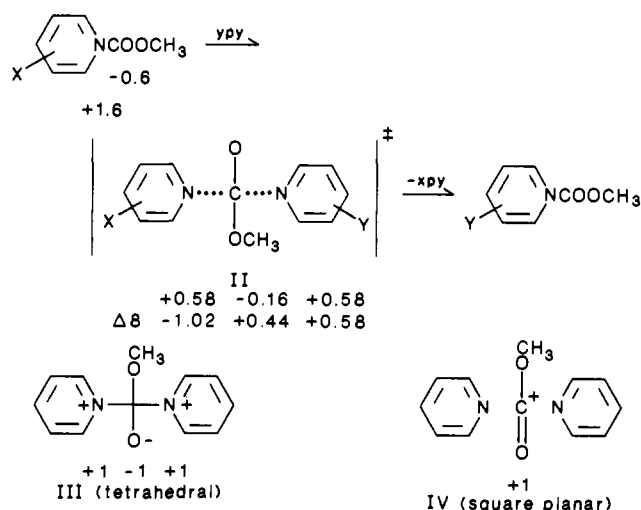
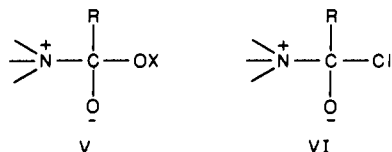


Scheme III



positively charged nitrogens in III would tend to distort a tetrahedral stereochemistry toward a square-planar one, and a transition state with full acylium ion character would be square planar (IV).

Concertedness in Acyl Group Transfer Reactions. This study has direct relevance to the tetrahedral intermediates V and VI demonstrated unequivocally in the pyridinolysis of acetic anhydride,¹³ methyl chloroformate,¹⁴ aryl acetates,¹⁵ aryl benzoates,¹⁶ and carbonates¹⁷ and in the aminolysis of anhydrides²⁸ and carbamate esters.²⁹ It is an immediate problem as to why the



intermediate I or III should be less stable than the above species

(28) Hall, W. E.; Higuchi, T.; Pitman, I. H.; Hekama, K. *J. Am. Chem. Soc.* **1972**, *94*, 8153.

(29) (a) Gresser, M. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 6963. (b) Gresser, M. J.; Jencks, W. P. *Ibid.* **1977**, *99*, 6970.

and why V and VI should have any stability at all in view of estimates for the lifetimes of tetrahedral adducts with good leaving groups.³⁰⁻³³

Those tetrahedral intermediates which have been demonstrated kinetically for interaction of pyridines and amines with neutral acyl compounds^{13-17,28,29} possess a zwitterionic form (V and VI); it is our contention that the electrostatic interaction is sufficient to stabilize the adduct to give an energy "well" in the potential energy surface of the acyl transfer reaction. The stabilization afforded by the electrostatic interaction in the zwitterion is about 14 kcal/mol if the microscopic dielectric constant is taken as 10.

Acyl group transfer with a single transition state has been proposed for several systems in polar solvents; the cases studied involve donor and acceptor groups which therefore possess considerable leaving ability. The solvolysis of benzoyl chloride has been demonstrated to involve competing stepwise and concerted mechanisms by use of a free energy correlation with the solvolysis of adamantyl chloride in the same solvents.³⁴ Reaction of aryl oxide ions with 2-aryloxazolin-5-ones exhibits bond formation which is balanced by a similar amount of endocyclic bond fission as measured by the change in effective charges on the entering and leaving atoms.³⁰ This behavior is explained by a concerted mechanism, and it is argued that the acylium ion is stabilized electrostatically forcing the transition state "north-west" along the diagonal A-C in the potential energy surface of the reaction (Figure 1).

Arguments based on estimated rate constants for decay of tetrahedral adducts too great to support a stepwise process have been advanced to indicate that concerted acyl group transfer could occur with weakly basic acceptors and donors.^{30,32} Ritchie, Van Verth, and Virtanen³¹ estimated that the decomposition of the adduct between ethanethiol and 2,4-dinitrophenyl acetate has a rate constant greater than 10^{13} s^{-1} in water and about 10^{19} s^{-1} in dimethyl sulfoxide. The cyanide adduct may exist in water but not in dimethyl sulfoxide.

Acknowledgment. We are grateful to the SERC for a research studentship (EC) and to Dr. R. B. Moodie for helpful advice.

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Kinetic and Stereochemical Effect of a Fluorine Substituent on the Cope and the Homodienyl 1,5-Hydrogen Shift Rearrangements

William R. Dolbier, Jr.,* Adam C. Alty, and Otto Phanstiel, IV

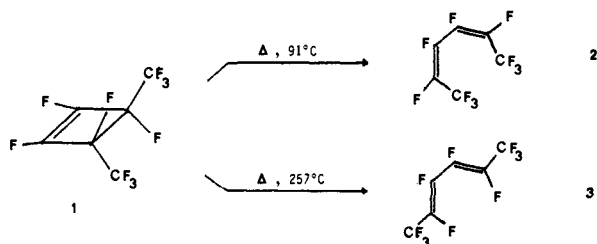
Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. Received November 3, 1986

Abstract: The kinetics and stereochemical outcome for the thermal rearrangements of 3-fluoro-1,5-hexadiene and 1-(fluoromethyl)-2-vinylcyclopropane have been investigated. The relative proportions of *Z* and *E* products in each case reflected their relative stability, thus indicating the lack of any dramatic kinetic effects due to the presence of the fluorine substituents in contrast to the very dramatic effects of this nature observed in cyclobutene-butadiene interconversions.

