Table III. Temperature Dependence of $(1 + K_2 + K_2K_3)/k_4K_2K_3$ and $(1 + K_3)/k_4K_3$

temp, °C	$(1 + K_2 + K_2K_3)/k_4K_2K_3$, s	$(1 + K_3)/k_4K_4$, s
30	2350 ± 90	2320 ± 190
40	800 ● 50	820 ● 70
50	340 ± 30	340 ± 20

Accordingly it follows that $k_{-3} \gg k_2$ because $k_{-3}K_5^{-1} \gg k_2K_1$. These results show that the negative charge on the amide nitrogen atom **2e** is delocalized over the acetyl group [$-N^-COCH_3 \leftrightarrow -N{=}C(O^-)CH_3$], and thus the nucleophilicity of the amide ion is decreased, whereas the negative charge is concentrated on the alkoxyl oxygen atom (**4e**).

Although the differences in the solvents are taken into account, the k_2K_1 values are fairly low compared with those in the reaction of **1e** with sodium isopropoxide in the Me_2SO–2-propanol mixture (20:80, v/v),[12] which may be attributed to the lower reactivity of methoxide ion (Table I).

Comparison of k_3 with k_{-2} is very interesting: in Table I $k_3 \gg k_{-2}$ in agreement with the results obtained in aromatic nucleophilic reactions of alkyl aryl ethers with amines[15] and supporting the experimental fact that no **1e**, which should be formed as shown in Scheme I, was found in the reaction of **6e** with CH_3OK.

Stage II. It is very interesting that the k^O_{obsd} and k^N_{obsd} vs. [CH_3OK] plots or their inversion plots coincide with each other (Figure 3). These results are considered to support Scheme I. From the intercepts in the inversion plots the parameters $(1 + K_2 + K_2K_3)/k_4K_2K_3$ and $(1 + K_3)/k_4K_3$ can be estimated, which represent the lower limits of the reciprocals of k^O_{obsd} and k^N_{obsd} (Table III).

From the coincidence of the inversion plots the following relations are derived (eq 17 and 18). In order for eq 17

$$\frac{1 + K_1K_2K_3K_5}{k_4K_1K_2K_3} = \frac{K_5}{k_4} \quad (17)$$

$$\frac{1 + K_2 + K_2K_3}{k_4K_2K_3} = \frac{1 + K_3}{k_4K_3} \quad (18)$$

to be valid, $K_1K_2K_3$ should be much greater than 1. It follows, therefore, that $k_3 \gg ca.\ 10^{-2}$, because the K_1K_2 values are ca. 10^2. Therefore, the K_3 value is larger than that in the reaction of **6e** with sodium isopropoxide in the Me_2SO–2-propanol (20:80, v/v),[12] which would be attributable to the kinds of alcohols and compositions of mixed solvents.

As treatment of **1a–d** with alkoxides yields the rearranged products **5a–e**, it is expected that $K_2 \gg 1$.[9] Therefore, eq 18 holds.

From Table III the $k_4K_3/(1 + K_3)$ values are (4.31 ± 0.35) × 10^{-4} (30 °C), (1.22 ± 0.10) × 10^{-3} (40 °C), and (2.94 ± 0.17) × 10^{-3} (50 °C) s^{-1}. These numbers approximately represent the k_4K_3 value, since K_3 is expected to be much small than 1.[12] Therefore, the rate constants of rearrangement (**1** ⟶ **5**) depend almost entirely on the decomposition stages of anionic σ complexs and are essentially independent of their formation stages. The smaller K_3 values should contribute to the relatively low rates of rearrangement.

Registry No. **1e**, 70320-89-7; **2e**, 90246-21-2; **3e**, 90269-12-8; **4e**, 90246-22-3; **5e**, 90246-23-4; **6e**, 87666-43-1.

(14) Bowden, K. *Chem. Rev.* **1979**, *70*, 667.
(15) Terrier, F. *Chem. Rev.* **1982**, *82*, 77.
(16) The synthesis of **6a–d** were unsuccessful, because they might easily rearrange to protonated **5a–d** even if they are formed.
(17) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

(2 + 2) and (2 + 4) Cycloadditions of Fluorinated Allenes

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Various (2 + 2) and (2 + 4) cycloadditions of difluoroallene and fluoroallene are presented and discussed mechanistically. The results are interpreted as reinforcing the hypothesis that distinct, and at times competing, concerted (2 + 4) and nonconcerted (2 + 2) mechanisms are involved.

1,1-Difluoroallene (DFA) has been shown[1] to undergo regiospecific (2 + 4) cycloadditions with respect to DFA, with the C_2–C_3 bond being exclusively incorporated into the new ring, while, in contrast, little regioselectivity with respect to the diene component is observed. In comparison to its (2 + 4) behavior, the (2 + 2) cycloadditions of DFA exhibit a lack of regiospecifity with respect to the DFA and increased regioselectivity with respect to the other (2 + 2) component (Scheme I).[1]

Likewise, fluoroallene (MFA) has been reported to undergo (2 + 4) cycloadditions with similar regiochemical behavior (Scheme II).[2]

These results were interpreted as deriving from the involvement of distinct and, in the case of the acyclic dienes, competitive, concerted (2 + 4) and nonconcerted (2 + 2) mechanistic processes. We present, at this time, results from a number of additional (2 + 4) and (2 + 2) cycloadditions of fluorine-substituted allenes, results which we believe provide additional support for the hypothesis of distinct mechanisms for the two modes of reaction.

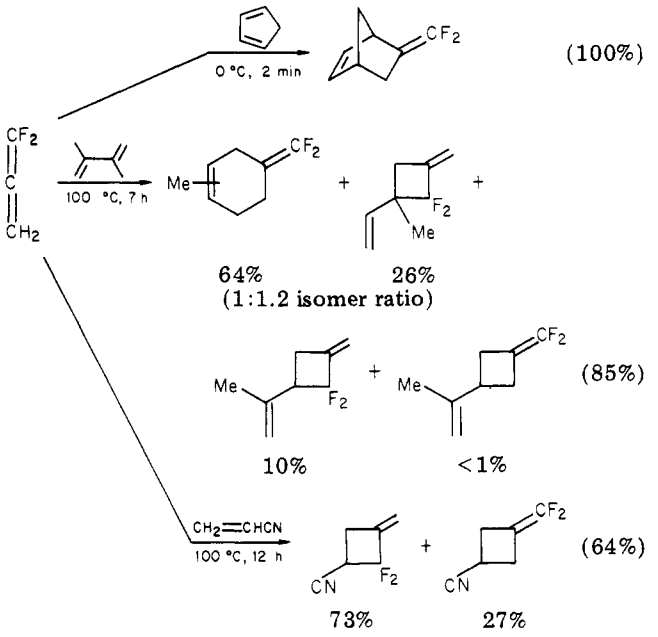
Results and Discussion

(2 + 4) Cycloadditions. A number of additional cycloaddition reactions of DFA were studied with the aim

