14 (m, 2, vinyl), 3.70 (s, 3, $-OCH_3$), 3.13–3.75 (m, 4, azetine and bridgehead), and 3.05 (d, J = 1.1 Hz, 2, α-carbonyl).

Anal. Calcd for $C_{18}H_{16}N\,O_3$: C, 70.11; H, 5.23; N, 9.09. Found: C, 69.93; H, 5.37; N, 8.99.

***N*-Phenylmaleimide Adduct of 14b.** A solution of 1.50 g (92 mmol) of **14b** and 1.59 g (92 mmol) of *N*-phenylmaleimide in 7 ml of xylene was refluxed for 5 hr. Removal of the solvent *in vacuo* and recrystallization of the residue from acetone afforded 1.88 g (61%) of **15b** as white needles: mp 194–195.5°; $\nu_{max}^{CHCl_3}$ 1705 and 1615 cm^{-1}; $\delta_{TMS}^{CD_3CN}$ 7.01–7.65 (m, 5, aryl), 6.01–6.27 (m, 2, vinyl), 3.65 (s, 3, $-OCH_3$), 3.19 (d, J = 1.1 Hz, 2, α-carbonyl), 2.75–3.28 (m, 2, bridgehead), 1.31 and 1.23 (s, 3 H each, methyls).

Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.37; H, 6.10; N, 8.29.

11-Oxo-10-aza[4.3.2]propell-3-ene (19a). Chlorosulfonyl isocyanate (71 g, 0.50 mol) was added dropwise to 60 g (0.50 mol) of 4,7-dihydrofuran (**18a**),[34] and the resulting reaction mixture was stirred for 1 hr under nitrogen. Scratching produced crude crystalline *N*-(chlorosulfonyl) β-lactam which was added in small portions to a 50% aqueous acetone solution maintained at neutrality by the dropwise addition of 4 *N* sodium hydroxide solution. The neutralized reaction mixture was extracted with ether and the combined organic layers were dried, filtered, and evaporated. Recrystallization of the residue from petroleum ether (60–110°) gave 50 g (62%) of **19a**, mp 61–63°; $\nu_{max}^{CHCl_3}$ 1748 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.50 (br s, 1, >NH), 5.80 (m, 2, vinyl), and 0.90–2.90 (m, 10, allyl and methylene).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.76; H, 8.04; N, 8.44.

11-Ethoxy-10-aza[4.3.2]propella-3,10-diene (20a). Treatment of 42.6 g (0.261 mol) of **19a** with 0.273 mol of triethyloxonium fluoroborate in methylene chloride solution for 6 hr at room temperature afforded 36 g (73%) of **20a** as a colorless oil: bp 65° (0.3 mm); ν_{max}^{film} 1620 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.72 (m, 2, vinyl), 4.17 (q, J = 7.0 Hz, 2, $-OCH_2-$), 0.90–2.84 (m, 10, allyl and methylene), and 1.29 (t, J = 7.0 Hz, 3, methyl).

The perchlorate salt of **20a** was obtained as colorless crystals, mp 120–122° (from ethanol–ether).

Anal. Calcd for $C_{12}H_{18}ClNO_5$: C, 49.40; H, 6.22; N, 4.80. Found: C, 49.29; H, 6.17; N, 4.73.

11-Ethoxy-10-aza[4.3.2]propella-2,4,10-triene (22a). A mixture of 30.6 g (0.16 mol) of **20a**, 30 g (0.17 mol) of *N*-bromosuccinimide, a trace of benzoyl peroxide, and 200 ml of carbon tetrachloride was refluxed for 1 hr under a nitrogen atmosphere. After filtration, the solvent was evaporated, the residual oil was dissolved in 50 ml of dry tetrahydrofuran, and this solution was added dropwise to an ice-cold slurry of 29.0 g (0.258 mol) of potassium *tert*-butoxide in 50 ml of anhydrous tetrahydrofuran. After 2 hr at 0°, the mixture was processed as above to yield 14.4 g (47%) of **22a**, bp 50–52° (0.1 mm), a portion of which was purified further by preparative vpc at 140°; ν_{max}^{film} 1603 cm^{-1}; calcd *m/e* 189.1154; observed *m/e* 189.1154.

