# Ene Reaction of Allene with Perfluorocyclobutanone: Deuterium Isotope Effect†

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Summary A study of primary and secondary deuterium isotope effects indicates that the ene reaction between allene and perfluorocyclobutanone can be mechanistically rationalized best as a concerted process

KETONES have been known for over seventy years to undergo what is now known as the ene reaction with olefins [1] The most reactive species in such ene reactions are a group of polyfluoro-ketones including perfluoro-acetone,[2,3] αα'-dichlorotetrafluoroacetone,[3] and perhaps best of all perfluorocyclobutanone [4] Perfluorocyclo-butanone (1), which reacts with most olefins rapidly below room temperature, has been shown by England to react essentially *quantitatively* with allene at temperatures below 100° [4]
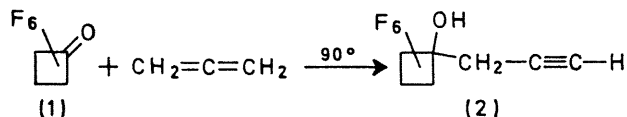
While the mechanism of the ene reaction is generally conceived in terms of a six-membered transition state,[5] it seems reasonable that with a linear molecule such as allene, there would be a possibility of a *non-concerted* ene process Indeed, Adelman has reported results which he interprets as being most consistent with a cyclic, dipolar intermediate, for the reactions of perfluoroacetone with simple olefins [3]

We have attempted to elucidate the mechanisms of the allene reaction with perfluorocyclobutanone by means of a study of the primary and secondary deuterium isotope effects for the reaction For Adelman's mechanism [shown as pathway (a) in the Scheme] which involves a rate-determining attack of the olefin upon the electrophilic carbonyl bond, one would expect in the case of [1 1-^{2}H$_2$]-allene to observe *only* a secondary isotope effect which would favour deuterium ending up at the centre of C–C bond formation, and for [1 3-^{2}H$_2$]allene while no secondary isotope effects are possible a primary isotope effect could be observed if the dipolar intermediate allowed the vinyl cation to rotate In the event of a concerted process, however, both allenes would give rise to primary isotope

effects with the [1,1-^{2}H$_2$]allene also producing a secondary isotope effect
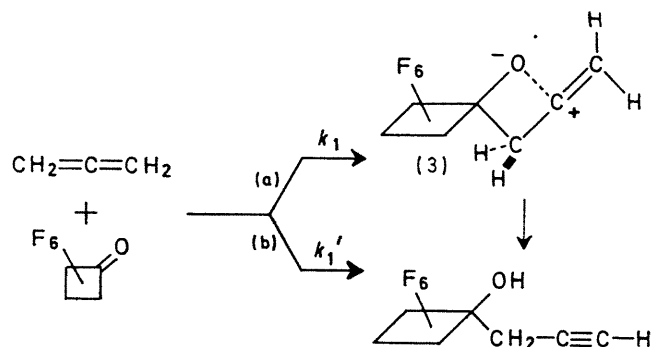
SCHEME

The reactions of an excess of [1,3-^{2}H$_2$]- and [1,1-^{2}H$_2$]-allene[6] with purified perfluorocyclobutanone were carried out neat in sealed tubes at 85—90° for 12—14 h The desired products, formed in >95% yield and free of 2:1 adduct,‡ were isolated by preparative g c and the isotope effects were determined simply by a comparison of the n m r intensities of the acetylenic and allylic protons which were at δ 2 02 and 2 65 p p m respectively The Table gives the results of these isotope effect determinations

Since secondary isotope effects are not expected for this system, the value of $k_H/k_D = 2$ 33 ± 0 11 for the [1 3-^{2}H$_2$]allene reactions was taken as the basic value for the primary isotope effect for hydrogen transfer This value compares with the intramolecular values of 6 1 ± 1 8 and 2 8—4 1 of Goldstein[7] and Huisgen[8] respectively for the reactions of diethyl azodicarboxylate with [7-^{2}H$_1$]cyclo-heptatriene and [1,4-^{2}H$_2$]-1,4-dihydronaphthalene The smaller size of our isotope effect can be rationalized by visualizing the necessarily *distorted* six-membered transition state for the reaction A maximum isotope effect in hydrogen transfer should be observed when the transition state of transfer is linear Non-linear transition states lead to diminished effects with the smaller the angle β the smaller the isotope effects [9]

