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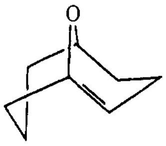
9-Oxabicyclo[3.3.1]non-1-ene[1,2]

Sir:

Over the past few years we and others have demonstrated that bridgehead alkenes in moderately sized ring systems are stable enough to permit their synthesis and purification at ordinary temperatures.[3] To date all isolable bridgehead alkenes have had the bridgehead double bond endocyclic in a ring of at least eight members.[3a] In smaller ring systems there is ample evidence for the existence of compounds with bridgehead unsaturation,[4] but none of these very highly strained compounds has yet been isolated in pure form. The torsional constraints on the double bonds in these compounds lead to interesting effects on their chemical behavior and reactivity.[3,4]

We have initiated a research program for the study of the chemical properties of some bridgehead alkenes substituted with heteroatoms within the bicyclic framework.[5] In ordinary unstrained systems the heteroatoms of enamines, enol ethers, and vinyl halides exert a very considerable influence on the chemical properties of the carbon double bond through the operation of inductive and resonance effects in the alkenes themselves and in the intermediates and products of their reactions. By constraining the heteroatom-substituted alkene in a bridged bicyclic framework, it should be possible to inhibit the resonance of the heteroatom with the double bond while leaving the inductive effect essentially unchanged.[6]

We now report on the synthesis and chemical behavior of 9-oxabicyclo[3.3.1]non-1-ene (**1**). Hydroboration oxidation of 1,5-cyclooctadiene[7,8] produced *cis*-1,5-cyclooctanediol which was oxidized with Jones' reagent to 1-hydroxy-9-oxabicyclo[3.3.1]nonane (**2a**)[9] in 49% overall yield.



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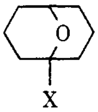

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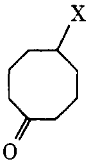

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a, X = HO
b, X = CH_3CO_2
c, X = CH_3SO_3
d, X = *p*-$CH_3C_6H_4SO_3$
e, X = CH_3CH_2O
f, X = Cl
g, X = H

The hemiketal **2a** is more stable than the hydroxy ketone **3a** as the infrared spectrum shows no carbonyl band. Nevertheless, most attempts to derivatize the hydroxyl group of **2a** gave derivatives of **3a** due to the greater reactivity of the secondary alcohol. Thus, reaction of **2a** with *p*-toluenesulfonyl chloride in pyridine gave **3d** exclusively,[10] and reaction with acetic anhydride in pyridine gave a mixture of acetates **2b** and **3b**.[9] Successful derivatization was achieved by the use of methanesulfonyl chloride and triethylamine[11] which gave mesylate **2c** as a stable white crystalline solid in 84% yield.[12] Treatment of mesylate **2c** with potassium *tert*-butoxide in *tert*-butyl alcohol at 80° caused a smooth elimination of methanesulfonic acid with production of the bridgehead olefin **1** in 32% yield after purification by distillation on a spinning band column.

The spectra of **1** indicate the absence of conjugation of the bridging oxygen with the double bond. The infrared spectrum shows a *weak* split band at 1640 cm^{-1} in contrast to the very intense bands usually observed for vinyl ethers,[13-16] and the nmr spectrum shows the vinyl proton at δ 5.74 (t, J = 6 Hz), shifted by 1.4 ppm from the "expected" position.[14,15] In the ultraviolet, **1** absorbs at 190 nm (ϵ 6200).

Hydrolysis of **1** in 50% aqueous acetone containing 1

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(1) Paper VI in the Bredt's Rule series. For previous papers in the series see ref 3 and 4.

(2) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society, and by a grant from Eli Lilly and Co.

(3) (a) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, **92**, 956 (1970); (b) J. A. Marshall and H. Faubl, *ibid.*, **92**, 948 (1970); (c) J. R. Wiseman, H.-F. Chan, and C. J. Ahola, *ibid.*, **91**, 2812 (1969); (d) W. Carruthers and M. I. Qureshi, *Chem. Commun.*, 832 (1969); (e) N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968); (f) G. L. Buchanan and G. Jamieson, *Tetrahedron*, **28**, 1123 (1972); (g) G. L. Buchanan and G. Jamieson, *ibid.*, 1129 (1972).

(4) (a) J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, **91**, 7775 (1969); (b) J. A. Chong and J. R. Wiseman, *ibid.*, **94**, 8627 (1972); (c) S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, **21**, 2997 (1965); (d) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); (e) R. Keese and E. P. Krebs, *ibid.*, **11**, 518 (1972); (f) P. Warner, R. LaRose, C.-M. Lee, and J. C. Clardy, *J. Amer. Chem. Soc.*, **94**, 7607 (1972); (g) J. E. Gano and L. Eizenberg, *ibid.*, in press.