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 75.74; H, 8.32; N, 7.02.

12-Oxo-11-aza[4.4.2]propell-3-ene (19b). Addition of 73 g (0.52 mol) of chlorosulfonyl isocyanate to 73 g (0.54 mol) of 5,8-dihydrotetralin (**18b**),[35] followed by the usual hydrolysis, afforded 51 g (54%) of β-lactam as colorless crystals: mp 90–91° (from petroleum ether, bp 60–110°); $\nu_{max}^{CHCl_3}$ 1748 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.80 (br s, 1, >NH), 5.82 (m, 2, vinyl), and 1.22–2.57 (m, 12, allyl and methylene).

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.68; H, 8.68; N, 7.91.

Hydrogenation of 19b. A solution of 150 mg (0.846 mmol) of **19b** in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure over 10% palladium-on-carbon. After filtration of the catalyst, evaporation of the solvent, and recrystallization of the residue from hexane, there was obtained 145 mg (96%) of 12-oxo-11-aza[4.4.2]-propellane (**28**), mp 51–53°, identical in all respects with an authentic sample.

12-Ethoxy-11-aza[4.4.2]propella-3,11-diene (20b). A 55.0-g (0.310 mol) sample of **19b** was treated with a slight excess of triethyloxonium fluoroborate in the predescribed manner to give 52.0 g (82%) of **20b** as a colorless oil, bp 62–64° (0.25 mm); ν_{max}^{film} 1623 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.72 (m, 2, vinyl), 4.22 (q, J = 7.0 Hz, $-OCH_2-$), 1.12–2.57 (m, 12, allyl and methylene), and 1.33 (t, J = 7.0 Hz, 3, methyl).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.23; H, 9.37; N, 6.87.

12-Ethoxy-11-aza[4.4.2]propella-2,4,11-triene (22b). *N*-Bromosuccinimide (5.3 g, 0.03 mol) bromination of **20b** (6.0 g, 0.029 mol), followed by treatment of the crude allylic bromide with 6.7 g (0.06 mol) of potassium *tert*-butoxide in tetrahydrofuran at 0° for 1.5 hr, gave 2.2 g (38%) of **22b** as a colorless oil, bp 56–57° (0.04 mm); ν_{max}^{film} 1603 cm^{-1}.

Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.35; H, 8.53; N, 6.68.

6,9-Dihydrobenzocycloheptene (18c). To a mechanically stirred mixture of 14.7 g (0.092 mol) of benzocycloheptene[36] and 27.6 g (0.60 mol) of ethanol in 150 ml of liquid ammonia was added 9.2 g (0.4 g-atom) of sodium metal in small pieces. Each successive piece of sodium was added upon the disappearance of the dark blue color, and the ammonia was allowed to reflux gently during the addition. The ammonia was allowed to evaporate, and 200 ml of water was added cautiously. The mixture was extracted with 200-ml portions of ether, and the combined extracts were washed with water, dried, and evaporated. Vpc analysis of the resulting oil indicated that considerable benzocycloheptene remained and therefore the sample was resubmitted to the Birch reduction. The recycled product was fractionally distilled utilizing a spinning band column; there was obtained 7.1 g (52%) of **18c**, bp 78° (5 mm);

(33) W. Hückel and R. Cramer, *Justus Liebigs Ann. Chem.*, **630**, 89 (1960).

(34) E. Giovannini and H. Wegmuller, *Helv. Chim. Acta*, **41**, 933 (1958).

(35) W. Hückel and U. Worfell, *Chem. Ber.*, **89**, 2098 (1956).

(36) N. L. Allinger and E. S. Jones, *J. Org. Chem.*, 27, 70 (1962).

$\delta_{TMS}^{CDCl_3}$ 5.62 (t, J = 1.2 Hz, 2, vinyl), 2.64 (d, J = 1.2 Hz, 4, doubly allylic), 2.03 (m, 4, allylic), and 1.55 (m, 6, methylene).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.42; H, 10.76.

