Generation of Strained Alkene by the Elimination of β-Halosilane. On the Nature of the Double Bond of a Bicyclo[2.2.2] Bridgehead Alkene

Sir:

The study of bicyclic bridgehead alkenes which violate Bredt's rule is a topic of much current interest.[1-3] A number of transient species, in violation of Bredt's rule, have been claimed to have been generated. A fundamental question in the investigation of these alkenes is the nature of the "double bond". Is it better represented in the ground state as a diradical or as a C-ylide[4] or is it a matter of semantics as some have claimed?[2] The study of bridgehead alkenes may also contribute to the understanding of the photochemistry of simple alkenes.

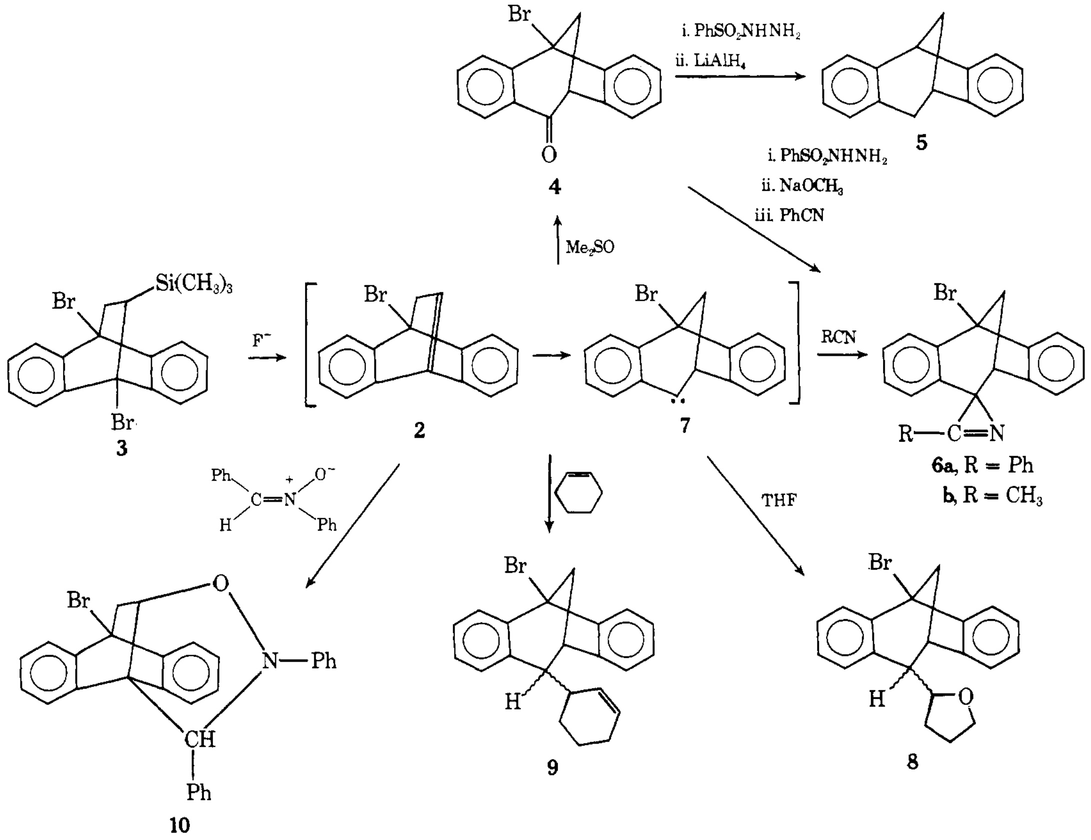
Recently we have reported that the fluoride ion-promoted elimination of β-halosilane is a powerful method to generate strained alkenes.[5] An advantage of this method is the fact that the reagent, alkali fluoride, as well as the products, alkali halide and trimethylfluorosilane, are generally neutral and inert toward most functionalities. We have now applied this reaction to the generation of 4-bromo-5,6;7,8-dibenzobicyclo[2.2.2]octa-1,5,7-triene (**2**), a derivative of **1**.[6]

Heating a mixture of 9,10-dibromoanthracene (5.0 g) and trimethylvinylsilane (12 g) in an autoclave at 220 °C for 14 h gave the cycloadduct **3**, mp 92–94 °C in quantitative yield (6.5 g).

