with a 9:1 solvent mixture of benzene and ether showed five bands. The first band, R_f 15.2, was shown by nmr to be composed of $(NO_2)_2$-**E** and the tricyclic **12**. The second band, R_f 10.2, was obtained as $(NO_2)_2$-**D**(ax)-OAc; the third band, R_f 9.6, as $(NO_2)_2$-**D**(eq)-OAc; the fourth band, R_f 8.5, as $(NO_2)_2$-**A**-OAc; the fifth band, R_f 6.2, as $(NO_2)_2$-**B**-OAc. The yields in Table II were determined by nmr spectroscopy and from the relative amounts of the thus isolated products. Because of insufficient amounts, isolation of samples of $(NO_2)_2$-**E** and **12**, satisfactory for analysis, was unsuccessful. The 100-MHz nmr of the crude **12** shows H_{6x} and H_{8x} at τ 8.03 (quartet, $J_{6x,6n}$ and $J_{8x,8n}$ = 11.6 Hz, $H_{6x,5}$ and $J_{8x,5}$ = 5.0 Hz), H_{6n} and H_{8n} at 9.03 (doublet), H_5 at 6.75 (triplet), H_2 at 7.66 (triplet, $J_{H_2H_1}$ and $J_{H_2H_7}$ = 7.4 Hz), and H_1, H_7 at 8.07 (doublet). Studies of products from other nitro brosylates were carried out in a similar way.

Infrared Hydroxyl Stretching Bands.—Spectra were taken in carbon tetrachloride and the concentration of alcohols were less than 0.003 *M*. **A**-OH, 6-NO_2-**A**-OH, and 7-NO_2-**A**-OH show only a free band at 3622, 3620, and 3620 cm^{-1}, respectively. **B**-OH shows a week free band at 3619 cm^{-1} and an associated band (OH$\cdots\pi$) at 3584 cm^{-1}. 6-NO_2-**B**-OH and 7-NO_2-**B**-OH show free bands at 3615 and 3613 cm^{-1}, respectively, as well as associated bands at 3594 and 3593 cm^{-1}, respectively. In both the nitro alcohols, the intensities of the associated bands are a little weak relative to those of the free bands.

Registry No.—**A** (Z, X) (6-CH_3O, 2-OH), 27142-14-9; (6-CH_3O, 2-Cl), 27142-15-0; (7-CH_3O, 2-Cl), 27142-16-1; (H, 2-Cl), 27189-22-6; (H, 2-OH), 13153-77-0; (H, 2-OBs), 16938-83-3; (H, 2-OAc), 16938-84-4; (6-NO_2, 2-OH), 27142-17-2; (6-NO_2, 2-OBs), 27142-18-3; (7-NO_2, 2-OH), 27142-19-4; (7-NO_2, 2-OBs), 27142-20-7; (7-NO_2, 2-OAc), 27142-21-8; (6,7-$(NO_2)_2$, 2-OH), 27142-22-9; (6,7-$(NO_2)_2$, 2-OBs), 27189-23-7; (6,7-$(NO_2)_2$, 2-OAc), 27150-76-1; **B** (Z, X) (H, 2-OH), 13153-78-1; (H, 2-OBs), 16938-82-2; (H, 2-OAc), 27149-76-4; (6-NO_2, 2-OH), 27149-77-5; (6-NO_2, 2-OBs), 27149-78-6; (7-NO_2, 2-OH), 27149-79-7; (7-NO_2, 2-OBs), 27149-80-0; (7-NO_2, 2-OAc), 27149-81-1; (6,7-$(NO_2)_2$, 2-OH), 27149-82-2; (6,7-$(NO_2)_2$, 2-OBs), 27149-83-3; (6,7-$(NO_2)_2$, 2-OAc), 27149-84-4; **C** (Z, X) (H, 2-OH), 16938-90-2; (H, 2-OAc), 27149-86-6; (8-NO_2, 2-OAc), 27149-87-7; (7-CH_3O, 2-OAc), 27149-88-8; **D** (Z, X) (7-NO_2, 2(ax)-OAc), 27149-89-9; (7-NO_2, 5(ax)-OAc), 27149-90-2; (6,7-$(NO_2)_2$, 2(ax)-OAc), 27149-91-3; (6,7-$(NO_2)_2$, 2(eq)-OAc), 27149-92-4; (7,8-$(NO_2)_2$, 5(ax)-OAc), 27149-93-5; **E** (Z) (CH_3O), 27150-77-2; **F** (Z, X) (6-NO_2, 2-one), 27150-78-3; (7-NO_2, 2-one), 27150-79-4; (6,7-$(NO_2)_2$, 2-one), 27150-80-7; **2**, 27150-81-8.

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The 1-Aza-2,4,6-cyclooctatriene–7-Azabicyclo[4.2.0]octadiene Valence Tautomeric Equilibrium. A Study of Substituent Effects and an Attempted Synthesis of Azetes (Azacyclobutadienes)[1]

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Five derivatives of the 1-aza-2,4,6-cyclooctatriene system have been prepared. The concentration of each polyene in equilibrium with its valence tautomeric 7-azabicyclo[4.2.0]octatriene form has been evaluated quantitatively by nmr spectroscopy. It was noted that the bicyclic form is favored in all instances, although to varying degrees, and explanations of such behavior are advanced. The attempted utilization of these substances in the preparation of azete (azacyclobutadiene) derivatives is described.

The last two decades have witnessed the methodical compilation of much experimental data concerning reversible transformations that occur without the migration of atoms or groups, now commonly referred to as valence tautomeric equilibria.[3] However, despite the fact that quantitative evidence for a wide variety of structural types is currently available, our basic understanding of the causative factors that control the individual positions of equilibrium is lacking in many instances. Particularly relevant examples in this connection are the cycloheptatriene–norcaradiene,[4] cyclooctatriene–bicyclo[4.2.0]octadiene,[5] oxepin–benzene oxide,[3d,f] 1*H*-azepine–azanorcaradiene,[3f,6] and azocine–azabicyclo[4.2.0]octatriene[7] tautomeric pairs. To illustrate, Huisgen and coworkers[5d] have recently determined the equilibrium position of the 1,3,5-cyclooctatriene (**1**)–bicyclo[4.2.0]octadiene (**2**) valence tauto-

1 **2**

(1) Unsaturated Heterocyclic Systems. LXXVII. For the previous paper in this series, see L. A. Paquette and T. Kakihana, *J. Amer. Chem. Soc.*, **93**, 174 (1971).

(2) Goodyear Tire and Rubber Co. Fellow, 1969–1970.

(3) For recent reviews, consult (a) E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **2**, 1 (1963); (b) W. von E. Doering and W. R. Roth, *ibid.*, **2**, 115 (1963); (c) S. J. Rhoads, "Molecular Rearrangements," part I, P. de Mayo, Ed., Wiley, New York, N. Y., 1963, p 655; (d) E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967); (e) G. Maier, *ibid.*, **6**, 402 (1967); (f) L. A. Paquette, "Nonbenzenoid Aromatics," Vol. I, J. Snyder, Ed., Academic Press, New York, N. Y., 1969, pp 249–310.

(4) (a) E. J. Corey, H. J. Burke, and W. A. Remers, *J. Amer. Chem. Soc.*, **78**, 180 (1956); (b) R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *ibid.*, **79**, 4127 (1957); (c) J. B. Lambert, L. J. Burham, P. Lepoutre, and J. D. Roberts, *ibid.*, **87**, 3896 (1965); (d) H. Günther and H. H. Hinrichs, *Tetrahedron Lett.*, 787 (1966); (e) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964); (f) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964); (g) M. Battiste, *Chem. Ind. (London)*, 550 (1961); (h) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 657 (1965); **88**, 3617 (1966); (i) E. Ciganek, *ibid.*, **87**, 652, 1149 (1965); **89**, 1454, 1458 (1967); (k) T. Mukai, H. Yubota, and T. Toda, *Tetrahedron Lett.*, 3581 (1967); (k) T. Toda, M. Nitta, and T. Mukai, *ibid.*, 4401 (1969).