13-Oxo-12-aza[5.4.2]propell-9-ene (19c). To an ice-cold, magnetically stirred solution of 6.0 g (0.041 mol) of **18c** in 10 ml of methylene chloride was added under a nitrogen atmosphere 5.2 g (37 mmol) of chlorosulfonyl isocyanate over a 10-min period. The reaction mixture was allowed to warm to room temperature during 1 hr with continued stirring. Hydrolysis in the customary manner gave an oil which was triturated with petroleum ether and refrigerated. After 2 days, the crystalline β-lactam was filtered and air dried, 2.24 g (28.6%), mp 58–68°. An analytical sample, mp 67–70°, was obtained after chromatography on neutral alumina (activity III) followed by recrystallization from petroleum ether: $\nu_{max}^{CHCl_3}$ 1742 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.60 (br s, 1, >NH), 5.62 (m, 2, vinyl), 2.18 (m, 4, allyl), and 1.64 (m, 10, methylene).

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.07; H, 9.19; N, 7.30.

13-Ethoxy-12-aza[5.4.2]propella-9,12-diene (20c). Exposure of 2.20 g (12 mmol) of **19c** to a slight excess of triethyloxonium fluoroborate in methylene chloride (4 hr, room temperature) yielded 1.10 g (42%) of a colorless oil, bp 84–88° (0.3 mm); ν_{max}^{film} 1625 cm^{-}; $\delta_{TMS}^{CDCl_3}$ 5.70 (m, 2, vinyl), 4.19 (q, J = 7.0 Hz, $-OCH_2-$), 1.03–2.39 (m, 14, allyl and methylene), and 1.28 (t, J = 7.0 Hz, 3, methyl).

The perchlorate of **20c** was obtained as colorless crystals, mp 108.5–110°, from ethanol–ether.

Anal. Calcd for $C_{14}H_{22}ClNO_5$: C, 52.58; H, 6.94; N, 4.38. Found: C, 52.32; H, 6.90; N, 4.22.

13-Ethoxy-12-aza[5.4.2]propella-8,10,12-triene (22c). *N*-Bromosuccinimide (1.28 g, 7.19 mmol) bromination of **20c** (1.50 g, 6.85 mmol), followed by treatment of the crude allylic bromide with 1.53 g (14 mmol) of potassium *tert*-butoxide in tetrahydrofuran at 0° for 2 hr, gave 0.70 g (47%) of **22c** as a pale yellow oil: bp 92–94° (0.3 mm); ν_{max}^{film} 1603 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.15; H, 8.66; N, 6.04.

7,10-Dihydrobenzocyclooctene (18d). To a mechanically stirred solution of 20.0 g (0.125 mol) of benzocyclooctene,[37] 56.4 g (1.25 mol) of ethanol, and 25 ml of anhydrous ether in 1.0 l. of liquid ammonia was added 7 g (1.0 g-atom) of lithium wire in small pieces over a 3-hr period. The ammonia was allowed to evaporate. The customary work-up gave 18 g of a colorless liquid, bp 68–69° (0.5 mm), which consisted of **18d** (~85%) and three minor components (~15%). Pure **18d** was obtained by preparative vpc; $\delta_{TMS}^{CDCl_3}$ 5.56 (t, J = 1 Hz, 2, vinyl), 2.47 (d, J = 1 Hz, 4, doubly allylic), 2.10 (m, 4, allylic), and 1.45 (m, 8, methylene).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.14; H, 11.16.

14-Oxo-13-aza[6.4.2]propell-10-ene (19d). To an ice-cold, magnetically stirred, nitrogen-blanketed solution of **18d** (8.20 g, 50.6 mmol) in 30 ml of methylene chloride was added dropwise 5.70 g (41 mmol) of chlorosulfonyl isocyanate. After 2 hr at 25°, hydrolysis was accomplished in the usual manner and there was obtained 4.3 g (51%) of **19d**, mp 80–95°. Five recrystallizations of this material from ether at −20° gave pure **19d**: mp 90–100°; $\nu_{max}^{CHCl_3}$ 1742 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.45 (br s, 1, NH), 5.76 (m, 2, vinyl), and 1.19–2.77 (m, 16, methylene).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.95; H, 9.37; N, 6.66.

