Fluorination of coumarin (28) was carried out on 1.0 g (6.8 mmol) as described previously. After the usual workup two compounds were obtained and eluted by HPLC using 15% EtOAc in cyclohexane. The major fraction was identified as 3,4-dihydro-3,4-difluorocoumarin (**29**) obtained in 55% yield as an oily solid which failed attempted crystallization: IR 1725 cm^{-1}; ^1H NMR δ 7.60–7.10 (4 H, m), 5.41 (1 H, three d, $^2J_{HF}$ = 46 Hz, $^3J_{HF}$ = 30 Hz, J_{HH} = 3.0 Hz), 5.76 (1 H, ddd, $^2J_{HF}$ = 55 Hz, $^3J_{HF}$ = 6 Hz, J_{HH} = 3.0 Hz); ^{19}F NMR -176.5 (1 F, three d, $^2J_{HF}$ = 55 Hz, $^3J_{HF}$ = 30 Hz, $^3J_{FF}$ = 15 Hz), -206.0 (1 F, three d, $^2J_{HF}$ = 49 Hz, $^3J_{HF}$ = 6 Hz, $^3J_{FF}$ = 15 Hz); MS, *m/e* 184 $(M)^+$, 164 $[(M - HF)^+]$, 136 $[(M - HF - CO)^+]$. Anal. Calcd for $C_9H_6F_2O_2$: C, 58.69; H, 3.26. Found: C, 57.90; H, 3.95. The minor fraction proved to be the known dehydrofluorinated product **30**,[12] 15% yield: mp 150 °C (from MeOH); IR 1710 cm^{-1}; ^1H NMR δ 7.60–7.26 (m); ^{19}F NMR -130.5 (d, $^3J_{HF}$ = 9 Hz). The transformation **29** → **30** could be quantitatively achieved by absorbing the difluoro adduct on a silica gel column for a period of 24 h.

Fluorination of 2-cyclopentylidenecyclopentanone (31) was carried as described previously. After the usual workup the crude reaction mixture was purified by vacuum flash chromatography using 5% EtOAc in petroleum ether as eluent. The difluoro adduct (**32**) was thus obtained in 35% yield as an oil: IR 1760 cm^{-1}; ^1H NMR δ 2.6–1.8 (m); ^{19}F NMR -159.6 (1 F, t, $^3J_{HF}$ = 26 Hz), -150.7 (1 F, quintet, $^3J_{HF}$ = 30 Hz); MS, *m/e* 188 $(M)^+$, 168 $[(M - HF)^+]$. Anal. Calcd for $C_{10}H_{14}F_2O$: C, 63.83; H, 7.45. Found: C, 63.21; H, 7.22.

Acknowledgment. We thank the Fund for Basic Research Administrated by The Israel Academy of Science and Humanities for supporting this research.

Registry No. 1, 3681-82-1; (±)-**2**, 103225-29-2; **3**, 3681-71-8; (±)-**4**, 103239-64-1; **5**, 4192-77-2; **6**, 4610-69-9; (±)-**7**, 103225-30-5; (±)-**8**, 103225-31-6; **9**, 645-49-8; *meso*-**10**, 14090-31-4; (±)-**11**, 52795-54-7; **12**, 628-92-2; **13**, 103225-32-7; (*E*)-**14**, 1486-75-5; (*Z*)-**14**, 1129-89-1; (±)-**15**, 103225-33-8; *meso*-**16**, 103302-88-1; (*E*)-**17**, 41446-63-3; (*Z*)-**17**, 41446-60-0; (±)-**18**, 103225-34-9; *meso*-**19**, 103225-35-0; **20**, 111-66-0; **21**, 112-41-4; (±)-**22**, 103225-36-1; (±)-**23**, 103225-37-2; (±)-**24**, 103225-38-3; (±)-**25**, 103225-39-4; **26**, 18402-83-0; (±)-**27**, 103225-40-7; **28**, 91-64-5; (±)-**29**, 103225-41-8; **30**, 704-60-9; **31**, 825-25-2; **32**, 103225-42-9; F_2, 7782-41-4.

Cycloaddition of Chloro-, Cyano-, Methoxy-, and (Phenylthio)allene with 1,1-Dichloro-2,2-difluoroethene (1122). Competitive Cyclodimerization and Trapping of the Cyclodimers with 1122

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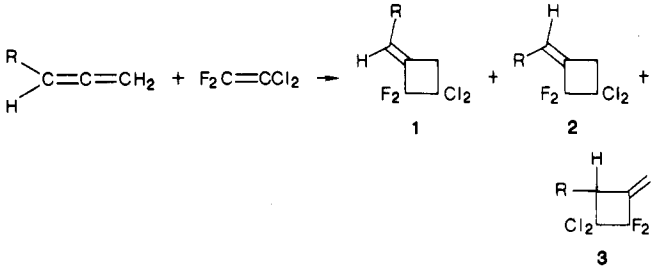
Received February 11, 1986

The cycloaddition reactions of chloro- (ClA), cyano- (CNA), methoxy- (MEOA), and (phenylthio)allene (PHSA) with 1,1-dichloro-2,2-difluoroethene (1122) have been investigated. Cycloadducts are derived by initial attack of 1122 at both C_2 and C_3 in ClA, CNA, and MEOA, and only at C_2 of PHSA. Competitive cyclodimerization of the substituted allenes occurs extensively with ClA and CNA and to lesser extents with MEOA and PHSA. The cyclodimerization of ClA produces a mixture of tail-to-tail (T–T), head-to-tail (H–T), and head-to-head (H–H) cyclodimers, while CNA forms only T–T and H–T cyclodimers, PHSA forms only H–T and H–H cyclodimers, and MEOA apparently forms only the H–H cyclodimer. Only the T–T cyclodimerization of ClA and CNA has been previously detected. The H–T and H–H cyclodimers react further with 1122 to produce 2:1 adducts. The T–T cyclodimers do not react with 1122.

Recent studies in our laboratories have focused on gaining an understanding of the mechanistic details of the free-radical[1,2] and cycloaddition reactions of substituted allenes with dienophiles.[3-5] The results of these studies have shown that the cycloaddition reactions proceed via two-step, diradical-intermediate pathways and have provided valuable information concerning the structures of the diradical intermediates and the factors affecting the relative rates of cleavage, internal rotation, and ring closure.[3-5] One of our objectives has been to determine the effect of substituents on the rates of formation of the diradical intermediates and to measure activation parameters for their formation. Our early observations indicated that all substituents, regardless of their electron-donating or electron-withrawing properties, accelerated the rate of formation of the diradical intermediate relative to hydrogen,[3,4] suggesting a rather late transition state. Two criteria must be met in order to accurately measure relative and/or specific rate constants for diradical intermediate formation: (1) the formation of the intermediate must be irreversible and (2) the reactions should occur cleanly involving attack only at the central carbon atom of the allene to produce the normal cycloaddition products. Our previous studies suggested that 1,1-dichloro-2,2-difluoroethene (1122) might be an excellent choice as the substituted alkene, the reactions of 1122 with monoalkylallenes occurring in a clean manner to produce the cycloadducts **1–3**,[3] and the formation of the diradical intermediate in



the reaction with phenylallene appearing to be irreversible.[6]

(1) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* **1981**, *46*, 2837.
(2) Pasto, D. J.; Warren, S. E. *J. Org. Chem.* **1981**, *46*, 2842.
(3) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3670.
(4) Pasto, D. J.; Heid, P. F.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3676.
(5) Pasto, D. J. Yang, S. H. *J. Am. Chem. Soc.* **1984**, *106*, 152.
(6) Pasto, D. J.; Yang, S. H. *J. Org. Chem.* **1986**, *51*, 1676.