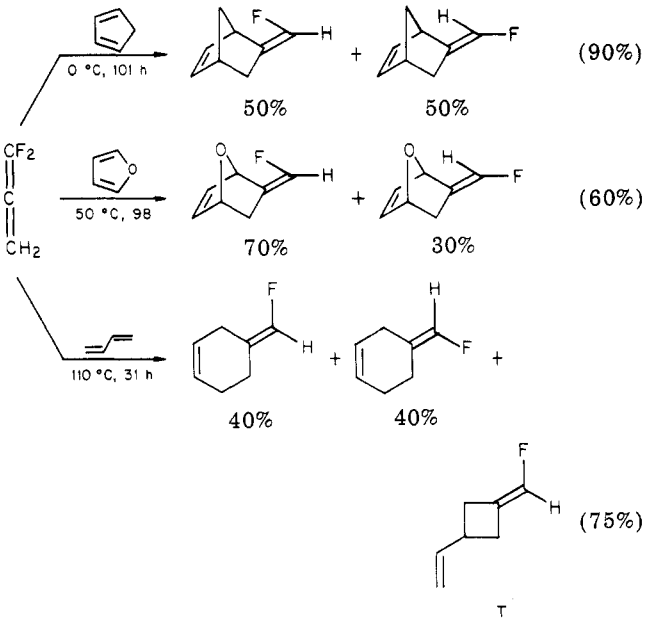
(1) Dolbier, W. R., Jr.; Piedrahita, C. A.; Houk, K. N.; Strosier, R. W.; Gandour, R. W. *Tetrahedron Lett.* **1978**, 2231.
(2) Dolbier, W. R., Jr.; Burkholder, C. R. *Tetrahedron Lett.* **1980**, *21*, 785.

0022-3263/84/1949-2381$01.50/0

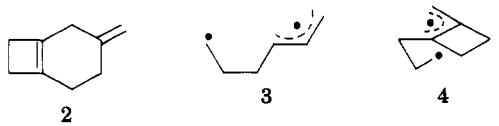
Scheme I



Scheme II



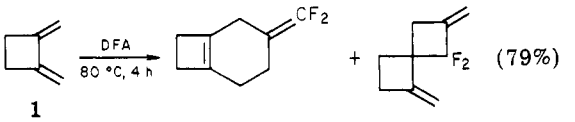
of further elucidation of the mechanism of these reactions. The reaction of DFA with 1,2-dimethylenecyclobutane, **1**, was examined in the hope of detecting some amount of the as yet unobserved adduct of the type **2**, which would be



2 3 4

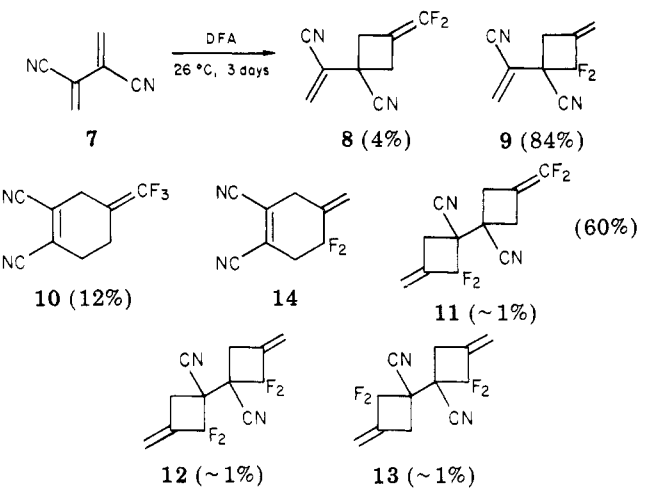
indicative of a diradical pathway for the (2 + 4) reaction. The particular cisoid geometry of **1** has been demonstrated to impose an inhibition on its potential concerted (2 + 4) cycloadditions because of the unusually large distance (3.35 Å) between the termini of **1** as opposed to that of cyclopentadiene (2.44 Å) or cisoid butadiene (2.89 Å).[3] Acyclic dienes are likely to undergo (2 + 2) reactions largely via such extended diradicals as **3** that are structurally incapable of forming (2 + 4) adducts, while cyclic dienes such as cyclopentadiene apparently will, at least with DFA and MFA, not form diradicals competitive with the concerted (2 + 4) process. However, if such a rigid cisoid diene as **1** should form a diradical (i.e., **4**), then one might expect there to be a reasonable chance of observing *some* diradical-derived (2 + 4) adduct.

Indeed a considerable amount of (2 + 2) adduct was observed in the reaction of DFA with **1**. However, the *only* observed (2 + 4) adduct was that one expected from the concerted reaction.



1 5 76:24 6

In looking at the reaction of DFA with the electron-deficient diene, 2,3-dicyano-1,3-butadiene, **7**, it was expected that the concerted cycloaddition would be inhibited, with concomitant enhancement of all diradical processes.



7 8 (4%) 9 (84%)

10 (12%) 14 11 (~1%)

12 (~1%) 13 (~1%)

While the (2 + 4) reaction was indeed significantly diminished, with the (2 + 2) products dominating, the elusive type of adduct **14** was still nowhere to be found. As can be seen, some 2:1 adducts could be isolated from this reaction as well.

In each of the above reactions, as well as in those communicated earlier,[1] the major (2 + 2) adducts proved to be those with the CF_2 group *in the ring*, the position of greater thermodynamic stability.[4,5]

As mentioned earlier, the (2 + 4) cycloadditions of fluoroallene are as regiospecific as those of DFA, although fluoroallene is significantly *less* reactive in such reactions than DFA. In the reaction with cyclopentadiene at 0 °C, DFA's reaction is effectively instantaneous, while fluoroallene requires ~100 h for complete reaction. (In stark contrast to both, allene requires ~200 °C for 6 h in a very poor yield reaction.)[6]

The composite picture of those (2 + 4) cycloadditions of DFA and fluoroallene that have been examined provides us with a clear picture of such reactions. In each case regiospecificity is strictly observed such that the fluorine-substituted allene terminus is never involved in ring

(3) Bartlett, P. D.; Wingrove, A. S.; Owyang, R. *J. Am. Chem. Soc.* **1968**, *90*, 6067.

(4) Dolbier, W. R., Jr.; Medinger, K. S.; Greenberg, A.; Liebman, J. F. *Tetrahedron* **1982**, *38*, 2415.

(5) Dolbier, W. R., Jr.; Piedrahita, C. A. *Tetrahedron Lett.* **1979**, 2957.

(6) Pledger, H., Jr. *J. Org. Chem.* **1960**, *25*, 278.

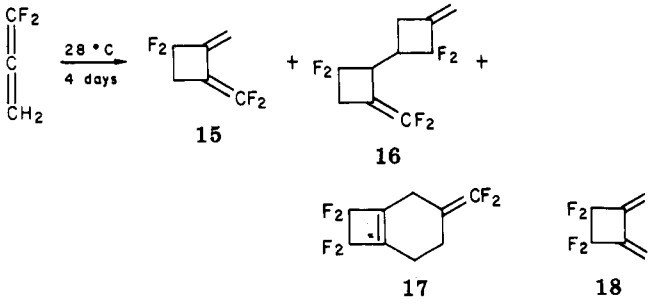
formation. Moreover no evidence has been found in any of these reactions for either inverse electron demand or biradical-involved (2 + 4) processes.

