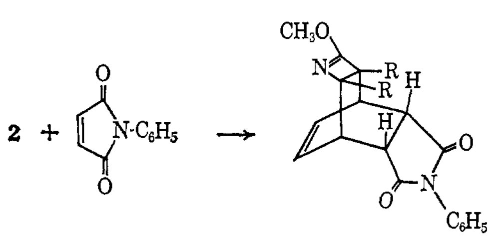
Further support for the existence of this reversible equilibrium was provided by the Diels–Alder reaction of **2a** with N-phenylmaleimide in refluxing toluene. The resulting colorless crystalline ((4 + 2)π) adduct, mp 205–207°,[8] exhibited spectral properties in unique agreement with structure **10a**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.0–7.6 (multiplet, 5 H), 6.0–6.2 (multiplet, 2 H), 3.70 (singlet, 3 H), 2.9–3.6 (multiplet, 4 H), and ~1.9 (multiplet, 2 H). The product is formulated with the imide moiety *syn* to the double bond in accordance with established precedence.[3,16]



10a, R = H
b, R = CH_3

In similar fashion, 1,2-dimethyl-1,4-cyclohexadiene (**3b**) afforded **4b**, mp 91–92°,[8] in 72% yield. The derived imino ether **5b** was quite stable in this instance and afforded a perchlorate salt, mp 139–140°.[8] The two-step dehydrogenation of **5b** proceeded without difficulty, and **2b** was obtained as a stable yellow oil: bp 47° (0.35 mm);[8] $\nu_{\max}^{\mathrm{neat}}$ 1670 (s), 1640 (m), and 1625 cm^{-1} (w); $\lambda^{\mathrm{isooctane}}$ 212 (ϵ 12,900) and 297 mμ (ϵ 590); $\delta_{\mathrm{TMS}}^{\mathrm{C_6H_6}}$ 5.72 (singlet, 3 H), 4.95 (broad singlet, 1 H), and three three-proton singlets at 3.63, 1.92, and 1.82. The two methyl groups serve to protect the azocine from base-induced aromatization reactions but do not exert an influence which favors the bicyclic valence tautomer **7b**.[14b] However, the facile conversion of **2b** to **10b**, mp 194–195.5°,[8] attests to the existence of a spectroscopically undetectable equilibrium of the tetraene with **7b**.

The striking similarity of the C=C bond stretching frequencies of azocines **2a** and **2b** with those reported for **1**[17] and the excellent correspondence of the ultraviolet spectra of **2a** and **1**[18] suggest that these hetero analogs likewise exist in the strain-free puckered "tub" conformation known to be preferred by the hydrocarbon.[17,19]

The availability of azacyclooctatetraenes by means of this direct and apparently general synthesis now causes these heterocycles to become an attractive focus of further synthetic manipulations. Presently under active investigation are studies which deal with their photolability, their capability to support dianion (10π electron) character and to serve as precursors of azacyclobutadienes, and the various other phenomena which are logical consequences of these and related concepts.

[16] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[17] E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Am. Chem. Soc.*, **73**, 3370 (1951).

[18] A. C. Cope and C. G. Overberger, *ibid.*, **70**, 1433 (1948).

[19] (a) W. B. Person, G. C. Pimentel, and K. S. Pitzer, *ibid.*, **74**, 3437 (1952); (b) I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

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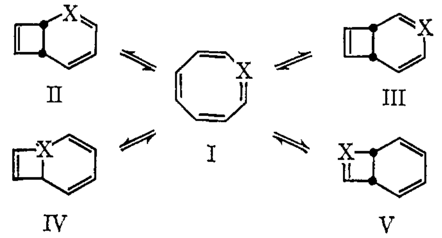
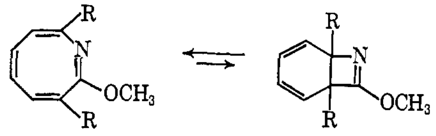
Concerning Azacyclooctatetraene Valence Tautomerism. Preparation of Annelated 7-Azabicyclo[4.2.0]octa-2,4,7-trienes[1,2]