(5) (a) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4867 (1952); (b) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, **19**, 3 (1965); (e) E. Vogel, O. Roos, and K.-H. Disch, *Justus Liebigs Ann. Chem.*, **653**, 55 (1962); (d) R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968).

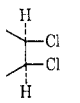
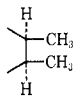
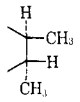
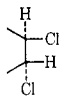
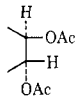
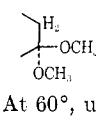
(6) (a) L. A. Paquette, J. H. Barrett, and D. E. Kuhla, *J. Amer. Chem. Soc.*, **91**, 3616 (1969); (b) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969); (c) L. A. Paquette, D. E. Kuhla, and J. H. Barrett, *ibid.*, **34**, 2879 (1969).

(7) (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); (c) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *ibid.*, **93**, 152 (1971).

merism as a function of the substituents at the 7 and 8 positions. Their results are summarized in Table I.

TABLE I

INFLUENCE OF 7 AND 8 SUBSTITUENTS ON THE VALENCE TAUTOMERIC EQUILIBRIUM OF CYCLOOCTA-1,3,5-TRIENES[a,b]

Substituents	% bicyclic	Substituents	% bicyclic
	0.01 (100°)		80
	0.4		81
	6.6		
	10.8		94
	35		99 (−30°)
	53		>95
			>95

[a] Values taken from ref 5d. [b] At 60°, unless otherwise specified.

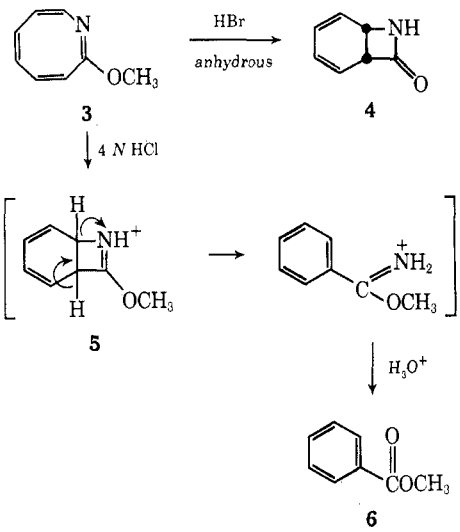
The German group was forced to conclude that the large variation in the proportions of the monocyclic and bicyclic forms of the 12 derivatives examined did not lend itself to ready theoretical interpretation at the present time.

A general synthesis of azocines (azacyclooctatetraenes) was devised recently in these laboratories.[7] Concurrently, an examination of the question of dynamic valence bond isomerization in nitrogen analogs of **1** and **2** was initiated. Because of the obvious structural relationship between the two series, knowledge of the behavior of 1-aza-2,4,6-cyclooctatriene derivatives was expected to provide valuable information on the influence of electronic, steric, and strain effects in medium ring compounds. The possibility of reconciling the behavior of cyclooctatrienes in such an indirect fashion also presented itself.

Synthetic Considerations.—Exposure of 2-methoxyazocine (**3**) to a dry solution of ethereal hydrogen bromide, followed by dissolution of the resulting salt in acetone at room temperature for 3 hr, gave 7-azabicyclo[4.2.0]octa-2,4-dien-8-one (**4**) in 17% yield. This lactam displayed an intense infrared carbonyl stretching vibration ($CHCl_3$) at 1765 cm^{-1} and exhibited ultraviolet absorption [$\lambda_{max}^{C_2H_5OH}$ 263 nm (ϵ 3220)] typical of 1,3-cyclohexadiene derivatives.[8] In contrast, aqueous hydrolysis of **3** with 4 *N* hydrochloric acid at room temperature for 20 min afforded methyl benzoate (**6**) in 47% yield. At the mechanistic level, the formation of

(8) The discussion of nmr spectra is deferred to the subsequent section of this paper.

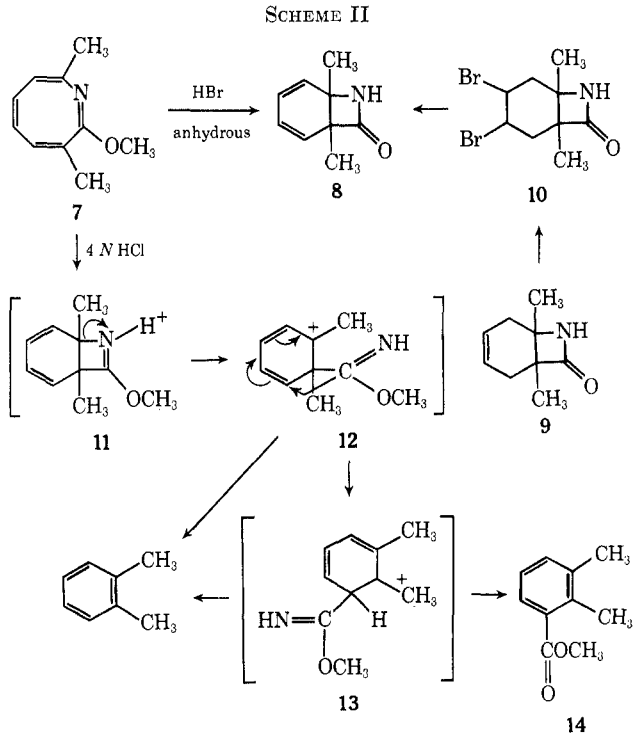
SCHEME I



6 may be attributed to the aromatization of **5**, the bicyclic valence tautomer of protonated **3** (Scheme I).

1,6-Dimethyl-7-azabicyclo[4.2.0]octa-2,4-dien-8-one (**8**) was similarly prepared by treating 3,8-dimethyl-2-methoxyazocine (**7**) with anhydrous hydrogen bromide. Lactam **8** was also available from the bromination of **9**, followed by dehydrobromination with 1,5-diazabicyclo[4.3.0]non-5-ene in benzene. On the other hand, **7** was found to undergo hydrolysis in 4 *N* hydrochloric acid with the formation of *o*-xylene and methyl 2,3-dimethylbenzoate (**14**). The presumed pathway leading to **14** is shown in Scheme II. Since aromatization is not

SCHEME II

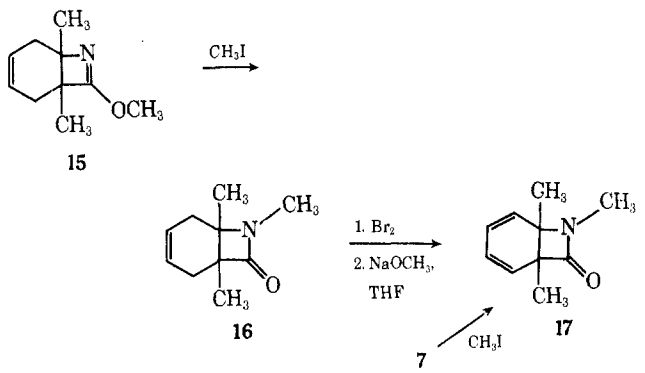


directly available to **11**, ionization to **12** apparently intervenes. At this point, the structure of the final product requires that imidate carbon migrate to an electron-deficient center with greater ease than a methyl group. However, this eventuality is not unexpected

in view of the established -COOR > $-CH_3$ reactivity order noted in certain related carbonium ion processes.[9,10] Finally, intermediate **13** may eject a proton to afford **14** or transform itself into *o*-xylene by loss of the functionalized side chain. The data do not, of course, rule out the possibility that *o*-xylene could result directly from cation **12**. β-Lactam **8** was characterized by an intense carbonyl band ($CHCl_3$) at 1750 cm^{-1} and an ultraviolet maximum (C_2H_5OH) at 261 nm (ε 3780).[8]