(2 + 2) Cycloadditions. As one can see from the nature of the (2 + 2) adducts reported earlier as well as in the reactions discussed above, the (2 + 2) cycloadditions of DFA and MFA proceed as one would expect for reactions involving *diradical* intermediates—that is, a *mixture* of regioisomers is obtained with the ratios of products generally being consistent with (1) the relative stabilities of potential diradical intermediates and (2) the relative stabilities of the products.

Nevertheless, such conclusions have been reached on the basis of only a few reactions. Therefore we report at this time a number of other related studies that allow one to gain a much broader perspective of the kinetic behavior of the diradicals involved in these reactions.

Since some dimerization was generally observed as a competitive process in each (2 + 2) cycloaddition study, this reaction was examined in detail. It had earlier been reported[7] that the dimerization of DFA gave only one product, **15**.

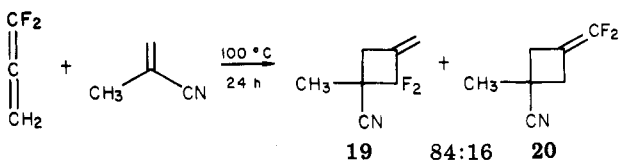
In our study difluoroallene was kept in a sealed tube at room temperature for 4 days. After this time, roughly half of the difluoroallene had reacted. In addition to polymeric material, three products were obtained. They proved to



be **15**, **16**, and **17**, which were present in relative yields of 33%, 17%, and 49%. The neat dimer **15** was very unstable to polymerization at room temperature and had to be kept at dry ice temperature. No dimer **18** could be detected in the reaction mixture. Presumably it is converted rapidly to trimer **17** under the reaction conditions by reaction with difluoroallene.

Due to the polymerization and the presence of minor products which were not isolated, the relative amounts of initial (2 + 2) cycloadducts cannot be determined accurately. However, it can reasonably be concluded that the dimerization of DFA is *not* a regiospecific reaction, that dimers **15** and **18** are both formed, probably in comparable amounts.

The reaction of difluoroallene with methacrylonitrile gave a 39% isolated yield of products **19** and **20** along with 9% of isolated DFA trimer **17**. It is worth noting that the observed regioselectivity in formation of adduct **19** (84%) in the reaction of DFA with methacrylonitrile is *greater* than that observed in its similar reaction with acrylonitrile (73%).[1,8]



(7) Banks, R. E.; Haszeldine, R. N.; Taylor, D. L. *J. Chem. Soc.* **1965**, 978.

(8) Burkholder, C. R. Ph.D. Dissertation, University of Florida, 1983.

Scheme III

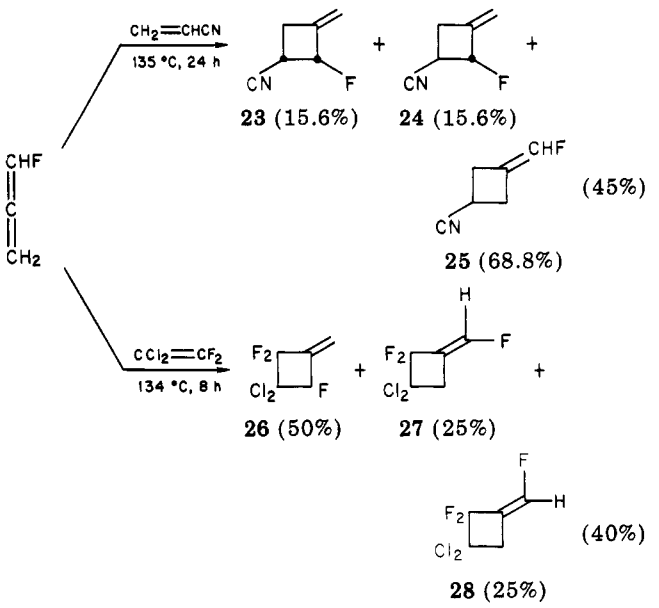
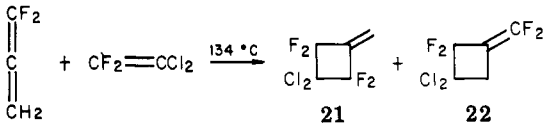


Table I. Summary of Product Ratios from Difluoroallene (2 + 2) Cycloadditions

$X_2C{=}CYZ$					
X	Y	Z	temp, °C	29	30
H	CN	$CH_2{=}CCN$	28	95	5
H	CN	CH_3	110	84	16
H	CN	H	110	77	23

It was also found that dichlorodifluoroethylene reacted with difluoroallene at 135 °C to give cycloadducts **21** and **22** in a ratio that was dependent upon the time of reaction. After 1 h the ratio was 51:49 while after 27 h this ratio was 27:73.



Fluoroallene offers a contrast to the behavior of DFA in (2 + 2) reactions. As can be seen in its reactions with butadiene, its fluorine-substituted carbon ends up vinylic, rather than on the ring.[2] Two further examples, the reactions of fluoroallene with acrylonitrile and with 1,1-difluoro-2,2-dichloroethylene demonstrate that, as for DFA, regiospecificity is not the rule in the (2 + 2) reactions of fluoroallene, but that, in general, the more thermodynamically stable isomers, i.e., the ones with *vinylic* CHF,[4] are formed preferentially (Scheme III).

It is also noteworthy that differences in reactivity are diminished in the (2 + 2) reactions of DFA, fluoroallene, and allene. (All three will react with acrylonitrile at 130 °C).

A summary of the (2 + 2) cycloadditions of olefins with difluoroallene where reliable kinetically controlled ratios were obtained is presented in Table I. The methylenecyclobutane products **29** and **30** are obtained in the indicated ratios. Though a number of 1,3-diene cycloadditions have been studied previously,[1] in only the reaction with dicyanobutadiene was one able to isolate a product with structure **30**.

While the number of examples is certainly limited, there seems to be a rough correlation between the stability of the biradical intermediate and the product ratio. This correlation may be explained by applying the Hammond

postulate to closure of the biradical intermediate. The longer lived, more stable the biradical intermediate, the later the transition state and the more the transition state resembles the products. Therefore the thermodynamic preference of geminal fluorines for an sp^3 carbon leads to predominant closure of CF_2 to give fluorines on the cyclobutane ring.

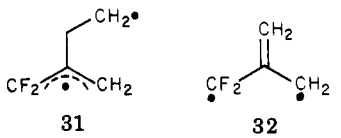
It should be noted that what little data there is for fluoroallene cycloadditions is also consistent with this hypothesis. Remembering that the thermodynamic preference for a single fluorine substituent is for sp^2 carbon[4] one would predict an *opposite* trend for the product ratios from the closure of the fluoroallyl biradical. This seems to be the case.

It should be mentioned that no (2 + 2) reactions of DFA or fluoroallene with *electron-rich* olefins have yet been carried out with success, although a number have been attempted.

