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The *In Situ* Generation and Trapping of Some Fluorine-substituted Ketenes

William R. Dolbier, Jr., Suk Kyu Lee and Otto Phanstiel IV
Dept. of Chemistry, University of Florida
Gainesville, FL 32611-2046

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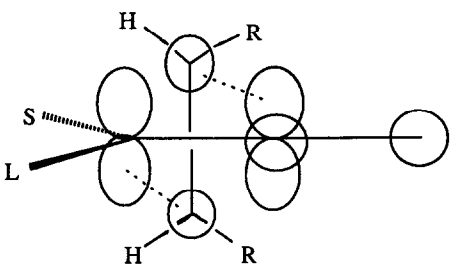
Abstract: Fluoroketene, difluoroketene, methylfluoroketene, trifluoromethylfluoroketene, and phenylfluoroketene were each generated, *in situ*, via dehydrohalogenation of the respective acid chlorides. In the presence of cyclopentadiene [2 + 2] adducts were obtained in all but the difluoroketene case. In the absence of cyclopentadiene, low temperature ^{19}F nmr indicated the presence of acyl ammonium salts and enolates, potential precursors of the ketenes, but no actual ketene species could unambiguously be detected. The stereochemical results were consistent with the currently accepted steric-based mechanistic rationale for stereochemical determination in ketene cycloadditions.

The cycloaddition of unsymmetrically substituted ketenes to cyclopentadiene and other cis alkenes has been reported to lead specifically to those adducts which have the larger substituent in the endo position.[1,2] The simplest and most generally accepted rationale for this stereochemical outcome is steric-based and derives from Woodward and Hoffmann's hypothesis[3] that the reaction is a concerted $[\pi 2_s + \pi 2_a]$ reaction wherein the olefinic portion of the ketene acts as the antarafacial component, a model which requires a perpendicular interaction of the ketene and the alkene as depicted below. Moore, however, has pointed out that a two-step variant of this



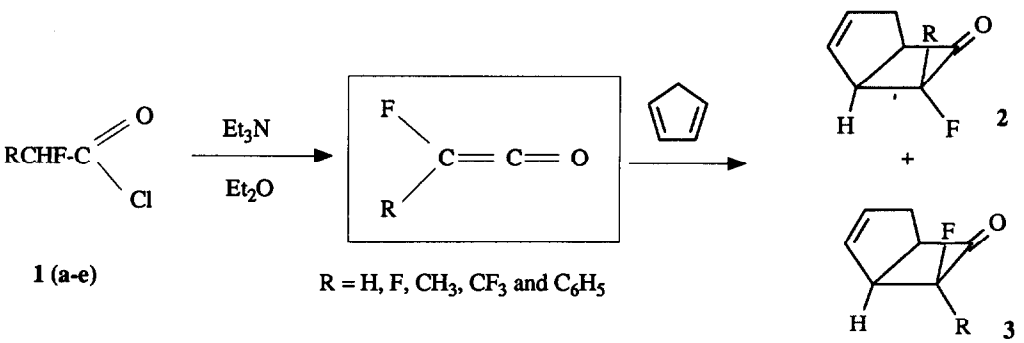
mechanism involving a zwitterionic intermediate is sometimes and perhaps even generally involved.[4] This mechanistic problem has attracted considerable recent theoretical interest,[5-7] with the net result being increased confidence in the early concerted model.

In recent years we have probed the effect of substituents, in particular fluorine substituents, on a number of pericyclic reactions the stereochemistries of which were also considered to be dominated by steric effects. In one case, the competitive conrotatory electrocyclic ring-openings of 3-substituted cyclobutenes,[8] it was found that *electronic* effects were clearly more important than steric effects, while in others electronic effects were found to be small[9] or, as in the case of the Cope rearrangement, insignificant.[10]

The results described in this paper derive from a study designed to resolve some remaining questions about *in situ*-generated ketene cycloaddition reactions and to provide a final test of whether electronic effects rather than steric effects might be involved in determining the stereochemistry of ketene [2 + 2] cycloadditions. Over the last

20 years, the groups of Brady, Dreiding and Ghosez have contributed much excellent work dealing with the stereochemistry of addition of unsymmetrically substituted ketenes to cyclopentadiene and other alkenes,[11-18] and the results were all consistent with the orthogonal/steric model. However, as we have demonstrated in our studies of fluoroallene,[19] *no* substituent is as effective as fluorine for distinguishing between steric and electronic effects. Until this work, the only published studies of cycloadditions of fluorine-substituted ketenes involved fluoroketene,[11,12,17,18] trifluoromethylfluoroketene,[20-22] chlorofluoroketene,[22] and briefly and ambiguously, difluoroketene.[23,24] It was our intention to specifically reexamine these three plus methylfluoro- and phenylfluoroketene, in order to more completely compare steric vs electronic effects. In addition, an attempt was made in this work to actually *detect* the ketenes or at least their immediate precursors directly by nmr. Direct detection of even moderately reactive ketenes has been rare, most of them having been generated and reacted *in situ*. Ambiguity always remains after such studies as to whether some moiety other than the ketene might have been the reactive species. For example, Brady claimed in his initial paper dealing with fluoroketene[11] that it was apparently "quite stable in the reaction mixture at -78°," but, of course, no attempt was made to directly detect the ketene. Later Brady did attempt to detect the more stable ketene, chloromethylketene, by low temperature nmr, without success.[25]

