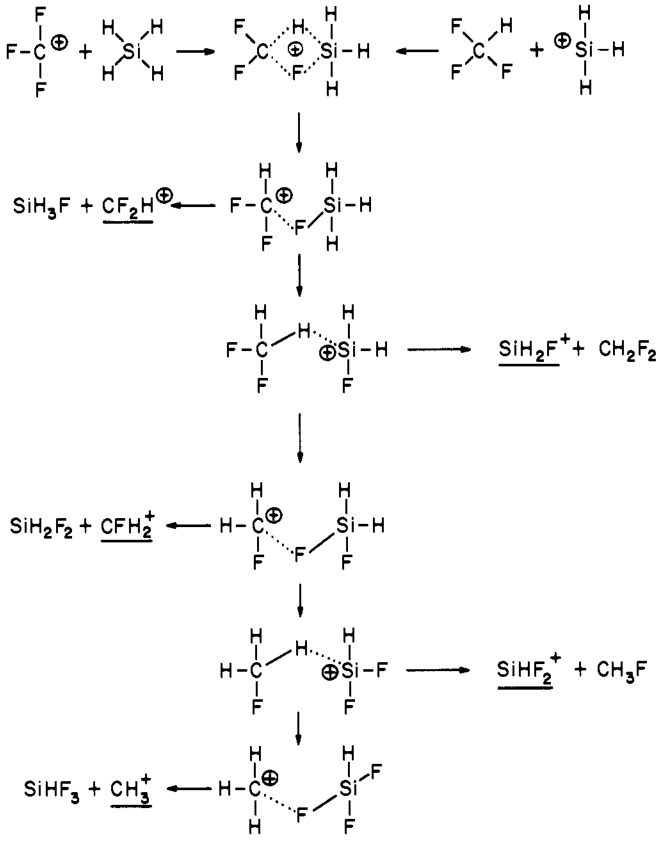
Scheme I



As the kinetic energy of the reactants is increased there is an enhanced formation of other products, including those such as SiH_2^+, SiH^+, CH_2^+, CH^+, and C^+ which are formed in endothermic processes.

The fact that eq 1 is the major reaction in CF_3^+–SiH_4 collisions is not surprising, since it is well documented that the major reaction of silanes with positive ions is hydride transfer.[6-9] Furthermore, kinematic studies of the H^- transfer from silanes have shown that the reaction proceeds mainly by a direct stripping-type mechanism as contrasted to the formation of a long-lived intermediate complex.[11] The surprising feature of the reaction is that at low kinetic energies ions such as CH_3^+, CH_2F^+, and $SiHF_2^+$, which represent extensive redistribution of H and F atoms, are formed.

The surprising feature alluded to arises from the fact that, at the pressures used, the mean free path in the collision cell is ~30 times longer than the ion path and, hence, all products must result from a *single collision* of CF_3^+ and SiH_4. Thus to form CH_3^+, for which only the neutral products $SiHF_3$ (or SiF_2 + HF) are possible, a collision complex must be formed which holds together long enough for six (or seven) bonds to be broken and six bonds to be formed. In view of the tendencies of positive carbon centers to abstract hydride from silanes[6-9] and of positive silicon centers to abstract fluoride from fluorocarbons,[12] and on the basis of the known bridging properties of hydrogen and fluorine in inorganic[13] and organosilicon[14] chemistry, we propose the mechanism shown in Scheme I. In this mechanism the necessary long-lived complex is held together by alternating hydrogen and fluorine bridges that arise as hydride and fluoride are successively exchanged and the center of positive charge alternates between carbon and silicon. As the redistribution proceeds, the complex is pictured as passing continually through double-bridged structures, the first of which is shown at the top of Scheme I. Stable product ions may be formed by random unimolecular break-up of the complex at various stages and those ionic products actually observed are underlined. The rate constant for the total reaction of CF_3^+ with SiH_4 at 1.3 eV is 6.5×10^{-10} cm^3/s.

In confirmation of the mechanism proposed in Scheme I is the fact that the same extensive redistribution products are formed in SiH_3^+ collisions with CF_3H, a system which results in the same intermediate collision complex and presumably the same mechanism. The entrance into the mechanistic sequence from these reactants is shown in the upper right of Scheme I. It is interesting that the extensive redistribution products are definitely not observed in collisions of SiH_3^+ with CF_4.

The fall-off in yield of CH_3^+ and CH_2F^+ at the higher energies (Table I) is in accord with a shorter complex lifetime and the existence of more energetically feasible reaction channels, as the internal energy of the complex is increased.