0022-3263/86/1951-3611$01.50/0

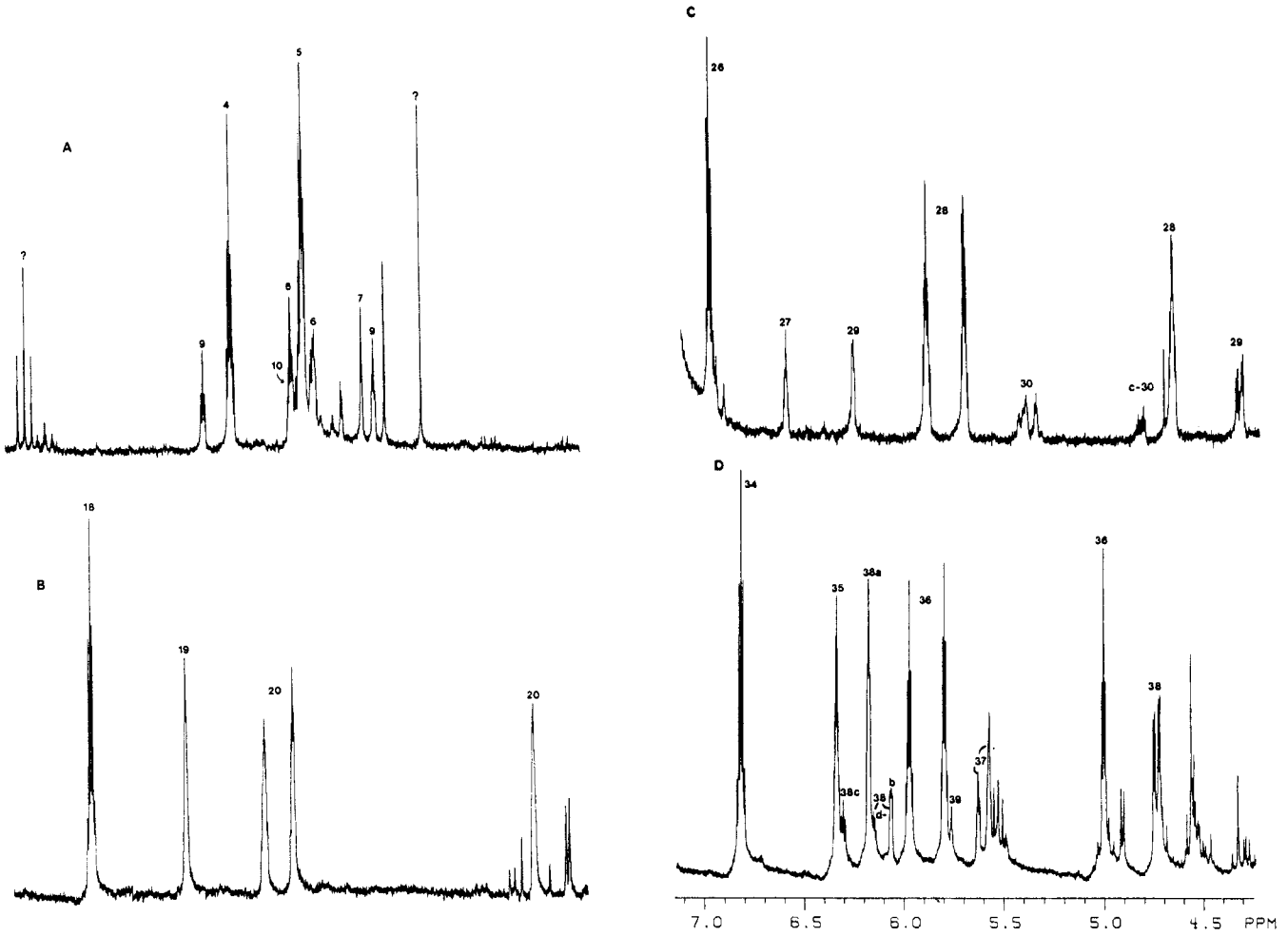


Figure 1. (A) Low-field portion of the ^1H NMR spectrum of the reaction mixture derived from CNA and 1122. The numbers above the resonances identify the structures. The singlet at δ 2.56 and multiplet at 5.47 did not appear in any of the NMR spectra of the isolated fractions. (B) Low-field portion of the ^1H NMR spectrum of the reaction mixture derived from the reaction of MEOA and 1122. (C) Low-field portion of the ^1H NMR spectrum of the reaction mixture derived from the reaction of PHSA with 1122. (D) Low-field portion of the ^1H NMR spectrum of the reaction mixture derived from the reaction of ClA with 1122.

We therefore undertook a study of the cycloaddition reactions of 1122 with several heterosubstituted allenes. These reactions have turned out to be much more complicated than originally anticipated, attack occurring at both the central and terminal carbon atoms of the allenes and cyclodimerization of the substituted allenes occurring competitively with the cycloaddition with 1122. The results of these studies have, however, provided interesting details on the cyclodimerization reactions which could not be extracted from the results of the direct cyclodimerization reactions due to further oligo- and polymerization reactions of some of the intermdiates.[7,8] The results of the studies of the cycloaddition reactions of cyano-, methoxyl-, (phenylthio)-, and chloroallene with 1122 are reported herein.

Results

Cyanoallene (CNA). The reaction of CNA with 1122 at 160 °C produces a complex mixture of the 1:1 cycloadducts **4–6**, the cyclodimers **7** and **8**, a mixture of the stereoisomeric 2:1 adducts **10a–f**, and the 1:2 – HCl adduct **11**, which could be partially separated into a number of fractions by thin-layer, rotating-disk chromatography (Scheme I). The 1:1 cycloadducts **4–6**, however, could not be isolated by chromatographic techniques, decomposition occurring during the chromatographic process. The formation of **4–6** is confirmed on the basis of the NMR spectral characteristics of such cycloadducts which appear in the ^1H NMR spectrum of the crude reaction mixture (see Figure 1). In the cycloadducts of 1122 derived from monoalkyl-substituted allenes the vinyl hydrogen resonances of the *E* stereoisomers appear at lower field than those of the *Z* isomers, with the (*Z*)-allylic H–H and H–F long-range coupling constants being greater than the (*E*)-allylic coupling constants.[3] The ^{19}F resonances of **4** and **5** appear as broadened singlets, the broadening arising from long-range allylic and cross-ring coupling (see ^{19}F NMR spectrum shown in Figure 2). The vinyl hydrogen resonances of **6** are superimposed on the vinyl hydrogen resonances of some of the stereoisomers of **10**. The ^{19}F spectrum of **6** shows a pair of broadened AB doublets for the diastereotopic fluorine atoms.

The cyclodimerization of CNA occurs in competition with the cycloaddition with 1122. The cyclodimers **7** and **8** were isolated, but the cyclodimer **9** was not isolated and appears not to have been formed by the lack of appropriate resonances in the ^1H NMR spectrum of the crude reaction mixture[7] and its lack of being isolated. The cyclodimers **7** and **8** do not appear to react further with the 1122 in that no 2:1 adducts corresponding to the expected structures derivable from **7** and **8** were isolated or indicated to be formed by a detailed analysis of the ^{19}F NMR spectrum

(7) Pasto, D. J.; Huang, N.-Z.; Yang, S. H.; Eigenbrot, C. W.; Barreto, R. D.; Fehlner, T. P. *J. Org. Chem.* **1985**, *50*, 5056.
(8) Pasto, D. J.; Yang, S. H., unpublished observations.

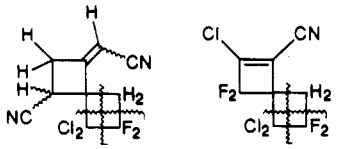
Table I. Relative Yields of Products Formed in the Reactions of CNA, MEOA, PHSA, and ClA with 1122

CNA		MEOA		PHSA		ClA	
product	relative yield (%)	product	relative yield (%)	product	relative yield (%)	product	relative yield (%)
4	24.2	**18**	32	**26**	40.5	**34**	19.8
5	8.8	**19**	25	**27**	9.8	**35**	15.6
6	4[a]	**20**	25	**28**	31.1	**36**	17.1
7	7.9	**21**	11	**29**	12.8	**37**	5.7
8	6.4	2:1 adducts	7	**30**	5.8	**38**	27.6
10a–f	21.8					**39**	3.2
11	14.5					**40**	10.0
unknown structures	12.4					**41**	~1.0

[a] Estimated yield. The resonances of **6** are superposed on those of **10** and an accurate assessment of the quantity of **6** formed cannot be made.

of the crude reaction mixture.

Cyclodimerization of CNA occurs to produce a mixture of the *E* and *Z* stereoisomers of **12** which undergo further cycloaddition with 1122 to produce a mixture of the stereoisomers of **10**. Of the eight possible stereoisomers for **10**, NMR evidence indicates that six of the stereoisomers were formed in detectable quantities which are designated **10a–f** (see Experimental Section). NMR data does not allow for assignment of the relative stereochemistries at any of the stereocenters in **10a–f**. The ^1H and ^{19}F NMR spectra of the stereoisomers of **10** are very characteristic. The ^1H NMR spectra show very characteristic A–MN–X proton and AB–XY proton–fluorine spin systems, the latter characteristic of a CH_2CF_2 fragment in a cyclic system containing a chiral center. (An expansion of a portion of the ^{19}F NMR spectrum is shown in Figure 2 showing the typical resonance pattern for one of the diastereotopic fluorine atoms in one of the isomers of **10**.) The mass spectra of **10** show characteristic cycloreversion modes of fragmentation illustrated below.



Also formed is a 1:2 adduct which has suffered the loss of hydrogen chloride. The ^1H NMR spectrum shows only a two-proton, AB–XY proton–fluorine spin system. The ^{19}F NMR spectrum shows the pattern characteristic of the AB–XY proton–fluorine spin system as well as a pair of sharp AB doublets for a pair of spin-isolated diastereotopic fluorine atoms. The mass spectrum of the adduct indicated a parent mass of 293, with the relative intensities of the M^+, $(M^+ + 2)$, and $(M^+ + 4)$ ions indicating the presence of three chlorine atoms. Major fragment ions are present for the loss of 1122 and H_2CCF_2. The data is consistent only with structure **11**. With the knowledge that 1122 reacts with π-systems with the formation of a CCl_2-centered radical,[6] a reasonable mechanism for the formation of **11** involves attack by 1122 at C_3 of CNA to form the diradical intermediate **13** which ring closes to form **14**. The further cycloaddition of **14** with 1122 to form **15** followed by the loss of hydrogen chloride produces **11**.

The relative yields of the products have been calculated from the integrals of the ^1H and ^{19}F NMR spectra and are given in Table I.