When a mixture of **3** (6.5 g) and potassium fluoride (2.6 g) in dimethyl sulfoxide (50 ml) was heated at 110 °C for 16 h, **3** was converted smoothly into a new compound, **4**, which was purified by column chromatography on silica gel with methylene chlride as eluent (yield, 63%). **4** has the following physical properties: mp 89–91 °C; molecular ion at *m/e* 298, 300; IR (KBr) 1690 cm^{-1}; UV 240 (6322), 269 (3161) nm (ethanol); ^{1}H NMR ($CDCl_3$) δ 6.9–7.8 (8 H), 3.32 (2 H), and 3.95 (1 H); ^{13}C NMR ($CDCl_3$) 57.51, 58.53, 65.81, 123.8, 125.0, 125.7, 126.8, 128.2, 128.4, 128.7, 133.8, 137.1, 147.0, 150.4, 193.8 ppm.[7] The structure of **4** was identified to be 1-bromo-2,3;6,7-dibenzobicyclo[3.2.1]octadiene-4-one from its physical data and by the following transformation. The phenylsulfonylhydrazone of **4**, mp 169–171 °C, on reduction with excess lithium aluminum hydride in refluxing tetrahydrofuran gave the hydrocarbon, dibenzobicyclo[3.2.1]octadiene (**5**), the spectroscopic data of which were identical in all respects with those of an authentic sample.[8] It is evident that when **3** was heated with fluoride ion, in addition to the elimination of trimethylbromosilane, a skeletal rearrangement has occurred, followed by the capture of oxygen from the solvent.

Similar rearrangement also occurred when **3** (1.74 g) was heated in benzonitrile (30 ml) with cesium fluoride (1.2 g) at 120 °C for 5 days under nitrogen. The major product, mp 194–196 °C dec after purification by TLC on silica gel (20% yield), was assigned to have structure **6a**, on the basis of its spectroscopic properties. The IR spectrum of **6a** showed absorption at 1735 cm^{-1} typical of azirines.[9] Reaction of **3** in refluxing acetonitrile and cesium fluoride gave a similar

Scheme I

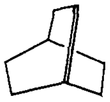


product **6b**, mp 170–172 °C dec.[9,10] The formation of azirines in these reactions suggests that the carbenoid intermediate, **7**, may have been involved.[11] Indeed, when the same carbene intermediate **7** was generated from the pyrolysis of the sodium salt of the phenylsulfonylhydrozone of **4** in benzonitrile at 140 °C, the same product **6a** could be formed.

Further evidence for the carbene intermediate **7** is provided by its reaction with tetrahydrofuran and with cyclohexene. When a mixture of **3** (0.66 g) and benzyltrimethylammonium fluoride (0.30 g) was refluxed in tetrahydrofuran (20 ml) for 9 days, the insertion product **8** was obtained in 25% isolated yield as a mixture of isomers.[12] The compound, **9**, was formed (17% yield)[13] with **8** (16% yield) when the same reaction was carried out in a 1:1 solution of tetrahydrofuran and cyclohexene.

From these results, there is little doubt that the carbene species **7** must have intervened. The carbene intermediate could have arisen from the rearrangement of the expected bridgehead alkene **2**. Various attempts to trap **2** with furan, 1,3-diphenylisobenzofuran, or azide ion have, however, all been unsuccessful. Eventually, evidence for the formation of **2** is adduced by trapping it with *C,N*-diphenylnitrone to give the cycloadduct **10**. A mixture of **3** (1.96 g), benzyltrimethylammonium fluoride (1.52 g) and *C,N*-diphenylnitrone (0.47 g) in 10 ml of tetrahydrofuran was refluxed for 5 days. The crude product (2.23 g) could be purified by TLC on silica gel to give pure **10**, mp 234 °C. The bicyclo[2.2.2] structure in **10** is clearly evident from its ^{1}H NMR spectrum which showed the aliphatic protons of the two-carbon bridge as ABX with $J_{AB} = 12$ Hz, $J_{AX} = 9$ Hz, and $J_{BX} = 4$ Hz. The regiochemistry of the adduct can be deduced from the chemical shift of the X proton (δ 5.0) and the coupling. There is apparently only one stereoisomer formed in the reaction.[14] When the same reaction was conducted in dimethyl sulfoxide as the solvent, **10** was formed in low yield, with **4** being the major product of the reaction. These results demonstrate that the course of events in the reaction of **3** with fluoride ion is the generation of the bridgehead alkene **2**, followed by rearrangement to the carbene **7** (Scheme I).

While the rearrangement of carbene to olefin is common, the reverse transformation **2** → **7**, under thermal conditions, appears to be rather unusual.[15] We note, however, that several reports of olefin to carbene under photochemical conditions have recently appeared.[16-18] The reactive species have variously been described as the Rydberg excited states[17] or the twisted excited state (π,π^*)[16] of the alkene. The alkene **2**, because of its geometry, must be considered as a twisted alkene. The parallel processes provide an interesting link between the photochemistry of alkenes and the thermal reaction of bridgehead alkenes.[19] In an illuminating article on the theory of photochemical reactions, Salem[20] recently argued that the zwitterionic state (Z) of the 90°-twisted ethylene would become stabilized relative to the diradical state (D) if the alkene is substituted by polar substituents or if one of the CH_2 groups is pyramidal. If it is assumed that **2** may indeed be better represented as its ground state by a dipolar structure (**2a**) than by a diradical, the bicyclo[2.2.2] to [3.2.1] rearrangement can readily be understood since similar rearrangement has been well documented in carbonium ion chemistry.[21] The rearrangement may also be facilitated by the resonance stabilization of the carbene by the benzo rings. The regioselectivity of the cycloaddition of **2** with *C,N*-diphenylnitrone could be interpreted on the same basis, using the frontier orbital model.[22]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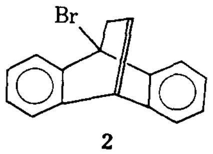