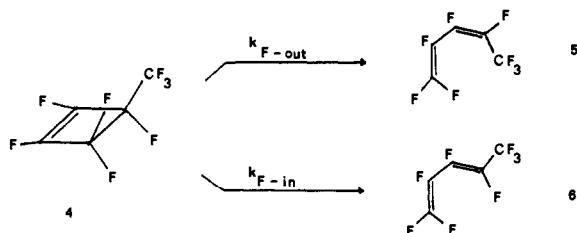
The recently reported dramatic kinetic effect of substituents, particularly fluorine substituents, upon electrocyclic cyclo-

butene-butadiene interconversions,^{1,2} combined with the subsequent theoretical explanation for these effects,^{2,3} induced us to

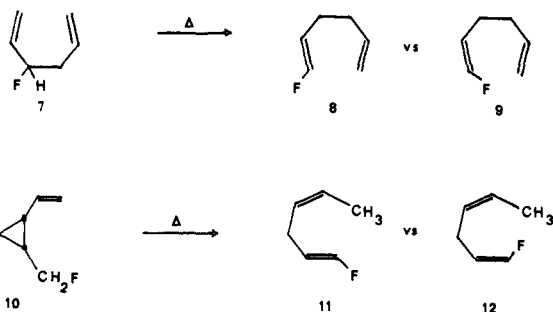
probe other pericyclic rearrangements with the hope of elucidating the requisite structural and mechanistic features necessary for their observation.



Since our studies on cyclobutene ring-opening demonstrated a very significant propensity for preferential *outward* vs. *inward* rotation for 3-fluoro substituents,^{1,4} it was decided to look for



similar stereochemical preferences in the Cope rearrangement and in homodienyl 1,5-hydrogen shift processes.



The interconversion of 3-fluoro-1,5-hexadiene with (*E*)- and (*Z*)-1-fluoro-1,5-hexadiene and the rearrangement of *cis*-1-(fluoromethyl)-2-vinylcyclopropane to (*E,Z*)- and (*Z,Z*)-1-fluoro-1,4-pentadiene were chosen as ideal model systems to demonstrate the importance of substituent effects in reactions of these types.

Syntheses

Samples of the 3-fluoro-1,5-hexadiene (7) and the (*E*)- and (*Z*)-1-fluoro-1,5-hexadienes (8 and 9) were necessary for the Cope study. The 3-fluoro isomer 7 was synthesized from treatment of 3-hydroxy-1,5-hexadiene with DAST,⁵ while the 1-fluoro dienes



(1) (a) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 1871. (b) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Heinze, P. L.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *J. Am. Chem. Soc.* **1987**, *109*, 219.

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Table I. Cope Rearrangement Rate Constants^a

temp, °C	k_{97}	k_{79}	k_{78}	k_{87}
236.15	2.65	0.871	0.404	2.69
246.4	5.06	1.55	0.818	5.90
256.9	10.0	3.04	1.67	10.9
268.35	20.8	6.65	3.77	23.6
277.2	34.2	10.8	5.72	35.7

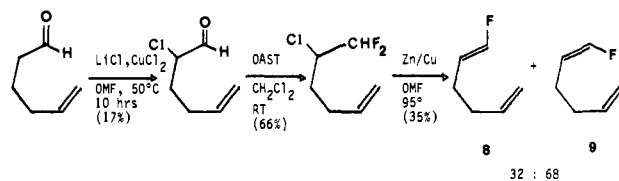
^a $\times 10^{-5} \text{ s}^{-1}$.

Table II. Activation Parameters for Cope Rearrangement

k	$\log A$	E_a^a	$\Delta H^\ddagger_{a,b}$	$\Delta S^\ddagger_{b,c}$	$\Delta G^\ddagger_{a,b}$
k_{97}	10.4 ± 0.1	35.0 ± 0.4	33.9	-14.0	41.3
k_{79}	9.84 ± 0.4	34.8 ± 0.9	33.7	-16.7	42.5
k_{78}	9.86 ± 0.7	35.5 ± 1.6	34.5	-16.5	43.2
k_{87}	10.4 ± 0.5	34.8 ± 1.2	33.8	-14.1	41.2

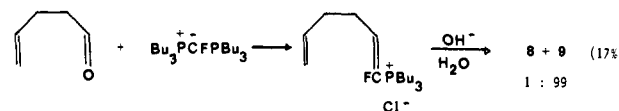
^a kcal/mol. ^b At 256.8 °C. ^c cal/deg.