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References and Notes

(1) U.S. Energy Research and Development Administration Document No. C00-3416-25.
(2) T. Y. Yu, T. M. H. Cheng, V. Kempter, and F. W. Lampe, *J. Phys. Chem.*, **76**, 3321 (1972).
(3) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. (U.S.), Tech. Note*, 270-3 (1968).
(4) T. A. Walter, C. Lifshitz, W. A. Chupka, and J. Berkowitz, *J. Chem. Phys.*, **51**, 3531 (1969).
(5) P. Potzinger and F. W. Lampe, *J. Phys. Chem.*, **73**, 3912 (1969).
(6) T. M. H. Cheng, T. Y. Yu, and F. W. Lampe, *J. Phys. Chem.*, **77**, 2587 (1973).
(7) G. W. Stewart, J. M. S. Henis, and P. P. Gaspar, *J. Chem. Phys.*, **57**, 1990 (1972).
(8) T. M. Mayer and F. W. Lampe, *J. Phys. Chem.*, **78**, 2433 (1974).
(9) J. R. Krause and P. Potzinger, *Int. J. Mass Spectrom. Ion Phys.*, **18**, 303 (1975).
(10) T. M. Mayer and F. W. Lampe, *J. Phys. Chem.*, **78**, 2195, 2429 (1974).
(11) R. Wolfgang, *Acc. Chem. Res.*, **3**, 48 (1970).
(12) J. R. Krause and F. W. Lampe, to be submitted for publication.
(13) B. L. Shaw, "Inorganic Hydrides", Pergamon Press, New York, N.Y., 1967.
(14) R. J. P. Corriu and M. Henner, *J. Organomet. Chem.*, **74**, 1 (1974).

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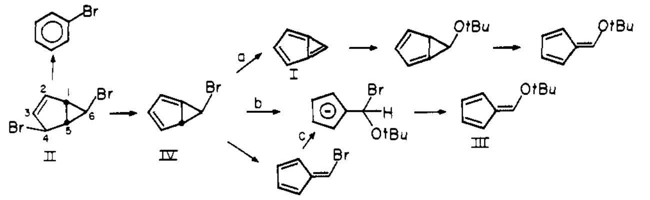
Deuterium Labeling Studies of Bicyclo[3.1.0]hexatriene

Sir:

We had previously reported preliminary results which were compatible with the intermediacy of bicyclo[3.1.0]hexatriene (I) when *exo,exo*-4,6-dibromobicyclo[3.1.0]hex-2-ene (II) was treated with potassium *tert*-butoxide.[1] A priori, the conversion of II to 6-*tert*-butoxyfulvene (III) in high yield resulted either from two HBr eliminations accompanied by the addition of *t*-BuOH or an HBr elimination followed by the substitution of *tert*-butoxide for bromide. III was accompanied by two minor side products, 6-bromofulvene and bromobenzene, which clearly arose by different mechanistic pathways. To further substantiate our initial claim, we examined the deuterium isotope effect on product distribution.

By labeling the halogens at C_4 and C_6 we demonstrated that bromobenzene was formed by loss of the C_4 hydrogen and C_6 halogen. The 6-bromofulvene presumably was the result of a cis 1,4 HBr elimination generating 6-bromobicyclo[3.1.0]hexa-1,3-diene (IV) which then underwent a disrotatory

Scheme I



electrocyclic ring opening converting the diene into the product triene. IV would also be the precursor of the 6-*tert*-butoxyfulvene III. As shown in Scheme I, path a, the transformation could entail a second HBr elimination generating the triene I followed by addition of *t*-BuOH and then a similar electrocyclic opening. Several alternative pathways would convert IV to III without necessitating further loss of HBr. Grohmann had suggested nucleophilic attack of *tert*-butoxide at C_6 with concomitant ring opening and loss of bromide (path b).[2] Addition–elimination to 6-bromofulvene would also form III (path c).

Invoking Scheme I, one can predict the result of replacement of a bridgehead hydrogen with deuterium. For example, the primary isotope effect of a deuterium at C_1 would enhance formation of bromobenzene at the expense of both fulvenes. However, if the deuterium were at C_5, IV deuterated at C_5 should be formed at a rate comparable to the undeuterated material. The partitioning of IV between 6-bromo and 6-*tert*-butoxyfulvene should be unchanged if both were the result of only one HBr elimination. However, if III arose via I, the amount of 6-*tert*-butoxyfulvene should decrease due to the primary isotope effect.

To test this analysis, we prepared the monodeuterated dibromide II, containing one deuterium equally distributed between the bridgehead carbons, from 6-deuterio-1,4-dioxa-6-spiro[4.4]nonene (V) which was prepared by bromination, dehydrobromination, and Na/*t*-BuOD reduction of 1,4-dioxa-6-spiro[4.4]nonene. V was converted to I by sequential reactions with $CH_2Br_2/LiN(SiMe_3)_2$, H_3O^+, SeO_2, AlH_3, and HBr.[3] Under conditions identical with those employed for the undeuterated dibromide, bridgehead deuterated II was converted in poor yield to 6-*tert*-butoxyfulvene; the major products were bromobenzene and 6-bromofulvene. These results demonstrate that the loss of both bridgehead hydrogens was required for the formation of the 6-*tert*-butoxyfulvene. This observation is consistent with a mechanism entailing the intermediacy of bicyclo[3.1.0]hexatriene I and not a pathway entailing only one HBr elimination.

