spectrometer was obtained through an Institutional Instrument Grant by the National Science Foundation.

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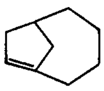
Bredt's Rule. II.[1] Synthesis of Bicyclo[4.2.1]non-1(2)-ene and Bicyclo[4.2.1]non-1(8)-ene

Sir:

We have postulated that a close relationship exists between the strain energy of bridged bicyclic bridgehead alkenes and the strain energy of *trans*-cycloalkenes.[1] This hypothesis leads to the prediction that bridged bicyclic alkenes in which the bridgehead double bonds are endocyclic in rings of at least eight members should be sufficiently stable to allow their synthesis and isolation. The pertinence of this simple relationship has been demonstrated in the synthesis of bicyclo[3.3.1]non-1-ene (**3**).[1,2] Lesko and Turner[3] have determined the strain energy of bicyclo[3.3.1]non-1-ene (**3**) to be of the same order of magnitude (*ca.* 12 kcal/mol) as the strain energies of *trans*-cyclooctene (9.2 kcal/mol) and *cis*-di-*t*-butylethylene (9.3 kcal/mol). An additional example of a bicyclic ring system having a bridgehead double bond endocyclic in an eight-membered ring has been provided in the synthesis of 9,9′-dehydrodianthracene.[4]

The bicyclo[4.2.1]nonanyl ring system offers an opportunity for further examination of the relationship between bridgehead alkenes and *trans*-cycloalkenes. Two bridgehead alkenes which have their double bonds endocyclic in eight-membered rings, bicyclo[4.2.1]non-1(8)-ene (**1**) and bicyclo[4.2.1]non-1(2)-ene (**2**), may be derived from this skeleton. We now report the synthesis and characterization of these highly strained alkenes using a synthetic sequence similar to that used to prepare bicyclo[3.3.1]non-1-ene (**3**).

Alkylation of the sodium enolate of 2-ethoxycarbonylcyclopentanone with 1,4-dibromobutane in dimethylformamide produced the bromo keto ester **4** in 65% yield. Addition of the bromo keto ester **4** to a suspension of sodium hydride in benzene and dimethylformamide produced ethyl 9-oxobicyclo[4.2.1]nonane-1-carboxylate (**5**) in 21% yield along with the enol ether **6** in 31% yield. The keto function of **5** was reduced by conversion to the ethylene dithioketal followed by desulfurization with Raney nickel. The ester **7**, produced in 65% yield, was hydrolyzed to the corresponding acid **8**, mp 48°, which was transformed by the Curtius procedure into the bridgehead amine **9**, mp 56°, in 80% yield. The primary amine **9** was methylated by the Clark–Eschweiler technique to give the tertiary amine **10**, and treatment of **10** with methyl iodide afforded the quaternary salt **11**, mp 284–287°, in 86% yield. The quaternary iodide **11** was transformed into the corresponding hydroxide **12** by treatment with silver oxide.



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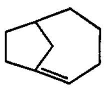

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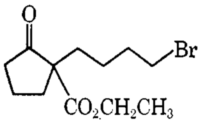

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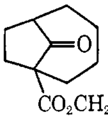

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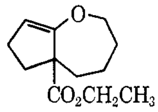

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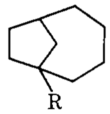

7, R = $CO_2CH_2CH_3$
8, R = CO_2H
9, R = NH_2
10, R = $N(CH_3)_2$
11, R = $^{+}N(CH_3)_3I^{-}$
12, R = $^{+}N(CH_3)_3OH^{-}$
13, R = $OCOCH_3$

Pyrolysis of the quaternary ammonium hydroxide **12** at 140° produced two isomeric hydrocarbons in a 5:1 ratio, a solid, mp 44–46°, and a liquid, with retention times[5] 3.7 and 5.0 min, respectively. Also formed in the pyrolysis was the tertiary amine **10**. The hydrocarbons were separated and purified by preparative vpc. The major isomer was shown to possess structure **1**, and the minor isomer was shown to have structure **2** by the following spectral analysis and chemical degradation.