Methoxyallene (MEOA). The reaction of MEOA with 1122 occurs to produce mainly the 1:1 cycloadducts **18–20** and the 1:2 adduct **21** (see Figure 1B) which were isolated by preparative GLC (Scheme II). The structures of **18–20** are readily assigned on the basis of their ^1H and ^{19}F NMR spectra. The structure of the 1:2 adduct is assigned **21** on the basis its ^1H and ^{19}F NMR spectra and its mass spectral fragmentation pattern which involves the characteristic

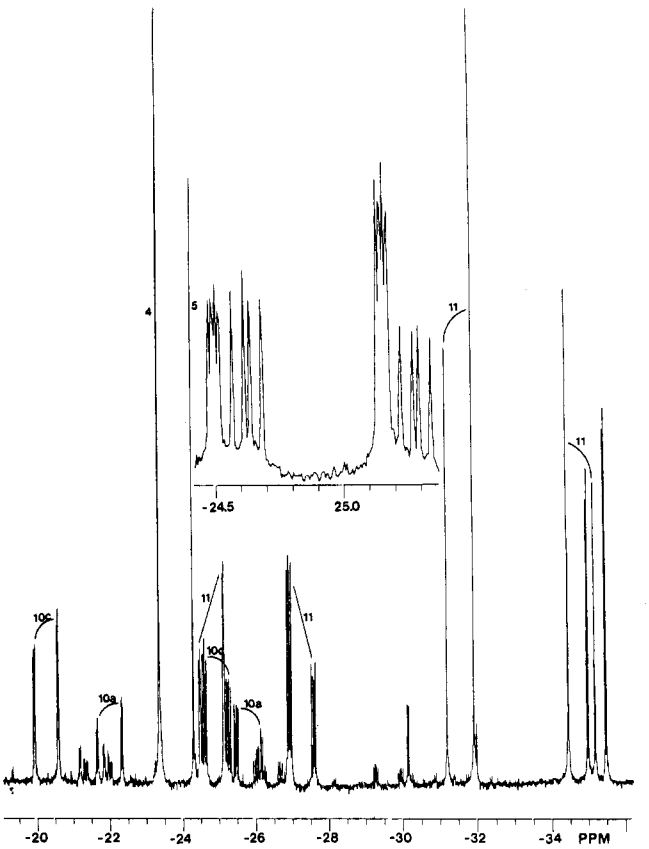
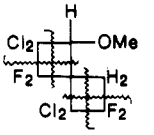


Figure 2. ^{19}F NMR spectrum of the reaction mixture derived from CNA and 1122. The numbers associated with the resonance patterns represent the structural assignments. Of the isomeric structures **10**, only the resonances of **10a** and **10c** are indicated. Other lower intensity resonances represent structures **10b** and **10d–f**. The expanded insert shows the ddd patterns for one of F atoms in structures **11** and **10c**.

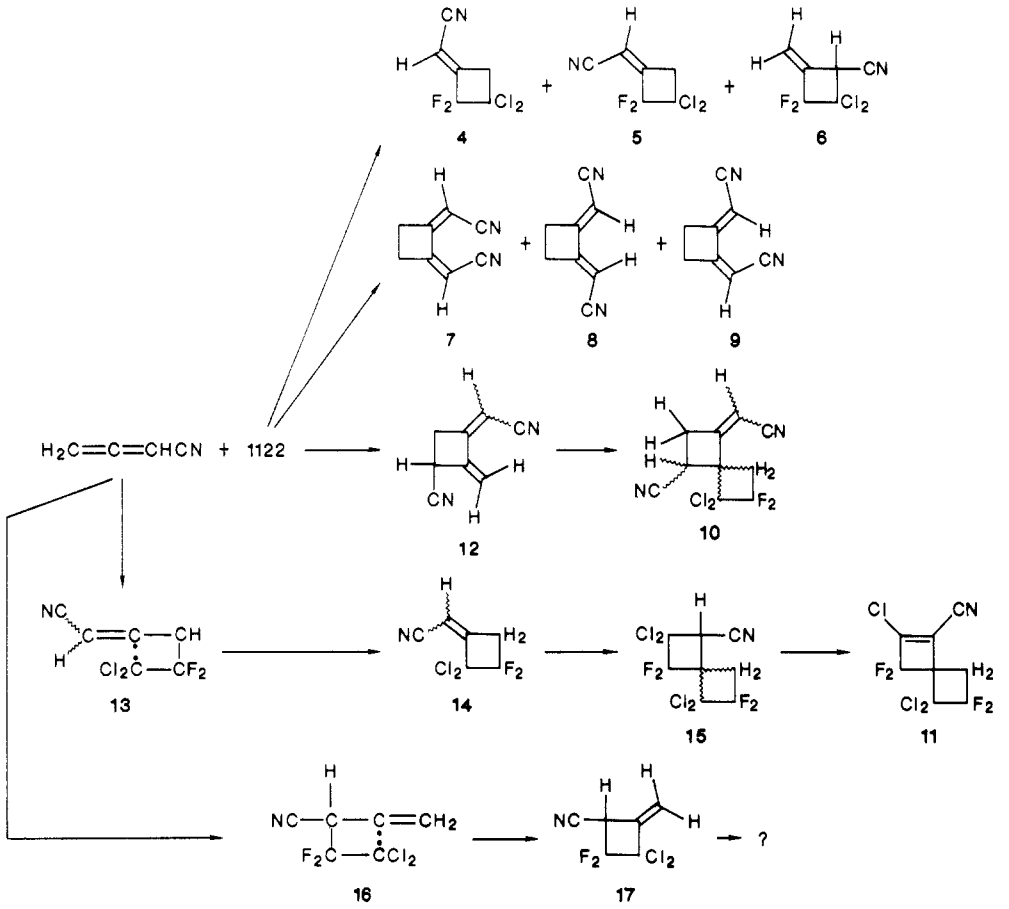
cleavages of the saturated four-membered rings as shown in the following diagram.



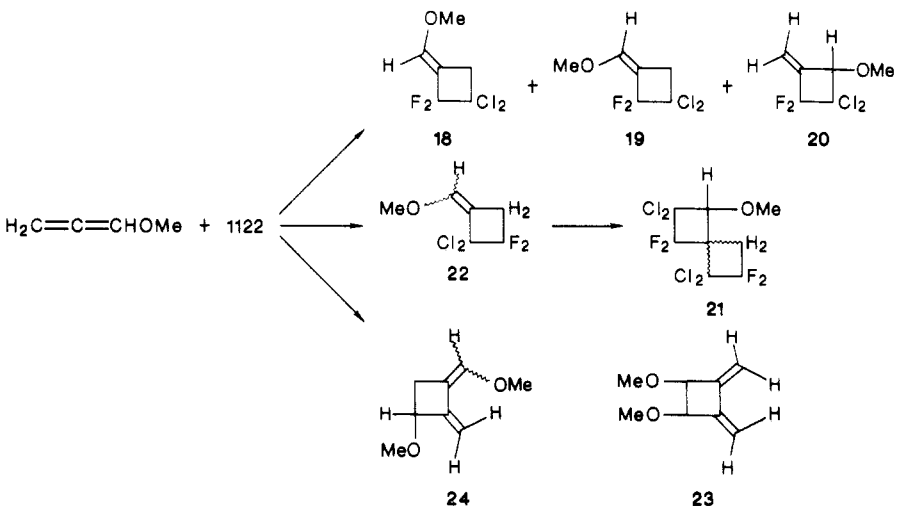
Adduct **21** is formed by attack of 1122 at C_3 of MEOA to produce **22** which reacts further with 1122 to produce **21**. The structure of **21** is similar to that of the 1:2 adduct derived from CNA except that **21** has not undergone the elimination of hydrogen chloride.

The ^{19}F NMR spectrum of the crude reaction mixture and the analysis by GC–MS indicated the formation of a small amount of a mixture of three stereoisomeric 2:1 adducts. These 2:1 adducts could not be isolated by either preparative GLC or TLC. The ^{19}F NMR spectrum of the

Scheme I



Scheme II



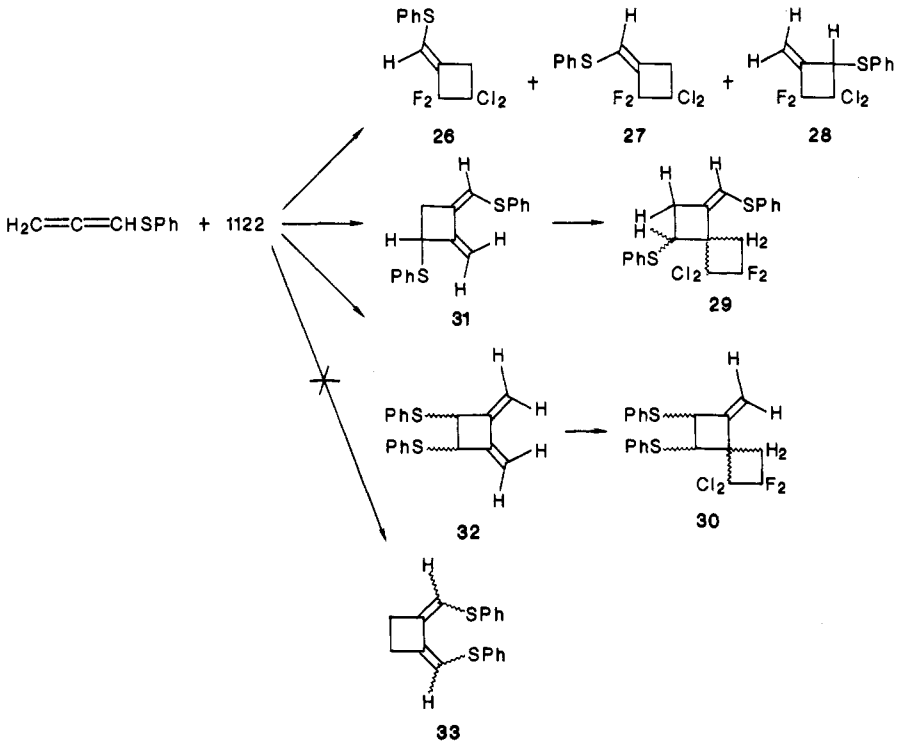
crude reaction mixture indicates that all of the 2:1 adducts contain a $-CH_2CF_2-$ segment in the presence of a chiral center, suggesting that these adducts are derived from **23** or **24**. The doublet at δ 4.37 in the ^1H NMR spectrum of the crude reaction mixture (see Figure 1B) suggests that the 2:1 adducts are derived from **23**.

