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DIELS-ALDER REACTIONS OF FLUOROALLENE. AN AFFIRMATION OF HOMO-LUMO CONTROL.

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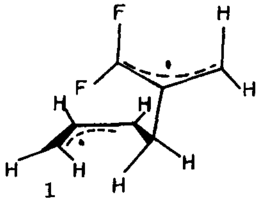
Summary: The Diels-Alder reactions of fluoroallene proceed with regiospecific addition to the C_2-C_3 bond. Mechanistic implications of these results are discussed.

In an earlier report the regiospecificity of [2+4] reactions of 1,1-difluoroallene (DFA) was demonstrated by its reactions with cyclopentadiene, butadiene and other dienes, where the cycloadditions occurred exclusively with DFA's C_2-C_3 π-bond. This regiospecificity was rationalized in terms of the Frontier Molecular Orbital Theory of concerted cycloadditions,[1,2] since the LUMO of DFA should be at the C_2-C_3 π^* orbital.[3] Nevertheless a "steric" explanation, involving a diradical intermediate, could not be unambiguously ruled out. Although fluorine is a relatively small substituent,[4] intermediate 1 (for cycloaddition of DFA to butadiene) might well be destabilized relative to the alternative 2 because of the interaction of the lower fluorine substituent with the former diene unit.[5]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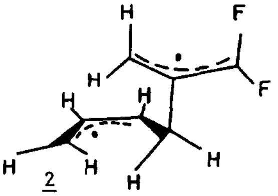
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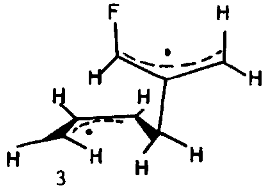
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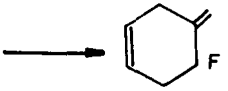
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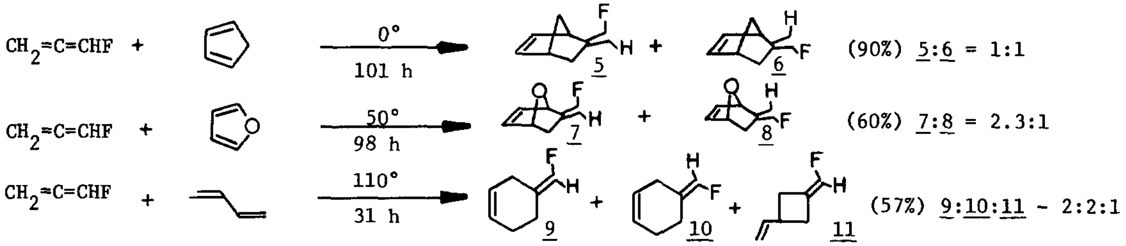
In order to exclude this steric rationale from consideration, a study of the [2+4] cycloadditions of fluoroallene was undertaken. While it was by no means certain that the inductive effect of a single fluorine substituent should induce complete regiospecificity in its Diels-Alder reactions, the thought was that if regiospecificity were indeed observed, then the steric argument for regiospecificity could be effectively excluded. If the regiospecificity were simply due to steric interaction of a fluorine substituent with the diene system, then intermediate 3 certainly should be a viable one and cycloadduct 4 should be observable.

Fluoroallene was prepared as outlined in the scheme below.[6]

$$CHFBr_2 + CH_2{=}CH_2 \xrightarrow[\Delta]{ROOR} BrCH_2CH_2CHBrF\ (46\%) \xrightarrow[EtOH]{KOH} CH_2{=}CHCHBrF + BrCH_2CH{=}CHF\ (39\%)$$

$$\xrightarrow{Br_2} BrCH_2CHBrCHBrF\ (82\%) \xrightarrow[EtOH]{KOH} CHF{=}CBrCH_2Br + BrFCHCBr{=}CH_2\ (75\%) \xrightarrow[EtOH]{Zn} CHF{=}C{=}CH_2\ (77\%)$$

The cycloaddition of fluoroallene were carried out in glass ampoules containing 100 mg fluoroallene and a 10-fold excess of diene. The [2+4] adducts were each characterized as having a fluorine-substitued double bond by strong absorption at 1700-1710 cm^{-1} in the IR and by the presence in the NMR of only 3 vinyl protons.[7] No other products (>1%) were observed for the cyclopentadiene and furan reactions, while at least one [2+2] adduct was obtained in the butadiene case. Three other, yet unidentified, minor products were also observed in 0.5 1 and 2% yeilds. Details about the [2+2] reactions of fluoroallene will be reported later.



Thus, fluoroallene is very similar to DFA in its [2+4] cycloadditions, while being intermediate in reactivity between allene and 1,1-difluoroallene. The results indicate that a single fluorine substituent on allene has sufficient effect upon the LUMO's of the two double bonds to make the Diels-Alder reaction as regiospecific as those of DFA, thus effectively ruling out a steric driving force for the regiospecificity of such DFA cycloadditions.

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References and Footnotes

1. W. R. Dolbier, Jr., C. A. Piedrahita, K. N. Houk, R. W. Strozier and R. W. Gandour, Tetrahedron Lett. 2231 (1978).
2. K. N. Houk, Accounts Chem. Res., 8, 361 (1975).
3. K. N. Houk, W. R. Dolbier, Jr., L. N. Domelsmith and C. A. Piedrahita, J. Am. Chem. Soc., 100, 6908 (1978).
4. H. Forster and F. Vogtle, Angew. Chem. Int. Ed., 16, 429 (1977).
5. The endothermic transition states for diradical formation should resemble intermediates 1-3.
6. Fluoroallene had previously been prepared, in very small yield, for use in spectroscopic studies: A. P. Zens, P. D. Ellis and R. Ditchfield, J. Am. Chem. Soc., 96, 1309 (1974).
7. The products are undoubtedly *kinetically* controlled, inasmuch as *much* higher temperatures have been required to isomerize methylene bicyclo[3.2.0]- or bicyclo[2.2.1]heptanes: W. R. Dolbier, Jr. and C. A. Piedrahita, Tetrahedron Lett., 2957 (1979) and D. Hasselmann, Tetrahedron Lett., 3465 (1972).

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