The mass spectra[6] of both isomers are nearly identical and show molecular ions at *m/e* 122 with isotope peaks at *m/e* 123 and 124 of the appropriate intensities for the formula C_9H_{14}. Both isomers reacted with acetic acid at room temperature to give bicyclo[4.2.1]nonan-1-yl acetate (**13**) which was identified by comparison of its infrared spectrum with that of an authentic sample.[7] The nmr of the major isomer (**1**) shows a broad "singlet" at τ 4.6 (1 H), a septet ($J = 2.1$ Hz) centered at τ 7.2 (1 H), and a complex absorption from τ 7.55 to 9.05 (12 H). The infrared spectrum (CCl_4) of **1** shows peaks at 3060 (=CH stretching) and 1607 cm^{-1} (C=C stretching). The nmr spectrum of the minor isomer (**2**) shows a triplet ($J = 7$ Hz) at τ 4.7 (1 H) and a complex absorption at τ 7.15–9.40 (13 H). The infrared spectrum of **2** shows bands at 3055 and 1655 cm^{-1}. Since vinyl protons in cyclopentene rings generally show small coupling constants with adjacent aliphatic protons and the frequency observed for the carbon–carbon double bond stretching in the infrared ordinarily decreases with decreasing ring size, the spectral data indicate the major isomer has structure **1** and the minor isomer structure **2**. Chemical degradation allowed definitive assignment of the position of the double bond in each compound. Oxidation of the major isomer (**1**) with potassium permanganate and sodium periodate[8] followed by methylation with diazomethane produced a keto ester which absorbed in the infrared at 1710 (seven-membered ketone) and 1745 cm^{-1} (ester carbonyl). Oxidation of the minor isomer (**2**) and esterification with diazomethane produced a keto ester

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[1] Previous paper in the series: John R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967).

[2] J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967).

[3] P. M. Lesko and R. B. Turner, *ibid.*, **90**, 6888 (1968).

[4] N. M. Weinshenker and F. D. Greene, *ibid.*, **90**, 506 (1968).

(5) Separations were effected on a 5 ft × 0.25 in. column packed with 20% Carbowax 20M and 10% KOH on 60–80 mesh Chromosorb W at 110° and 60 cc/min He flow.

(6) We are indebted to Dr. M. Green for the mass spectra.

(7) It is a pleasure to acknowledge the assistance of Professor W. G. Dauben in furnishing reference spectra.

(8) E. von Rudloff, *Can. J. Chem.*, **34**, 1413 (1956).

which absorbed in the carbonyl region only at 1745 cm^{-1} (five-membered ring ketone and ester carbonyl).

Inspection of models indicates that bicyclo[4.2.1]non-1(8)-ene (**1**) is more strained than bicyclo[4.2.1]non-1(2)-ene (**2**). We believe that the predominant production of the less stable isomer is the result of kinetic control during the Hofmann elimination. The Hofmann elimination has been shown to proceed by both *syn* and *anti* mechanisms.[9] Models of the quaternary ammonium hydroxide **12** indicate the alkenes **1** and **2** are most likely formed by *syn* elimination of the *exo* hydrogens at C-8 and C-2, respectively. Whereas the *exo* hydrogen at C-8 is held rigidly in a *syn* and coplanar orientation with respect to the trimethylammonium group, the *exo* C-2 hydrogen may be in various orientations due to the greater mobility of the four-membered bridge. Thus, kinetically preferred removal of the favorably oriented *exo* C-8 hydrogen should result in formation of the less stable isomer (**1**) in greater amount.

We are currently investigating the chemistry of this and other highly strained alkenes in our efforts to define the limits of Bredt's rule.[10]

(9) (a) M. P. Cooke, Jr., and J. L. Coke, *J. Amer. Chem. Soc.* **90**, 5556 (1968); (b) J. L. Coke and M. C. Mourning, *ibid.*, **90**, 5561 (1968).

(10) This research was generously supported by Grants 916G and 3740A from the Petroleum Research Fund.