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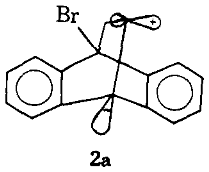

2a

In view of the rather special structure of **2**, it is obviously not possible to extend the conclusions from this work to other bridgehead alkenes. Nevertheless, it is clear that the fluoride ion-promoted elimination of β-halosilane is a superior method of generating even extremely strained alkenes and can be added to the arsenal of reactions for the study of bridgehead alkenes.[3] Investigation of other bicyclic systems is actively pursued in our laboratories.

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References and Notes

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(5) T. H. Chan and D. Massuda, *Tetrahedron Lett.*, 3383 (1975).
(6) For the generation of **1**, see H. H. Grootveld, C. Blomberg, and F. Bickelhaupt, *J. Chem. Soc., Chem. Commun.*, 542 (1973), and A. D. Wolf and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 8209 (1973).
(7) The ^{13}C NMR of **4** shows only 15 signals presumably because two of the aromatic carbons have nearly the same chemical shift, most likely at 128.4 ppm which has almost twice the intensity as the other signals.
(8) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *J. Am. Chem. Soc.*, **87**, 2870 (1965). We are grateful to Professor Cristol for providing us with the spectra of dibenzobicyclo[3.2.1]octadiene.
(9) Cf. S. Sato, *Bull. Chem. Soc. Jpn.*, **41**, 1440 (1968), who reported absorption at 1740 cm^{-1} for phenylazirines, and D. F. Morrow, M. E. Butler, and E. C. Y. Huang, *J. Org. Chem.*, **30**, 579 (1965), who reported 1754 cm^{-1} for methylazirines.
(10) The cycloadduct appears to be unstable on purification by TLC.
(11) Formation of azirines from nitriles and carbene precursors has recently been reported, M. I. Komendantov, R. R. Bekmukhametov, and V.G. Novinskii, *Chem. Abstr.*, **82**, 72849z (1975).
(12) Compound **8** was purified by TLC (silica gel) with methylene chloride as eluent. Its mass spectrum showed molecular ions at *m/e* 354, 356. Its ^{1}H NMR spectrum ($CDCl_3$) showed absorptions at δ 1.4–2.5 (m, 4 H), 2.6–3.4 (m, 3 H), 3.4–4.2 (m, 4 H), and 7.0–7.9 (m, 8 H) ppm.
(13) Compound **9** was purified by TLC (silica gel) with petroleum ether (bp 30–60°) as eluent. Its mass spectrum showed molecular ions at *m/e* 364, 366, and prominent fragments at *m/e* 383, 385 ($M - C_6H_9$) and at *m/e* 204 ($M - C_6H_9 - Br$). Its ^{1}H NMR spectrum ($CDCl_3$) showed absorptions at δ 1.4–3.4 (m, 11 H), 5.6 (m, 2 H), and 6.9–7.8 (m, 8 H) ppm. In an early experiment, a compound with spectroscopic data consistent with addition of carbene **7** to the double bond of cyclohexene was obtained in low yield together with **8** and **9**. Subsequent experiments, however, did not lead to isolable yield of that compound.
(14) Study of CPK molecular model revealed that the isomer with the C-phenyl and the C–H *syn* to each other in the isoxazolidine ring to be sterically less crowded.
(15) There have been reports of rearrangements of strained cyclopropene to vinyl carbene. See, for example, (a) W. E. Bullips, L. P. Lin, and W. Y. Chow, *J. Am. Chem. Soc.*, **96**, 4026 (1974); (b) I. J. Landleer, W. H. de Wolf, and F. Bickelhaupt, *Tetrahedron Lett.*, 2813 (1974); and (c) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Am. Chem. Soc.*, **95**, 5680 (1973).
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(18) S. J. Cristol and C. S. Ilenda, *J. Am. Chem. Soc.*, **97**, 5862 (1975).
(19) Another possible similarity between the photochemistry of alkenes and the thermal reaction of bridgehead alkenes is the addition of alcohol across the double bond.[1,20]
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(22) For a frontier orbital explanation of the regioselectivity of 1,3-dipolar addition of nitrone, see J. Sims and K. N. Houk, *J. Am. Chem. Soc.*, **95**, 5798 (1973). For the alkene **2**, because of poor overlap, it will have a high energy HOMO. Thus, it is the interaction of the nitrone LUMO with the HOMO of **2** which controls the regioselectivity.[23,24]
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(24) K. N. Houk, J. Sims, R. E. Duke, R. W. Strozier, and J. K. George, *J. Am. Chem Soc.*, **95**, 7287 (1973).
(25) This paper is dedicated to Professor R. B. Woodward of Harvard University on the occasion of his 60th birthday.

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