Conclusions

There can be little doubt as to the overwhelming effect of fluorine substituents on the behavior of allene in Diels–Alder reactions. In every case studied thus far, the fluorine substituents have directed and enhanced (2 + 4) cycloaddition to the non-fluorine-substituted π bond. We have rationalized this effect earlier[9] in terms of fluorine's unique π-donating and σ-withdrawing character. Photoelectron spectra indicate a lack of significant orbital energy change upon direct attachment of fluorine to a π system. Allylic fluorine, in contrast, lowers energies by "negative hyperconjugation", that is by admixture of the π^* CF_2 orbital into the π in a bonding fashion. Thus the C_1–C_2 π orbitals of DFA and monofluoroallene are influenced little by the fluorine substituents, so that C_1–C_2 is, like allene, an electron-rich double bond and unreactive in (2 + 4) reactions; the C_2–C_3 π orbitals are very electron deficient and thus reactive in (2 + 4) reactions as are other alkenes with allylic fluorine substituents. In fact, because of the rigid eclipsing of the C–F bonds with the C_2–C_3 π bond and the greater proximity of these interacting orbitals, the activating effects in the allenes shoud be (and apparently are) even greater than they are for simple allylic fluorine-substituted systems. Thus the behavior of the fluorine-substituted allenes in (2 + 4) cycloadditions is completely consistent with expectations based upon the FMO theory of concerted cycloadditions.[10]

Our understanding of the (2 + 2) reactions is more less complete, largely because the general lack of understanding of those factors which control the kinetic behavior of diradicals such as **31**. This is an area of considerable interest



31 **32**

to us. Indeed we have just communicated our first results on the kinetic behavior of fluorine-substituted trimethylenemethane diradicals such as **32**.[11] For such diradicals as **32** there is strong evidence that their relative rates of cyclization are *completely unrelated* to the thermodynamic stability of the products. In contrast, the results presented in this paper, as well as those in earlier communications,[1,2] seem to indicate a significant correlation of kinetic behavior of diradicals such as **31** with thermodynamic stability of the cyclization products.

Because of the virtual lack of a "steric" factor in fluorine-substituted diradicals, studies of diradicals such as **31** and **32** have special significance. Such studies may indeed be able to provide us with insights into the intrinsic behavioral patterns of diradicals that are unobtainable elsewhere.

Experimental Section

Infrared spectra were determined either as films between KBr plates or in solution with matched liquid cells (0.1 mm). Gas-phase spectra were determined by using a gas IR cell with KBr windows and a 5-cm path length using 10–20 mm pressure of sample. NMR chemical shifts for ^1H spectra are reported in parts per million downfield from internal Me_4Si in $CDCl_3$ solution. Chemical shifts for ^{19}F spectra are reported in parts per million upfield from internal $CFCl_3$ in $CDCl_3$ solution. Chemical shifts for ^{13}C spectra are reported in parts per million downfield from internal Me_4Si in $CDCl_3$ solution. All assignments of ^{13}C NMR resonances are made with the aid of off-resonance spectra or pulse-sequence spectra.

3-(Difluoromethylene)bicyclo[4.2.0]oct-1(6)-ene (5) and 2,5-Bis(methylene)-1,1-difluorospiro[3.3]heptane (6). Into a 5-mL glass tube containing 200 mg (2.50 mmol) of 1,2-dimethylenecyclobutane[12] was condensed 206 mg (2.71 mmol) of difluoroallene.[13] The tube was sealed under vacuum and kept at room temperature for 2 days and then heated at 80 °C for 4 h. The tube was cooled and opened. The products were isolated by preparative GLPC (20 ft by $^1/_4$ in 20% SE-30 at 120 °C 80 mL/min) to give 223 mg (57%) of **5** and 86 mg (22%) of **6**.

5: bp 156.0–156.8 °C; IR (film) 2923, 2845, 1760 (s), 1690 (w), 1438, 1270, 1236, 1210, 1080, 1007, 940 cm^{-1}; ^1H NMR (100 MHz) δ 2.59 (m, 2 H), 2.46 (m, 4 H), 2.24 (m, 2 H), 2.03 (m, 2 H); ^{19}F NMR (100 MHz) ϕ 94.4 and 99.3 (AB pattern), J_{FF} = 59.8 Hz); ^{13}C NMR (100 MHz) δ 152.0 (t, J_{CF} = 281.6 Hz, CF_2), 141.9 (C_6), 138.7 (d, J_{CF} = 2.4 Hz, C_1), 84.9 (t, J_{CF} = 18.9 Hz, C_3), 30.5 (CH_2), 30.2 (CH_2), 25.1 (t, J_{CF} = 2.1 Hz, CH_2), 24.1 (t, J_{CF} = 1.8 Hz), 2].2 (dd, J_{CF} = 3.1 and 1.2 Hz); mass spectrum gave M^+ 156.074 06 ± 0.001 37 (9 ppm), calcd for $C_9H_{10}F_2$ 156.075 06, deviation −0.0010 (6 ppm). Anal. ($C_9H_{10}F_2$) C, H.

6: bp 142.5–143.0 °C; IR (film) 3090, 2997, 2960, 2935, 1680, 1428, 1278, 1090, 1017, 990, 918, 886 cm^{-1}; ^1H NMR (100 MHz) δ 5.52 (d of pentet, 1 H, J_{gem} = 0.98, J = 2.9 Hz), 5.19 (d of pentet, 1 H, J_{gem} = 0.98, J = 2.4 Hz), 4.99 (m, 1 H), 4.94 (m, 1 H), 2.8–2.4 (complex m, 5 H), 1.96 (m, 1 H; ^{19}F NMR (100 MHz) ϕ 105.4 (complex m); ^{13}C NMR (100 MHz) δ 147.8 (t, J_{CF} = 2.4 Hz, C_5), 144.0 (t, J_{CF} = 21.4 Hz, C_2), 118.4 (t, J_{CF} = 283.8 Hz, CF_2), 112.1 (=CH_2), 107.3 (=CH_2), 56.8 (t, J_{CF} = 22.6 Hz, C_4), 36.8 (t, J_{CF} = 8.5 Hz, C_3), 28.0 (C_6), 24.3 (t, J_{CF} = 4.0 Hz, C_7); mass spectrum gave M^+ 156.073 83 ± 0.001 69 (11 ppm), calcd for $C_9H_{10}F_2$ 156.075 06, deviation −0.001 23 (8 ppm).

The combined yield of isolated products was 79%. Order of elution was **6** and then **5**. The GLPC relative yields were 76% for **5** and 24% for **6**.

1-(1-Cyanoethenyl)-2,2-difluoro-3-methylenecyclobutanecarbonitrile (9), 1-(1-Cyanoethenyl)-3-(difluoromethylene)cyclobutanecarbonitrile (8), 4-(Difluoromethylene)-1-cyclohexene-1,2-dicarbonitrile (10), 3,3′-Bis(methylene)-2,2,2′,2′-tetrafluoro[1,1′-bicyclobutyl]-1,1′-dicarbonitrile (12 and 13), and 2,2-Difluoro-3′-(difluoromethylene)-3-methylene-[1,1′-bicyclobutyl]-1,1′-dicarbonitrile (11). Into a 30-mL glass tube containing a solution of 1.00 g (9.6 mmol) of 1,3-butadiene-2,3-dicarbonitrile[14] in 10 mL of $CHCl_3$ was condensed 2.89 g (38.0 mmol) of difluoroallene.