The following procedure was used to analyze for deuterium content and location. The standard conditions for the transformation of deuterated II to 6-dimethylaminofulvene (VI) were as follows: 1 mM of II in 1 ml of THF was added under argon over 30 min to 3 ml of THF at −75 °C containing 6 mM of KO-*t*-Bu and 8 mM of $HNMe_2$. After stirring for 1 h at −75 °C, the solution was quenched by H_2O. To prevent any possibility of exchange, the aqueous washes were kept neutral or alkaline.[4] The deuterium content of the product aminofulvene VI was determined by mass spectral analysis after conversion to 6-phenylfulvene.[5,6] To ascertain the location of the deuterium, we utilized the observation that the hydrogens at C_1 and C_4 of VI are easily exchanged by mild acid catalysis.[7] Moreover, under more vigorous conditions, exchange will even occur at C_2 and C_3. Typically, the product VI was split into two portions: only one of which was exchanged. Both samples were then converted to the 6-phenylfulvene. Comparison of the deuterium content of each established the location of the label as being distributed at one or more of the three distinct sets of positions: C_6, C_1 and C_4, and C_2 and C_3. We could not distinguish between C_1 and C_4 or between C_2 and C_3 by this method. Consistent with formation of I, the mixture of bridgehead monodeuterated dibromides was converted in poor yield to VI containing a total of 0.09 D (0.03 D at C_2 and C_3 and 0.06 D at C_1 and C_4).

To exclude the possibility of hidden skeletal rearrangements, we prepared II deuterated at C_3 and at C_6. II deuterated at C_3 was prepared by acid catalyzed exchange of the α-methylene protons of 6-bromo-2-bicyclo[3.1.0]hexanone followed by the procedure stated above. The dibromide II containing 0.5 D at C_3 was converted in excellent yield to VI containing 0.32 D at C_2 and C_3 and 0.06 D at C_1 and C_4.

To label C_6, II was prepared from deuterated benzvalene.[8] The labeled dibromide contained 1.5 total D of which 0.75 was at C_6, 0.22 at C_2 and C_4, respectively, and 0.15 at C_1 and C_5, respectively. Upon conversion in high yield to the aminofulvene VI, followed by exchange, 0.7 D remained in the molecule. By ^1H NMR, all the deuterium was at C_6.

From these two labeling studies it is apparent that no skeletal rearrangements occurred. Moreover, deuterium at C_3 or C_6, or as will be seen at C_2 or C_4, had no effect on the reaction course.[9] Only deuterium at either bridgehead position adversely affected the formation of 6-*tert*-butoxy or 6-dimethylaminofulvene. These results are consistent only with the formation of bicyclo[3.1.0]hexatriene, the chemistry of which is described in the following communication.[9]

Acknowledgments. We thank Research Corporation for financial support.

References and Notes

(1) W. Washburn, *J. Am. Chem. Soc.*, **97**, 1615 (1975).
(2) A. H. Amaro and K. Grohmann, *J. Am. Chem. Soc.*, **97**, 5946 (1975).
(3) The 3:1 exo/endo mixture of epimers of C_6 was separated as the enones.
(4) Separate control experiments with VI dideuterated at C_1 and C_4 and C_2 and C_3 confirmed that no deuterium loss occurred either under the reaction or workup conditions.
(5) Mass spectral analysis of VI to ascertain deuterium content was unreliable since controls revealed appreciable loss of deuterium from the ring carbons.
(6) 6-Phenylfulvenes were prepared by addition of phenyllithium to VI followed by dilute acetic acid. Control experiments established that deuterium could not be washed in or out under these conditions.
(7) A. Mannschreck and U. Kolle, *Chem. Ber.*, **102**, 243 (1969).
(8) T. J. Katz and N. Acton, *J. Am. Chem. Soc.*, **95**, 2738 (1973).
(9) W. Washburn and R. Zahler, *J. Am. Chem. Soc.*, following paper in this issue.

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Chemistry of Bicyclo[3.1.0]hexatriene

Sir:

This paper focuses on two aspects of the chemistry of bicyclo[3.1.0]hexatriene (I): (1) the acidity of I and (2) the transformation of I to fulvenes.

The complex nature of the latter was revealed by the examination of the products arising from a mixture of 2- and 4-deuterio-*exo,exo*-4,6-dibromobicyclo[3.1.0]hexenes (II) prepared by alane-d_3 reduction of 6-bromo-2-bicyclo[3.1.0]hexenone followed by exposure to HBr. By ^1H NMR the sole deuterium was equally divided between C_2 and C_4. Under the standard conditions previously outlined,[1] this labeled dibromide was converted to 6-dimethylaminofulvene (III) containing 0.3 D distributed between C_1 and C_4.[2] The amount of deuterium washed out varied between 0.6 and 0.8 D, depending on the reaction conditions. The S_N2' products isolated from the reaction had not lost deuterium as judged by ^1H NMR, thus precluding prior exchange of II.