8 and 9 could both be obtained in reasonable amount by the following short scheme:⁶

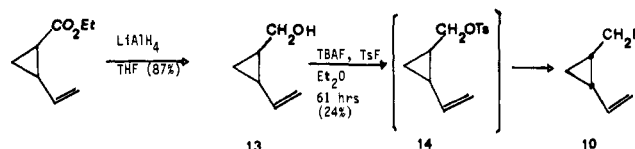


32 : 68

Application of Burton's Wittig-type olefination procedure⁷ to the synthesis of the 1-fluoro-1,5-hexadienes led to the selective synthesis of the *Z*-diene 9 in 17% overall yield.



cis-1-(Fluoromethyl)-2-vinylcyclopropane, (10) was synthesized from 1-carboethoxy-2-vinylcyclopropane⁸ with the key step being displacement by fluoride (using "anhydrous TBAF")^{9,10} on the tosylate, 14, formed in situ from alcohol 13. In this synthesis



a mixture of *cis* and *trans* isomers (*trans*:*cis* = 60:40) was carried through until the final stage at which 10 was separated by GC from its *trans* isomer. Treatment of alcohol 13 with DAST unfortunately led to no 10 but only products where the cyclopropane ring was not intact. Tosylate 14 could be prepared separately and then treated by anhydrous TBAF, but the overall yields for the two-step procedure were inferior to the *in situ* method.

Results and Discussion

Cope Rearrangement. In an earlier exploratory study of the pyrolysis of 3-fluoro-1,5-hexadiene (7)⁵ it was found that its surface-catalyzed loss of HF to form 1,3,5-hexatriene dominated the desired sigmatropic process such that the reaction could not readily be studied. For the purpose of the current study, it was considered sufficient to examine the relative rates of Cope rear-

(6) Daub, G. W.; Zuckermann, R. N.; Johnson, W. S. *J. Org. Chem.* **1985**, *50*, 1599.

(7) Cox, D. G.; Gurusamy, N.; Burton, D. J. *J. Am. Chem. Soc.* **1985**, *107*, 2811.

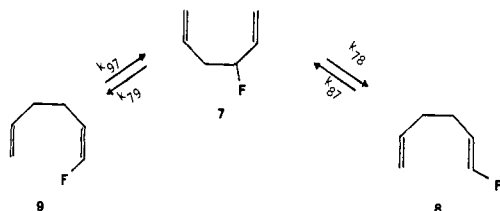
(8) Vogel, E.; Erb, R.; Lenz, G.; Bothner-by, A. A. *Liebigs Ann. Chem.* **1964**, *682*, 1.

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rearrangement of the (*E*)- and (*Z*)-1-fluoro-1,5-hexadienes to **7**, assuming that **7** would immediately lose HF and create a first-order kinetic system for the rearrangements of **8** and **9**. However, upon preliminary examination of these rearrangements, it was found that the loss of HF from **7** was not immediate and as a result some reversibility could be observed. Indeed with further effort conditions were found which allowed the reversible system to be studied completely normally, with little loss of HF being observed on the time scale of the study.

Because the kinetic system $A \rightleftharpoons B \rightleftharpoons C$ cannot be solved directly, the Simplex Approximation method was applied to the analysis of the kinetic data in order to obtain the four rate constants needed. Starting from a mixture ($\sim 73:27$) of the (*Z*)-

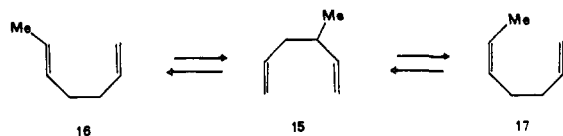


and (*E*)-1-fluoro-1,5-hexadiene isomers, **9** and **8**, the concentrations of the three-component mixture as a function of time were determined at five temperatures and a fit of rate constants to the concentration data was obtained with the Simplex method.¹¹ At each temperature an equilibrium value was obtained for a time in excess of 10 half-lives. Table I provides the so-obtained rate constants for each temperature, while Table II gives the activation parameters which are derived from the respective sets of rate constants.

As can be seen from the kinetic data, there was evidenced *no* dramatic kinetic effect due to the fluorine substituent wherein preferential formation (or conversion) of (*Z*)- or (*E*)-1-fluoro-1,5-hexadiene would have been observed. Indeed the kinetic ratio for formation of **9** and **8** (k_{79}/k_{78}) is 1.82 at 256.9 °C, while the thermodynamic *Z* to *E* ratio ($k_{87}/k_{78}; k_{79}/k_{97}$) is 1.98.

The observed thermodynamic preference for the *Z* over the *E* isomer is consistent with earlier work wherein (*Z*)-1-fluoropropene was found to be similarly more stable than (*E*)-1-fluoropropene.⁵ Therefore the kinetic ratio is simply reflective of the thermodynamic preference for the *Z* diene. *No* special effect in any way similar to that observed in the cyclobutene-butadiene equilibria can be inferred.