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‡ If less than a 10 fold excess of allene was used some 2 1 adduct could be detected The i r spectrum indicated that it was the expected allene product (ref 2)

The larger value of $k_H/k_D = 3.53 \pm 0.03$ for [1,1-^{2}H$_2$]-allene can be understood readily since this value is a composite product of the above primary effect and a secondary deuterium isotope effect. By taking the ratio of [k_H/k_D-(1,1)]/[$k_H/k_D(1,3)$] one obtains $(k_H/k_D)_{sec} = 1.51 \pm 0.09$ or 1.26 ± 0.05 per deuterium, a value somewhat larger than

established and thus k_1 (Scheme) becomes rate determining, then $k_H/k_D(1,3)$ should be *greater* than $k_H/k_D(1,1)$. A free radical, initial-hydrogen-abstraction mechanism seems unlikely, but must be considered since isotope effects for hydrogen abstraction by oxy-radicals can be quite small[13] and a propargyl radical should be more stable than the

The reactions of perfluorocyclobutanone with [1,1-^{2}H$_2$]- *and* [1,3-^{2}H$_2$]-*allene: isotope effects*

| Run	Allene used	N.m.r. ratio acetylenic/allylic[b]	Hk/k_D	(k_H/k_D)corr.[a]
1	[^{2}H$_0$]-	0.499 ± .008	1.00 ± .02	1.00 ± .02
2	[1,1-^{2}H$_2$]-	1.70 ± .02	3.40 ± .03	3.53 ± .03
3	[1,1-^{2}H$_2$]-	1.70 ± .02	3.40 ± .03	3.53 ± .03
4	[1,3-^{2}H$_2$]-	0.320 ± .005	2.12 ± .04	2.35 ± .05
5	[1,3-^{2}H$_2$]-	0.327 ± .005	2.06 ± .05	2.27 ± .05
6	[1,3-^{2}H$_2$]-	0.317 ± .004	2.15 ± .04	2.39 ± .05

[a] Corrected for [^{2}H$_1$] content (allene purity: 91.7—93.7% [^{2}H$_2$], 8.3—5.7% [^{2}H$_1$] as determined by low-voltage m.s.).

[b] Controls have shown that no exchange of acetylene protons occurs under the reaction conditions.

those obtained for solvolyses[10] and the usual cycloadditions,[11] although not sufficiently different to warrant further discussion at this time.§

These results are most consistent with the concerted reaction passing through a dipolar transition state such as (4). The Adelman mechanism is of course ruled out.¶ However, the *reversible* formation of the intermediate (3) should be considered. If the equilibrium is *completely* established then our results would be consistent. However, this possibility is unlikely as the dipolar species *needed* is the one not *expected* in such a reaction.

(4)
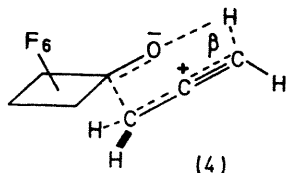
In both electrophilic additions and cycloadditions to allene[12] the orientation of addition is *via* the *most stable intermediate*, which means that intermediate (5) and not (3) should be formed. Another argument against a reversible first step is that to the extent the equilibrium is *not*

initially formed allenyl radical. Clear evidence against this, however, comes from the knowledge that propyne reacts similarly and *specifically* to yield an allene product and also we have found that (1) will not abstract hydrogen from cumene under similar conditions.
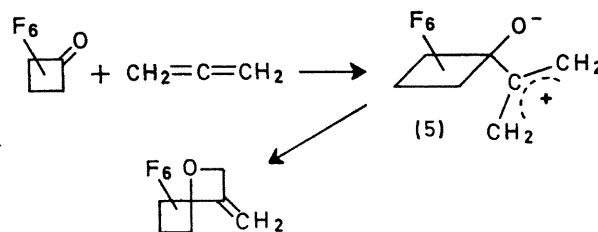
(5)

§ It should also be noted that if, as expected, an $sp^2 \rightarrow sp$ conversion gives rise to a secondary isotope effect comparable to the $sp^3 \rightarrow sp^2$ effect, then this would contribute to the disparity between k_H/k_D (1,3) and k_H/k_D (1,1).

¶ While intermolecular trapping is considered *prima facie* evidence for the existence of an intermediate, intramolecular trapping such as that observed by Adelman, can be just as easily rationalized in terms of two competing concerted processes.

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