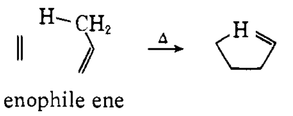
Allene–Perfluorocyclobutanone Ene Reaction. Kinetic Isotope Effects[1a]

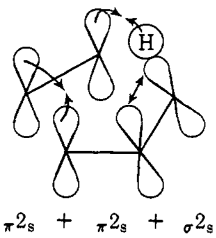
Sheng-Hong Dai[1b] and William R. Dolbier, Jr.*[1c]

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32601. *Received July 29, 1971*

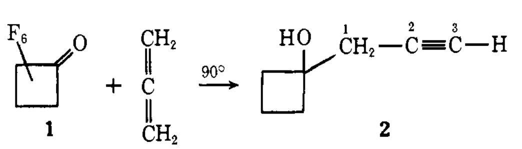
Abstract: Primary and secondary deuterium isotope effects have been utilized to elucidate the mechanism of the reaction between allene and perfluorocyclobutanone. The data obtained from intramolecular studies using 1,1- and 1,3-dideuterioallene and from an intermolecular study using tetradeuterioallene are most simply rationalized in terms of a *concerted* mechanism.

Theoretical considerations of the ene reaction result in the conclusion that it is mechanistically very similar to both the Diels–Alder reaction and 1,5-hydrogen shifts. Applying Woodward–Hoffmann principles, each of these reactions is considered a symmetry-allowed totally suprafacial concerted thermal process. Indeed there is much kinetic[3] and stereochemical[4] data which provide impressive, if not conclusive evidence that the ene reaction is a synchronous process.





Ketones have been known for over 70 years to be effective as the *enophile* component in ene type reactions.[5] The most reactive enophiles known today, in fact, are a group of polyfluoroketones including perfluoroacetone,[6] α,α'-dichlorotetrafluoroacetone,[6b] and perhaps the very best, perfluorocyclobutanone.[7] Perfluorocyclobutanone (**1**), which reacts with most olefins rapidly below room temperature, has been shown by England to react with the relatively poor ene component, allene, essentially quantitatively at temperatures below 100°.[7]



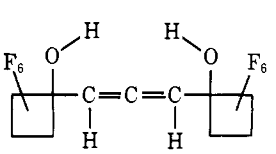
In this paper, the mechanism of the reaction of perfluorocyclobutanone (**1**) with allene is examined using a combination of primary and secondary kinetic deuterium isotope effects as the probe.

Experimental Section

Glpc was performed using a Model A-90-P3 Varian Aerograph gas chromatograph equipped with a Varian Model G2010 strip chart recorder. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer, mass spectra on a Hitachi Model RMU-6E spectrometer, and nmr spectra on a Varian Model A-60A spectrometer. 1,1-Dideuterio-, 1,3-dideuterio-, and tetradeuterioallene were prepared using the method of Morse and Leitch[8] with slight modifications.[9]

Perfluorocyclobutanone–Allene Reaction.[7] **1** (5.3 mmol) and a 15-fold excess of allene (80 mmol) were transferred *via* vacuum line to a 10-ml capacity, thick-walled tube which was then sealed under atmospheric (N_2) pressure. After heating at 90° for 12 hr in a tube furnace, the tube was opened, excess allene recovered in the vacuum line, and the volatile product transferred to a collecting tube *via* vacuum line transfer, room temperature to $-190°$. Only a trace of yellow solid was nontransferrable. The product was shown by glpc (using a 8 ft × 0.25 in. 20% SE-30 column at 80°) to be 97.5% pure propynyl perfluorocyclobutanol (**2**): bp 76° (350 mm); ir (gas) 3550, 3300, 2120, 1645, 1405, 1355, 1258, 1205, 1135, 1080, 1010, 974, 908, and 715 cm^{-1}; nmr (CCl_4) δ 1.99 (t, J = 2.6 cps, 1 H), 2.63 (m, 2 H), and 3.20 ppm (s, 1 H); mass spectrum (70 eV) *m/e* 218 (parent), 203, 170, 151, 131, 118, 100, 90, 67, and 39.

If a smaller excess of allene was used, significantly amounts of the 2:1, **1**:allene, adduct (**3**) was obtained: ir (KBr) 3340, 1955, 1630, 1385, 1270, 1190, 1002, 909, and 765 cm^{-1}; nmr (CCl_4) δ 5.60 (s, 2 H) and 6.22 ppm (s, 2 H). (*I.e.*, when the ratio of **1**:allene was 1:1.5, a 20% yield of the 2:1 adduct could be obtained.)



