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THE EFFECT OF STYRENE α-SUBSTITUENTS ON THE REGIOCHEMISTRY OF [2+2] CYCLOADDITIONS WITH DIFLUOROALLENE.

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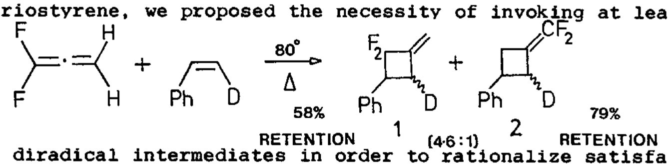
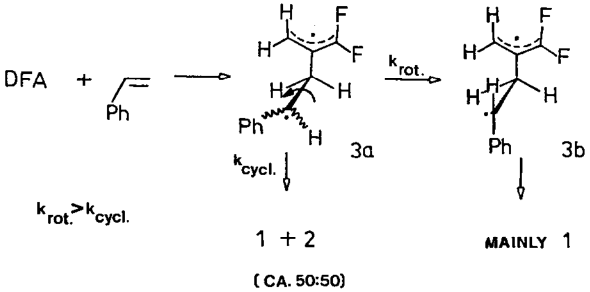
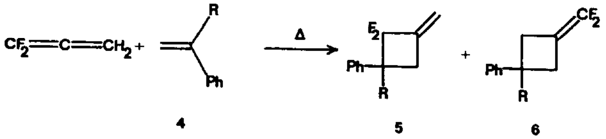
Summary: Consistent with our hypothesis for a mechanism involving two kinetically-distinct diradical intermediates, the observed effects of styrene α-substituents can be explained as deriving either from steric effects or radical stabilizing effects.

In a detailed study of the stereochemistry of the [2+2] cycloaddition of difluoroallene (**DFA**) with Z-β-deuteriostyrene, we proposed the necessity of invoking at least two kinetically-distinct diradical intermediates in order to rationalize satisfactorily the observed differences in degree of retention in the two products 1 and 2.[1] Pasto and Yang, in explaining similar results for cycloadditions of dimethylallene, proposed a similar rationalization.[2] A simplified representation of the proposed mechanism is presented below:





In an effort to probe the details of this mechanism, so as to more fully elucidate those factors which should have an impact upon the regiochemical and stereochemical outcome of such reactions, we sought to perturb the system systematically through substitution of the styrene component at the α-position. It was considered probable that an increase in radical



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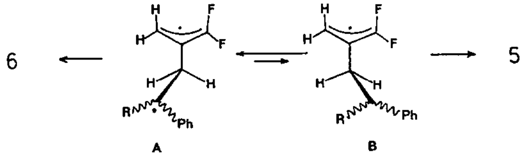
stabilizing ability would decrease the reactivity of the proposed "highly-reactive, non-regioselective and highly stereoselective" first intermediate, **3a**, and hence enhance its fraction of conversion to the second, "less reactive, more-regioselective and less stereoselective" intermediate, **3b**. Therefore it might be expected that substituents such as chlorine or phenyl would lead to greater regioselectivity. On the other hand, as we increase the steric bulk of the α-substituent, R, one might expect an increased reluctance for **3a** to undergo rotation to form **3b**, which would be expected to be more sterically crowded. Hence as we were to change R from H to methyl, ethyl, etc. one might expect more product deriving from the **3a**, with a resultant diminishment of regioselectivity.

Table Regiochemistry for [2+2] Cycloadditions of **DFA** with α-R-Styrenes.

R	Reaction Temp, °C	Isolated Yield[4]	%5(+0.3%)	%**6**(+0.3%)[5]
H	100°C, 3hrs	35%	81.1	18.9
Me	100°C, 3hrs	37%	79.6	20.4
Et	100°C, 3hrs	28%	70.6	29.4
isobu	100°C, 3hrs	22%	69.7	30.3
isopr	100°C, 3hrs	15%	31.3	68.7
F	100°C, 3hrs	26%	79.6	20.4
Cl	100°C, 3hrs	23%	85.5	14.5
Ph	100°C, 3hrs	18%	84.4	15.6

The results[3] which are presented in the Table are generally consistent with the above-mentioned expectations. However, our simplistic mechanistic model does not take into account the effect of steric bulk at the α-position on conformational equilibria such as that shown below. The relative concentrations of conformations **A** and **B** could exert considerable influence upon the ratio of products. Without such steric considerations the ratio of **5**:**6** should not go below 50:50. The result for R=isopropyl makes it clear that a steric effect of this type must be playing a role. [2+2] Cycloadditions are generally very sensitive to steric inhibition, which is consistent with our observed drop-off in yield as R increases in size. F vs H steric effects have not been observed in our cycloaddition studies before, but they appear to be required at least to some degree to explain all of the results in this study.



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References and Footnotes.

1. Dolbier, W. R. Jr.; Wicks, G. E. J. Am. Chem. Soc. **1985**, 107, 3626.
2. Pasto, D. J.; Yang, S. H. J. Am. Chem. Soc. **1984**, 106, 152.
3. Products 5 and **6** for each R were fully characterized by ^{1}H, ^{13}C, and ^{19}F NMR.
4. Title reaction is very clean one; low yields caused by competitive oligomerisation of DFA.
5. Product ratios determined by g.c..

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