The results can be compared to the related study by Frey and Solly of the 3-methyl-1,5-hexadiene system,¹² wherein the *E* isomer, **16**, was found to be preferentially formed from **15**. Such



a preference was again reflective of the thermodynamic preference of the *E* isomer over the *Z* isomer. A ΔE_a^\ddagger of 1.52 kcal/mol for **16** vs. **17** formation could be compared to an expected thermodynamic difference between **16** and **17** of only ~ 1 kcal/mol.¹³ The more substantial activation energy difference in this case is likely due to a transition-state effect. In the assumed chair-like transition states for *E*- and *Z*-diene formation the methyl substituent must take on an equatorial or an axial configuration, respectively, the latter being about 1.8 kcal/mol less stable.

In our fluorine-substituted system, the equatorial-axial differences should be relatively unimportant (~ 0.5 kcal/mol),¹⁴ thus making relative product stability the dominant factor in determining the ratio of products.

(11) Serena Software, 489 Serena Lane, Bloomington, IN 47401: KINETICS PACKAGE.

(12) Frey, H. M.; Solly, R. K. *Trans. Faraday Soc.* **1968**, *64*, 1858.

(13) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, **1976**; p 273.

(14) Jensen, F. R.; Bushweller, C. H. *Adv. Alicyclic Chem.* **1971**, *3*, 140.

Table III. Rate Constants^a for Rearrangement of *cis*-1-(Fluoromethyl)-2-vinylcyclopropane

temp, °C	12/11	k_{overall}	k_Z	k_E
193.25	1.90	2.83	1.85	0.98
201.25	1.94	5.24	3.46	1.78
209.75	1.90	10.0	6.55	3.45
219.25	1.89	19.4	12.7	6.72
227.25	1.82	35.4	22.8	12.6

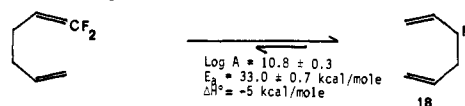
^a $\times 10^{-5} \text{ s}^{-1}$.

Table IV. Activation Parameters for Rearrangement of *cis*-1-(Fluoromethyl)-2-vinylcyclopropane

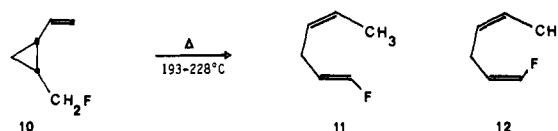
k	$\log A$	E_a^a	$\Delta H^\ddagger a,c$	$\Delta S^\ddagger b,c$	$\Delta G^\ddagger a,c$
k_Z	11.2 ± 0.1	34.1 ± 0.2	33.1	-10.0	38.0
k_E	11.2 ± 0.2	34.7 ± 0.4	33.7	-10.1	38.6

^a kcal/mol. ^b cal/deg. ^c At 210.0 °C.

In terms of the overall kinetic effect of a 3-fluoro substituent on the rate of the Cope rearrangement, it would appear that there is little effect. For unsubstituted 1,5-hexadiene the E_a for rearrangement is 35.5 ($\log A = 11.1$),¹⁵ while for the 3-methyl-1,5-hexadiene system, the E_a is 34.2 ($\log A = 10.5$).¹² These values should be compared with our $E_a = 34.8$ ($\log A = 9.8$) for k_{79} . Recognizing that our $\log A$ may be low (hence the actual E_a might be a bit higher), it is obvious that there is little effect due to the presence of a fluorine substituent. In contrast the E_a for rearrangement of 3,3-difluoro-1,5-hexadiene (**18**) shows a significant inhibition ($E_a \approx 38$ kcal/mol) due to the presence of the *gem*-difluoro substituents.⁵ This is likely a manifestation of the special thermodynamic effect which bestows unusual stabilization to saturated *gem*-difluoro compounds in comparison to vinylic *gem*-difluoro compounds.



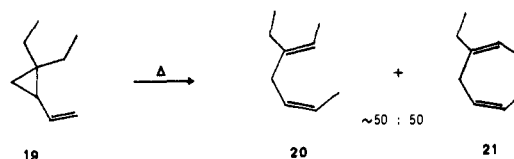
Homodieryl 1,5-Hydrogen Shift. The rearrangement of *cis*-1-(fluoromethyl)-2-vinylcyclopropane is a well-behaved, irreversible, first-order process, which forms competitively the (*E,Z*)- and (*Z,Z*)-1-fluoro-1,4-hexadienes (**11** and **12**).



The kinetic data for the rearrangement are found in Table III, while the activation parameters for the two competitive processes are in Table IV.

Again, it can be seen that the *Z* isomer, **12**, is formed preferentially, about to the same degree as in the Cope rearrangement. Assuming that the thermodynamic preference of **12** over **11** would be about the same as for **9** and **8**, one can see that the same rationale which was applied to explain product preference in the Cope rearrangement can be applied also to this homodieryl 1,5-hydrogen shift system.