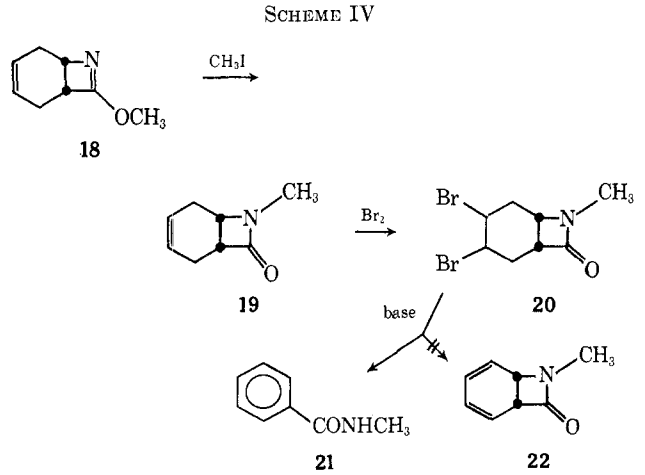
For comparison purposes, the *N*-methyl derivatives of **4** and **8** were sought. To this end, azetine **15** was allowed to react with methyl iodide at ambient temperature for 7 hr.[11] There was obtained by direct distillation a 93% yield of **16** (Scheme III). Bromination of **16** and dehydrohalogenation of the resultant dibromide with sodium methoxide in refluxing tetrahydrofuran gave **17** in 34% overall yield. In a less favorable reaction, heating of **7** in excess methyl iodide for 45 hr also afforded **17**, but only in low yield (12%).

SCHEME III



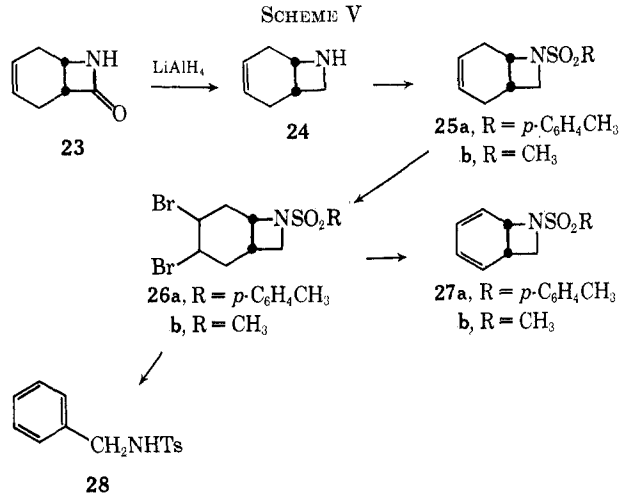
Similarly, azetine **18** was found to give rise to **19** when refluxed with methyl iodide for 9 hr. Although the bromination of **19** proceeded as expected, all attempts to dehydrohalogenate this intermediate (**20**) led only to *N*-methylbenzamide (**21**, Scheme IV). Attempts to transform **3** directly into **22** by reaction with methyl iodide were also to no avail.

SCHEME IV

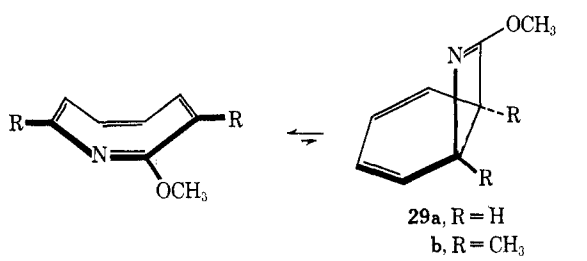


Reduction of **23** with lithium aluminum hydride furnished azetidine **24**, treatment of which with *p*-toluenesulfonyl and methanesulfonyl chlorides gave **25a** and **25b**, respectively, in quantitative yield. Bromination of these sulfonamides with an equivalent amount of bromine was readily achieved. However, as expected from earlier observations, the dehydrobromination of **26a** and **26b** required strictly controlled conditions to arrive at **27a** and **27b** (Scheme V). To illustrate, it soon became apparent that the action of excess potassium *tert*-butoxide on **26a** invariably led to **28**. In contrast, when 2 equiv of base was employed at 0°, **27a** could be isolated in 69% yield.

SCHEME V



Valence Tautomeric Considerations.[12]—Previously, **3** and **7** were shown to exhibit temperature invariant (−75 to 185°) nmr spectra which fail to provide any suggestion of the presence of bicyclic imino ethers of type **29**.[7] However, the presence in **3** and **7** of spectroscopically undetectable quantities of **29a** and **29b**, respectively, was apparent from the diene behavior of 2-methoxyazocines in Diels–Alder reactions and the ease with which **3** is converted to benzonitrile with strong base. A reliable estimate of the proportion of **29** in these equilibria is ≤2%. The high equilibrium concentrations of the monocyclic forms suggests that the strain generated in passing to the bicyclic 1-azetine derivatives (**29**) is sufficiently large to overcome the loss of stabilization derived from the noncontiguous overlap of π orbitals in **3** and **7** (due to the preferred tub conformation). These characteristics therefore parallel closely those of cyclooctatetraene in which the concentration of the bicyclic tautomer at 100° is only 0.01%.[5b,d]



(9) H. Plieninger, L. Arnold, and W. Hoffmann, *Chem. Ber.*, **101**, 981 (1968).

(10) The virtually complete absence of methyl migration was evidenced by the fact that the isolated ester showed no contamination by methyl 2,6-dimethylbenzoate (vpc analysis).

(11) (a) L. A. Paquette and N. A. Nelson, *J. Org. Chem.*, **27**, 1085 (1962); (b) L. A. Paquette and G. Slomp, *J. Amer. Chem. Soc.*, **85**, 765 (1963).

(12) For a preliminary report of these results, see L. A. Paquette, T. Kakihana, J. F. Kelly, and J. R. Malpass, *Tetrahedron Lett.*, 1455 (1969).

In marked contrast, 1,2-dihydroazocin-2-one (**30a**) exists predominantly as bicyclic tautomer **4**. The percentage composition values for **30a** (and also **31a** and **31b**) were derived from the following equation

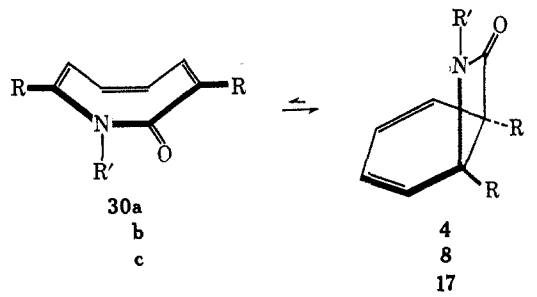
$$\% \text{ monocyclic} = \frac{\text{area of vinyl absorption} - 2(\text{area of bridgehead absorption})}{\text{total area}}$$

and the pertinent chemical shifts are collected in Table II. Variable temperature nmr studies gave evidence

TABLE II
PERTINENT CHEMICAL SHIFT DATA FOR THE DIHYDROAZOCINES (δ UNITS)

Tautomeric pair	Vinyl protons	Bridgehead protons
4–30a	5.62–6.08	3.86–4.26
27a–31a	5.48–6.04	4.58–4.85, 2.75–3.15
27b–31b	5.62–6.20	4.98–5.27, 3.05–3.55
Tautomeric pair	**>C—CH₃**	**>C—CH₃**
8–30b	1.94 (broad)	1.39, 1.40 (sharp)
17–30c		1.24, 1.28 (sharp)

that the concentration levels of **30a** rise progressively with temperature. For example, in tetrachloroethylene solution the percentage of **30a** in the mixture varied in the following fashion: 60°, 2.4%; 85°, 3.5%; 100°, 8.4%; 115°, 15.3%.