The tube was sealed under vaccum and kept at room temperature for 4 days. The clear, colorless solution was concentated

(9) Domelsmith, L. N.; Houk, K. N.; Piedrahita, C. A.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6908.
(10) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.
(11) Dolbier, W. R., Jr.; Burkholder, C. R. *J. Am. Chem. Soc.* **1984**, *106*, 2139.
(12) Doering, W. von E.; Dolbier, W. R., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 4534.
(13) Dolbier, W. R., Jr.; Burkholder, C. R.; Piedrahita, C. A. *J. Fluorine Chem.* **1982**, *20*, 637.
(14) Bellus, D.; Weis, C. D. *Tetrahedron Lett.* **1973**, 999.

by rotary evaporation at reduced pressure to approximately 2 mL and then filtered to remove a minute amount of insoluble material.

The products were isolated by preparative GLPC (10 ft by $^1/_4$ in. 20% SE-30 at 160 °C, 60 mL/min): **8** and **9** eluted together, then **11** and **12** together, and finally **10** and **13** together. The yields were 1.22 g for **8** and **9**, 85 mg for **11** and **12**, and 168 mg for **10** and **13**. Further separation by preparative GLPC (10 ft by $^1/_4$ in. 10% DEGS at 160 °C, 60 mL/min) gave 989 mg (57.2%) of white solid **9**: mp 35.0–36.1 °C (sublimed); IR (CCl_4) 3120, 3000, 2250, 2230, 1930, 1870, 1790, 1690, 1616, 1283 (s), 1164 (s), 1125 (s) cm^{-1}; ^1H NMR (100 MHz) δ 6.44 and 6.41 (AB pattern, 2 H, J = 1.3 Hz), 5.85 (hextet, 1 H, J = 2.4 Hz), 5.60 (hextet, 1 H, J = 2.4 Hz), 3.27 (non-first-order m, 2 H); ^{19}F NMR (300 MHz) ϕ 91.9 and 98.4 (AB pattern, J_{FF} = 205 Hz); ^{13}C NMR (100 MHz) δ 138.6 (t, J_{CF} = 20.1 Hz, C_3), 136.9 (=CH_2), 118.4 (=CH_2), 115.7, 115.4 (t, J = 293.6 Hz, CF_2), 114.5, 49.6 (dd, J_{CF} = 22.6 and J_{CF} = 26.2 Hz, C_1), 35.4 (t, J_{CF} = 6.7 Hz, C_4); mass spectrum gave M^+ 180.049 66 ± 0.0019 (11 ppm), calcd for $C_9H_6N_2F_2$ 180.0499, deviation −0.00024 (1 ppm). Anal. ($C_9H_6N_2F_2$) C, H, N.

8: 30 mg (1.7%) of white solid; mp 32.3–34.0 °C; IR (CCl_4) 3120 (w), 2943 (w), 2245 (w), 2230 (w), 1794 (s), 1617 (w), 1277 (s) cm^{-1}; ^1H NMR (60 MHz) δ 6.33 (d, 1 H, J = 1 Hz), 6.25 (d, 1 *H*, J = 1 Hz), 3.4 (t, 4 H, J_{HF} = 4.0 Hz); ^{19}F NMR (300 MHz) ϕ 91.5 (pentet, J_{FH} = 3.9 Hz); ^{13}C NMR (100 MHz) δ 151.6 (t, J_{CF} = 286.3 Hz, =CF_2), 132.7 (=CH_2), 121.6, 119.0, 114.3, 78.7 (t, J_{CH} = 29.3 Hz, =CR_2), 35.9 (CH_2); mass spectrum gave M^+ 180.484 ± 0.0012 (7 ppm), calcd for $C_9H_6N_2F_2$ 180.0499, deviation −0.0015 (8 ppm).

10: 25 mg (1.4%) of white solid; ^1H NMR (100 MHz) δ 3.14 (pentet, 2 H, J = 2.2 Hz), 2.5–2.4 (non-first order m, 4 H); ^{19}F NMR (100 MHz) ϕ 90.1 and 94.0 (AB pattern with pentet fine structure, J_{FF} = 47.5 and J_{HF} = 2.0 Hz).

12 (or **13**): 20 mg (0.81%) white solid; mp 142–145.5 °C; IR ($CHCl_3$) 2255 (w), 1880 (w), 1794 (w), 1738 (w), 1690 (w), 1431, 1379 (s), 1159 (s), 1124 (s), 1012 936 cm^{-1}; ^1H NMR (100 MHz) δ 5.9 (m, 1 H, J = 2 Hz), 5.6 (m, 1 H, J = 2 Hz), 3.2 (non-first-order m, 2 H); ^{19}F NMR (300 MHz) ϕ 88.9 and 98.6 (AB pattern, J_{FF} = 211.1 Hz); ^{13}C NMR (300 MHz) δ 138.4 (t, J_{CF} = 20.7 Hz, C_3), 119.4 (=CH_2), 115.5 (dd, J_{CF} = 288.8 and J_{CF} = 295.4 Hz, CF_2), 113.3 (d, J_{CF} = 3.2 Hz, CN), 48.4 (t, J_{CF} = 23 Hz, C_1), 34.2 (dd, J_{CF} = 6.0 and J_{CF} = 8.7 Hz, C_4); mass spectrum gave M^+ 255.054 66 ± 0.0020 (8 ppm), calcd for $C_{12}H_7N_2F_4$ 255.054 53, deviation 0.000 12 (0.5 ppm).

13 (or **12**): 21 mg (0.85%) white solid; mp 82–86.5 °C; IR (CCl_4) 1745 (w), 1711 (w), 1431 (w), 1288 (s), 1135, 907 cm^{-1}; ^1H NMR (60 MHz) δ 5.9 (m, 1 H, J = 2.5 Hz), 5.6 (m, 1 H, J = 2.5 Hz), 3.1 (m, 2 H); ^{19}F NMR (300 MHz) ϕ 90.7 and 98.8 (AB pattern, J_{FF} = 215.4 Hz); ^{13}C NMR (300 MHz) δ 138.4 (t, J_{CF} = 21.1 Hz, C_3), 119.2 (=CH_2), 114.8 (t, J_{CF} = 292 Hz, CF_2), 113.9 (d, J_{CF} = 2.7 Hz, CN), 47.9 (dd, J_{CF} = 22.2 and J_{CF} = 27.3 Hz, C_1), 33.6 (br s, C_4) mass spectrum gave M^+ 255.053 79 ± 0.0016 (6 ppm), calcd for $C_{12}H_7N_2F_4$ 255.054 53, deviation −0.000 74 (3 ppm).