The only related results in the literature are those for the rearrangement of *cis*-1,1-diethyl-2-vinylcyclopropane (**19**), where again little preference is exhibited for disposition of the methyl substituent in the *E* or the *Z* geometry of products **20** and **21**.¹⁶



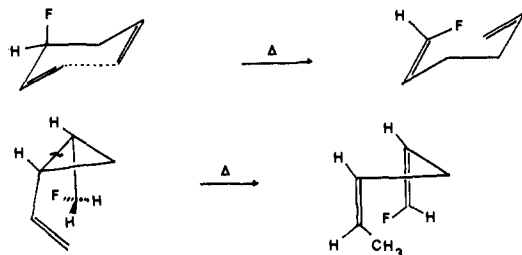
(15) Doering, W. E.; Toscano, V., unpublished results cited in Table X: Benson, S. W.; O'Neal, H. E. *J. Chem. Phys.* **1967**, *71*, 2903.

(16) Frey, H. M.; Skinner, R. F. unpublished results cited in the following: *Chem. Rev.* **1969**, *69*, 114.

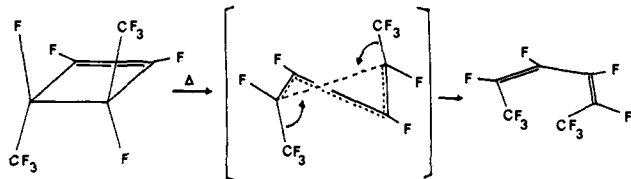
Kinetically the presence of the α -fluorine substituent had a significant effect upon the activation energy for the hydrogen transfer. Comparison of the observed E_a of 34.1 kcal/mol (log $A = 11.2$) with that for the parent system (31.2 kcal/mol, log $A = 11.0$)¹⁷ indicates an inhibition of 2.9 kcal/mol in the rearrangement of **10**. There is little data on the effect of α -fluorine substituents on C-H bond strengths and what there is indicates an irregular but generally strengthening effect of α -fluorination upon C-H bond strength.¹⁸

Conclusion

The lack of significant transition-state-derived kinetic effect or stereochemical preference in the two types of pericyclic reactions examined in this study provides considerable insight into those factors which give rise to such effects. An examination of the transition state for these rearrangements shows that little rotation



or torsional movement is required at the site of substitution in the creation of the new sp^2 site in these reactions, in contrast to the very significant torsional, twisting motion required in the transition state for cyclobutene ring opening:



It is expected that if dramatic effects such as those observed in the cyclobutene system are to be observed in any other pericyclic reactions, it will be for those which the substituent must undergo considerable torsional motion in reaching the transition state.

Experimental Section

NMR spectra are reported as δ , ppm downfield from TMS for ^1H and ^{13}C spectra, and as ϕ , ppm upfield from CFC_3 in the case of ^{19}F spectra. Unless otherwise indicated, preparative GC was done on a 10 ft \times 1/4 in., 20% SE 30 on Chrom P 60/80 column, and analytical GC was done on a 16 ft \times 1/8 in., 5% ODPN on Chrom P 60/80 column.

3-Fluoro-1,5-hexadiene (7). This was made by our previously reported procedure⁵ and obtained in a 24% yield with >97% purity after preparative GC.

1-Fluoro-1,5-hexadienes (8 and 9). (a) **From 4-Pentenal via a Wittig Olefination.**¹⁰ A 250-mL flask, equipped with magnetic stir bar, rubber septum, and nitrogen tee was charged with tributylphosphine (29.3 g, 145 mmol) and cooled to -5°C , and a solution of trichlorofluoromethane (6.6 g, 48 mmol) in dry chlorobenzene (35 mL) was added in one portion via syringe. Stirring was continued at 0°C for 1 h and at 20°C for 3 h before 4-pentenal¹⁹ (3.25 g, 38.7 mmol) was added; after a further 8 h 58 mL of 10% NaOH was slowly added to the cooled mixture and stirring was continued for 15 h. The organic layer was then separated, dried (MgSO_4), and distilled to give 1.1 g of crude product. Final purification by preparative GC gave 0.65 g (6.44 mmol, 17%) of a colorless liquid composed of (*Z*)-1-fluoro-1,5-hexadiene [NMR, ^1H (300 MHz), δ 6.4 (ddt, 1 H, CHF), 5.8 (ddt, 1 H, olefinic), 5.0 (c, olefinic, CH_2), 4.7 (ddt, 1 H, olefinic), and 2.2 (c, 4 H, $-\text{CH}_2\text{CH}_2-$); ^{19}F (282 MHz), ϕ 130.8 (ddt, $J_{\text{FH}(1)} = 85.7$ Hz, $J_{\text{FH}(2)} = 43.1$ Hz, $J_{\text{FH}(3)} = 1.7$ Hz); ^{13}C (75.46 MHz) δ 147.9 (d, $J_{\text{CF}} = 256.5$ Hz, C_1), 137.8 (s, C_3), 115.1 (s, C_6), 110.25 (d, $J_{\text{CF}} = 5.29$ Hz), 33.4 (d, $J_{\text{CF}} = 1.88$ Hz, C_4), and 22.2 (d, $J_{\text{CF}} = 4.95$ Hz, C_3); mass spectrum, m/z (relative intensity) 101 ($\text{M}^+ + 1$, 0.14), 100 (M^+ , 2.13), 85 (23.07), 80 (11.98), 72 (22.58),