30a **4**
b **8**
c **17**

R = R′ = H
R = CH_3; R′ = H
R = R′ = CH_3

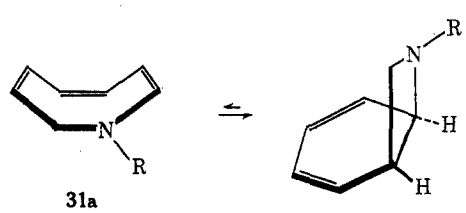
Lactam **30b** behaved analogously. For **30b** and **30c**, integration of the areas of the C-methyl absorptions was employed to establish the positions of equilibrium (see Table II). By comparison to **30a**, however, the percentage of monocyclic form was seen to be relatively greater and to vary somewhat less with temperature: 38°, 19.5%; 95°, 20.7% (CCl_2=CCl_2 solution). Also, the position of equilibrium did not appear to be affected significantly by changes in solvent (all measurements at 38°): benzene-d_6, 20.3%; acetone-d_6, 20.4%; acetic acid-d_4, 22.2%. It should be mentioned that throughout this entire study, the solutions were allowed to equilibrate for 4–5 hr prior to spectral examination. Additionally, the spectra were rerecorded after 1 week to guard against a situation where a particularly slow rate of valence isomerization was operative.

The effect of a methyl group on the lactam nitrogen of **30b** influences the positions of equilibrium to an amazing extent. Thus, the nmr spectrum of **30c** indicated the substance to be totally bicyclic (at least at the spectroscopic detection limit) over a substantial temperature range (38–120°). Above 120°, **17** decomposes rapidly to *o*-xylene and methyl isocyanate.[13] These data are to be contrasted with the valence tautomeric situation prevalent in cyclooctatrienone which is 93.4% monocyclic at 60°.[5d]

The presence of the amide function in **30** clearly has several consequences. First, the strain in the β-lactam portion of the valence tautomers is not so great as in a 1-azetine ring. Secondly, for electrostatic reasons the electropositive carbon of the carbonyl group can be expected to exercise a preference for bonding to sp^3- rather than sp^2-hybridized carbon (the former is less electronegative). These factors, in conjunction with the stabilization resulting from more effective π overlap in the planar diene tautomers (**4**, **8**, and **17**), can be anticipated to favor the bicyclic structures. The somewhat greater concentration of the monocyclic tautomer in **8** ⇆ **30b** can be attributed to the eclipsed methyl–methyl interactions in **8** which are relieved in passing to **30b**. In **17** ⇆ **30c**, this eclipsing interaction exists also, but relief of the newly generated steric interference between *N*-methyl and carbonyl oxygen is overriding. The bicyclic form is favored to a greater extent in this instance because the external bond angles in the four-membered ring are appreciably wider than those in the azocine tautomer, thereby substantially reducing this destabilizing interaction. Pronounced changes in the reactivity of medium-ring lactams have been reported to occur upon N-methylation, presumably because of analogous nonbonded interactions.[14]

It now becomes important to reconcile the differing behavior of cyclooctatrienone and the 1,2-dihydroazocinones. Dreiding models of **30** indicate that the amide linkage in the medium-sized ring is noticeably distorted from planarity. This out-of-plane twisting causes reduced resonance interaction between the nonbonded nitrogen electron pair and the carbonyl π bond. In the bicyclic tautomers, however, the planar conformation enforced on the β-lactam ring results in restoration of total delocalization and accordant stabilization. On the other hand, cyclooctatrienone enjoys no such prerogative and the strain associated with the cyclobutanone ring in the bicyclic form is the dominant destabilizing factor.

Sulfonamides **31a** and **31b** likewise give evidence of existing only as azabicyclooctadienes **27a** and **27b**. Because **27a** and **27b** are air sensitive and thermally labile



31a **27a**
b **b**

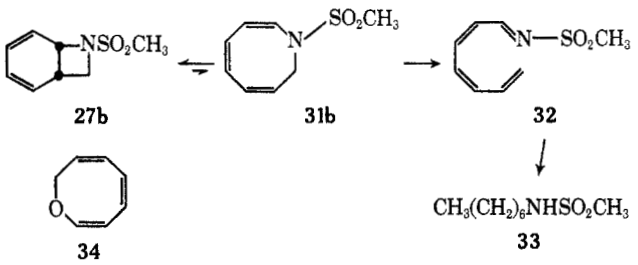
substances, temperatures in excess of 100° could not be employed. Under conditions such as refluxing toluene, for example, **27b** is transformed into unstable tetraene

(13) For a discussion of the stereochemical consequences of β-lactam thermolyses, see L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 1763 (1970). The relative ease of pyrolytic ring fission in this instance is attributable to the presence of aromatic character in the transition state (if a concerted process) or of enhanced free-radical stabilization (if stepwise).

(14) L. A. Paquette and L. D. Wise, *ibid.*, **87**, 1561 (1965).

32, presumably by thermal bond reorganization of **31b** with ring opening (Scheme VI). The imine was cata-

SCHEME VI

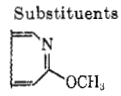
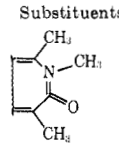
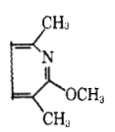
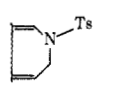
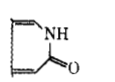
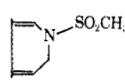
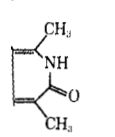


lytically hydrogenated to sulfonamide **33** which was identical with material prepared in unequivocal fashion from *n*-heptylamine. Demonstration of the feasibility of the electrocyclic reaction which is followed in the conversion of **27b** to **32**[15] may explain why oxocin (**34**) has proven to be a substance which has defied isolation and characterization to date.[16]

As with **17** ⇆ **30c**, the steric interference between the >NSO_2– substituent and the methylene group appears to be significant in causing **27a** and **27b** to be energetically favored. Also, other factors such as the absence of significant strain in the azetidine ring and effective diene π-orbital overlap in **27** can be expected to stabilize the bicyclic form relative to **31**. The data compiled herein is summarized in Table III.

TABLE III

INFLUENCE OF SUBSTITUENTS ON VALENCE TAUTOMERIC EQUILIBRIA IN THE AZOCINE SERIES (Cl_2C=CCl_2 SOLUTIONS)[a]

Substituents	% bicyclic	Substituents	% bicyclic
	<2		>98
	<2		>98
	97.6[b]		>98
	80.5[c]		

[a] Accuracy level is ±2%. [b] At 60°. [c] At 38°.

The Electronic Nature of Azete and Attempted Synthesis of Certain Derivatives.—Preliminary Hückel MO calculations for azete (azacyclobutadiene, **35**) have

35

indicated that this heterocycle can be expected to possess a greater degree of delocalization energy than cyclobutadiene.[17] Also, as with azocine,[18] the degeneracy of the NBMO's has been removed by the inclusion of the nitrogen atom in the molecular π framework. As always, the largest problem in calculations of this sort for heteroatomic systems is the selection of appropriate parameters.[19] Although numerous values for nitrogen have been assigned, k_{CN} is usually taken as unity and h_N as 0.5 or unity. The illustrated theoretical

$$\alpha_N = \alpha_0 + h_N\beta_0 \qquad \beta_{CN} = k_{CN}$$

results (Tables IV and V) suggest that **35** may, in fact,

TABLE IV

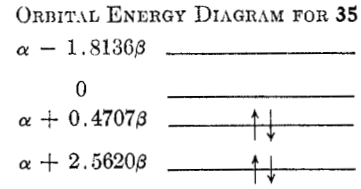
HÜCKEL MO TREATMENT OF **35**

h_N	k_{CN}	D.E. (β)[a]
1.0	1.0	0.391
0.5	1.0	0.224
0.1	1.0	0.049

[a] Delocalization energy for cyclobutadiene = 0.