14-Ethoxy-13-aza[6.4.2]propella-10,13-diene (20d). O-Ethylation of 3.13 g (15.3 mmol) of **19d** with a slight excess of triethyloxonium fluoroborate in the predescribed fashion afforded 2.58 g (73%) of **20d** as a colorless oil: bp 90–96° (0.1 mm); ν_{max}^{film} 1625 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.72 (m, 2, vinyl), 4.16 (q, J = 7.0 Hz, $-OCH_2-$), 1.03–2.43 (m, 16, allyl and methylene), and 1.22 (t, J = 7.0 Hz, 3, methyl).

The perchlorate of **20d** was obtained as colorless crystals, mp 145–147°, from ethanol–ether.

Anal. Calcd for $C_{15}H_{24}ClNO_5$: C, 53.97; H, 7.25; N, 4.20. Found: C, 53.72; H, 7.40; N, 4.20.

14-Ethoxy-13-azabicyclo[6.4.2]tetradeca-8,10,12,14-tetraene (22d). Allylic bromination of **20d** (1.73 g, 7.43 mmol) with *N*-bromosuccinimide (1.46 g, 8.2 mmol), followed by dehydrohalogenation of the resulting allylic bromide with potassium *tert*-butoxide in tetrahydrofuran (2 hr, 0°), yielded 0.50 g (29%) of **22d** as a yellow oil, bp 106–110° (0.2 mm). This material was eluted through a short column of basic alumina (activity I) with hexane and redistilled; ν_{max}^{film} 1672 and 1650 cm^{-1}; calcd *m/e* 231.1623; observed *m/e* 231.1623.

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15. Found: C, 77.24; H, 9.05.

***N*-Phenylmaleimide Adduct of 22a.** A solution of 931 mg (4.92 mmol) of **22a** and 850 mg (4.92 mmol) of *N*-phenylmaleimide in 10 ml of toluene was refluxed under nitrogen for 7 hr. The solvent was removed, and the residual gum was triturated with petroleum ether. The resulting crystals were filtered and air-dried to give 1.54 g (86%) of a cream-colored solid. Three recrystallizations of this material from benzene–hexane gave pure **23a**: mp 172–174.5°; $\nu_{max}^{CHCl_3}$ 1770, 1705, and 1608 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.0–7.56 (m, 5, aryl), 6.19 (m, 2, vinyl), 4.16 (q, J = 7.0 Hz, 2, $-OCH_2-$), 3.08–3.58 (m, 4, bridgehead and α-carbonyl), 1.08–2.37 (m, 6, methylene), and 1.28 (t, J = 7.0 Hz, 3, methyl).

Anal. Calcd for $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73. Found: C, 73.12; H, 6.25; N, 7.67.

***N*-Phenylmaleimide Adduct of 22b.** Heating a solution of 1.10 g (5.46 mmol) of **22b** and 0.95 g (5.46 mmol) of *N*-phenylmaleimide in 10 ml of toluene for 6 hr under nitrogen afforded 1.9 g (93%) of **23b**, mp 156–158°, from benzene–hexane: $\nu_{max}^{CHCl_3}$ 1775, 1710, and 1618 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.92–7.43 (m, 5, aryl), 6.08 (m, 2, vinyl), 4.10 (q, J = 7.0 Hz, 2, $-OCH_2-$), 2.83–3.29 (m, 4, bridgehead and α-carbonyl), 1.08–2.07 (m, 8, methylene), and 1.27 (t, J = 7.0 Hz, 3, methyl).

Anal. Calcd for $C_{23}H_{24}N_2O_3$: C, 73.38; H, 6.43; N, 7.44. Found: C, 73.53; H, 6.47; N, 7.39.

12-Oxo-11-aza[4.4.2]propella-3,8-diene (27). To 35.0 g (0.264 mol) of 1,4,5,8-tetrahydronaphthalene (**26**)[38] was added dropwise 36.5 g (0.258 mol) of chlorosulfonyl isocyanate under a nitrogen atmosphere. After 1 hr, the resulting oil was hydrolyzed in the customary way to give 17.8 g (39%) of **27** as colorless crystals, mp 111–112°, from benzene–hexane: $\nu_{max}^{CHCl_3}$ 1748 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.47 (br s, 1, >NH), 5.85 (m, 4, vinyl), and 1.62–2.68 (m, 8, allyl).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.39; H, 7.50; N, 7.98.