67 (17.35), 59 (100.00), 54 (14.33), 53 (5.54), 51 (6.32), 41 (60.37), 39 (35.57), 33 (10.28)] and (*E*)-1-fluoro-1,5-hexadiene [NMR, ^{19}F , ϕ 130.6 (ddt, $J_{\text{FH}(1)} = 85.6$ Hz, $J_{\text{FH}(2)} = 18.8$ Hz, $J_{\text{FH}(3)} = 2.1$ Hz); ^{13}C , 137.5 (s, C_3), 115.4 (s, C_6), 110.9 (d, $J_{\text{CF}} = 9.50$ Hz, C_2), 33.90 (d, $J_{\text{CF}} = 2.71$ Hz, C_4), 24.70 (d, $J_{\text{CF}} = 9.31$ Hz, C_3); mass spectrum, m/z (relative intensity) 100 (M^+ , 0.38), 63 (5.34), 57 (5.20), 56 (100.00), 55 (6.79), 43 (42.32), 41 (63.01), 39 (12.08). The ratio of *Z/E* isomers as calculated by analytical GC was 99:1.

(b) **From 5-Hexenal.**⁶ 5-Hexenal (9.40 g, 97.9 mmol) was chlorinated with copper(II) chloride (42.34 g; 248.4 mmol) and lithium chloride (5.25 g, 123.8 mmol) in DMF (200 mL) with magnetic stirring at 50°C . Monitoring by GC indicated that all the starting material had been consumed after 10 h, so the resulting green solution was worked up in the usual manner and gave, after preparative GC, two compounds as pale yellow liquids: 2-chloro-5-hexenal (2.2 g, 16.86 mmol, 17%) [^1H NMR, δ 9.51 (d, 1 H, $-\text{CHO}$), 5.75 (c, 1 H, olefinic), 5.06 (c, 2 H, olefinic), 4.19 (ddd, 1 H, $-\text{CHCl}$), 2.26 (c, 4 H, $-\text{CH}_2\text{CH}_2-$)] and 2,2-dichloro-5-hexenal (5.32 g, 32.24, 33%) [^1H NMR, δ 9.27 (s, 1 H, $-\text{CHO}$), 5.83 (c, 1 H, olefinic), 5.15 (c, 2 H, olefinic), 2.40 (br s, 4 H, $-\text{CH}_2\text{CH}_2-$)]. Treatment of the monochloroaldehyde (2.2 g, 16.86 mmol) with DAST (5.18 g, 32.17 mmol) in dry CH_2Cl_2 (20 cm^3) for 2 h at room temperature followed by an ice-cold sodium bicarbonate workup and distillation to remove CH_2Cl_2 gave 5-chloro-6,6-difluorohex-1-ene (1.7 g, 11.14 mmol, 66%) as a colorless liquid: ^1H NMR, δ 5.6-6.2 (c, 2 H, CHF_2 and olefinic), 5.17 (c, 2 H, olefinic), 4.00 (c, 1 H, $-\text{CHCl}$), 1.8-2.6 (c, 4 H, $-\text{CH}_2\text{CH}_2-$); mass spectrum gave $\text{M}^+ 154.03633 \pm 0.001280$ (8.31 ppm), calculated for $\text{C}_6\text{H}_9\text{F}_2\text{Cl}$ 154.03608, deviation = 0.000252 (1.6 ppm), m/z (relative intensity) 156 ($\text{M}^+ + 2$, 2.24), 155 ($\text{M}^+ + 1$, 0.46), 154 (M^+ , 7.04), 118 (12.63), 103 (17.49), 77 (10.64), 75 (10.63), 67 (21.43), 55 (100.00). With use of the method developed by Daub and co-workers⁶ reduction was conveniently achieved by heating 5-chloro-6,6-difluorohex-1-ene (1.47 g, 9.6 mmol) with freshly prepared zinc-copper couple (10 g) in DMF (50 mL) and a few drops of 1,2-dibromoethane. The reaction was monitored by GC with periodic additions every 24 h of fresh couple (10 g) and 1,2-dibromoethane (ca. 10 drops). After 3 days distillation followed by preparative GC gave a 0.34 g (3.4 mmol, 35%) yield of mixture of (*Z*)- and (*E*)-1-fluorohexa-1,5-dienes identical with the material prepared by method a. The *Z/E* ratio as determined by analytical GC was 68:32.

Kinetics Procedure for Cope Rearrangement. The kinetic parameters were determined on a *Z, E* mixture of 1-fluoro-1,5-hexadienes.