The yields of the products from the reaction of MEOA are given in Table I.

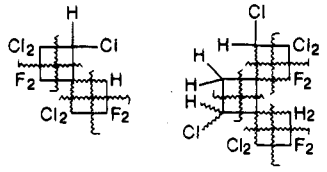
(Phenylthio)allene (PHSA). The reaction of PHSA with 1122 produces a mixture of the 1:1 cycloadducts **26–28** along with predominantly one stereoisomer of a 2:1 adduct of gross structure **29** (trace quantities of other stereoisomers of **29** are indicated to be formed by the ^{19}F NMR spectrum of the crude reaction mixture) and the cis and trans stereoisomers of the 2:1 adduct **30** (Scheme III). (The low-field portion of the ^1H NMR spectrum of the crude reaction mixture is shown in Figure 1C.) The 2:1 adducts **29** and **30** are formed by reaction of the intermediate PHSA cyclodimers **31** and **32** with 1122. Cyclodimer **33** appears not to have been formed. Attack by 1122 at C_3 of PHSA, to ultimately produce a 1:2 adduct similar in structure to **21**, also does not appear to occur. The relative yields of **26–30** are given in Table I.

Chloroallene (ClA). The reaction of CLA with 1122 produces a complex mixture of products (see ^1H NMR spectrum shown in Figure 1D), including the three 1:1 cycloadducts **34–36**, a single stereoisomer of the 2:1 adduct **37**, three major and four minor stereoisomers of the 2:1

Scheme III

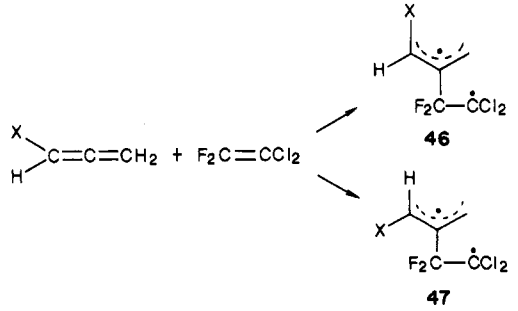


adduct **38** (designated **38a–g**), the 2:2 adduct **41**, the 1:2 adduct **40**, and the cyclodimer **39** (Scheme IV). Adducts **40** and **41** could not be isolated by preparative GLC, and their presence and structures were inferred from GC–MS data which showed the characteristic modes of fragmentation shown in the structures below. The relative yields of the products are given in Table I.



Discussion

1:1 Cycloadduct Formation. In all cases the *E* stereoisomer is formed in preference to the *Z* stereoisomer (for example, **4** vs. **5**, etc.). This is consistent with a two-step, diradical-intermediate cycloaddition process in which, for steric reasons,[3,4] the diradical intermediate **46** is formed preferentially over **47**, and in which diradical intermediate formation is essentially irreversible and there is no isomerization of **46** to **47**. The *E*:*Z* product ratio is



greatest in the case of PHSA (81:19), intermediate with CNA (73:27), and lowest with MEOA and ClA (both 56:44). If the *E*–*Z* product ratio reflects the ratio of **46** and **47** formed in the reaction of the substituted allenes with 1122, the phenylthio group is the most stereically demanding in the transition states for diradical intermediate formation, with the methoxy and chloro groups being the least sterically demanding.

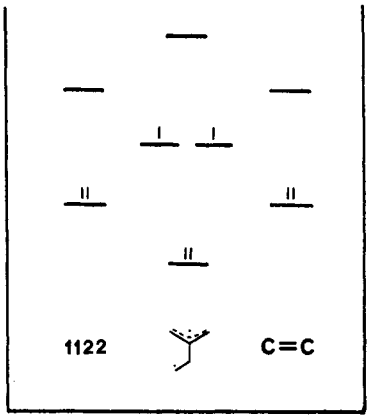
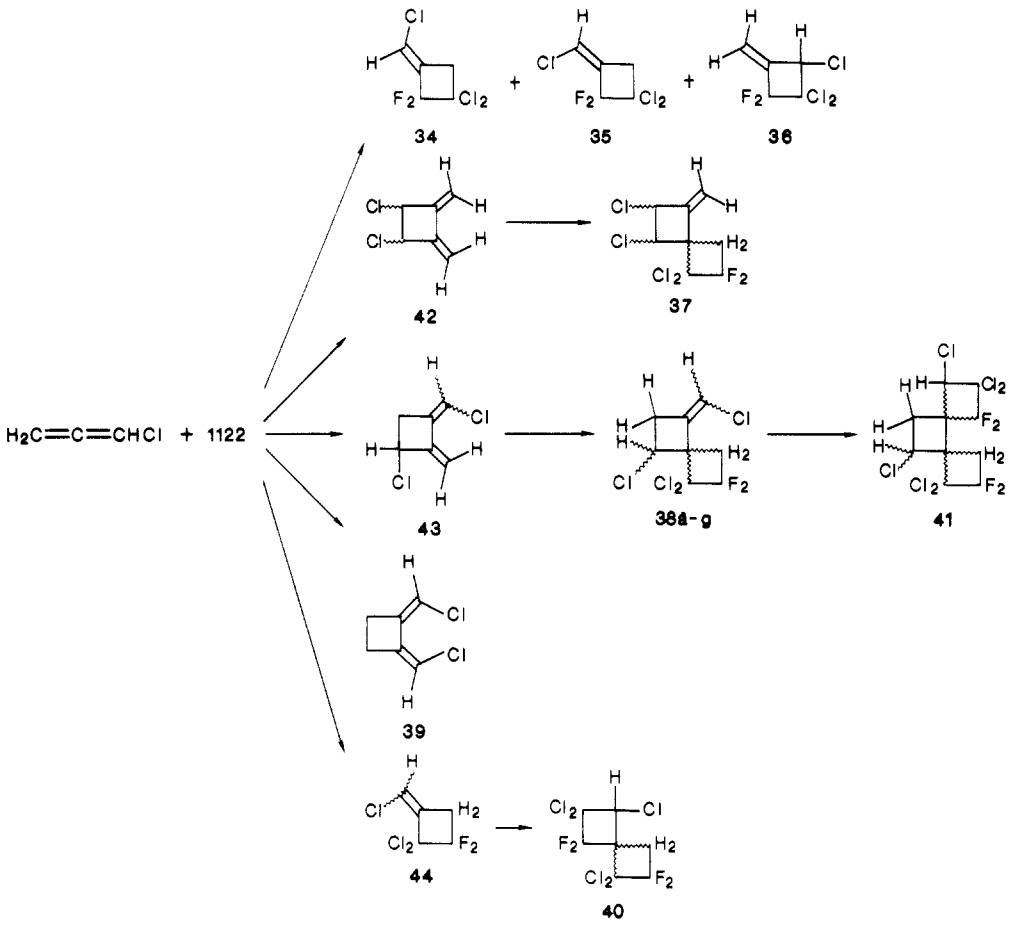


Figure 3. Relative orbital energy levels of 1122, an alkene, and the diradical intermediate.

Ring closure of the diradical intermediates favors the substituted-methylene cyclobutane structure in all cases (for example, **4** and **5** vs. **6**, etc.). The ratio is largest in the case of CNA (89:11) and quite similar in the cases of MEOA (69:31), PHSA, and ClA (67:33). The factors that govern the regioslectivity of the ring closure of **46** and **47** are not fully understood and are currently under further study in our laboratories.

