(11) Crude yields of chromatographically pure products were uniformly quantitative; the yields reported in this paper are for distilled or recrystallized products. All of the reactions reported herein have been carried out many times with completely reproducible results.

(12) A. McKillop, B. P. Swann, and E. C. Taylor, *J. Am. Chem. Soc.*, **95**, 3340 (1973).

(13) This is true both for 0.1 and 1.0 molar scale reactions.

Edward C. Taylor,* Chih-Shu Chiang
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

A. McKillop
School of Chemical Sciences, University of East Anglia
Norwich, England NR4 7TJ

J. F. White
Emery Industries
Cincinnati, Ohio 45232

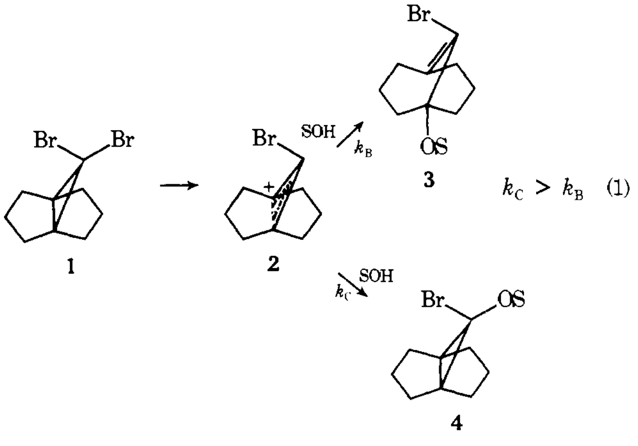
Received June 1, 1976

Propellanes. 12. A Bridgehead Olefin Transoid in a Six-Membered Ring. Formation of a Stable Cyclopropanone

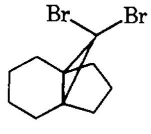
Sir:

A surge of interest[1] in the production and fate of bridgehead olefins has followed Wiseman's demonstration that these olefins are similar in strain energy and reactivity to their corresponding trans cycloolefins.[2] As expected, most work has been limited to cases where the bridgehead double bond is transoid in a ring of ≥ 7 carbons. While effort has been expended on the synthesis of examples of bridgehead double bonds transoid in six-membered rings,[3] no energy comparisons have been possible. We now report data which allow some perspective on the energetics of bridgehead olefin formation.

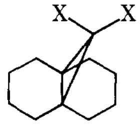
Our approach[4] to bridgehead olefins has been through the solvolysis of tricyclic cyclopropyl halides (i.e., propellanes); others have also utilized this route.[5] An obvious potential precursor for a bridgehead olefin transoid in a six-membered ring is 9,9-dibromo[3.3.1]propellane (9,9-dibromotricyclo[3.3.1.$0^{1,5}$]nonane, **1**),[6] although one would expect relatively more cyclopropyl product than in the earlier cases we reported[4b,c] (eq 1).



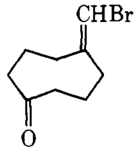
Solvolysis of **1** (HOAc, 0.012 M NaOAc, 125 °C) proceeded with a rate constant of 3.1×10^{-7} s^{-1}, some 6200 times slower than acetolysis of **5**. Unfortunately, however, 2 mol of acid was produced, indicating that both bromines had been lost. We pursued this no further, since our experience with **6a** indicated we were probably seeing HOAc addition to the cyclopropane ring followed by solvolysis; with **6a**, addition took place six times faster than the solvolysis of **1**.