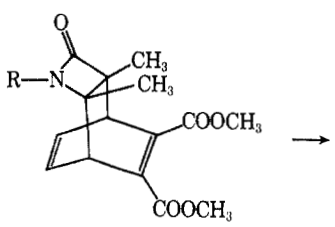
TABLE V

ORBITAL ENERGY DIAGRAM FOR **35**

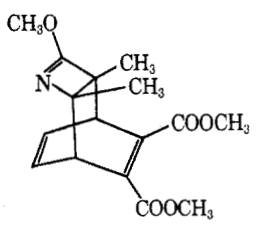


be endowed with modest stability. Also, in passing from the neutral molecule to the azete dianion, there should be a marked proclivity for the formation of the 6π electron "aromatic" structure.

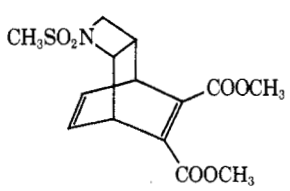
Accordingly, we investigated the retrograde Diels–Alder approach[20] to derivatives of azete. The condensation of **8** and **17** with dimethyl acetylenedicarboxylate proceeded readily to give **36a** and **36b**. O-Methylation of **36a** at the β-lactam functionality with



36a, R = H
b, R = CH_3



37



38

(15) Such an isomerization sequence may also be followed by the *N*-carbethoxy analog of **31b**: W. H. Okamura, *Tetrahedron Lett.*, 4714 (1969).

(16) R. W. Begland, unpublished results. For the preparation of a suitable precursor to **34**, see L. A. Paquette and R. W. Begland, *J. Org. Chem.*, **32**, 2723 (1967).

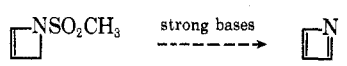
(17) For a recent MO treatment of cyclobutadiene, consult M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 3255 (1965).

(18) L. A. Paquette, J. F. Hansen, and T. Kakihana, *ibid.*, **93**, 168 (1971).

(19) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 5.

(20) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968).

trimethyloxonium fluoroborate served to provide **37**.[21] Under similar cycloaddition conditions, **27b** was transformed into **38**. The intent in this last example was to prepare **39** which in the presence of strong bases could conceivably be subject to elimination of methanesulfinic acid[22] and formation of **35**. However, all attempts to pyrolyze **36a**, **36b**, and **38** (200–325°, usually under



39 **35**

reduced pressure) led uniquely to dimethyl phthalate and tarry residues. In contrast, **37** was notably more stable and could be heated to 300° for long periods of time in an inert atmosphere with minimal decomposition. Higher temperatures did cause composition, but only small amounts of dimethyl phthalate could be detected.

Increasingly frequent reports of successful photochemically induced reverse Diels–Alder reactions[23] prompted an examination of this alternative. However, it soon became clear that unsaturated four-membered nitrogen-containing rings could not be isolated from a variety of such photolyses. Low yields of dimethyl phthalate were again encountered, but attempts to trap the proposed azete derivatives with such dienes as *trans*-piperylene and isoprene[23d] were unsuccessful.[24]

Experimental Section[25]

7-Azabicyclo[4.2.0]octa-2,4-dien-8-one (4).—To a stirred solution of 3.78 g of a mixture of 2-methoxyazocine (40%) and benzonitrile (60%)[7c] in 100 ml of petroleum ether (bp 30–60°) cooled to −78° was added dropwise a saturated ethereal solution of hydrogen bromide until the yellow azocine color faded. The colorless mushy precipitate was separated by decantation while still cold, washed with petroleum ether, and dissolved in 70 ml of acetone. The solution was stirred at room temperature for 3 hr during which time a color change from pale yellow to dark brown was noted. Evaporation of the solvent under reduced pressure gave a dark viscous oil. Column chromatography of this oil on Florisil (12 g) using ether as eluent gave 248 mg (17%) of a faintly yellow solid. Recrystallization from hexane afforded **4** as white crystals: mp 70–73°; $\nu_{max}^{CHCl_3}$ 3350, 1765, 1650, and 1580 cm^{-1}; $\lambda_{max}^{ethanol}$ 263 nm (ε 3220); $\delta_{TMS}^{CDCl_3}$ 6.82–7.41 (br s, 1, >NH), 5.51–6.10 (m, 4, vinyl), and 3.84–4.35 (m, 2, allylic).

Anal. Calcd for C_7H_7NO: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.32; H, 5.88; N, 11.56.

Aqueous Acid Hydrolysis of 2-Methoxyazocine (3).—A solution of 328 mg (2.4 mmol) of **3** in 6 ml of 4 *N* hydrochloric acid was stirred at room temperature for *ca.* 20 min. The dark red solution was extracted with ether (three 30-ml portions) after initial dilution with water (50 ml). The combined organic layers were neutralized by washing with aqueous sodium bicarbonate, dried, and evaporated at 0° to yield an orange oil (171 mg). Molecular distillation (90°, 0.15 mm) afforded 154 mg (47%) of a colorless mobile liquid which was identical with authentic methyl benzoate (**6**) in all respects.

1,6-Dimethyl-7-azabicyclo[4.2.0]octa-2,4-dien-8-one (8). A. Hydrolysis of 7.—A 9.90-g (60 mmol) sample of **7**[7c] in 250 ml of pentane cooled to −78° was treated with ethereal hydrogen bromine as above, followed by 6 hr in acetone at 25°. After chromatography, there was obtained 3.26 g (37%) of **8** as white needles: mp 104–105° (from ethyl acetate–hexane); $\nu_{max}^{CHCl_3}$ 3370, 1750, 1630, and 1580 cm^{-1}; $\lambda_{max}^{ethanol}$ 261 nm (ε 3780); for discussion of nmr spectrum, see text.

Anal. Calcd for $C_9H_{11}NO$: C, 72.45; H, 7.55; N, 9.39. Found: C, 72.32; H, 7.55; N, 9.52.

B. Bromination–Dehydrobromination of 9.—To a stirred solution of 5.0 g (33 mmol) of **9**[7c] in 100 ml of methylene chloride cooled to −78° was added dropwise a solution of 5.8 g (36.3 mmol) of bromine in 10 ml of the same solvent during 15 min. The solution was allowed to warm during 30 min and evaporated under reduced pressure. Recrystallization of the product from ethyl acetate gave 4.91 g (47%) of **10** as colorless crystals: mp 149–149.5°; $\nu_{max}^{CHCl_3}$ 3400 and 1760 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.56–6.88 (br s, 1, >NH), 4.42–4.77 (m, 2, >CHBr), 2.00–2.82 (m, 4, methylene), 1.39 and 1.27 (s, 3 each, methyl groups).

Anal. Calcd for $C_9H_{13}Br_2NO$: C, 34.75; H, 4.21; N, 4.50. Found: C, 34.75; H, 4.21; N, 4.43.

A solution of 4.03 g (13 mmol) of **10** and 4.85 g (39 mmol) of 1,5-diazabicyclo[4.3.0]non-5-ene in 30 ml of anhydrous benzene was heated at 72° with stirring for 4.5 hr. After cooling, the supernatant liquid was poured into 100 ml of water, and the mixture was extracted with ether (two 100-ml portions). The ethereal solution was washed with 2 *N* sulfuric acid (two 30-ml portions) and 20% aqueous potassium carbonate (one 50-ml portion), dried, and filtered. Recrystallization of the resulting semisolid from ethyl acetate gave 380 mg (20%) of **8**, mp 148–149°.