Sir:

According to generalized theory, an unsubstituted π-equivalent heterocyclic congener of cyclooctatetraene such as I may theoretically be characterized by dynamic equilibrium with four structurally distinct valence bond tautomers (II–V). In actual fact, only one of the heteroatomic bicyclo[4.2.0]octatrienes is likely to be preferred for reasons such as more advantageous electronic interactions, more favorable conformational environments, and the like. However, placement of one or more substituents on the eight-membered ring could affect the original position of equilibrium sufficiently to cause an alternative bicyclic isomer to be more stable. The recent synthesis of the azacyclooctatetraene system[1] has permitted the first practical assessment of such a set of electrocyclic changes.

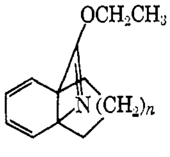


In 2-methoxyazocine (**1a**) and its 3,8-dimethyl analog (**1b**), the azacyclooctatetraene form is sufficiently stabilized that the proportion of valence tautomer in the equilibrium is below the spectroscopic detection limit (<5%). However, both substances readily form adducts with N-phenylmaleimide derived from the azetine form **2**.[1] This tautomer also appears to be the reacting species in the base-induced conversion of **1a** to benzonitrile.[1] Therefore, a detailed investigation of the spectral and chemical properties of such azetines was deemed advisable. This interest in valence bond tautomerizations has led us to prepare the annelated derivatives **3–5**.

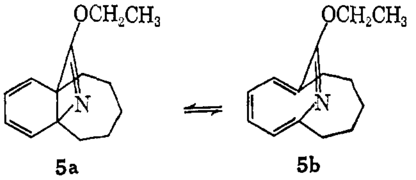


1a, R = H
b, R = CH_3

2



3, $n = 1$
4, $n = 2$



5a **5b**

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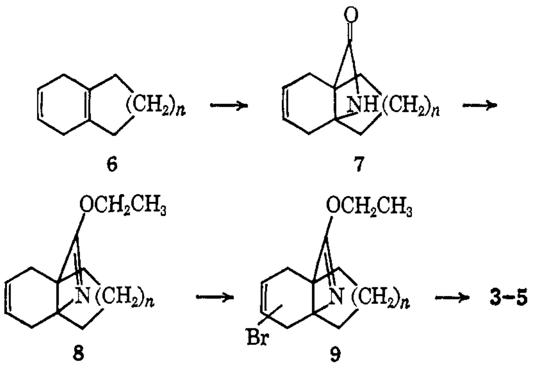
[1] Unsaturated Heterocyclic Systems. XLIV. For the previous paper in this series, see L. A. Paquette and T. Kakihana, *J. Am. Chem. Soc.*, **90**, 3897 (1968).

[2] We wish to express our gratitude to the National Institutes of Health for their generous financial support of this work.

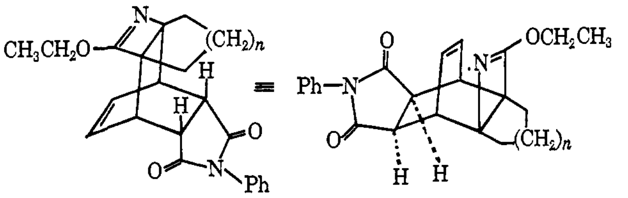
The synthesis of azacyclooctatetraene derivatives described earlier has proven to be extremely versatile and was employed as the means of entry into the annelated 7-azabicyclo[4.2.0]octa-2,4,7-trienes **3**–**5**. Cycloaddition of chlorosulfonyl isocyanate (CSI) to 4,7-dihydroindan (**6a**)[3] was performed in the usual fashion[4] to give the desired N-(chlorosulfonyl) β-lactam which, without purification, was hydrolyzed with 4 *N* NaOH in cold acetone to give **7a**, mp 61–63°,[5] in 60% over-all yield. The β-lactam was directly converted with triethyloxonium fluoroborate in dichloromethane solution to **8a** which was readily purified as its perchlorate salt, mp 120–122°.[5] Through the action of N-bromosuccinimide (1 equiv) in carbon tetrachloride, **8a** was transformed into a mixture of allylic bromides (**9a**), dehydrohalogenation of which was brought about by potassium *t*-butoxide in tetrahydrofuran at 0°. The stable azetine **3** was isolated by direct distillation [bp 44° (0.07 mm)][5] in 42% over-all yield. This new azapolyene exhibited ultraviolet absorption in isooctane at 220 (ε 1650) and 267 mμ (ε 2200) and revealed in its nmr spectrum a multiple line pattern at δ 5.55–6.20 expected[6] for the four vinyl protons.