5

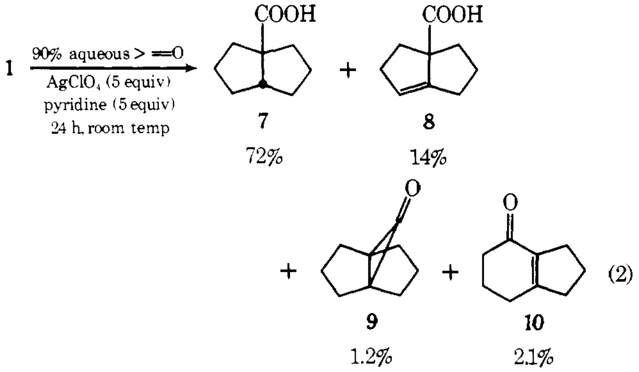


6a, X = Br
b, X = Cl



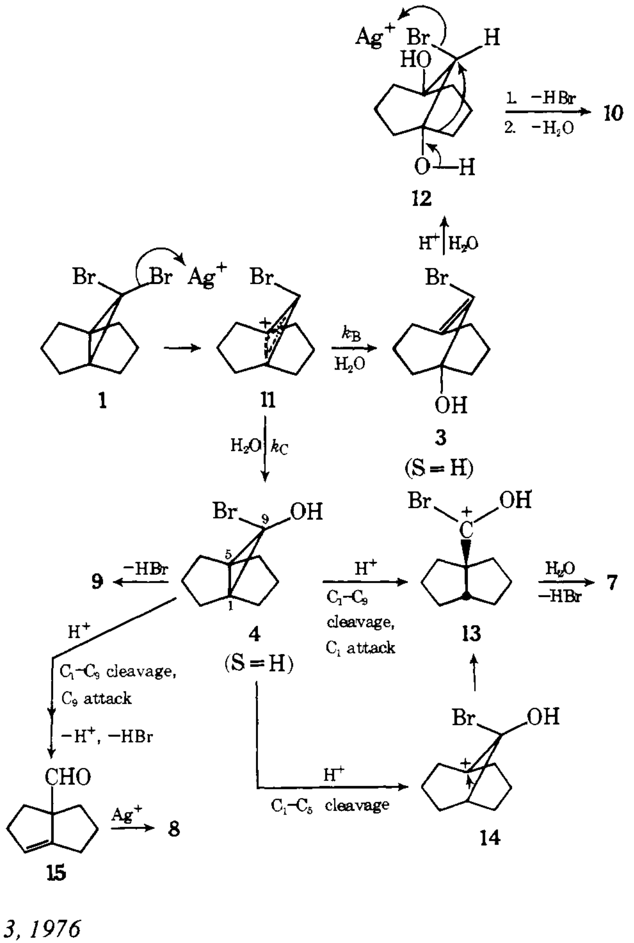
16

Silver assisted hydrolysis of **1** in aqueous acetone proved more fruitful. In 90% aqueous acetone, **1** reacted eight-ten times slower than **6a**, but two-three times faster than **6b**. The products isolated from hydrolysis (buffered to allow isolation of **9**) are shown in eq 2.



Thus the acid mixture of **7** and **8** was the major product. Catalytic hydrogenation (Pd/C, EtOH) gave pure **7**.[7] The olefinic resonance of **8** indicated its presence; the ^{13}C NMR of the mixture showed nine peaks not attributable to **7**, including two olefinic carbons (δ 151.9, 122.2). The diazomethane-derived esters showed separate resonances at δ 3.62 (7-OCH_3) and δ 3.67 (8-OCH_3). Cyclopropanone **9**, which led to primarily **7** when treated under unbuffered hydrolysis conditions or when shaken with aqueous base, was identified

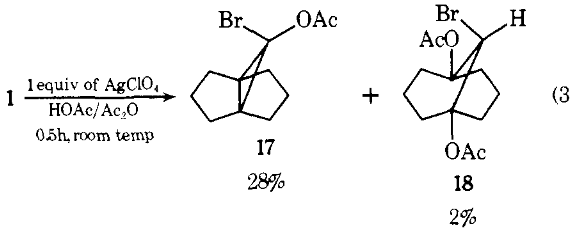
Scheme I



on the basis of its ir (CCl_4) carbonyl absorption at 1824 cm^{-1}, its mass spectrum (Calcd for $C_9H_{12}O$: m/e 136.0888. Found: m/e 136.0883. Calcd for C_8H_{12}: m/e 108.0939. Found (P − CO, rel. intensity 1.2): m/e 108.0938. Calcd for C_7H_8O: m/e 108.0575. Found (P − C_2H_4, rel. intensity 1.0): m/e 108.0575), and its ^{13}C NMR[12] ($CDCl_3$): δ 174.1, 32.8, 30.7, 30.4.[13,14] Compound **10** showed λ_{max} 250 (log ϵ 4.23) nm (lit.[16] 250 (log ϵ 3.95)); also calcd for $C_9H_{12}O$: m/e 136.0888. Found: m/e 136.0886.