3

Intramolecular Isotope Effect Determination. Using a 10- to 18-fold excess of 1,1- or 1,3-dideuterioallene resulted in consistent >95% yields of 1:1 adduct which was purified first as above and then by preparative glpc. Instead of a triplet, the acetylenic proton appears as a singlet for the adduct of allene-*1,1*-d_2 and as a doublet for that of allene-*1,3*-d_2. The intramolecular isotope effects were obtained using the ratio of acetylenic to allylic proton intensities using an average of ten continuous-sweep integrations to get each ratio value. Table I gives the results of these experiments.

Intermolecular Isotope Effect Determinations. The reactions were carried out using a 30-fold excess of an allene–tetradeuterio-

---

(1) (a) This work has been reported in part previously in communication form;[2] (b) taken in part from the Ph.D. dissertation of S.-H. D., University of Florida, June 1971; (c) A. P. Sloan Foundation Fellow, 1970–1972.

(2) W. R. Dolbier, Jr., and S.-H. Dai, *J. Chem. Soc. D*, 166 (1971).

(3) (a) G. Ahlgren and B. Akermark, *Tetrahedron Lett.*, 3047 (1970); (b) R. Huisgen and H. Pohl, *Chem. Ber.*, **93**, 527 (1960); (c) B. Franzus, *J. Org. Chem.*, **28**, 2954 (1963).

(4) (a) R. K. Hill and M. Rabinovitz, *J. Amer. Chem. Soc.*, **86**, 965 (1964); (b) J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187 (1966).

(5) O. Kriewitz, *Chem. Ber.*, **32**, 57 (1899).

(6) (a) W. H. Urry, J. H. Y. Nin, and L. G. Lundsted, *J. Org. Chem.*, **33**, 2302 (1968); (b) R. L. Adelman, *ibid.*, **33**, 1400 (1968).

(7) D. C. England, *J. Amer. Chem. Soc.*, **83**, 2205 (1961); we thank Dr. England for samples of purified PFC and for his helpful comments.

(8) A. T. Morse and L. C. Leitch, *J. Org. Chem.*, **23**, 990 (1968).

(9) S.-H. Dai and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **92**, 3946 (1972).

Table I. Intramolecular Isotope Effects

Allene used	Nmr ratio, acetylenic/allylic[b]	k_H/k_D	$k_H/k_{D\text{cor}}$[a]
d_0	0.499 ± 0.008	1.00 ± 0.02	1.00 ± 0.02
1,1-d_2	1.70 ± 0.02	3.40 ± 0.03	3.54 ± 0.03
1,1-d_2	1.70 ± 0.02	3.40 ± 0.03	3.54 ± 0.03
1,3-d_2	0.320 ± 0.005	2.12 ± 0.04	2.19 ± 0.04
1,3-d_2	0.327 ± 0.005	2.06 ± 0.05	2.12 ± 0.05
1,3-d_2	0.317 ± 0.004	2.15 ± 0.04	2.21 ± 0.05

[a] Corrected for d_1 content assuming $(k_H/k_{d_1})^2 = (k_H/k_{d_2})$ (allene purity; 91.7–93.7% d_2, 8.3–5.7% d_1 as determined by low voltage mass spectrometry). [b] Controls have shown that no exchange of acetylene protons occurs under the reaction conditions.

allene mixture, whose isotopic content was precisely known by low-voltage mass spectrometry. An internal hydrogen standard, $CHCl_3$, was used to obtain by nmr the ratio of undeuterated to deuterated product. The technique was quantitatively checked three times using only undeuterated allene. Table II contains the details and results of these experiments.

Table II. Intermolecular Isotope Effects

Mole ratio adduct/ $CHCl_3$	Nmr mole ratio[a] d_0-adduct/$CHCl_3$	Adduct mole ratio,[b] d_0/d_4	$(k_H/k_D)_{d_4}$[c]
1.136[d]	1.10 ± 0.01		
1.158[d]	1.16 ± 0.01		
1.194[d]	1.20 ± 0.01		
0.584[e]	0.386 ± 0.003	1.95 ± 0.05	2.01 ± 0.05
0.663[e]	0.437 ± 0.003	1.93 ± 0.04	1.99 ± 0.04
0.732[e]	0.484 ± 0.006	1.91 ± 0.10	1.97 ± 0.10
		Av	1.99 ± 0.07

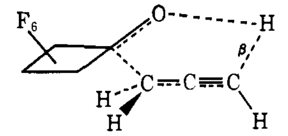
[a] ± values are standard deviations derived from the average of at least ten nmr integrations of acetylenic proton and $CHCl_3$ proton. [b] Obtained as follows for run 4: 0.584 − 0.386 = 0.198 = $d_4/CHCl_3$ ratio; d_0/d_4 adduct ratio = 0.386/0.198 = 1.95. [c] Corrected for deviation from 1.00 of ratio of d_0/d_4 allene as follows: $(k_H/k_D)_{d_4} = d_0/d_4$ adduct × d_4/d_0 starting allene. [d] Undeuterated allene alone used as control. [e] Composition of starting allene mixture was 47.6% d_4, 4.1% d_3, and 48.0% d_0.