Aqueous Acid Hydrolysis of 7.—A solution of 1.0 g of **7** in 6 ml of 4 *N* hydrochloric acid was refluxed with stirring for 30 min. The cooled reaction mixture was poured into an ice-cold aqueous solution containing 1 equiv of sodium hydroxide. Extraction with ether (two 50-ml portions) and normal processing yielded 651 mg of a pale yellow oil, vpc analysis of which indicated the composition to be 28% *o*-xylene and 72% methyl 2,3-dimethylbenzoate (**14**). Comparison of samples isolated by preparative vpc to authentic materials confirmed the structural assignments.

1,6,7-Trimethyl-7-azabicyclo[4.2.0]oct-3-en-8-one (16).—A mixture of 3.29 g (20 mmol) of **15**[7c] and 14.20 g (0.10 mol) of methyl iodide was stirred at room temperature for 7 hr. Evaporation of the excess methyl iodide, followed by distillation under reduced pressure afforded 3.06 g (93%) of **16** as a colorless oil, bp 62–63° (0.2 mm). The analytical sample was prepared by crystallization and recrystallization from cold hexane, followed by molecular distillation: $\nu_{max}^{CCl_4}$ 1750 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.45–6.03 (m, 2, vinyl), 2.56 (s, 3, >NCH$_3$), 1.45–2.68 (m, 4, allyl), 1.28 and 1.19 (s, 3 each, methyls).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.88; H, 9.16; N, 8.80.

1,6,7-Trimethyl-7-azabicyclo[4.2.0]octa-2,4-dien-8-one (17). A. Methylation of 7.—A mixture of 3.50 g (21.4 mmol) of **7** and 7.6 g (54 mmol) of methyl iodide was refluxed for 45 hr. The excess methyl iodide was evaporated and the residue was chromatographed on neutral alumina (40 g, Baker, activity I). Elution with ether led to the recovery of 362 mg (10.4%) of **7**, whereas elution with 10% methanol–ether gave a viscous brown semisolid. Recrystallization of this material from hexane gave 367 mg (11.5%) of **17**: mp 81–82.5°; $\nu_{max}^{CCl_4}$ 1750 and 1585 cm^{-1}; $\lambda_{max}^{ethanol}$ 262 nm (ε 3440); for discussion of nmr spectrum, see text.

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.21; H, 7.89; N, 8.46.

B. Bromination–Dehydrobromination of 16.—A 2.31-g (14 mmol) sample of **16** was brominated (3.36 g, 21 mmol) in the usual way in methylene chloride (30 ml) at −78°. A solution of the crude dibromide in 50 ml of anhydrous tetrahydrofuran was added during 10 min to a stirred, refluxing suspension of sodium methoxide (from 7.13 g of sodium) in 200 ml of the same solvent. Heating was continued for 4 hr, the solids were removed by filtration, and the dark filtrate was reduced to one-fifth its volume and diluted with 150 ml of water. Extraction of the product with ether, followed by the customary work-up afforded 4.37 g (34%) of **17**, mp 81–82.5°, after recrystallization from hexane.

7-Methyl-7-azabicyclo[4.2.0]oct-3-en-8-one (19).—A mixture of 1.85 g (13.4 mmol) of **18**[7c] and 9.60 g (67.5 mmol) of methyl iodide was refluxed for 9 hr. Evaporation of the excess methyl iodide and distillation of the residue gave 1.56 g (85%) of **19** as a colorless mobile liquid, bp 63° (0.20 mm). The analytical sample was obtained by preparative scale vpc followed by molecular distillation: $\nu_{max}^{CCl_4}$ 1760 cm^{-1}; $\delta_{TMS}^{CCl_4}$ 5.27–5.82 (m, 2, vinyl), 3.35–

(21) Not unexpectedly, attempts to condense 2-methoxyazocines with dimethyl acetylenedicarboxylate gave rise to ill-defined polymeric substances, presumably as a result of initial nucleophilic attack at the triple bond by the nitrogen atom.

(22) For examples of analogous elimination reactions of sulfonamides, consult (a) W. Paterson and G. R. Proctor, *J. Chem. Soc.*, 485 (1965); (b) E. Negishi and A. R. Day, *J. Org. Chem.*, **30**, 43 (1965).

(23) (a) B. B. Roquitte, *J. Amer. Chem. Soc.*, **90**, 415 (1968); (b) R. K. Murray, Jr., and H. Hart, *Tetrahedron Lett.*, 4995 (1968); (c) H. Nozaki, H. Kato, and R. Noyori, *Tetrahedron*, **25**, 1661 (1969); (d) R. D. Miller and E. Hedaya, *J. Amer. Chem. Soc.*, **91**, 5401 (1969).

(24) S. F. Nelsen and J. P. Gillespie, *Tetrahedron Lett.*, 5059 (1969).

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

3.52 (m, 1, >CHN<), 2.93–3.29 (m, 1, >CHCO–), 2.56 (s, 3, $>NCH_3$), and 1.70–2.42 (m, 4, allyl).

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08. Found: C, 70.25; H, 8.37.

3,4-Dibromo-7-methyl-7-azabicyclo[4.2.0]octan-8-one (20).—A 2.52-g (18.4 mmol) sample of **19** in 30 ml of methylene chloride was brominated with a solution of 3.22 g (20.2 mmol) of bromine in 10 ml of the same solvent at −78°. There was obtained 3.82 g (70%) of **20** as white crystals: mp 110–117° (from ethyl acetate); $\nu_{max}^{CHCl_3}$ 1750 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 4.31–4.69 (m, 2, >CHBr), 3.59–3.98 (m, 1, >CHN<), 3.16–3.55 (m, 1, >CHCO–), 2.82 (s, 3, $>NCH_3$), and 2.24–2.90 (m, 4, methylene).

Anal. Calcd for $C_8H_{11}Br_2NO$: C, 32.35; H, 3.73; N, 4.72. Found: C, 32.98; H, 3.92; N, 4.45.

Attempted Dehydrobromination of 20.—A solution of 2.97 g (10 mmol) of crude **20** in 10 ml of anhydrous tetrahydrofuran was added dropwise during 30 min to a stirred suspension of sodium methoxide (prepared from 570 mg of sodium metal) in 50 ml of the same solvent. After stirring at room temperature for 5 hr, the dark solution was filtered, concentrated *in vacuo* to one-fifth its volume, and diluted with 50 ml of water. The aqueous mixture was extracted with ether (two 60-ml portion), and the combined organic layers were dried, filtered, and evaporated to give a solid residue admixed with an oil. This mixture was filtered and the solid washed with a minimum amount of cold ether to afford 690 mg (51%) of *N*-methylbenzamide, mp 80–81° (from ether). The mother liquor gave upon molecular distillation 487 mg (36%) of methyl benzoate, which presumably arose from the action of acid on the 2-methoxyazocine contaminant.

7-Azabicyclo[4.2.0]oct-3-ene (24).—A solution of 61.5 g (0.5 mol) of 7-azabicyclo[4.2.0]oct-3-en-8-one (**23**)[7c] in 200 ml of anhydrous tetrahydrofuran was added during 30 min to a stirred slurry of 16 g (0.4 mol) of lithium aluminum hydride in 300 ml of the same solvent. The mixture was stirred for 3 hr at reflux and then cooled to 0° in an ice bath. Water (16 ml) was slowly added, followed by 16 ml of 30% sodium hydroxide solution, and 30 ml of water. Anhydrous magnesium sulfate (25 g) was added to the resulting mixture and this was filtered. The solvent was evaporated and the residue was distilled to give 19.5 g (38%) of **24**: bp 53° (3.5 mm); ν_{max}^{neat} 3410 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.95–6.20 (m, 2, vinyl), 4.00–4.35 (m, 1, bridgehead, >CHN<), 3.50–3.85 (m, 1, one $-CH_2N<$), 2.65–3.25 (m, 2, other $-CH_2N<$ and >NH), and 1.90–2.25 (m, 5, bridgehead and allyl).