The mode of product formation is shown in Scheme I. Thus ionization of **1** to partially opened ion **11**[17] is followed by collapse at $C_9(k_C)$ to give **4** (S = H), or at C_1 (C_5, k_B) to give **3** (S = H). Dehydrobromination of **4** gives **9**. While acid formation may funnel through **9**, we show the alternative protolysis of the cyclopropane ring of **4**. Ion **13** may be derived from **4** either directly or via **14**; production of the cis acid (**7**) is expected.[4c,18] The less favored formation of unsaturated acid **8** can involve the alternate direction of protolytic cleavage of the C_1–C_9 bond with concomitant elimination to aldehyde **15**; Tollens oxidation by Ag^+ then produces **8**.[19] Bridgehead olefin **3** suffers a fate similar to those derived from **5**[4b,d] and **6**.[4c]

While the small amount of **10** formed fits prior expectations for the mode of reaction of **11**, the absence of typical bridgehead olefin products **12** and/or **16** was worrisome. Hydrolysis in less aqueous media would be expected to enhance fragmentation to **16**;[4c] indeed Ag^+ assisted solvolysis of **1** in 99% aqueous acetone produced roughly equal amounts of **10** and **16** (^1H NMR δ 5.80 (s); ir $\nu_{C=O}$ at 1690 cm^{-1}. Calcd for $C_9H_{13}OBr$: m/e 216.0150. Found: m/e 216.0156). Additionally, the Ag^+ assisted acetolysis of **1** gave a derivative of **12** (**18**), as shown in eq 3. The spectral identification of **17** was made secure via its base catalyzed conversion to **7**. Similarly, **18** was converted to **12**, and subsequently **10**.



17
28%

18
2%

(3)

In 90% aqueous acetone, the ratio k_B/k_C, as measured by the percent bridgehead olefin products divided by the percent cyclopropyl products, is 0.024 for **1**, ≥360 for **5**, and 1.8 for **6a**. The difference between the bridgehead olefins derived from **1** and **5** is that the former is transoid in a six-membered ring, while the latter is transoid in a seven-membered ring; both are cisoid in six-membered rings. The energy required to produce the k_B/k_C change—roughly *6 kcal/mol*—is a first approximation to the energy difference between transoid seven and transoid six bridgehead olefins which *bear a halogen substituent* (the difference for alkyl or hydrogen substituted ones should be greater). Similarly, the difference between analogous cisoid seven and cisoid six bridgehead olefins (**5** vs. **6a**) is calculated to be ca. 3 kcal/mol.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for partial support of this work. We are indebted to Mr. Thomas Schleis for the synthesis of generous amounts of **1**.

References and Notes

(1) Reviews: (a) R. Keese, *Angew. Chem., Int. Ed. Engl.*, **14**, 528 (1975); (b) G. L. Buchanan, *Chem. Soc. Rev.*, **3**, 41 (1974); (c) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973).

(2) J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, **92**, 956 (1970).

(3) (a) A. Nickon, D. F. Covey, F. Huang, and Y.-N. Kuo, *J. Am. Chem. Soc.*, **97**, 904 (1975); (b) M. Kim and J. D. White, *ibid.*, **97**, 451 (1975); (c) W. G. Dauben and J. D. Robbins, *Tetrahedron Lett.*, 151 (1975); (d) D. Lenoir and J. Firl, *Justus Liebigs Ann. Chem.*, 1467 (1974); (e) W. Burns and M. A. McKervey, *J. Chem. Soc., Chem. Commun.*, 858 (1974); (f) A. D. Wolf and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 8209 (1973); (g) C. B. Quinn, J. R. Wiseman, and J. C. Calabrese, *ibid.*, **95**, 6121 (1973); (h) A. H. Alberts, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 3047 (1973); (i) J. E. Gano and L. Eizenberg, *J. Am. Chem. Soc.*, **95**, 972 (1973); (j) H. H. Grootveld, C. Blomberg, and F. Bickelhaupt, *J. Chem. Soc., Chem. Commun.*, 542 (1973); (k) D. Lenoir, *Tetrahedron Lett.*, 4049 (1972); (l) D. Grant, M. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972); (m) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **11**, 518 (1972); **10**, 262 (1971); (n) J. O. Reed and W. Lwowski, *J. Org. Chem.*, **36**, 2864 (1971).

(4) (a) P. Warner, R. LaRose, R. F. Palmer, C. Lee, D. O. Ross, and J. C. Clardy, *J. Am. Chem. Soc.*, **97**, 5507 (1975); (b) P. Warner, S. Lu, E. Myers, P. DeHaven, and R. A. Jacobson, *Tetrahedron Lett.*, 4449 (1975); (c) P. Warner and S. Lu, *J. Am. Chem. Soc.*, **97**, 2536 (1975); (d) P. Warner, J. Fayos, and J. C. Clardy, *Tetrahedron Lett.*, 4473 (1973); (e) P. Warner, R. LaRose, C. Lee, and J. C. Clardy, *J. Am. Chem. Soc.*, **94**, 7607 (1972).