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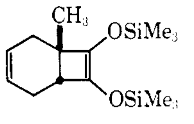
Application of Electron Spin Resonance Spectroscopy to a Study of Valence Isomerization and *cis–trans* Isomerization. Bicyclo[4.2.0]octane-7,8-semidione and Bicyclo[4.2.0]oct-3-en-7,8-semidione[1]

Sir:



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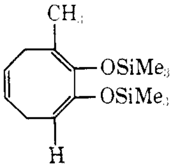

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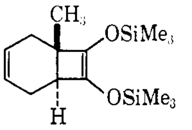

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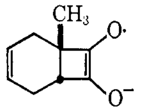


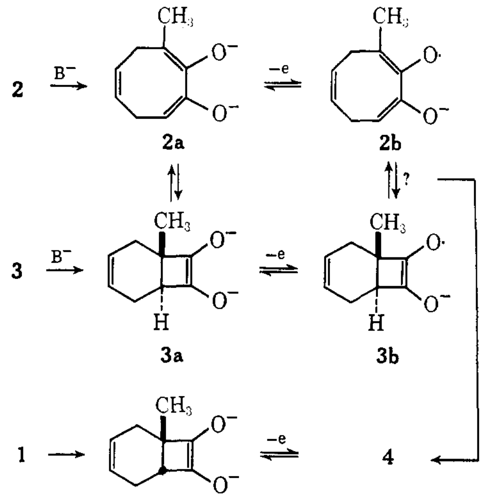
4

$a^H = 13.5, 1.2, 0.4, 0.4$ G

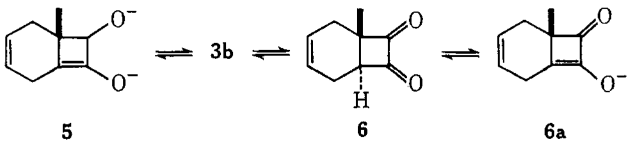
$a_{CH_3}{}^H = 0.2$ G

Treatment of **1**,[2] **2**,[2] or **3**[2] with a solution of potassium *t*-butoxide in dimethyl sulfoxide (DMSO) yields a single semidione[3] to which we assign structure **4**. Semidione **4**, when prepared from **1**, exchanges its α-hydrogen atom very slowly in DMSO-d_6 to give $a_\alpha{}^D = 2.1$ G. The mixture of the deuterated and undeuterated semidiones could be easily analyzed by esr spectroscopy. Under standard conditions 50% hydrogen–deuterium exchange was found in 420 min. Under similar conditions, the semidione formed from **3** had undergone 95% exchange in 40 min, while the initial[4] semidione formed from **2** in DMSO-d_6 had exchanged 50% of the α-hydrogen atoms. These results suggest that **2a** and **3a** (or **2b** and **3b**) are rapidly interconverted by a conrotatory motion and that hydrogen–deuterium exchange occurs rapidly in one or the other. Orbital symmetries predict that the dianion **2a** should undergo a conrotatory ring closure more readily than the radical anion **2b**. We conclude that the reaction sequence of Chart I is involved wherein the concentrations of **2b** and **3b** are always less than 10% of **4**.

Chart I

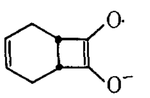


The process involved in the interconversion of **3b** to **4** and in the hydrogen–deuterium exchange may involve a radical dianion (**5**) or the diketone **6** and its enolate anion **6a**.



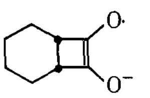
Alternately, protonation of **2a** will lead to hydrogen–deuterium exchange while a disrotatory ring closure of **2b** will yield **4**. A rapid but reversible conrotatory ring closure of **2a** or **2b** in competition with a slower but irreversible disrotatory closure to **4** is a distinct possibility.

We have previously demonstrated that, under the reaction conditions, the hydrogen–deuterium exchange of the α-methylene protons in bicyclo[3.1.0]hexane-2,3-semidione is highly stereoselective (the hydrogen *trans* to the cyclopropyl ring exchanges preferentially).[5] This observation is most consistent with a radical-dianion intermediate. Therefore, we examined **7**



7

$a^H = 13.5, 13.5, 0.60, 0.60, 0.35, 0.35$ G



8

$a^H = 13.5, 13.5, 0.5, 0.5, 0.25, 0.25$ G

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[1] Supported by the National Science Foundation.

[2] J. J. Bloomfield, *Tetrahedron Lett.*, 587 (1968).

[3] G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 6781 (1967).

[4] Spectrum recorded 15 min after mixing of reagents.

[5] G. A. Russell, J. J. McDonnell, and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 5516 (1967).