The results of the studies in our laboratories indicate that all functions, regardless of whether they are electron-donating or electron-withdrawing, activate the substituted allene toward diradical-intermediate formation suggestive of a late transition state. This is supported by the results of our earlier kinetic isotope effect studies.[3,4] In an early transition state the relative rates of diradical-intermediate formation from two π systems will depend in a complex manner on the orbital energies and coefficients of both the HOMO's and LUMO's of both reactants as is illustrated in Figure 3. An analysis of the orbital energies and coefficients of the substituted allenes[7] does

Scheme IV



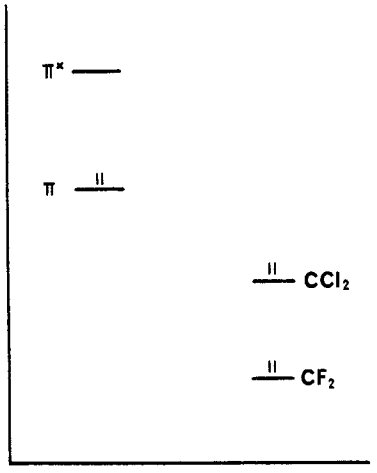
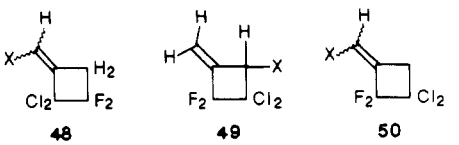


Figure 4. Relative orbital energy levels of an alkene π system and the π-type methylene orbitals of CCl_2 and CF_2 groups.

not provide a clear-cut explanation of the observations. In a late transition state the relative rates of diradical-intermediate formation will be dependent on the relative stabilization of the radical centers by the attached functional groups. A review of the literature reveals that thermodynamic radical stabilization energies have been only rarely determined, the only good example being that for the allyl radical.[9] Quantitative rate studies on the cycloaddition reactions of substituted allenes and the determination of thermodynamic radical stabilization energies will be required before an adequate understanding of the factors governing relative reactivities and regioselectivities in these reactions will be possible.

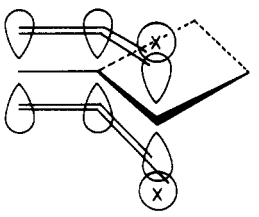
C_2 vs. C_3 Attack. The cycloaddition reactions of alkyl-substituted allenes with 1122 occurs only via attack at C_2 to produce the diradical intermediates **46** and **47** which undergo ring closure to produce cycloadducts of structures **1** and **2**. The cycloadducts **1** and **2** (R = alkyl) have not been observed to undergo further cycloaddition with 1122 across the exocyclic double bond. This would suggest that the formation of **11**, **21**, and **40** does not occur via further cycloaddition of 1122 to the cycloadducts **4** and **5**, **18** and **19**, or **34** and **35**, but involves attack by 1122 at C_3 of CNA, MEOA, and ClA to form the cycloadducts **14**, **22**, and **44**, respectively, which undergo further reaction with 1122.

This would indicate an interesting difference in the reactivities of **48** vs. **49** and **50** toward further cycloaddition.



This difference is reactivity appears to arise from the difference in the extent of the interaction of the adjacent CX_2 π-type group orbital with the π and π^* MO's of the π system as shown in Figure 4. The CCl_2 π-type group orbital is expected to lie closer in energy to the π MO of the double bond than does the lower lying CF_2 π-type group orbital and will thus interact with the π MO to a greater extent as illustrated in **51**. This orbital interaction will elevate the energy of the π MO of **48** to a greater extent than in **49** or **50**, thus increasing the reactivity of **48** toward further cycloaddition with 1122. The increased nuclear

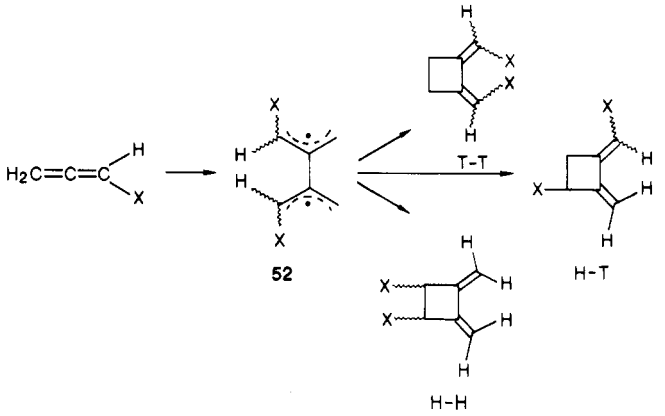
(9) Rossi, M.; King, K. D.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1223.



51

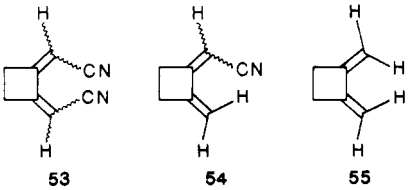
potential field effect by the fluorine atoms (the inductive effect) will lower the energy of the π MO in **49** and **50** and decrease the reactivity of the adducts of structure type **49** and **50** toward cycloaddition with 1122.

Cyclodimerization Reactions. In the cycloaddition reactions of alkyl-substituted allenes with 1122 competitive cyclodimerization of the allenes was not observed. In the present studies extensive cyclodimerization was observed, occurring to the greatest extent with CNA (51:49 ratio of cycloaddition to cyclodimerization) and ClA (58:42) and to the lesser extents with PHSA (81:19) and MEOA (92:8). Thus, these substituted allenes are more reactive toward both cycloaddition and cyclodimerization. In the direct cyclodimerization of CNA, only the tail-to-tail (T–T) cyclodimers **7**, **8**, and **9** have been isolated[7] and with ClA only the T–T dimer **39** has been isolated.[8,10] Extensive oligo- and/or polymerization occurs in both cases in the attempted cyclodimerization reactions. The results of the present studies indicate that heat-to-tail (H–T) and head-to-head (H–H) cyclodimers are also formed, which in the presence of 1122 are trapped as the 2:1 adducts. In



the absence of 1122, as in the direct cyclodimerization reactions of CNA and ClA, the H–T and H–H cyclodimers must also be formed, but must undergo further reaction to produce oligo- and/or polymeric products which precludes their isolation.

The lack of reactivity of the cyclodimers of structure similar to **7–9** must be electronic in origin, the coefficients at the C_1 and C_4 positions in the π fragment **53** in both the HOMO and LUMO being quite small.[11] In the cyclodimers of general structure **54**[12] and **55**,[13] the coefficients



53 54 55

at C_4 are greater than those in **7–9**, thus resulting in greater reactivity toward reaction with 1122.

Interesting trends are apparent in the regioselectivity for ring closure of the substituted bisallyl diradical intermediates **52** encountered in this study. The diradical intermediate derived from CNA undergoes ring closure to form the T–T and H–T cyclodimers in a 60:40 ratio, ClA the T–T, H–T, and H–H cyclodimers in a 9:76:15 ratio, PHSA the H–T and H–H cyclodimers in a 69:31 ratio, while MEOA apparently produces only the H–H cyclodimer. An interpretation of these results is complicated by the fact that three stereoisomers of **52** are possible which may exhibit different regioselectivities for ring closure and the fact that little is known about the factors that control the regioselectivity of reactions of substituted allyl radicals. It is also not known whether the results represent kinetically or thermodynamically (reversible) controlled processes. Further studies in this area are currently in progress in our laboratories.

Experimental Section

General Methods. All ^1H and ^{19}F NMR spectra were recorded in $CDCl_3$ solutions on a Nicolet NB-300 NMR system. ^{19}F chemical shifts are relative to δ 0.0 for boron trifluoride etherate in $CDCl_3$ solution. Extensive decoupling experiments allowed assignment of H–H and H–F coupling constants. Mass spectra were recorded either on a DuPont 102 GC-MS or a AEI MS-902 high-resolution mass spectrometer.

Reaction of Cyanoallene (CNA) with 1,1-Dichloro-2,2-difluoroethene (1122). Into a thick-walled Pyrex tube was placed 200 μL of CNA. The tube was placed in dry ice and ~1.0 mL of 1122 was condensed into the tube. The contents of the tube were triply freeze degassed, and the tube was sealed under reduced pressure. The tube was placed in a sand bath at 160 °C for 24 h, after which time the tube was removed, cooled, and opened. The excess 1122 was allowed to evaporate. The ^1H and ^{19}F NMR spectra of the reaction mixture were recorded (see Figures 1 and 2). The yields of the products were determined by the integrals of the ^1H and ^{19}F NMR spectra (see Table I). The attempted separation of the reaction mixture by GLC resulted in extensive decomposition. The reaction mixture was subjected to thin-layer, rotating disk chromatograph on a 1-mm thick silica gel plate using hexane–dichloro-methane gradient elution giving several fractions. The ^1H and ^{19}F NMR and mass spectra were recorded.

Fraction 1 (**11**, 13.2%): ^1H NMR δ 2.90 (dddd, J_{HH} = 14.47 Hz, J_{HF} = 12.62, 3.95, 2.25 Hz, 1 H), 3.40 (dddd, J_{HH} = 14.47 Hz, J_{HF} = 20.05, 7.61, 1.31 Hz, 1 H); ^{19}F NMR δ −24.82 (ddd, J_{FF} = 186.3 Hz, J_{HF} = 7.61, 3.95 Hz, 1 F), −27.20 (ddd, J_{FF} = 186.3 Hz, J_{HF} = 20.05, 12.62 Hz, 1 F), −31.60 (d, J_{FF} = 204.70 Hz, 1 H), −34.78 (br d, J_{FF} = 204.70 Hz, broadening due to long-range coupling to H, 1 H); MS, M^+ calcd for $C_9H_2Cl_3F_4N$ 293, found 293.

Fractions 2 and 3. Fractions 2 and 3 showed no resonances in the ^1H NMR region and are 1122 oligomers.