Anal. Calcd for $C_7H_{11}N$: C, 77.01; H, 10.16. Found: C, 76.98; H, 10.17.

***N*-Tosyl-7-azabicyclo[4.2.0]oct-3-ene (25a).**—To a well-stirred, cold mixture of 5.5 g (0.05 mol) of **24** and 25 ml of 30% aqueous sodium hydroxide was added 12 g (0.065 mol) of *p*-toluenesulfonyl chloride in small portions over a 10-min period. The mixture was stirred at 0° for another 15 min and extracted, and the residue was recrystallized from hexane to give 13.2 g (100%) of **25a**: mp 100–101°; ν_{max}^{KBr} 1333 and 1170 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}NO_2S$: C, 63.90; H, 6.61; N, 5.24. Found: C, 63.86; H, 6.51; N, 5.32.

3,4-Dibromo-7-tosyl-7-azabicyclo[4.2.0]octane (26a).—Treatment of 13.2 g (0.05 mol) of **25a** with 8.0 g (0.05 mol) of bromine in the predescribed fashion furnished 17.5 g (82.9%) of **26a**: mp 143–154° (from tetrahydrofuran–hexane); ν_{max}^{KBr} 1333 and 1165 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.20–7.80 (m, 4, aryl), 4.25–4.80 (m, 2, >CHBr), 3.15–4.15 (m, 3, >CHN<), 2.10–3.00 (m, 7, other ring protons), and 2.46 (s, 3, methyl).

Anal. Calcd for $C_{14}H_{17}Br_2NO_2S$: C, 39.60; H, 4.04; N, 3.26. Found: C, 39.73; H, 4.03; N, 3.31.

Dehydrobromination of 26a. A. With Excess Base.—To a cold (0°) stirred solution of 1.05 g (2.50 mmol) of **26a** in 10 ml of dry tetrahydrofuran was slowly added a suspension of 1.12 g (0.01 mol) of potassium *tert*-butoxide in 10 ml of the same solvent. The resulting mixture was stirred for 1 hr at 0°, evaporated *in vacuo*, and extracted with ether (two 25-ml portions). Evaporation of the ether and recrystallization of the residue from ether–hexane afforded 450 mg (69%) of *N*-tosylbenzylamine, mp 115°. This substance was identical with an authentic sample prepared from benzylamine and tosyl chloride.

B. With an Equivalent of Base.—Treatment of 4.23 g (0.01 mol) of **26a** with 2.20 g (0.0195 mol) of potassium *tert*-butoxide in analogous fashion at 0° gave 1.6 g (62%) of **27a**, mp 89–91°. The product was isolated by evaporation of the tetrahydrofuran *in vacuo*, extraction of the residue with ether, filtration through Celite, and evaporation, followed by extraction with boiling petroleum ether (30–60°), and cooling of the extracts to −20°. Principal infrared bands were seen at 1610, 1342, 1165, and 1148 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.35–8.05 (m, 4, aryl), 5.60–6.35 (m, 4, vinyl), 4.65–4.95 (m, 1, bridgehead, >CHN<), 3.85–4.35 (m, 2, $-CH_2N<$), 2.75–3.30 (m, 1, methine), and 2.50 (s, 3, methyl).

This substance decomposed somewhat rapidly and satisfactory elemental analyses could not be obtained. Therefore its *N*-phenylmaleimide adduct was prepared (ether solvent, 12 hr, 25°) in 91% yield, mp 281–282° (from acetone).

Anal. Calcd for $C_{24}H_{22}N_2O_4S$: C, 66.34; H, 5.10; N, 6.45. Found: C, 66.38; H, 5.15; N, 6.41.

***N*-Methanesulfonyl-7-azabicyclo[4.2.0]oct-3-ene (25b).**—From 5.5 g (0.05 mol) of **24** and 7.0 g (0.062 mol) of methanesulfonyl chloride, there was obtained a quantitative yield of **25b**: mp 89–90° (from hexane); ν_{max}^{KBr} 1318, 1160, and 1135 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.95–6.20 (m, 2, vinyl), 4.45–4.80 (m, 1, bridgehead, >CHN<), 3.74 (m, 2, $-CH_2N<$), 2.85–3.10 (m, 1, methine), 2.86 (s, 3, methyl), and 1.90–2.50 (m, 4, allyl).

Anal. Calcd for $C_8H_{13}NO_2S$: C, 51.31; H, 7.00; N, 7.48. Found: C, 51.34; H, 7.16; N, 7.49.

3,4-Dibromo-7-mesyl-7-azabicyclo[4.2.0]octane (26b).—Bromination of **25b** (3.75 g, 0.02 mol) in the customary fashion afforded 4.6 g (66.3%) of **26b**: mp 109–126° (from ether–hexane); ν_{max}^{KBr} 1350, 1155, and 1147 cm^{-1}.

Anal. Calcd for $C_8H_{13}Br_2NO_2S$: C, 27.68; H, 3.78; N, 4.04. Found: C, 27.91; H, 3.91; N, 3.90.

7-Mesyl-7-azabicyclo[4.2.0]octa-2,4-diene (27b).—To a solution of 1.80 g (5.2 mmol) of **26b** in 40 ml of dry tetrahydrofuran was added dropwise at 0° a suspension of 1.10 g (9.9 mmol) of potassium *tert*-butoxide in 30 ml of the same solvent. The mixture was stirred for 30 min upon completion of the addition and the solvent was then evaporated. Work-up in the predescribed fashion afforded 0.70 g (70%) of **27b**: mp 59–60° (from pentane); ν_{max}^{KBr} 1332, 1315, and 1135 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 265 nm (ϵ 2800); $\delta_{TMS}^{CDCl_3}$ 5.60–6.30 (m, 4, vinyl), 5.00–5.30 (m, 1, bridgehead, >CHN<), 4.20 (m, 2, $-CH_2N<$), 3.10–3.55 (m, 1, methine), and 2.90 (s, 3, methyl).

Because of the ease of decomposition of this substance, satisfactory combustion data could not be obtained. Therefore, its *N*-phenylmaleimide adduct was prepared (ether solvent, 24 hr, 25°) in 99% yield, mp 251–252° (from acetone).

Anal. Calcd for $C_{18}H_{18}N_2O_4S$: C, 60.32; H, 5.06; N, 7.82. Found: C, 60.23; H, 5.15; N, 7.58. Found: C, 60.23; H, 5.06; N, 7.82.

Thermal Rearrangement of 27b.—A solution of 100 mg of **27b** in 20 ml of toluene was refluxed under nitrogen for 2 hr. The crude product was distilled *in vacuo* to give a small quantity of **32**: ν_{max}^{neat} 1342, 1320, and 1160 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 264 nm (ϵ 3160), 273 (3860), and 289 (3860); $\delta_{TMS}^{C_2Cl_4}$ 6.40–6.60 (br d, J = 7 Hz, $-CH{=}N-$), 4.90–6.10 (m, 7, vinyl), and 2.83 (s, 3, methyl).

A second pyrolysis sample (70 mg) was immediately hydrogenated over Adams catalyst at 50 psig in ethanol solution. The catalyst was separated by filtration, the solvent evaporated, and the residue recrystallized several times from methanol to give 20 mg (26.7%) of *N*-mesylheptylamine, mp 55–56°, which was identical with an authentic sample prepared from the reaction of *n*-heptylamine and methanesulfonyl chloride: $\delta_{TMS}^{CDCl_3}$ 2.75–3.30 (m, 2, $-CH_2N<$), 2.96 (s, 3, $-SO_2CH_3$), 1.00–1.80 (m, 10, methylene), and 0.89 (t, J = 7 Hz, 3, methyl).