Hydrogenation of 27. A solution of 45.8 mg (0.261 mmol) of **27** in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure over 10% palladium-on-carbon. After filtration of the catalyst and evaporation of the solvent, the residue was recrystallized from hexane to give colorless crystals (45 mg, 96%), mp 51–53°, identical in all respects with authentic **28**.

12-Oxo-11-aza[4.4.2]propellane (28). To an ice-cold stirred solution of $\Delta^{9,10}$-octalin (**29**, 5.2 g, 0.038 mol)[39] in 50 ml of methylene chloride was added dropwise under nitrogen 5.2 g (0.037 mol) of chlorosulfonyl isocyanate. After 1 hr at 25°, the usual hydrolysis was performed. There was obtained 1.9 g (30%) of **28**, mp 52–53.5°, from hexane at −20°: $\nu_{max}^{CHCl_3}$ 1740 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.17 (br s, 1, >NH) and 1.63 (br peak, 16, methylene).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.53; H, 9.56; N, 7.68.

12-Ethoxy-11-aza[4.4.2]propella-3,8,11-triene (30). Exposure of 13.8 g (0.079 mol) of **27** to a slight excess of triethyloxonium fluoroborate in the predescribed manner gave 8.5 g (53%) of **30** as a colorless oil: bp 65–66° (0.2 mm); ν_{max}^{film} 1630 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.72 (m, 4, vinyl), 4.13 (q, J = 7.0 Hz, $-OCH_2-$), 1.67–2.67 (m, 8, allyl), and 1.27 (t, J = 7.0 Hz, 3, methyl).

The perchlorate salt of **30** was obtained as colorless crystals, mp 129–131°, from ethanol–ether.

Anal. Calcd for $C_{13}H_{18}ClNO_4$: C, 51.41; H, 5.97; N, 4.61. Found: C, 51.39; H, 6.08; N, 4.46.

Typical Attempted Preparation of 12-Ethoxy-11-aza[4.4.2]propella-2,4,7,9,11-pentaene (25). A mixture of 2.89 g (14.3 mmol) of **30**, 5.35 g (30 mmol) of *N*-bromosuccinimide, and a trace of benzoyl peroxide in 50 ml of carbon tetrachloride was refluxed for 1 hr under a nitrogen atmosphere. After cooling, the succinimide was removed by filtration, the solvent was evaporated, and the residual oil was dissolved in 50 ml of tetrahydrofuran. This solution was added dropwise under nitrogen to a magnetically stirred slurry of 4.82 g (42.9 mmol) of potassium *tert*-butoxide in 50 ml of dry tetrahydrofuran at −50°. The reaction mixture was allowed to stir at −20° for 2 hr. Ether and ice-cold water were cautiously added so that the temperature of the reaction mixture did not exceed 0°. The organic layer was separated, washed with ice water, and dried over

(37) R. Huisgen and W. Rapp, *Chem. Ber.*, **85**, 826 (1952).

(38) W. Hückel and H. Schlee, *ibid.*, **88**, 346 (1955).

(39) R. A. Benkeser and E. M. Kaiser, *J. Org. Chem.*, **29**, 955 (1964).

magnesium sulfate at −20°. The solvent was evaporated *in vacuo* and the residue was immediately examined by nmr spectroscopy. The presence of naphthalene was easily confirmed, but other absorptions were too broad and overlapping for possible assignment. Vpc indicated the presence of naphthalene and a number of less volatile components. Column chromatography on Woelm basic alumina (activity I) with petroleum ether gave 0.40 g (22%) of naphthalene. Continued elution with more polar solvents gave only dark viscous oils which could not be characterized.

Acknowledgment. The authors are grateful to the National Institutes of Health and the Lilly Research Laboratories for grants which contributed to the financial support of this research.