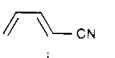
Fraction 4 (unknown structure, 8.4%): ^1H NMR δ 5.07 (s, 1 H), 7.04 (t, J_{HF} = 10.47 Hz, 1 H); ^{19}F NMR δ −35.48 (d, J_{HF} = 10.47 Hz); MS, M^+ 282, 247 (P − Cl) and 212 (P − 2 Cl).

Fraction 5 (unknown structure, 3.0%): ^1H NMR δ 4.18 (dd, J_{HH} = 10.86 Hz, J_{HF} = 6.02 Hz, 1 H), 4.21 (dd, J_{HH} = 10.86 Hz, J_{HF} = 5.71 Hz, 1 H), 7.52 (dd, J_{HF} = 5.71, 3.30 Hz, 1 H), 7.68 (dd, J_{HF} = 5.67, 3.29 Hz, 1 H). Double resonance of the δ 4.2, 7.52, and 7.68 regions resulted in no change in the ^1H NMR spectral regions.); MS, highest m/e peak 279, with the relative intensities of the M + 2 and M + 4 peaks indicating the presence of two

(10) Jacobs, T. L.; McClenon, J. R.; Musico, O. J., Jr. *J. Am. Chem. Soc.* **1969**, 91, 6038.

(11) 3-21B ab-initio calculations of **7–9** give c(I)'s and c(0)'s of 0.18 and 0.22 in the HOMO and 0.18 and 0.36 in the LUMO.

(12) In the model fragment i the c(I)'s and c(0)'s at the $=CH_2$ terminus are 0.22 and 0.29 in the HOMO and 0.22 and 0.47 in the LUMO.



i

(13) In butadiene the c(I)'s and c(0)'s at the terminal positions are 0.26 and 0.32 in the HOMO and 0.24 and 0.55 in the LUMO.

chlorine atoms. Major fragment peaks appear at m/e 167 and 149 which do not contain chlorine.

Fraction 6 (10a, 4.1%): ^{1}H NMR δ 2.98 (m, 1 H), 3.3 (m, 2 H), 3.81 (dd, J_{HH} = 9.98, 7.15 Hz), 5.68 (t, J_{HH} = 2.85); ^{19}F NMR δ −22.02 (ddd, J_{FF} = 188.1 Hz, J_{HF} = 8.45, 7.00 Hz, 1 F), −25.82 (ddd, J_{FF} = 188.1 Hz, J_{HF} = 17.66, 12.54 Hz, 1 F); GC–MS; M$^+$ 262; major fragment ions at m/e 227 (M − Cl), 198 (M − CH_2CH_2), 132 (1122), 130 (M − 1122), 64 (CH_2CF_2). (All fractions containing isomers of **10** showed similar GC–MS spectra.)

Fraction 7 [obtained as a mixture of **8** (7.2%)[7] and **10b** (1.2%)]. **10b**: ^{1}H NMR δ 3.3 (m), 3.8 (m), 3.9 (m), 5.73 (t, J = 2.73 Hz); ^{19}F NMR δ −21.73 (ddd, J_{FF} = 187.7 Hz, J_{HF} = 8.58, 6.19 Hz, 1 F), −26.52 (ddd, J_{FF} = 187.7 Hz, J_{HF} = 17.78, 12.69 Hz, 1 F).

Fraction 8 (10c, 10.0%): ^{1}H NMR δ 3.02 (ddd, J_{HH} = 17.30, 3.02, 1.98 Hz, 1 H), 3.34 (ddd, J_{HH} = 17.30, 10.00, 2.91 Hz, 1 H), 3.80 (dd, J_{HH} = 10.00, 3.02 Hz, 1 H), 3.03 (ddd, J_{HH} = 14.88 Hz, J_{HF} = 14.24, 3.84 Hz, 1 H), 3.70 (ddd, J_{HH} = 14.88 Hz, J_{HF} = 20.02, 7.80 Hz, 1 H), 5.67 (dd, J_{HH} = 2.91, 1.92 Hz, 1 H); ^{19}F NMR δ −20.29 (ddd, J_{FF} = 185.4 Hz, J_{HF} = 7.80, 3.84 Hz, 1 F), −24.91 (ddd, J_{FF} = 185.4 Hz, J_{HF} = 20.02, 14.24 Hz, 1 F).

Fraction 9 [mixture of **10c**, **10d** (1.4%), and **10e** (2.8%)]. **10d**: ^{1}H NMR δ 3.02 (dd, J_{HH} = 10.07, 7.05 Hz, 1 H), 3.20 (ddd, J_{HH} = 18.09, 7.05, 2.81 Hz, 1 H), 3.36 (ddd, J_{HH} = 18.09, 10.07, 2.81 Hz, 1 H), 3.1 (partially obscured ddd, J_{HF} = 12.61, 6.53 Hz, 1 H), 3.7 (partially obscured ddd, J_{HF} = 17.58, 8.42 Hz, 1 H), 5.66 (t, J_{HH} = 2.81 Hz, 1 H); ^{19}F NMR δ −21.96 (ddd, J_{FF} =188.2 Hz, J_{HF} = 8.42, 6.53 Hz, 1 F), −25.76 (ddd, J_{FF} = 188.2 Hz, J_{HF} = 17.58, 12.52 Hz, 1 F).

10e: ^{1}H NMR δ 5.73 (t, J = 2.70 Hz) (The remainder of the spectrum is obscured by the peaks of **10c** and **10d**.); ^{19}F NMR δ −21.58 (ddd, J_{FF} = 188.2 Hz, J_{HF} = 6.53, 1.4 Hz, 1 F), −29.52 (ddd, J_{FF} = 188.2 Hz, J_{HF} = 21.34, 13.77 Hz, 1 F).

Fraction 10 [mixture of **7**,[7] **10d**, **10e**, and **10f** (0.3%)]. **10f**: ^{1}H NMR δ 5.69 (t, J_{HH} = 2.78 Hz) (The remainder of the spectrum is obscured by the peaks of **10d** and **10e**.); ^{19}F NMR δ −21.27 (ddd, J_{FF} = 186.6 Hz, J_{HF} = 6.9, 4.3 Hz, 1 F), −26.31 (ddd, J_{FF} = 186.6 Hz, J_{HF} = 18.7, 12.4 Hz, 1 F).

Cycloadducts **4**, **5**, and **6** apparently underwent decomposition on the silica gel plate; no fractions were isolated whose ^{1}H NMR spectra contained vinyl hydrogen resonances at δ 6.02, 5.68, 5.61, and 5.63. The structures of **4–6** are assigned on the basis of the resonances appearing in the ^{1}H and ^{19}F NMR spectra of the reaction mixture. **4**: ^{1}H NMR δ 6.02 (tt, J_{HH} = 2.43 Hz, J_{HF} = 2.92 Hz); ^{19}F NMR δ −23.33. **5**: ^{1}H NMR δ 5.68 (tt, J_{HH} = 2.52 Hz, J_{HF} = 1.26 Hz); ^{19}F NMR δ −24.28. **6**: The ^{1}H resonances of **6** appear as distorted multiplets superposed on the vinyl hydrogen resonances of the isomers of **10**.

Reaction of Methoxyallene (MEOA) with 1,1-Dichloro-2,2-difluoroethene (1122). To 200 μL of MEOA in a thick-walled Pyrex tube cooled in dry ice was condensed ~1.0 mL of 1122. The contents of the tube were triply freeze degassed, and the tube was sealed under vacuum. The tube was heated in a sand bath at 160 °C for 1 day. The tube was removed, allowed to cool, and opened, and the excess 1122 was allowed to evaporate. The ^{1}H (see Figure 1B) and ^{19}F NMR spectra of the reaction mixture were recorded. Attempts to separate the reaction mixture by preparative thin-layer rotating disk chromatography resulted in complete decomposition. No products were isolated that corresponded to those indicated to be present in the crude reaction mixture. Separation of the mixture by preparative GLC on a 10 ft. × $^1/_4$ in. SE-30 on Chromasorb P column at 150 °C gave two major fractions containing a mixture of **18** and **19** and pure **20**. Several very small fractions were isolated; however, the NMR spectra of these fractions did not correspond to any of the minor resonance patterns appearing in the δ 2.4–4.0 region of the NMR spectrum of the reaction mixture. Analysis by GC–MS indicated the formation of three 1:1 cycloadducts, one 1:2 adduct, and a 2:1 fraction. The structures of the 1:2 and 2:1 adducts have been assigned on the basis of recognizable patterns in the ^{1}H and ^{19}F NMR spectra of the crude reaction mixture and the mass spectral fragmentation patterns. The relative yields have been determined from the integrals and the ^{1}H and ^{19}F NMR spectra.

18 and **19** (obtained as a mixture). **18** (32%): NMR δ 3.31 (dt, J_{HH} = 2.92 Hz, J_{HF} = 1.13, 2 H), 3.74 (s, 3 H), 6.75 (dt, J_{HH} =2.92 Hz, J_{HF} = 2.92 Hz, 1 H); ^{19}F NMR −15.8 (br s); GC–MS, M$^+$ 202; major fragment ions at m/e 167 (M$^+$ − Cl, base peak).

19 (25%): ^{1}H NMR δ 3.24 (dt, J_{HH} = 2.11 Hz, J_{HF} = 1.10 Hz, 2 H), 3.81 (s, 3 H), 6.27 (dt, J_{HH} = 2.11 Hz, J_{HF} = 1.45 Hz, 1 H); ^{19}F NMR δ −13.5 (s).