11: 28 mg (1.1%) white solid; mp 78.6–80.0 °C; IR (CCl_4) 2940 (w), 1794 (s), 1430, 1278 (s), 1155, 1126, 1112 cm^{-1}; ^1H NMR (60 MHz) δ 5.9 (pentet, 1 H, J = 3 Hz), 5.6 (pentet, 1 H, J = 2.5 Hz), 3.3 (m, 4 H), 3.1 (m, 2 H); ^{19}F NMR (300 MHz) ϕ 89.9 and 101.2 (AB pattern, 2 F, J_{FF} = 214.3 Hz), 90.8 (pentet, F, J_{HF} = 1.9 Hz); ^{13}C NMR (300 MHz) δ 151.6 (t, J_{CF} = 287.0 Hz, =CF_2), 138.4 (t, J_{CF} = 20.5 Hz, C_3), 119.1 (=CH_2), 118.8, 115.2 (dd, J_{CF} = 289.4 and J_{CF} = 293.2 Hz, CF_2), 114.2 (d, J_{CF} = 3.6 Hz), 78.4 (t, J_{CF} = 32 Hz, $C_{3'}$), 51.2 (t, J_{CF} = 24.8 Hz, C_1), 33.7 ($C_{2'}$), 34.2 (d, J_{CF}= 2.5 Hz, $C_{1'}$), 33.0 (dd, J_{CF} = 6.6 and J_{CF} = 7.9 Hz, C_4); mass spectrum gave M^+ 255.053 34 ± 0.0021 (8 ppm), calcd for $C_{12}H_7N_2F_4$ 255.054 53, deviation −0.0012 (5 ppm).

The total combined yield was 63%. The order of elution on DEGS was **8**, **9**, **11**, **12**, **13**, and then **10**. The relative yields were 4.1%, 79.3%, 2.7%, 1.4%, 1.4%, and 11.2%, respectively, as determined by GLPC integration as well as ^{19}F NMR integration.

1,1-Difluoro-3-(difluoromethylene)-2-methylenecyclobutane (15), 7-(Difluoromethylene)-2-methylene-1,1,5,5-tetrafluorospiro[3.3]heptane (16), and 3-(Difluoromethylene)-7,7,8,8-tetrafluorobicyclo[4.2.0]oct-1(6)-ene (17). Into a 10-mL glass tube containing 20 mg of hydroquinone was condensed 1.10 g (14.5 mmol) of difluoroallene. The tube was sealed under vacuum and kept in the dark at room temperature for 108 h. The tube was cooled and opened. The volatile components were transferred on the vacuum line to a flask, and the products were isolated by preparative GLPC (10 ft by $^1/_4$ in. 10% TCP at 28 °C, 60 mL/min) to give 67 mg (6.1%) of dimer **15**: IR (gas) 1765 (s), 1430 (w), 1320, 1290, 1204, 1133, 1070, 1023 cm^{-1}; ^1H NMR (100 MHz) δ 5.58 (m, 1 H), 5.35 (m, 1 H), 3.20 (tt, 2 H, J_{HF} = 4.3 and J_{HF} = 10.0 Hz); ^{19}F NMR (100 MHz) ϕ 80.0 (dtt, 1 F, J_{FF} = 31.0, J_{HF} = 4.3, and J_{HF} = 1 Hz, 98.4 (tt, 2 F, J_{HF} = 10.1 and J_{HF} = 2.6 Hz).

From the nonvolatile liquid fraction was isolated by preparative GLPC (10 ft by $^1/_4$ in. 10% TCP at 120 °C, 60 mL/min) 35 mg (3.2%) of trimer **16** and 100 mg of trimer **17**.

16: bp 143.5–144.0 °C; IR (film) 2955 (w), 1972 (s), 1430, 1305, 1280, 1262, 1110, 955, 880 cm^{-1}; ^1H NMR (100 MHz) δ 5.62 (m, 1 H), 5.30 (m, 1 H), 3.3–3.0 (complex m, 3 H), 2.7 (d of m, 1 H, J = 16.7 Hz); ^{19}F NMR (100 MHz) ϕ 85.6 (dd, 1 F, J_{FF} = 48.7 and J_{HF} = 12.3 Hz), 86.9 (d, 1 F, J_{FF} = 48.7 Hz), 98.1 (dd, 1 F, J_{FF} = 220.1 and J_{HF} = 11.8 Hz), 101.1 (non-first-order m, 2 F), 104.9 (dd, 1 F, J_{FF} = 220.1 and J_{HF} = 27.7 Hz); mass spectrum gave M^+ 228.036 88 ± 0.001 95 (8 ppm), calcd for $C_9H_6F_6$ 228.037 37, deviation −0.000 49 (2 ppm).

17: bp 173.0–174.5 °C; IR (film) 2930, 1766 (s), 1436, 1334 (s), 1304, 1254, 1212, 1103 (s), 953, 918, 874 cm^{-1}; ^1H NMR (60 MHz) δ 2.92 (m, 2 H), 2.39 (m, 4 H); ^{19}F NMR (300 MHz) ϕ 90.7 (d of pentet, 1 F, J_{FF} = 50.3 and J_{HF} = 1.7 Hz), 94.4 (d of pentet, 1 F, J_{FF} = 50.3 and J_{HF} = 2.0 Hz), 113.6 and 113.7 (non-first-order AB pattern, 2 F); ^{13}C NMR (100 MHz) δ 153.0 (t, J_{CF} = 284.7 Hz, =CF_2), 119.6 (t with non-first-order fine structure, J_{CF} = 287, J_{CF} = 30.8, and J_{CF} = 25.3 Hz, CF_2CF_2), 81.7 (dd, J_{CF} = 19.8 and J_{CF} = 21.7 Hz, C_3), 20.2 (d, J_{CF} = 2.4 Hz, CH_2), 19.5 (t, J_{CF} = 1.8 Hz, CH_2), 19.1 (t, J_{CF} = 2.1 Hz, CH_2); mass spectrum gave M^+ 228.037 80 ● 0.000 96 (4 ppm) calcd for $C_9H_6F_6$ 228.037 37, deviation 0.000 43 (2 ppm).

The combined yield of isolated products was 18.4%. The reaction was roughly 50% complete judging from the amount of unreacted difluoroallene. Order of elution was **15**, **16**, and then **17**. The relative yields were 33% for **15**, 17% for **16**, and 62% for **17**. There were numerous minor products that were not isolated dur to their small concentrations.

2,2-Difluoro-1-methyl-3-methylenecyclobutanecarbonitrile (19) and 1-Methyl-3-(difluoromethylene)cyclobutanecarbonitrile (20). Into a 20-mL glass tube containing 4.00 g (59.6 mmol) of methacrylonitrile was condensed 641 mg (8.43 mmol) of difluoroallene. The tube was sealed under vacuum and heated at 110 °C for 24 h. After cooling and opening, the excess methacrylonitrile was removed by distillation. After vacuum transfer of the residue, preparative GLPC (20 ft by $^1/_4$ in. 20% Carbowax 20M at 130 °C, 40 mL/min) gave 402 mg (33%) of **19** and 147 mg of a mixture of **20** and trimer **17**.