(5) For examples of compounds with bridgehead unsaturation involving a heteroatom see (a) J. O. Reed and W. Lwowski, *J. Org. Chem.*, **36**, 2864 (1971); (b) M. Toda and Y. Hirata, *Chem. Commun.*, 1597 (1970); (c) H. Newman and T. L. Fields, *Tetrahedron*, **28**, 4051 (1972); (d) P. G. Gassman, R. L. Cryberg, and K. Shudo, *J. Amer. Chem. Soc.*, **94**, 7600 (1972); (e) R. D. Fisher, T. D. Bogard, and P. Kovacic, *ibid.*, **94**, 7599 (1972); (f) C. A. Grob and A. Sieber, *Helv. Chim. Acta*, 2531 (1967).

(6) For examples of steric inhibition of resonance see (a) M. S. Newman, Ed., "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956; (b) H. Pracejus, M. Kehlen, H. Kehlen, and H. Matscheiner, *Tetrahedron*, **21**, 2257 (1965); (c) G. Wittig and G. Steinhoff, *Justus Liebigs Ann. Chem.*, **676**, 21 (1964); (d) K. C. Dewhirst and D. J. Cram, *J. Amer. Chem. Soc.*, **80**, 3115 (1958); (e) B. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); (f) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

(7) R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *Chem. Ind.* (*London*), 2087 (1962).

(8) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280 (1968).

(9) C. Ganter and J. F. Moser, *Helv. Chim. Acta*, **52**, 725 (1969). The ratio of acetates **2b** and **3b** is determined kinetically. *p*-Toluenesulfonic acid in acetic acid catalyzes the quantitative conversion of **2b** to **3b**.

(10) J. K. Crandall, R. D. Huntington, and G. L. Brunner, *J. Org. Chem.*, **37**, 2911 (1972).

(11) J. F. King and T. Durst, *J. Amer. Chem. Soc.*, **86**, 287 (1964); W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964); G. Stork and I. J. Borowitz, *ibid.*, **84**, 313 (1962).

(12) Mesylate **2c** is a stable compound, but does isomerize on long storage at room temperature to **3c**. The isomerization apparently is catalyzed by traces of methanesulfonic acid. On heating to 75°, **2c** decomposes to 4-cyclooctenone and methanesulfonic acid.

(13) (a) Y. Mikawa, *Bull. Chem. Soc. Jap.*, **29**, 110 (1956); (b) G. D. Meakins, *J. Chem. Soc.*, 4170 (1953).

(14) J. Feeney, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1962).

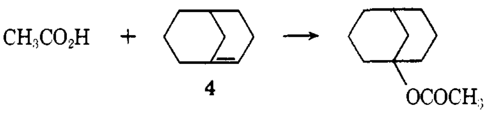
(15) Spectra for 2-methyl-5,6-dihydropyran;[16] ir (CCl_4) 1680 (s) cm^{-1}; (CCl_4) vinyl H, δ 4.34; uv (pentane) 190 nm (ϵ 5700).

(16) (a) W. H. Perkin, Jr., *J. Chem. Soc.*, **51**, 702 (1887); (b) J. G. Montaigne, *Ann. Chim.*, (*Paris*), 314 (1954); (c) I. S. Trubnikov and Yu. A. Tentin, *Zh. Obshch. Khim.*, **32**, 3590 (1962).

drop of 70% perchloric acid afforded the hemiketal **2a**, and reaction of **1** with acetic acid gave exclusively acetate **2b**.[9] Hydrogenation of **1** (5% Pd–C in 20 ml of ethanol with 2 drops of acetic acid) afforded 9-oxabicyclo[3.3.1]nonane (**2g**).[17]

Comparisons of the chemical reactivity of **1** have proved interesting. Whereas the half-life of the reaction of **1** with acetic acid at 25° is 68 hr, the reaction of bicyclo[3.3.1]non-1-ene (**4**)[3a] with acetic acid at 25° is complete in 2 min ($t_{1/2} < 1$ min). The hydrocarbon **4** is at least 4000 times as reactive as the enol ether **1**, just the opposite of the case for unstrained compounds where enol ethers are vastly more reactive.