20 (25%): ^{1}H NMR δ 3.60 (s, 3 H), 4.51 (br m, 1 H), 5.73 (tt, J_{HHgem} = $J_{HHallylic}$ = ~1.7 Hz, J_{HF} = 2.27 Hz, 1 H), 5.88 (ddt, $J_{HHallylic}$ = ~1.8 Hz, J_{HHgem} = ~1.7 Hz, J_{HF} = 2.99 Hz, 1 H); ^{19}F NMR δ −22.37 (br d, J_{FF} = 184.0 Hz, 1 F), −28.54 (d, J_{FF} = 184.0 Hz, 1 F); GC–MS, M$^+$ 202, major fragment ions at m/e (M$^+$ − CH_2O), 167 (M$^+$ − Cl).

1:2 adduct 21 (GC–MS fraction 7 and very minor component in preparative GLC fraction 7, 11%): partial ^{1}H NMR δ 3.11 (ddd, J_{HH} = 13.3 Hz, J_{HF} = 3.77, 9.5 Hz, 1 H), 3.64 (s, 3 H), 3.93 (partially obscured ddd, J_{HH} = 13.3 Hz, J_{HF} = 7.2 Hz, 1 H); ^{19}F NMR δ −15.29 (ddd, J_{HF} = 7.21, 9.65 Hz, J_{FF} = 184.4 Hz, 1 F), −33.12 (ddd, J_{HF} = 3.77, 13.62 Hz, J_{FF} = 184.4 Hz, 1 F), −33.277 (br d, J_{FF} = 198.2 Hz, 1 F), −35.50 (dd, J_{HF} = 5.0 Hz, J_{FF} = 198.2 Hz, 1 F); GC–MS, M$^+$ calcd for $C_8H_6{}^{35}Cl_4F_4O$, 334, found, 334; major fragment ions appear at m/e 299 (M$^+$ − Cl), 202 (M$^+$ − 1122), 126 ($Cl_2ClCHOCH_3^+$), 64 ($H_2C{=}CF_2^+$).

2:1 adducts: major isomer (5%); ^{19}F NMR δ −19.18 (dd, J_{HH} = 3.86, 8.14 Hz, J_{FF} = 181.6 Hz, 1 F), −28.09 (ddd, J_{HH} = 14.04, 19.20 Hz, J_{FF} = 188.6 Hz, 1 F). Two very minor isomers (total of ~2%) were indicated to be present by the appearance of ddd patterns at δ −16.7 and −24.2, and −21.8 and −24.4.

Reaction of (Phenylthio)allene (PHSA) with 1,2-Dichloro-2,2-difluoroethene (1122). In a thick-walled Pyrex tube containing 200 μL of PHSA cooled in dry ice was condensed to ~1.0 mL of 1122. The contents of the tube were triply freeze degassed and the tube was sealed under reduced pressure. The tube was placed in a sand bath and heated at 160 °C for 1 day. The tube was removed from the sand bath and allowed to cool. The tube was opened and the unreacted 1122 was allowed to evaporate. The ^{1}H and ^{19}F NMR spectra of the residue were recorded and integrated to calculate the relative yields of the products.

The residue was subjected to thin-layer, rotating disk chromatography on a 1-mm-thick plate of silica gel using hexane–dichloromethane gradient elution giving several fractions.

Fraction 1 [mixture of **26** (40.5%) and **28** (31.1%)]. **26**: ^{1}H NMR δ 3.17 (dt, J_{HH} = 2.61 Hz, J_{HF} = 1.38 Hz, 2 H), 6.98 (p, J_{HH} = J_{HF} = 2.61 Hz, 1 H), 7.2–7.5 (m); ^{19}F NMR δ −18.21 (br s); MS (of mixture), exact mass calcd for $C_{11}H_8{}^{35}Cl_2F_2S$, 279.969, found, 279.970.

28: ^{1}H NMR δ 4.68 (dddd, J_{HH} = 3.17, 1.96 Hz, J_{HF} = 2.22, 1.58 Hz, 1 H), 5.75 (ddt, J_{HH} = 1.96, 1.96 Hz, J_{HF} = 1.96 Hz, 1 H), 5.94 (ddt, J_{HH} = 3.17, 1.96 Hz, J_{HF} = 2.02 Hz, 1 H), 7.2–7.5 (m); ^{19}F NMR δ −22.65 (br d, J_{FF} = 198.2 Hz, 1 F), −23.82 (br d, J_{FF} = 198.2 Hz, 1 F); MS, exact mass calcd for $C_{11}H_8{}^{35}Cl_2F_2S_1$, 279.969, found, 279.970.

Fraction 2 (**27**, 9.8%): ^{1}H NMR δ 3.47 (dt, J_{HH} = 2.32 Hz, J_{HF} = 1.34 Hz, 2 H), 6.63 (tt, J_{HH} = 2.32 Hz, J_{HF} = 1.42 Hz, 1 H), 7.3–7.5 (m, 5 H); ^{19}F NMR δ −22.33 (br s); GC–MS, M$^+$ 280, major fragment ions at m/e 245 (M$^+$ − Cl), 183, 147, and 109 ($C_6H_5S^+$).

Fraction 3 [an inseparable mixture of **29** (12.8%) and *trans*- and *cis*-**30** (3.4% and 2.4%)]. **29**: ^{1}H NMR δ 2.61 (ddd, J_{HH} = 15.85, 2.69, 2.17 Hz, 1 H), 3.37 (ddd, J_{HH} = 15.85, 8.64, 2.46 Hz, 1 H), 4.37 (dd, J_{HH} = 8.64, 2.69 Hz, 1 H), 2.95 (ddd, J_{HH} = 14.42 Hz, J_{HF} = 5.53, 5.53 Hz, 1 H), 3.73 (ddd, J_{HH} = 14.42 Hz, J_{HF} = 18.22, 9.11 Hz, 1 H), 6.29 (dd, J_{HH} = 2.46, 2.17 Hz, 1 H), 7.3–7.5 (m); ^{19}F NMR δ −19.18 (ddd, J_{FF} = 183.3 Hz, J_{HF} = 9.11, 5.53 Hz, 1 F), −22.35 (ddd, J_{FF} = 183.3 Hz, J_{HF} = 18.22, 5.53 Hz, 1 F) [The ^{1}H and ^{19}F NMR spectra also indicated the presence of a very small amount (<0.3%) of an isomer of **29**.]; MS (of mixture), exact mass calcd for $C_{29}H_{16}{}^{35}Cl_2F_2S_2$, 428.004, found, 428.003.

***cis*-30**: ^{1}H NMR δ 2.71 (ddd, J_{HH} = 13.46 Hz, J_{HF} = 13.03, 6.07 Hz, 1 H), 3.16 (ddd, J_{HH} = 13.46 Hz, J_{HF} = 18.48, 9.01 Hz, 1 H), 4.71 (d, J_{HH} = 8.26 Hz, 1 H), 4.85 (dt, J = 8.26, 2.60 Hz, 1 H), 5.37 (br m, 1 H), 5.43 (br m, 1 H), 7.2–7.5 (m); ^{19}F NMR δ −21.25 (ddd, J_{FF} = 184.5 Hz, J_{HF} = 9.01, 6.07 Hz, 1 F), −26.23 (ddd, J_{FF} = 184.5 Hz, J_{HF} = 18.48, 13.03 Hz, 1 F).

***trans*-30**: ^{1}H NMR δ 2.66 and 3.25 (multiplets partially obscured by the peaks of *cis*-**30**), 4.05 (d, J_{HH} = 6.7 Hz, 1 H), 4.08 (dt, J_{HH} = 6.7, ~2.6 Hz, 1 H), 5.45 and 5.47 (br m), 7.2–7.5 (m); ^{19}F NMR δ −21.20 (ddd, J_{FF} = 184.2 Hz, J_{HF} = 8.92, 5.45 Hz, 1 F), −26.07 (ddd, J_{FF} = 184.2 Hz, J_{HF} = 19.27, 13.44 Hz, 1 F).

Reaction of Chloroallene (ClA) with 1122. Into a thick-walled Pyrex tube containing 200 μL of ClA cooled in dry ice was condensed ~1.0 mL of 1122. The contents of the tube were triply freeze degassed, and the tube was sealed under vacuum and heated in a sand bath at 160 °C for 24 h. The tube was allowed to cool and was opened, and the excess 1122 was allowed to evaporate. The ^1H (see Figure 1D) and ^{19}F NMR spectra were recorded. The reaction mixture was separated into several fractions by preparative GLC on a 18 ft × $^1/_4$ in. Carbowax 20M (column A) and a 12 ft × $^1/_4$ in. SE-30 (column B) on Chromosorb P. The mixture was subjected to GC–MS, indicating the presence of a 1:1 fraction, a single 1:2 adduct, one major and two intermediate and four minor 2:1 adducts, and a 2:2 adduct fraction. The yields of the major adducts has been estimated by a combination of the integrations of the ^1H and ^{19}F NMR and GC–MS spectra.