The kinetic apparatus and procedure was as usual,^{1b} the only difference being that a "virgin" Pyrex kinetic bulb was used; routinely a 7-10-mmHg sample was used and GC analyses were carried out on a FID GC machine with a 16 ft \times 1/8 in., 5% ODPN column at a temperature of 30°C (detector set at 150°C). A minimum of 3 GC traces were obtained for each sample. The averaged values of the time/concentration points were then fed into the SMPLXKS program¹¹ which used approximate rate constants (calculated from initial points at each temperature) and fitted them to the experimental data. An error factor of 0.00001 was used for each rate constant which required >200 iterations.

1-(Hydroxymethyl)-2-vinylcyclopropane (13).²⁰ Into a clean three-necked 500-mL round-bottomed flask equipped with a 125-mL pressure-equalized addition funnel with N_2 inlet, a mechanical stirrer, and a vertical water condenser that was attached to a drying tube of calcium chloride was placed under a positive N_2 pressure LiAlH_4 (3.53 g; 0.093 mol) in 150 mL of THF (dried by CaH_2 , then distilled from LiAlH_4 onto activated 4Å sieves). This solution was stirred mechanically for 20 min. Ethyl (2-vinylcyclopropane)carboxylate⁷ (13.0 g; 0.093 mol) was added dropwise via the addition funnel. This mixture was then refluxed for 2.5 h. The reaction was monitored by GC and additional hydride (1.03 g; 0.03 mol) was added after 2.5 h.

After 2 h of additional stirring the dark grey reaction mixture was then cooled to 0°C and the excess hydride quenched by the *very slow* addition of water. A 20% HCl solution was added until all the white precipitate was dissolved. This clear solution was then extracted with 3 \times 100 mL of diethyl ether, dried by MgSO_4 , and filtered and the ether was removed. The crude product, a yellow oil, was vacuum distilled at 64°C (12 mmHg, bath temperature 105°C) to give 7.96 g (87%) of 1-(hydroxymethyl)-2-vinylcyclopropane (13): ^1H NMR (100 MHz) δ 5.55-4.78 (m, 3 H, olefinic), 3.87 (s, 1 H, $-\text{OH}$), 3.62-3.42 (m, 2 H, CH_2-O), 1.33-0.40 (m, 4 H, cyclopropyl H); IR (neat) 890, 1040, 1630, 2880, 3000, 3080, 3350 cm^{-1} ; high-resolution mass spectrum gave $\text{M}^+ 98.0744 \pm 0.0014$, calcd for $\text{C}_6\text{H}_{10}\text{O}$ 98.0731 \pm 0.0013.

1-(Fluoromethyl)-2-vinylcyclopropane (10). Into a preweighed three-necked 100-mL round-bottomed flask equipped with two stoppers, vacuum adapter, and stirring bar was placed 13.0 g of tetrabutyl-

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ammonium fluoride trihydrate (TBAF·3H₂O, Aldrich). This flask was attached to a vacuum line (<2 mmHg) and heated at 45 °C for 48 h.⁸ To the dry TBAF (calcd 16% H₂O loss) was added a mixture of tosyl fluoride (3.56 g, 0.0204 mol) and 1-(hydroxymethyl)-2-vinylcyclopropane (1.0 g, 0.0102 mol) in 30 mL of diethyl ether (dried from LiAlH₄ onto activated 4 Å sieves). The TBAF/TsF/alcohol mixture formed two layers upon combination. The TBAF formed an orange gelatinous solid which could be stirred freely upon use of ultrasonics (E/MC Model 250, RAI Reseach) and slight heating (not >40 °C). This mixture was stirred for 61 h. At this time the product mixture (2 layers) was poured into a 200-mL separatory funnel and 20 mL of deionized H₂O was added. The ether layer was separated and the aqueous layer extracted with 2 × 20 mL diethyl ether. The ether layers were combined, dried with MgSO₄, and filtered. The ether was removed at atmospheric pressure pot temperature <48 °C). The yellow oil was vacuum transferred twice. The *cis* and *trans* isomers of 1-(fluoromethyl)-2-vinylcyclopropane (10) (24%) were separated by GC.

The *cis*-1-(fluoromethyl)-2-vinylcyclopropane was further GC purified on a 10 ft × 1/4 in., 10% ODPN column (98% GC pure). The kinetic studies were done on this purified sample.

trans-1-(Fluoromethyl)-2-vinylcyclopropane: ¹H NMR (300 MHz), δ 5.42 (ddd, 1 H, C—CH=C), 5.10 (dd, 1 H, t—C=CH), 4.92 (dd, 1 H, C—C=CH), 4.28 (ddd, 2 H, CH₂F) 1.5–0.7 (complex m, 4 H, cyclopropyl H); ¹⁹F NMR, φ 210.46 (t d, J_{HF}² = 48.9 Hz), J_{HF}³ = 7.3 Hz; mass spectrum, *m/z* (relative intensity) 101 (M⁺ + 1, 1.36), 100 (M⁺, 30.07).