Results and Discussion

The two intramolecular isotope effects, $(k_H/k_D)_{1,1} = 3.54 \pm 0.03$ and $(k_H/k_D)_{1,3} = 2.17 \pm 0.05$, and the intermolecular isotope effect, $(k_H/k_D)_{d_4} = 1.99 \pm 0.07$, are clearly nonidentical in value. All can clearly be understood as being different combinations of primary and secondary deuterium isotope effects, acting in a *concerted* mechanism.

In a concerted process one would expect a significant primary isotope effect due to proton transfer, as well as two secondary isotope effects due to changes in hybridization at both C-1 ($sp^2 \rightarrow sp^3$) and C-3 ($sp^2 \rightarrow sp$).

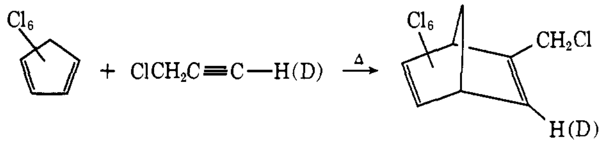
Letting X be the primary effect, Y be the former secondary effect, and Z be the latter secondary effect one sees that $(k_H/k_D)_{1,1} = XZ/Y^2$, $(k_H/k_D)_{1,3} = X/Z$, and $(k_H/k_D)_{d_4} = XY^2Z$. Solving the three simultaneous equations, we find that $X = 2.41$, $Y = 0.868$, and $Z = 1.10$, all this assuming a concerted mechanism.



A small primary isotope effect such as 2.41 might be expected for a reaction where the hydrogen transfer does not take place through a *linear* transition state. More O'Ferrall has found that primary isotope effects depend smoothly upon the β angles in the transition state, with a maximum being obtained where $\beta = 180°$.[10] Using this method of calculation, an angle of 100° for β is obtained for our transition state, a value which certainly would be consistent with expectations.

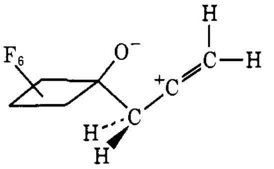
The magnitude of the secondary deuterium isotope effect for $sp^2 \rightarrow sp^3$ rehybridization at C-1 was estimated to be $(k_H/k_D) = 0.868$. This is certainly comparable to values obtained in a number of solvolysis reactions (for the inverse rehybridization process) where $k_H/k_D \approx 1.15$.[11] Such a result is consistent with substantial C–C bond formation in the concerted transition state.

Lastly, the value of the secondary deuterium isotope effect for $sp^2 \rightarrow sp$ rehybridization at C-3 was estimated to be $k_H/k_D = 1.10$. There are no other reported values for such a process although a negligibly small effect has been observed for the reaction of propargyl chloride with hexachlorocyclopentadiene.[12] Certainly a value of 1.10 is not inconsistent with the concerted mechanism.



$(k_D\ k_H) = 1.03 \pm 0.05$

Rate-determining formation of an intermediate such as **4** can be clearly ruled out by the above data. For an abstraction–recombination mechanism, all isotope effects should have been nearly identical and a *larger* primary effect might have been expected since the transition state could have been linear. Moreover, PFC was found *not* to be able to abstract the weaker bound hydrogen atom in cumene under similar reaction conditions. A mechanism involving *fully established* preequilibrium formation of **4** is also consistent with the data, however. To the extent that such an equilibrium were *not* established, $(k_H/k_D)_{1,3}$ should have been greater than $(k_H/k_D)_{1,1}$. The inverse was actually observed.



4

In conclusion, the isotope effect data can be rationalized very nicely assuming concerted C–C bond formation and H migration in this ene reaction. Nevertheless, kinetic data alone cannot *conclusively* rule out a preequilibrium followed by a rate-determining step.

Acknowledgments. We wish to acknowledge with thanks the National Science Foundation (Grants GP 8320 and GP 20598) for their generous support of this research.

---

(10) R. A. More O'Ferrall, *J. Chem. Soc. B*, 785 (1970).

(11) A. Streitwieser, Jr., R. A. Jajow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, 89, 2326 (1958).

(12) S. H. Dai and W. R. Dolbier, Jr., unpublished results.