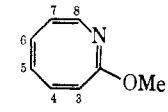
Electrochemical Studies of the Reduction of 2-Methoxyazocines in Aprotic Solvents. Comparison with the Cyclooctatetraene System[1]

Larry B. Anderson, John F. Hansen, Tsuyoshi Kakihana,[2a] and Leo A. Paquette[2b]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 7, 1970*

Abstract: The polarographic reduction of each of the five different 2-methoxyazocines studied was observed to be nonnernstian. In tetrahydrofuran (THF) or dimethylformamide (DMF) solutions containing 0.1 *M* tetra-*n*-butylammonium perchlorate (TBAP) background electrolyte, the reduction occurs by the addition of two electrons to the parent azocine to form directly the dianion product. Cyclic voltammetry of the azocines indicates that the dianion product is not reoxidized at the mercury drop electrode until the potential is scanned nearly 1-V anodic of the initial reduction wave. This behavior is in strong contrast to the previously reported mechanism for the reduction of cyclooctatetraene (COT), the hydrocarbon analog. COT and its derivatives undergo two nearly nernstian one-electron reductions separated by ~0.24 V. A mechanism is proposed for the azocine reduction process. Addition of the first electron is thought to be accompanied by considerable ring flattening, producing a planar or nearly planar anion radical. This radical is more easily reduced than the parent heterocycle, resulting in the immediate introduction of a second electron to form the stable dianion. The reason for the spontaneous addition of a second electron at the same potential as the addition of the first is thought to be the favorable energy gain upon formation of a ten π-electron aromatic dianion. The significance of these results in interpreting the previously reported behavior of cyclooctatetraene and its derivatives is discussed.

Electrochemical techniques are recognized to be capable of providing invaluable diagnostic information concerning the generation and chemical reactivity of cyclic conjugated olefins containing $(4n + 2)$ π electrons.[3-9] A case in point is the direct correlation that exists between the free energy of the electron-transfer reaction and the energy of the molecular orbital accepting or donating the electron.[10] Most importantly, electron-transfer reactions that take place at inert electrode surfaces are devoid of undesirable side reactions generally associated with alkali metal reductions. Because alkali metal ions are known to form strong ion-pair complexes with radical anions and dianions, the utilization of metal cation-free reduction techniques are best suited to the study of electron transfer reactions *per se*. Recently a convenient synthesis of π-equivalent nitrogen analogs of cyclooctatetraene (COT) was developed in this laboratory.[1] Because of the ready availability of 2-methoxyazocines and their close structural, but electronically different, relationship with COT, a study of their electrochemical behavior was undertaken.[11]



1a, 2-methoxyazocine (MA)
b, 8-methyl-2-methoxyazocine (MMA)
c, 3,8-dimethyl-2-methoxyazocine (DMMA)
d, 4,6,8-trimethyl-2-methoxyazocine (TMMA)
e, 3,5,6,8-tetramethyl-2-methoxyazocine (TTMA)

In a chemical system composed of a parent compound and its dianion in equilibrium with an inert electrode, the following chemical and electrochemical reactions may be defined.

(1) Unsaturated Heterocyclic Systems. LXXIV. For the previous paper in this series, see L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *J. Amer. Chem. Soc.*, **93**, 152 (1971).
(2) (a) Goodyear Tire and Rubber Co. Fellow, 1969–1970; (b) to whom correspondence should be addressed.
(3) D. H. Geske, *J. Amer. Chem. Soc.*, **81**, 4145 (1959).
(4) L. E. Craig, R. M. Elofson, and I. J. Ressa, *ibid.*, **75**, 480 (1953).
(5) (a) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *ibid.*, **84**, 802 (1962); (b) T. J. Katz, M. Yoshida, and L. C. Siew, *ibid.*, **87**, 4516 (1965); (c) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963).
(6) R. D. Allendoerfer and P. H. Reiger, *ibid.*, **87**, 2336 (1965).
(7) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed, Vol. 2, Interscience, New York, N. Y., 1952, p 634 ff.
(8) J. Proszt, V. Cieleszky, and K. Gyorbiro, "Polarographie," Akademiai Kiado, Budapest, Hungary, 1967, pp 384 ff.
(9) N. Tokel, V. Katovic, K. Farmery, L. B. Anderson, and D. H. Busch, *J. Amer. Chem. Soc.*, **92**, 400 (1970).
(10) (a) G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **74**, 1525 (1955); (b) G. J. Hoijtink, E. deBoer, P. H. van der Meij, and W. P. Weijland, *ibid.*, **75**, 487 (1956).
(11) A preliminary account of a portion of this work is to be found in L. A. Paquette, J. F. Hansen, T. Kakihana, and L. B. Anderson, *Tetrahedron Lett.*, 533 (1970).