Anal. Calcd for $C_8H_{19}NO_2S$: C, 49.71; H, 9.91; N, 7.25. Found: C, 49.66; H, 9.93; N, 7.15.

Diels–Alder Reactions with Dimethyl Acetylenedicarboxylate.—A solution of 326 mg (2.18 mmol) of **8** and 342 mg (2.4 mmol) of dimethyl acetylenedicarboxylate in 6 ml of benzene was heated at reflux for 6 hr. Removal of the solvent under reduced pressure gave a viscous yellow oil, crystallization of which from ethyl acetate afforded 433 mg (67%) of **36a**: mp 140–141°; $\nu_{max}^{CHCl_3}$ 3490, 1775, 1740, 1655, and 1615 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.22–6.64 (m, 3, vinyl and NH), 3.63–4.03 (m, 2, bridgehead), 3.79, 1.37, and 1.28 (s, 6, 3, and 3, methyls).

Anal. Calcd for $C_{15}H_{17}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.28; H, 5.05; N, 5.24.

From 2.48 g (1.5 mmol) of **17** and 2.14 g (1.5 mmol) of dimethyl acetylenedicarboxylate in 30 ml of benzene (10 hr reflux), there was obtained 3.78 g (82%) of **36b** as colorless crystals: mp 132–133° (from ethyl acetate); $\nu_{max}^{CHCl_3}$ 1745, 1725, 1645, and 1610 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.24–6.71 (m, 2, vinyl), 3.59–4.08 (m, 2, bridgehead), 3.82, 2.59, 1.32, and 1.26 (s, 6, 3, 3, and 3, methyls).

Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 63.11; H, 6.25; N, 4.72.

From 100 mg (0.54 mmol) of **27b** and 70 mg (0.50 mmol) of dimethyl acetylenedicarboxylate in 10 ml of ether (48 hr, 25°), there was obtained 130 mg (76.4%) of **38**: mp 116–117° (from ether); ν_{max}^{KBr} 1755, 1718, 1310, 1160, and 1138 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.40–6.70 (m, 2, vinyl), 4.00–4.45 (m, 2, bridgehead), 3.60–3.85 (m, 1, >CHN<), 3.75 (s, 6, carboxylate methyls), 3.00–3.25 (m, 2, $-CH_2N<$), 2.81 (s, 3, CH_3SO_2-), and 2.50–2.90 (m, 1, methine).

Anal. Calcd for $C_{14}H_{17}NO_6S$: C, 51.37; H, 5.23. Found: C, 51.57; H, 5.40.

O-Methylation of 36a.—A mixture of 6.49 g (24 mmol) of **36a** and 3.5 g (2.8 mmol) of trimethyloxonium fluoroborate in 60 ml of dry methylene chloride was stirred at 0° for 10 hr. Aqueous sodium carbonate solution was carefully added until the solution became neutral. The organic layer was separated, washed with water, dried, and evaporated to give a viscous oil. This oil was dissolved in 50 ml of anhydrous ether and ethanolic perchloric acid (1:1) was added dropwise with cooling until the supernatant liquid showed no cloudiness. Filtration of the crystals, followed by thorough rinsing with ether and drying, afforded 7.86 g (86%) of **37** perchlorate, mp 162–164.5° (from methanol). Liberation of the free base from the purified perchlorate furnished **37** as a colorless crystalline solid: mp 85–87° (from ether–pentane); $\nu_{max}^{CCl_4}$ 1745, 1725, 1635, 1623, and 1603 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.54–6.73 (m, 2, vinyl), 3.99 (s, 9, $-OCH_3$), 3.90–4.25 (m, 2, bridgehead), 1.61 and 1.49 (s, 3 and 3, methyls).

Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.95; H, 6.27; N, 4.59. Found: C, 63.22; H, 6.27; N, 4.52.

Registry No.—**4**, 27070-39-9; **8**, 24321-92-4; **10**, 27062-83-5; **16**, 27062-84-6; **17**, 27062-85-7; **19**, 27062-86-8; **20**, 27062-87-9; **24**, 27062-88-0; **25a**, 27062-89-1; **25b**, 27062-90-4; **26a**, 27062-91-5; **26b**, 27062-92-6; **27a**, 27062-93-7; **27a** *N*-phenylmaleimide adduct, 27062-94-8; **27b**, 27062-95-9; **27b** *N*-phenylmaleimide adduct, 27062-96-0; **36a**, 27111-68-8; **36b**, 27062-43-7; **37**, 27062-44-8; **37** perchlorate, 27062-45-9; **38**, 27062-46-0.

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Neighboring-Group Participation by Sulfonamide Nitrogen. The 7-Azabicyclo[4.2.0]oct-3-ene to 6-Azabicyclo[3.2.1]oct-2-ene Rearrangement[1]

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The addition of bromine to *N*-sulfonyl derivatives of 1,6-dimethyl-7-azabicyclo[4.2.0]oct-3-ene (**3**) resulted in skeletal rearrangement and formation of *N*-sulfonyl-1,2-dimethyl-4-bromo-6-azabicyclo[3.2.1]oct-2-enes (30–37%). The structures (including exo stereochemistry for the bromo substituent) were assigned on the basis of their 100-MHz nmr spectra, their ready dehydrohalogenation to conjugated dienes, and the chemical behavior of these dienes. The rearrangements probably proceed by way of intramolecular SN2 displacement of trans-disposed bromine by neighboring sulfonamide nitrogen. Furthermore, a significant portion of **3** undergoes rupture of the azetidine ring with ultimate formation of dibromide **5** and the derived sulfonamide. A possible mechanism is presented.

Despite the extensive amount of research which has been accorded to skeletal rearrangements of carbobicyclic structures, similar transformations of related nitrogen heterocycles are notably few in number at the present time. The first reported example appears to be the racemization of L-(+)-2-α-tropanol,[2] which proceeds with participation of an amino nitrogen. At a later date, the isoquinuclidine system was shown to be particularly prone to conversion into derivatives of azabicyclo[3.2.1]octane, even when neighboring-group participation by amide nitrogen is required.[3] More recently, skeletal rearrangement of bicylic nitrenium ions has been demonstrated to be a general reaction type.[4] In the course of work directed at the synthesis of polyolefinic medium-ring nitrogen compounds,[1] we observed an unprecedented and unusual example of sulfonamide nitrogen migration with skeletal reorganization. In this paper we describe the details of several such transformations together with a number of affiliated chemical changes.

Results

cis-1,6-Dimethyl-7-azabicyclo[4.2.0]oct-3-ene (**2**) was prepared by treating previously described β-lactam **1**[5] with lithium aluminum hydride. Reaction of **2** with *p*-toluenesulfonyl, benzenesulfonyl, and methanesulfonyl chlorides readily afforded **3a**, **3b**, and **3c**, respectively. After addition of bromine to **3a** at 0°, the product was refluxed in hexane for 30 min. Direct crystallization of the reaction mixture led to the isolation of **4b** in 37% yield; chromatographic purification of the residual material on silica gel afforded 4,5-dibromo-4,5-dimethyl-1-cyclohexene (**5**, 17%), *p*-toluenesulfonamide (**6**, 29%), and a dibromosulfonamide identified as **7** (12%). *N*-Sulfonylazetidines **3b** and **3c** have similarly been found to undergo ready conversion to **4b** and **4c**. The structures of **4a–4c** follow from analyses, infrared and ultraviolet, and particularly nmr spectra. Spin-decoupling studies of **4b** at 100 MHz, for example, showed that vinyl proton H_c is coupled vicinally to H_d (J = 4.4 Hz), allylically to the low field methyl absorp-

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