19: bp 171.8–172.0 °C; IR (film) 3000, 2950, 2248, 1694 (w), 1432, 1279, 1123, 1100, 1053, 1022, 933 cm^{-1}; ^1H NMR (100 MHz) δ 5.71 (m, 1 H), 5.43 (hextet, 1 H, J = 2.2 Hz), 3.08 (d of m, 1 H, J = 16.0 Hz), 2.57 (d of m, 1 H, J = 16.0 Hz), 1.6 (dd, 3 H, J = 1.8 and J = 0.7 Hz); ^{19}F NMR (100 MHz) ϕ 97.9 (d of septet, 1 F, J_{FF} = 206.4 and J_{HF} = 2.2 Hz), 105.5 (d of m, 1 F, J_{FF} = 206.4 Hz); ^{13}C NMR (100 MHz) δ 140.7 (dd, J_{CF} = 20.1 and J_{CF} = 21.4 Hz, C_3), 118.5 (d, J_{CF} = 4.3 Hz, CN), 116.6 (d, J_{CF} = 1.2 Hz, =CH_2), 116.2 (dd, J_{CF} = 282.9 and 293.9 Hz, CF_2), 41.6 (dd, J_{CF} = 20.4 and 25.3 Hz, C_1), 37.0 (dd, J_{CF} = 9.2 and 5.5 Hz, C_4), 18.4 (d, J_{CF} = 5.5 Hz, CH_3); mass spectrum gave $(M-1)^+$ 142.045 68 ± 0.000 84 (6 ppm), calcd for $C_7H_6NF_2$ 142.046 83, deviation −0.001 16 (8 ppm). Anal. ($C_7H_7NF_2$) C, H, N.

20 and **17**: further separation by preparative GLPC (20 ft by $^1/_4$ in. 20% SE-30 at 110 °C, 45 mL/min) gave 50.5 mg (7.9%) of trimer **17** and 76 mg (6.3%) of pure **20**: bp 160.5–161.0 °C; IR (film) 2985, 2943, 2880 (w), 2853 (w), 2240, 1795 (s), 1766 (w), 1430, 1260 (s), 1058 cm^{-1}; ^1H NMR (100 MHz) δ 3.24 (d of quartet, 2 H, J = 15.0 and 3.5 Hz), 2.69 (d of quartet, 2 H, J = 15.0 and 3.2 Hz), 1.58 (s, 3 H); ^{19}F NMR ϕ 94.0 (pentet, J_{HF} = 3.8 Hz); ^{13}C NMR (100 MHz) δ 151.8 (t, J_{CF} = 284.7 Hz, =CF_2), 123.8 (CN), 80.3 (t, J_{CF} = 28.4 Hz, C_3), 36.5 (t, J_{CH} = 2.1 Hz, C_2), 28.0 (C_1), 24.9 (CH_3); mass spectrum gave M^+ 143.053 93 ± 0.0012 (8 ppm), calcd for $C_7H_7NF_2$ 143.054 66, deviation −0.000 73 (5 ppm). Anal. ($C_7H_7NF_2$) C, H, N.

The combined yield of isolated products was 39.3%. Order of elution on Carbowax 20M was **17** and **20** and then **19**. On SE-30 the order was **20** and then **17**. The GLPC relative yields were 84% for **19** and 16% for **20**.

2,2-Dichloro-4-methylene-1,1,3,3-tetrafluorocyclobutane (21) and 1,1-Dichloro-2,2-difluoro-3-(difluoromethylene)-cyclobutane (22). Into a 20-mL glass tube was condensed 2.31 g (17.4 mmol) of 1,1-dichloro-2,2-difluoroethylene and 110 mg (1.45 mmol) of difluoroallene. The tube was sealed under vacuum and heated at 134 °C for 27 h. The tube was cooled and opened. The mixture was subjected to preparative GLPC (10 ft by $^1/_4$ in. 10% TCP at 80 °C, 60 mL/min) to give 150 mg of dichlorodifluoroethylene dimer, 10.6 mg (3.5%) of **21** and 49.3 mg (16.3%) of **22**:

21: IR (CCl_4) 1718 (w), 1700 (w), 1438 (w), 1300, 1180, 1091, 924, 890 cm^{-1}; ^1H NMR (60 MHz) δ 6.23 (pentet, J_{HF} = 2.1 Hz); ^{19}F NMR (100 MHz) ϕ 94.4 (t, J_{HF} = 2 Hz).

22: IR (CCl_4) 1787 (s), 1432, 1321 (s), 1150, 990, 782 cm^{-1}; ^1H NMR (100 MHz) δ 3.35 (t, J = 4.6 Hz); ^{19}F NMR (100 MHz) ϕ 65.6 (d of m, 1 F, J_{FF} = 22.5 Hz), 72.3 (d of m, 1 F, J_{FF} = 22.5 Hz), 88.2 (dd, 2 F, J_{FF} = 7.8 and 4.1 Hz); mass spectrum gave M^+ 207.947 82 ± 0.002 63 (13 ppm), calcd for $C_5H_2F_4Cl_2$ 207.946 97, deviation 0.000 85 (4 ppm).

The combined yield of isolated products was 20%. Order of elution was **22**, dichlorodifluoroethylene dimer, and then **21**. The GLPC relative yields were 73% for **22** and 27% for **21**. At low conversion (134 °C, 1 h) the relative yields were 50.6% for **21** and 49.4% for **22**.

(*E*)-1,1-Dichloro-2,2-difluoro-3-(fluoromethylene)cyclobutane (27), 1,1-Dichloro-2,2,4-trifluoro-3-methylenecyclobutane (26), and (*Z*)-1,1-Dichloro-2,2-difluoro-3-(fluoromethylene)cyclobutane (28). Into a 5-mL glass tube was condensed 2.50 g (18.8 mmol) of 1,1-dichloro-2,2-difluoroethylene and 105 mg (1.8 mmol) of fluoroallene. The tube was sealed under vacuum and heated at 134 °C for 8 h. The tube was cooled and opened. The products were isolated by preparative GLPC (10 ft by $^1/_4$ in. 10% TCP at 130 °C, 60 mL/min) to give 220 mg of dichlorodifluoroethylene dimer and 40.3 mg (11.7%) of **27**. **27**: IR ($CDCl_3$) 1732 (s), 1425, 1290, 1237, 1205, 1150 (s), 1100, 1030, 1000, 978 cm^{-1}; ^1H NMR (100 MHz) δ 7.17 (d of pentet, 1 H, J_{HF} = 77.4 and J = 3.1 Hz), 3.39 (m, 2 H); ^{19}F NMR (100 MHz) ϕ 96.4 (dd, 2 F, J_{HF} = 3.2 and J_{FF} = 5.2 Hz), 124.8 (d of pentet, 1 F, J_{HF} = 77.4, and J = 4.9 Hz); mass spectrum gave M^+ 189.955 66 ± 0.001 68 (9 ppm), calcd for $C_5H_3Cl_2F_3$ 189.956 39, deviation −0.000 73 (4 ppm).

There was also isolated 65.4 mg (19.0%) of **26**: IR (CCl_4) 1300, 1149, 1084, 876, 735 (s) cm^{-1}; ^1H NMR (100 MHz) δ 6.09 (m, 1 H), 5.97 (m, 1 H), 5.39 (d of pentet, 1 H, J_{HF} = 56.2 and J = 2.5 Hz); ^{19}F NMR (100 MHz) ϕ 99.1 (dd of quartet, 1 F, J_{FF} = 203.9, J_{FF} = 9.2 and J_{HF} = 2.5 Hz), 102.3 (dd of quartet, 1 F, J_{FF} = 203.9, J_{FF} = 8.4, and J_{HF} = 2.5 Hz), 174.1 (dtt, 1 F, J_{HF} = 56.2, J_{FF} = 8.8, and J_{HF} = 3.7 Hz); mass spectrum gave M^+ 189.956 78 ± 0.003 27 (17 ppm) calcd for $C_5H_3Cl_2F_3$ 189.956 39, deviation 0.000 39 (2 ppm).