$$CH_3CO_2H + \mathbf{1} \longrightarrow \mathbf{2b}$$



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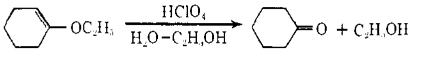
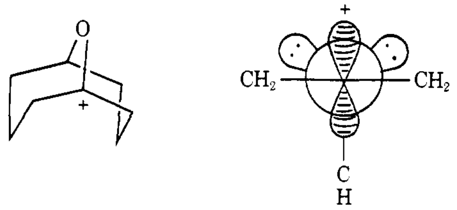
Similarly, we have compared the rate of perchloric acid-catalyzed hydrolysis (and ethanolysis) of **1** in 95% aqueous ethanol with that of 1-ethoxycyclohexene (**5**);[18] see Table I. Enol ether **5** is 10^5 times as reactive as the enol ether **1**, in spite of the strain energy of **1** which should accelerate its reaction. We attribute the low reactivity of **1** in these reactions to inhibition of resonance of the bridging oxygen atom with the positive bridgehead carbon in cation **6**. The bridging oxygen atom is assumed to have distorted tetrahedral geometry as shown in the projection view of **6** along the 1–9 bond. In a strain-free model the empty p orbital at the bridgehead carbon bisects the angle between the oxygen orbitals containing the nonbonding electrons. The strain energy of **1** may be estimated as approximately 12 kcal/mol,[19] relative to **2a**, while cation **6** should be nearly strainless.[20] If the strain of **1** is relieved entirely at the transition state for protonation, the rate of the reaction should be accelerated by approximatly 10^9. Therefore, the real rate retardation seen in comparing the rates of hydrolysis of **1** and **5** may be as great as 10^{14}.

Table I. Rates of Hydrolysis of Enol Ethers

	k_2, l. mol^{-1} sec^{-1}
$1 \xrightarrow[H_2O-C_2H_5OH]{HClO_4} 2a + 2e$	8.8×10^{-4} (27°)
 **5**	8.0×10^{1} (25°)[1]



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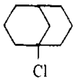
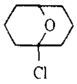
Finally, we have compared the rates of solvolysis of 1-chlorobicyclo[3.3.1]nonane (**7**)[20] and 1-chloro-9-oxabicyclo[3.3.1]nonane[21] in 60% aqueous ethanol. The results, summarized in Table II, show that some resonance must still persist in cation **6** since the inductive effect of oxygen should retard the reaction by more than a factor of 3.[22]

Table II. Rates of Solvolysis of Bridgehead Chlorides in 60% Aqueous Ethanol

	Temp, °C	k_1,[a] sec^{-1} × 10^5
 (**7**)	65.10	21.8
	55.00	6.83
	44.85	2.11
 (**2f**)	65.05	6.43
	55.00	2.08
	44.85	0.646

[a] The rates for **7** are in good agreement with earlier work.[20]

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[17] F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966).

[18] Rates are first order in both acid and enol ether and were measured spectrophotometrically at 208 nm. Rates for **5** are from A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne, and D. S. Sagatys, *ibid.*, **93**, 413 (1971).

[19] The strain energy of **4** is 12 kcal/mol. P. M. Lesko and R. B. Turner, *ibid.*, **90**, 6888 (1968). The strain energy of **1** is unknown. See also N. L. Allinger and J. T. Sprague, *ibid.*, **94**, 5734 (1972).

[20] W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968).

[21] Prepared from **2a** with thionyl chloride.

[22] See H. Stetter, P. Tacke, and J. Gartner, *Chem. Ber.*, **97**, 3480 (1964), for a similar comparison in the adamantyl ring system.

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Reaction of Carbon Vapor with Lithium Atoms. A Direct Synthesis of Polylithium Compounds

Sir:

The reaction of lithium atoms with chlorocarbons has been shown to produce tetralithiomethane and hexalithioethane from analogous chlorocarbon starting materials.[1] It is well known that carbon vapor, usually produced with a carbon arc or by vaporizing carbon with a laser, consists of the carbon species C^1 through C_6[2] with C_3 in highest concentration. Carbon vapor is known to be reactive.[3] A study of the reaction of atomic lithium with carbon vapor species was therefore deemed worthwhile since it was very unlikely that these reactive species would combine to give only lithium carbide C_2Li_2.

A stainless steel reactor was used (Figure 1) in which carbon vapor was generated by an arc between movable graphite electrodes positioned at the orifice of the lithium Knudsen cell. The reaction vessel was evacuated to 10^{-5} Torr, and the Knudsen cell, containing 11 g of lithium, was heated to 800–850° by induction or resistance heating. The lower walls of the reactor were cooled to −196°, and the arc was initiated with an 18-V, 250-A ac source. After 45 min the reaction

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[1] C. Chung and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 1078 (1972).

[2] J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, *J. Chem. Phys.*, **31**, 1131 (1959).

[3] P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 1135 (1965).