34 (fraction 1 from column A and fraction 5 from column B, 20.0%): ^1H NMR δ 3.38 (dt, J_{HH} = 2.93 Hz, J_{HF} = 0.86 Hz, 2 H), 6.83 (p, $J_{HH} \simeq J_{HF}$ = 2.93 Hz, 1 H); ^{19}F NMR δ −20.02 (s); MS, exact mass calcd for $C_5H_3{}^{35}Cl_3F_2$, 205.927, found, 205.929; GC–MS (fraction 1, of mixture of **34**, **35**, and **36**), major fragments at m/e 171 (M − Cl), 136 (M − 2Cl), 111 (M − Cl_2CCH_2), 74 (M − Cl_2CCF_2).

35 (fraction 3 from column A and fraction 6 from column B, 15.8%): ^1H NMR δ 3.47 (dt, J_{HH} = 2.56 Hz, J_{HF} = 0.89 Hz, 2 H), 6.35 (tt, J_{HH} = 2.56 Hz, J_{HF} = 1.24 Hz, 1 H); ^{19}F NMR δ −23.83 (s); MS, exact mass calcd for $C_5H_3{}^{35}Cl_3F_2$, 205.927, found, 205.928.

36 (not isolated from Column A, fraction 4 from column B containing some **35**, 17.3%): ^1H NMR δ 5.02 (ddd, J_{HH} = 2.22, 2.02 Hz, J_{HF} = 0.60 Hz, 1 H), 5.81 (ddt, J_{HH} = 2.22, 2.02 Hz, J_{HF} = 2.02 Hz, 1 H), 5.99 (ddt, J_{HH} = 2.22, 2.22 Hz, J_{HF} = 2.69 Hz, 1 H); ^{19}F NMR δ −23.06 (br d, J_{FF} = 200.9 Hz, 1 F), −23.44 (br d, J_{FF} = 200.9 Hz, 1 F).

37 (fraction 5 from column A and fraction 2 from column B as one very major isomer, 5.8%): ^1H NMR δ 2.67 (ddd, J_{HH} = 13.68 Hz, J_{HF} = 13.68, 4.41 Hz, 1 H), 3.32 (ddd, J_{HH} = 13.68 Hz, J_{HF} = 20.05, 8.71 Hz, 1 H), 4.57 [(apparent dt, J_{HH} = 4.45 (trans), 2.29 (long-range allylic) Hz, 1 H], 4.59 (d, J_{HH} = 4.45 Hz, 1 H), 5.59 (m, 1 H), 5.64 (m, 1 H); ^{19}F NMR δ −21.17 (ddd, J_{HF} = 8.71, 4.41 Hz, J_{FF} = 185.1 Hz, 1 F), −26.37 (ddd, J_{HF} = 20.05, 13.68 Hz, J_{FF} = 185.1 Hz, 1 H); GC–MS, M^+ 280; major fragment ions at m/e 245 (M^+ − Cl), 209 (M^+ − Cl − HCl), 148 (M^+ − 1122).

38 (fraction 7 from column A, fraction 3 from column B, 17.2%): ^1H NMR δ 2.73 (ddd, J_{HH} = 16.46, 2.44, 1.91 Hz, 1 H), 3.04 (ddd, J_{HH} = 14.81 Hz, J_{HF} = 13.09, 7.44 Hz, 1 H), 3.36 (ddd, J_{HH} = 16.46, 7.54, 1.91 Hz, 1 H), 3.50 (ddd, J_{HH} = 14.81 Hz, J_{HF} = 15.83, 9.55 Hz, 1 H), 4.76 (dd, J_{HH} = 7.54, 2.44 Hz, 1 H), 6.19 (t, J_{HH} = 1.91 Hz, 1 H); ^{19}F NMR δ −20.34 (ddd, J_{HF} = 7.44, 9.55 Hz, J_{FF} = 183.9 Hz, 1 F), −22.05 (ddd, J_{HF} = 15.83, 13.09 Hz, J_{FF} = 183.9 Hz, 1 F); GC–MS, M^+ m/e 280; major fragment ions at 245 (M −Cl), 209 (M − Cl, HCl), 148 [M − 1122 (ClA dimer)], 113 (ClA dimer − 35), 86, 77, and 64 (H_2CCF_2). (The GC–MS spectra of the other isomers of **38** were essentially identical.)

38b and **38c** (fraction 6 from column A as a mixture of diastereoisomers, present as a minor components in fraction 2 from column B). **38b** (5.5%): ^1H NMR δ 2.71 (ddd, J_{HH} = 13.74, 12.95, 2.45 Hz, 1 H), 3.30 (ddd, J_{HH} = 13.93 Hz, J_{HF} = 9.09, 19.71 Hz, 1 H), ~3.3 (ddd, J_{HH} = 13.74, 6.15, 0.98 Hz, 1 H), 5.55 (dd, J = 12.95, 6.15 Hz, 1 H), 6.08 (dd, J_{HH} = 2.45, 0.98 Hz, 1 H) (One hydrogen resonance appears in a complex multiplet at δ ~2.7 which could not be unambiguously assigned.); ^{19}F NMR δ −21.17 (ddd, J_{HF} = 4.33, 9.26 Hz, J_{FF} = 185.6 Hz, 1 F), −26.37 (ddd, J_{HF} = 19.71, 14.03 Hz, 1 F).

38c (5.2%): ^1H NMR δ 2.77 (ddd, J_{HH} = 15.46, 6.45, 2.99 Hz, 1 H), 3.30 (ddd, J_{HH} = 15.46, 8.69, 2.99 Hz, 1 H), 4.74 (dd, J_{HH} = 8.69, 6.45 Hz, 1 H), 6.32 (t, J_{HH} = 2.99 Hz, 1 H) [Two hydrogens appear in the δ 2.7–2.8 region which could not be unambiguously identified.]; ^{19}F NMR δ −22.27 (ddd, J_{HF} = 5.7, 8.3 Hz, J_{FF} = 185.8 Hz, 1 F), −25.88 (ddd, J_{HF} = 18.95, 13.31 Hz, 1 F).

38d–g (isolated as a complex mixture as fraction 7 from column B, total < 5%). Vinyl region of ^1H NMR: δ 5.82, 5.91, 6.06, 6.17, and 6.72 (multiplets). The remainder of the ^1H NMR spectrum was too complex to interpret. The ^{19}F NMR spectrum contained many ddd patterns consistent with the structures **38d–g**.

39 (not isolated from column A, fraction 8 from column B as a mixture of **39** and isomers of **38**, 3.2%): ^1H NMR δ 2.61 (br s, 4 H), 5.78 (br s, 2 H).[10]

40 (not isolated from either column A or B, fraction 5 from GC–MS, estimated 5% yield): GC–MS M^+, m/e 338, major fragment ions at m/e 303 (M^+ − Cl), 274 (M^+ − H_2CCF_2), 239 (274 − Cl), 206 (M^+ − $ClCHCCl_2$), 130 ($ClCHCCl_2$), 64 (H_2CCF_2).

41 (not isolated from either column A or B, fraction 15 from GC–MS; estimated yield, ~1%): GC–MS, M^+, m/e 412, major fragment ions at m/e 375 (M^+ − Cl), 350 (M^+ − $ClCHCH_2$), 348 (M^+ − H_2CCF_2), 280 (M^+ − 1122), 245 (M^+ − 1122 − Cl), 216 (280 − H_2CCF_2).

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Registry No. **4**, 10373-79-2; **5**, 103732-80-5; **6**, 103732-81-6; **7**, 96095-73-7; **8**, 96095-72-6; **10**, 103732-78-1; **11**, 103732-77-0; **18**, 103732-82-7; **19**, 103732-83-8; **20**, 103732-84-9; **21**, 103732-85-0; **26**, 103732-86-1; **27**, 103732-87-2; **28**, 103732-88-3; **29**, 103732-89-4; **30**, 103732-90-7; **34**, 103732-91-8; **35**, 103732-92-9; **36**, 103732-93-0; **37**, 103732-94-1; **38**, 103732-95-2; **39**, 103732-96-3; **40**, 103732-97-4; **41**, 103732-98-5; 1,1-dichloro-2,2-difluoroethene, 79-35-6; cyanoallene, 1001-56-5; methoxyallene, 13169-00-1; (phenylthio)allene, 1595-38-6; chloroallene, 3223-70-9.

An Excess Acidity Analysis of Acylal and Thioacylal Hydrolysis in Sulfuric Acid. Variation of ρ with Acidity[1]

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The excess acidity method has been applied to the hydrolysis reactions of some acylals and thioacylals in aqueous sulfuric acid mixtures. At low acidities, aryl thioacylals (RCH_2OCOCH_3, R = ArS) react by an A-2 mechanism involving two water molecules, but for aryl acylals (R = ArO) only one is involved. Both undergo a mechanistic switch to an A-1 pathway at high acidity. Linear free energy relationships for both substrates and both mechanisms were found to give acidity-dependent ρ values. Methoxymethyl (R = CH_3O) and (methylthio)methyl acetate (R = CH_3S) only show the A-1 reaction. Methylene diacetate (R = CH_3COO) has two A-1 hydrolysis pathways, one of them A-2-like, involving attack by an internal nucleophile.

Hammett ρ values are valuable sources of mechanistic information.[2] In acid-catalyzed hydrolysis process, ρ values of −3.64 (in 95% H_2SO_4 at 25 °C)[3] and −3.21 (99.99% H_2SO_4, 45 °C)[4] for methyl benzoates, and +1.99

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