Finally there was isolated 47.1 mg (14%) of **28**: IR (film) 1723 (s), 1429, 1361, 1257, 1147, 1118, 990, 977, 872 cm^{-1}; ^1H NMR (60 MHz) δ 6.65 (d of m, 1 H, J_{HF} = 77.4 Hz), 3.32 (dd, 2 H, J_{HF} = 4.9 and J_{HH} = 2.5 Hz); ^{19}F NMR (100 MHz) ϕ 98.1 (d, 2 F, J_{FF} = 9.1 Hz), 116.6 (d of septet, 1 F, J_{HF} = 77.4 and J = 4.8 Hz; mass spectrum gave m/e 190 (M^+, 7), 155 (100), 132 (20), 96 (55).

The combined yield of isolated products was 45%. Order of elution was dichlorodifluoroethylene dimer, **27**, and then **26**, followed by **28**. The GLPC relative yields were 25.3% for **27**, 49.3% for **26**, and 25.4% for **28**. In a separate experiment at 80 °C for 30 h, the relative yields were 23.4%, 51.1%, and 25.5%.

***cis*- and *trans*-2-Fluoro-3-methylenecyclobutanecarbonitriles (23 and 24) and 3-(Fluoromethylene)cyclobutanecarbonitrile (25).** Into a 10-mL, thick-walled, glass tube was condensed 2.00 g (0.0377 mol) of distilled, degassed acrylonitrile and 91 mg (1.57 mmol) of fluoroallene **13**. The tube was sealed under vacuum and heated in a tube furnace at 135 °C for 21 h. After being cooled to room temperature, the tube was opened and the clear, yellow liquid containing clumps of white solid was filtered. From the filtrate, the three products were separated by preparative GLPC using a $^3/_8$ in. × 10 ft 10% SE-30 column at 122 °C (72 mL/min He, T_i = 197 °C, T_d = 191°). The three products were collected separately and identified by their spectra.

The first eluted isomer was *trans*-2-fluoro-3-methylenecyclobutanecarbonitrile (**24**) that was obtained in 7% isolated yield (12 mg); IR 2950 (w), 2250 (m), 1690 (w), 1440 (m), 1420 (w), 1360 (w), 1220 (w), 1180 (w), 1090 (s), 910 cm^{-1} (s) (acrylonitrile impurity at 2220 cm^{-1}); ^1H NMR (60 MHz), δ 2.5–3.5 (3 H, br m, CH_2 and CH), 5.07 and 5.30 (2 H, two br s, $=CH_2$), 6.34 (1 H, d, CHF), [J_{FH}(CHF) = 51 Hz]; ^{19}F NMR (100 MHz) ϕ 164.6 (1 F, d of d), [J_{FH}(CHF) = 54, J_{FH}(CH, CHF) = 15 Hz]; mass spectrum, e/m (relative intensity) 112 (8), 111 (87), 110 (12), 96 (1), 91 (67), 84 (100), 83 (20), 72 (25), 71 (20), 65 (84), 64 (84), 58 (92), 57 (46), 54 (23), 40 (61), 39 (67); M^+ 189.956 78 ± 0.003 27, M^+ 111.047 83 ± 0.000 97 (9 ppm), calcd for C_6H_6FN 111.048 43, deviation 0.000 60 (5 ppm).

The second eluted isomer was 3-(fluoromethylene)cyclobutanecarbonitrile (**25**) obtained in 31% isolated yield (55 mg): IR 2940 (w), 2240 (m), 1720 (s), 1420 (w), 1330 (w), 1240 (w), 1130 (m), 1090 (s), 1000 (w), 840 (m), 780 cm^{-1} (w); ^1H NMR (60 MHz) δ 3.17 (5 H, br s, CH_2 and CH), 6.38 (1 H, br d, =CHF), [J_{FH}(=CHF) = 82 Hz]; ^{19}F NMR (100 MHz) ϕ 138.7 (1 F, br d), [J_{FH}(=CHF) = 82 Hz]; mass spectrum, m/e (relative intensity) 112 (5), 111 (61), 110 (6), 92 (2), 91 (5), 90 (2), 85 (5), 84 (53), 83 (15), 78 (3), 72 (10), 71 (13), 65 (47), 58 (100), 57 (55), 54 (58), 39 (20); M^+ 111.047 74 ± 0.001 00 (9 ppm), calcd for C_6H_6FN 111.048 43, deviation 0.000 69 (6 ppm).

The third eluted isomer was *cis*-2-fluoro-3-methylenecyclobutanecarbonitrile **23** obtained in 7% isolated yield (12 mg): IR 2940 (m), 2250 (m), 1700 (w), 1430 (m), 1400 (w), 1340 (m), 1240 (m), 1100 (s), 970 (w), 910 cm^{-1} (s); ^1H NMR (60 MHz), δ 2.72–3.72 (3 H, br m, CH_2 and CH), 5.18 and 5.38 (2 H, two br s, $=CH_2$), 5.40 (1 H, d of d, CHF), [J_{FH}(CHF) = 54, J_{HH}(CH, CHF) = 7.5 Hz]; ^{19}F NMR (100 MHz) ϕ 171.6 ppm (1F, br d), [J_{FH}(CHF) = 54 Hz]; mass spectrum, m/e (relative intensity): 112 (6), 111 (65), 110 (10), 109 (4), 103 (3), 101 (2), 96 (2), 91 (14), 85 (8), 84 (88), 83 (20), 72 (28), 71 (20), 65 (78), 64 (21), 58 (100), 57 (51), 54 (69), 52 (15), 51 (23), 40 (68), 39 (64); M^+ 111.0454 (one scan), calcd for C_6H_6FN 111.0483, deviation 0.0029 (26 ppm).

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Registry No. **1**, 14296-80-1; **5**, 90029-26-8; **6**, 90029-27-9; **7**, 19652-57-4; **8**, 90029-28-0; **9**, 90029-29-1; **10**, 90029-30-4; **11**, 90029-31-5; ***R**,*S**-12**, 90029-32-6; ***R**,*R**-13**, 90029-33-7; **15**, 2557-72-4; **16**, 90029-34-8; **17**, 90029-35-9; **18**, 7704-59-8; **19**, 90029-36-0; **20**, 90029-37-1; **21**, 90029-38-2; **22**, 90029-39-3; **23**, 90029-40-6; **24**, 90029-41-7; **25**, 90029-42-8; **26**, 90029-43-9; **27**, 90029-44-0; **28**, 90029-45-1; DFA, 430-64-8; MFA, 51584-22-6; CF_2=CCl_2, 79-35-6; CH_2=CHCN, 107-13-1; methacrylonitrile, 126-98-7.