cis-1-(Fluoromethyl)-2-vinylcyclopropane: ¹H NMR (200 MHz), δ 5.7 (m (ddd?), 1 H, C—CH=C), 5.2 (m (dd?), 1 H, t—C=CH), 5.1 (m (dd?), 1 H, C—C=CH), 4.4–4.0 (ddm, 2 H, CH₂F), 1.8–0.5 (complex m, 4 H, cyclopropyl H); ¹⁹F NMR, φ 211.3 (t, J_{HF}² = 48.9 Hz); ¹³C NMR, δ 135.8 (s, HC=), 115.9 (s, =CH₂), 84.0 (d, J_{C-F} = 166 Hz, CH₂F), 19.7 (d, J_{CF} = 5 Hz, H₂C cyclopropyl), 17.8 (d, J_{CF} = 25 Hz, HC—CH₂F cyclopropyl), 9.6 (d, J_{CF} = 5 Hz, HC—C= cyclopropyl); mass spectrum, *m/z* (relative intensity) 101 (M⁺ + 1, 1.50), 100 (M⁺, 27.46).

Thermal Rearrangement of cis-1-(Fluoromethyl)-2-vinylcyclopropane. *cis*-1-(Fluoromethyl)-2-vinylcyclopropane (80.0 mm) was expanded into a well-conditioned pyrolysis bulb and pyrolyzed at five temperatures between 193.25 and 227.25 °C. The reaction was followed by GC with a 10 ft. × 1/8 in., 10% ODPN column at 55 °C. The rate constants are given in Table III. The pyrolysis afforded only two products: (*Z,Z*)-1-fluoro-1,4-hexadiene (12) and (*E,Z*)-1-fluoro-1,4-hexadiene (11) in the ratio of 65:35, respectively.

(*Z,Z*)-1-Fluoro-1,4-hexadiene: ¹⁹F NMR, φ 131.64 (ddt, J_{HF}¹ = 85.4 Hz, J_{trans HF}² = 42.6 Hz, J_{HF}³ = 1.7 Hz, =CHF).

(*E,Z*)-1-Fluoro-1,4-hexadiene: ¹⁹F NMR, φ 131.87 (ddt, J_{HF}¹ = 85.5 Hz, J_{cis HF}² = 18.8 Hz, J_{HF}³ = 2.6 Hz, =CHF).

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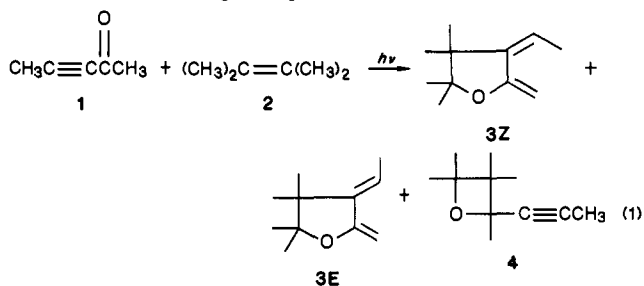
Photochemistry of 4,4-Dimethyl-1-mesityl-2-pentyn-1-one¹

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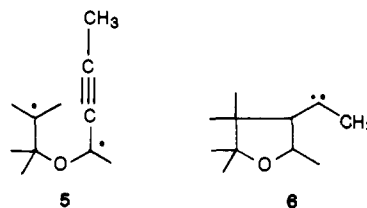
Abstract: The photochemistry of 4,4-dimethyl-1-mesityl-2-pentyn-1-one (7) in solution has been examined by using a combination of product studies, quantum yield measurements, and laser flash photolysis techniques. The main products of reaction are the indanones 10 and 11, believed to be formed via the intermediacy of carbene 9. Transient phenomena are dominated by the photoenolization of the parent ketone 7, which occurs following hydrogen abstraction by the triplet leading to biradical (or triplet enol) 8. The biradical has a lifetime of 38 ± 4 ns in methanol and 45 ± 7 ns in heptane (for 7D) at room temperature. Biradical decay leads to a mixture of enols 18Z and 18E. The syn enol 18Z usually accounts for >90% of the mixture and decays with first-order kinetics with *k*_d = 2.7 × 10⁷ s⁻¹ in hexane at 293 K. For comparison the deuterio analogue 18Z-D decayed with *k*_d = 3.7 × 10⁶ s⁻¹ under the same experimental conditions. The anti enol was extremely long-lived, and under carefully controlled conditions its lifetime was 22 s in hexane at room temperature.

Several recent reports have provided a number of examples of photochemical [3 + 2] cycloaddition of α,β-acetylenic ketones with various olefins, e.g.,⁵⁻⁷ eq 1. The reaction has been proposed



to involve the intermediacy of biradical 5, which cyclizes to carbene

6, which is ultimately responsible for product formation. The



products of [3 + 2] cycloaddition have been shown to be triplet-derived, and trapping studies, in particular using alcohols, have provided unequivocal evidence for the intermediacy of carbene 6.

The biradical shown above (5) and all those included in the earlier publications contain an oxygen atom in their backbone; this is known to have a great influence on the biradical lifetimes in other systems.⁸ Recently, Agosta et al. have reported an example of a reaction involving an all-carbon alkyl propargyl

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