a, *n* = 1; **b**, *n* = 2; **c**, *n* = 3

On being subjected to the same sequence of reactions, 5,8-dihydrotetralin (**6b**)[7] was transformed sequentially into β-lactam **7b**, mp 90–91°,[5] imino ether **8b**, bp 62° (0.1 mm),[5] and ultimately **4**, bp 56–57° (0.04 mm),[5] $\lambda_{\max}^{\text{isooctane}}$ 230 (ε 1250) and 272 mμ (ε 2100); the *temperature-independent* nmr spectrum of **4** likewise displayed a pattern assignable to the vinyl protons of a 1,3-cyclohexadiene system.[6] On the basis of the spectral properties of **3** and **4**,[8] it is apparent that for steric reasons the tri- and tetramethylene bridges achieve complete displacement of the azacyclooctatetraene equilibrium in favor of the azabicyclooctatriene tautomer.

In refluxing toluene, **3** and **4** reacted readily with N-phenylmaleimide to give the colorless (4 + 2)π adducts **10a**, mp 172.5–174.5°,[5] and **10b**, mp 152.5–154°,[5] respectively. The stereochemistry of these products has been assigned on the basis of vicinal proton coupling constants[9] and analysis of nonbonded interactions operating in the various possible transition states.



10a, *n* = 1
b, *n* = 2

The imino ether [bp 68–70° (0.15 mm)] obtained from **6c**[10] was also found to be uniform at room temperature; the spectral properties of this compound, particularly its ultraviolet [$\lambda_{\max}^{\text{isooctane}}$ 230 (ε 1800) and 268 mμ (ε 2000)] and nmr spectra, provide clear evidence for the 1-azetine formulation **5a**. However, contrary to the behavior of **3** and **4**, the pentamethylene-bridged heterocycle ($Cl_2C{=}CCl_2$ solution) exhibits a temperature-dependent nmr spectrum. 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 4H low-field and a 6H 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 the bridged azacyclooctatetraene **5b** at the elevated temperatures.

Thus, in contrast to the bridged norcaradiene–cycloheptatriene and arene oxide–oxepin systems wherein the triene tautomers predominate when a chain length of five methylene groups is reached, the strain imposed on the azacyclooctatetraene form **5b** remains sufficiently great that measurable concentrations of this tetraene are attainable only in the vicinity of 100° and above.

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

[4] R. Graf, *Ann.*, **661**, 111 (1963); *Org. Syn.*, **46**, 51 (1966).

[5] Satisfactory elemental and spectral analyses were obtained for the indicated new compounds.

[6] H. Günther and H.-H. Hinrichs, *Ann.*, **706**, 1 (1967).

[7] W. Hückel and V. Worffel, *Chem. Ber.*, **89**, 2098 (1956).

[8] For reviews in which the properties of annelated cyclohexadienes are discussed, see (a) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963); (b) E. Vogel and H. Günther, *ibid.*, **6**, 385 (1967); (c) G. Maier, *ibid.*, **6**, 402 (1967).

[9] These data will be presented in detail in the full paper.

[10] Prepared by the lithium in liquid ammonia reduction of benzocycloheptene.

[11] National Institutes of Health Predoctoral Fellow, 1966–present.

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