(5) (a) C. B. Reese and M. R. Stebles, *J. Chem. Soc., Chem. Commun.*, 1231 (1972); (b) D. B. Ledlie, T. Swan, J. Pile, and L. Bowers, *J. Org. Chem.*, **41**, 419 (1976); (c) D. B. Ledlie and L. Bowers, *ibid.*, **40**, 792 (1975); (d) D. B. Ledlie, J. Knetzer, and A. Gitterman, *ibid.*, **39**, 708 (1974); (e) D. B. Ledlie and J. Knetzer, *Tetrahedron Lett.*, 5021 (1973).

(6) P. Warner, R. LaRose, and T. Schleis, *Tetrahedron Lett.*, 1409 (1974).

(7) Mp 43–44 °C (lit.[8] 40–43 °C). Calcd for $C_9H_{14}O_2$: m/e 154.0994. Found: m/e 154.0996. The ^{13}C NMR showed only six peaks: δ 186.0, 59.8, 49.8, 38.1, 34.0, 26.3.

(8) A. C. Cope and E. S. Graham, *J. Am. Chem. Soc.*, **73**, 4702 (1951).

(9) Compare $\nu_{C=O}$ 1822 cm^{-1} for 1,1-di-*tert*-butylcyclopropanone[10] and 1825 for *trans*-1,2-di-*tert*-butylcyclopropanone.[11]

(10) J. K. Crandall and W. H. Machleder, *J. Am. Chem. Soc.*, **90**, 7347 (1968).

(11) J. F. Pazos, J. G. Pacifici, G. O. Pierson, D. B. Sclove, and F. D. Greene, *J. Org. Chem.*, **39**, 1990 (1974).

(12) The carbonyl absorption at δ 174.1 is some 40 ppm upfield from that of *trans*-di-*tert*-butylcyclopropanone,[11] which is the only other case reported. In the presence of 2.5 equiv of CrAcAc, the ^{13}C NMR peaks appeared at δ 173.6, 35.3, 33.8, and 29.9. Importantly, we recovered **9** unchanged (ir, ^1H NMR) after ^{13}C NMR analysis.

(13) Also ^1H NMR (CCl_4): δ 2.5–1.1 (m); uv (CH_2Cl_2) 325 (ϵ 27), 336 (ϵ 22) nm.

(14) As might be expected from its structure, **9** was relatively inert. It was stable to oxygen and, after stirring for 16 h at room temperature in anhydrous MeOH, was recovered unchanged. After refluxing for 8 h in MeOH, a ca. 75% yield of a very acrid smelling material was obtained. ^1H NMR absorptions at δ 5.35 and 2.8–1.1, as well as ir peaks at 1700 and 1640 cm^{-1}, were observed for the unidentified product(s). Furthermore, **9** did not hydrogenate appreciably (Pt/C, EtOH, 50 psi, 2 h), although a small peak at 1730 cm^{-1} was observed ($\nu_{C=O}$ 1726 cm^{-1} for bicyclo[3.3.1]nonan-9-one[15]).

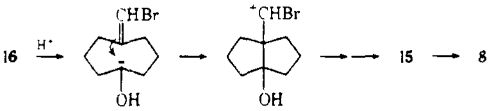
(15) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).

(16) V. Prelog, K. Schenker, and W. Kung, *Helv. Chim. Acta*, **36**, 471 (1953).

(17) (a) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **7**, 588 (1968); (b) P. Warner and S. Lu, submitted for publication.

(18) An alternate mode for production of **7** and **8** is direct electrophilic attack on **1** by $HClO_4$. To test this, 1 equiv of EtBr was allowed to react with 0.9 equiv of $AgClO_4$ in 90% aqueous acetone. To the resulting 0.9 equiv of $HClO_4$ was added 1 equiv of **1**, and the mixture stirred 12 h at room temperature; 92% of **1** was recovered. Even less likely than protonolysis of **1** is Ag^+ cleavage. When the more susceptible [3.3.1]propellane was exposed to $AgClO_4$ in aqueous acetone (which contained 1 equiv of $HClO_4$) for 17 h, only 28% starting material was recovered. However, no other tractable products resulted. We thus feel confident that **1** reacts via initial C–Br bond heterolysis.

(19) The possibility that **8** arose from **16**, i.e.,



was excluded by a control experiment, as it also was for the analogous nine- and ten-membered ring compounds.

(20) Fellow of the Alfred P. Sloan Foundation, 1976–1978.

Philip Warner,*[20] Shih-Lai Lu
Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received June 14, 1976

Stabilization of Aryldiazonium Ions by Crown Ether Complexation

Sir:

Despite an early beginning, the chemistry of aromatic diazonium compounds remains in vogue as additional synthetic