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CYCLOADDITIONS OF 1,1-DIFLUOROALLENE. A NOVEL PROBE OF MECHANISM.

William R. Dolbier, Jr.* and Carlos Piedrahita
Department of Chemistry, University of Florida
Gainesville, Florida 32611

K. N. Houk, R. W. Strozier, and Ruth Wells Gandour
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

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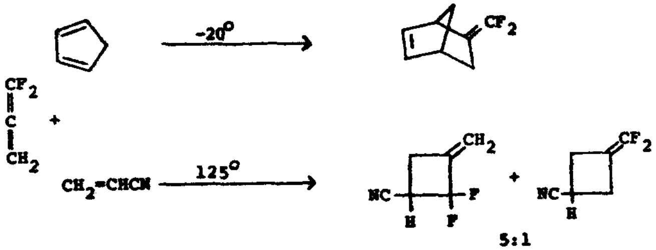
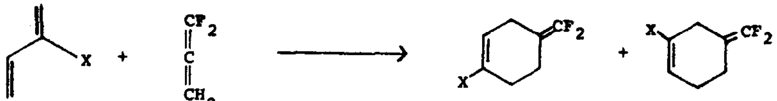
Fluoroolefins have exceptional reactivity in cycloaddition reactions, particularly with regard to [2+2] processes.[1] This enhanced reactivity probably derives from the dramatic thermodynamic advantage which accrues to a system containing a CF_2 group when that group is converted from sp^2 to sp^3 hybridization.[2,3]

We wish to report preliminary results from our investigation of cycloadditions of 1,1-difluoroallene,[4] a molecule which readily undergoes both [2+2] and [2+4] cycloadditions, but with dramatically contrasting regiospecificities for the two types of reactions.

1,1-Difluoroallene has received only scant attention in the chemical literature since its synthesis in 1949.[5,6,7] In 1960 Knoth and Coffman published a very interesting, but brief and certainly non-definitive report on some of the cycloaddition chemistry of difluoroallene including its dimerization.[8] We initially reexamined the two reactions below, verifying the contrasting modes of addition and demonstrating that the products were indeed, in each case, kinetic-controlled. These surprising reactions foreshadowed strikingly the general observations of regioselectivity for cycloaddition reactions of 1,1-difluoroallene.

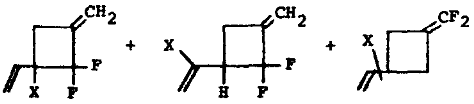


In a classic series of investigations, Bartlett contrasted effectively many aspects of [2+2] and [2+4] cycloadditions, particularly their stereochemical differentiation.[9] We have now scrutinized, in terms of their total regioselectivity, three cycloadditions of 1,1-difluoroallene which produce both [2+2] and [2+4] adducts. In these reactions, which yield significant



2 3

1a, X=H
1b, $X=CH_3$
1c, $X=OSiMe_3$



4 5 6

Table Yields of Cycloaddition Adducts

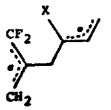
Diene Used	Temp °C	Time (hrs)	2	3	4	5	Absolute Total Yield
1a	110°	7	63	-	37	-	90%
1b[10]	110°	7.5	(29)[b]	(35)[b]	26	10	85%
1c[11]	140°	5.5	23	23	37	17	60%

[a] Relative yields of products were found to be independent of time of reaction.
[b] Distinction between 2 & 3 was not made; all spectra of 2 & 3 were of mixtures and relative amounts were detd. by capillary glpc; product identifications were by spectroscopic analyses of glpc isolated materials.

amounts of both [2+2] and [2+4] adducts, the [2+4] adducts were exclusively those with an exocyclic difluoromethylene group, while the [2+2] adducts were, in stark contrast, almost exclusively those with endocyclic CF_2.[12] It can also be seen that orientation effects in the [2+4] and [2+2] reactions are significantly different. While no significant orientational preference is observed in the [2+4] adducts of 1b and 1c, ratios of 4:5 in these reactions are 2.6 and 2.2, respectively. Such ratios of 4:5 are, of course, consistent with preferential formation of the more stable transoid diradical 7 rather than the less stable species 8. In cases of cycloaddition of 2-substituted butadienes, where there is competition between [2+2] and [2+4] processes, the two processes generally evidence similar orientational preferences.[13] This is true except in those instances, such as with 2-t-butylbutadiene, where a significant steric effect exists at the 2-position.

The observed contrasting regiospecificities for these competitive [2+2] and [2+4] reactions, regarding both the disposition of the CF_2 group and the orientational preferences of the diene unit, make a common intermediate a very unattractive proposition.

The invocation of steric effects on conformational equilibria which might favor exclusive formation of cisoid diradical 9 rather than the "sterically-more hindered" 10, is not consistent with the experimental fact that fluorine is a *very* small substituent.[14] For example, equatorial is favored over axial position for fluorocyclohexane by only 0.12 kcal/mole,[15] in contrast to the 1.7 kcal/mole value for a methyl substituent.



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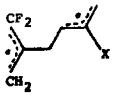

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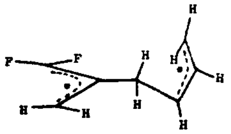

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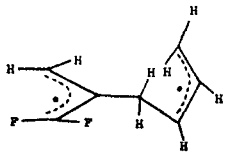

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We choose to rationalize the results as a competition between a concerted [2+4] reaction and a non-concerted [2+2] reaction. The [2+2] results are completely consistent with expectations for a reaction involving a diradical intermediate,[16] the preferential cyclization of the difluoroallyl radical moiety at the difluoromethylene site probably being related to the aforementioned preference for the CF_2 group to be sp^3 hybridized.[18] On the other hand the [2+4] results can be nicely rationalized in terms of a concerted process using the Frontier Molecular Orbital Theory of Cycloadditions.[20] *Ab initio* (STO-3G) calculations have been carried out on 1,1-difluoroallene and indicate that its LUMO is the C_2-C_3 π^* orbital, and not the C_1-C_2 π^* orbital. Qualitatively this could have been predicted using earlier described generalizations.[20] Thus the C_2-C_3 π and π^* orbitals are lowered in energy, relative to those of allene, by mixing with the $\pi^*_{CF_2}$ acceptor orbital, while the C_1-C_2 π and π^* orbitals are raised by antibonding interactions with the fluorine lone pairs. The inductive effect of fluorine lowers all orbital energies. The LUMO coefficients, 0.73 at C_2 and -0.78 at C_3 are nearly identical, and a very slight preference for formation of 2 over 3 is predicted (opposite to diradical intermediate prediction).[21]

In conclusion, it appears that the cycloaddition reactions of 1,1-difluoroallene provide an easily discernible mechanistic probe, whereby concerted and non-concerted mechanisms may be distinguished by mere identification of the products. 1,1-Difluoroallene, moreover, appears to be a particularly reactive species in cycloadditions. Therefore this probe should be amenable to application to a large number of cycloaddition reactions.

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