Cycloaddition Results and Discussion. The methodology which we employed in our generation of the desired ketenes was the standard one of dehydrohalogenation of the respective acyl chlorides, **1 a-e**. (These acid



1 (a-e)

R = H, F, CH_3, CF_3 and C_6H_5

halides were themselves synthesized by known procedures.)[26-29] When carried out in the presence of a five-fold excess of cyclopentadiene (CPD) in Et_2O, [2 + 2] cycloadducts were obtained in all cases, except for difluoroketene precursor **1-b**, as shown in the Table below. The stereochemistries of the adducts were easily determined from their ^{19}F nmr spectra as a result of the magnitude of the coupling between the F substituent and the β-methine proton. When the F substituent is endo (as in **3**), and thus trans to the β-methine H, the coupling is almost negligible, while when the F is exo (as in **2**), and thus cis to the β-methine H, the coupling is quite significant (i. e., 15-24 Hz). No adduct could be detected for the cycloaddition between difluoroketene and CPD, although as we will see below the precursors to the ketene appeared to be formed.

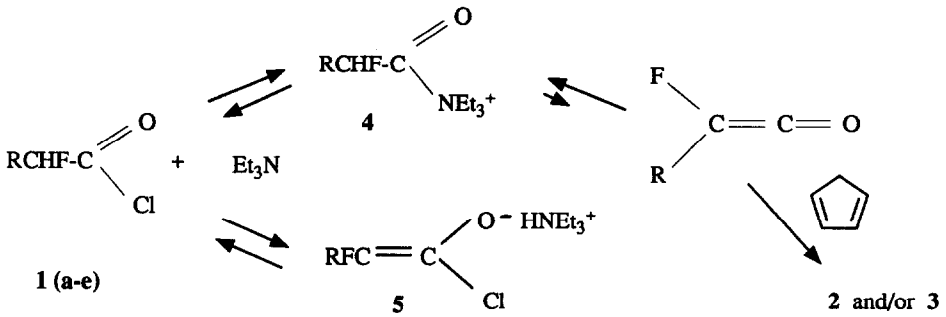
Table I. Cycloadditions of Fluorinated Ketenes with Cyclopentadiene

Acyl chloride	Solvent	Adduct (yield)	^{19}F nmr data ϕ(ppm)	J_{HF}(Hz)
1-a	Et_2O	**2-a** (3%)	178.5	15.3
		3-a (29%)	185.8	-
1-c	Et_2O	**2-c** (23%)	144.8	24.4
1-d	Et_2O	**2-d** (10%)	164.9	19
1-e	Et_2O	**2-e** (38%)	138.0	17.9
	$CHCl_3$	(69%)		
	THF	(16%)		

The results which we obtained were totally consistent with the accepted steric rationale for determination of stereochemistry. There was no evidence for the intervention of electronic effects in these cycloadditions. In all cases the more sterically demanding ketene substituent was observed to be preferentially incorporated into the endo position in the cyclobutanone adducts. In fact, this study pointedly indicates just how sensitive ketene cycloadditions are to the steric demand of the ketene substituents. Fluorine is recognized to be the *smallest* substituent other than hydrogen or its isotopes, and it is generally considered to exert little, if any, steric effect on reactions. Nevertheless, in the reaction of fluoroketene with CPD there was observed a 10 : 1 preference for fluorine versus hydrogen to end up in the endo position. Then, in all of the other examples, where there was competition of F with methyl, trifluoromethyl and phenyl for the endo position, the reactions were found to be completely stereospecific, with *none* of the smaller F substituent having become incorporated into the endo position.

It was attempted to utilize a number of other alkenes in these ketene-trapping reactions, with a general lack of success. Included were electron-rich alkenes, such as 2,3-dihydrofuran, vinyl acetate, 1,3-butadiene, α-methylstyrene, and 2,3-dimethyl-2-butene, all of which ordinarily would be expected to be quite reactive with ketenes. Only in the case of the reaction between phenylfluoroketene and 2,3-dihydrofuran was any other adduct detected (by nmr, ϕ140.6). (In this case the yield was small and the product not fully characterized.) Thus the only alkene which was generally reactive enough to successfully trap the fluorinated ketenes was CPD. Brady found that the analogous chloro- and bromomethylketenes were able to be trapped in good yield by other olefins,[14] similar to the ones we tried. Cyclopentadiene was, as in our study, found to consistently be the most reactive olefin in these reactions. It is likely that the general inability to trap our fluorinated ketenes with olefins other than CPD is due to their relative instability at the temperatures required for them to undergo cycloaddition. Likewise our total inability to trap difluoroketene indicates that it likely decomposes even more rapidly than the other ketenes. Knunyants has suggested that such lack of observed cycloaddition is due to a competitng polymerization process.[22]

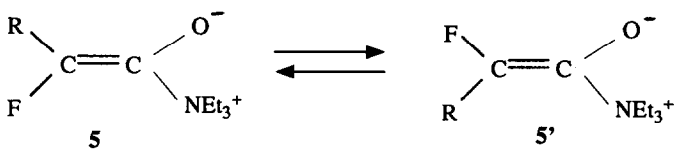
Mechanistic Results and Discussion. It is commonly accepted that the mechanism of reactions of acyl chlorides with Et_3N involves the formation of acyl ammonium salts (**4**) and/or enolates (**5**) as precursors of the



reactive ketene species.[25,30-35] Acyl ammonium salts have actually been isolated in those systems where ketenes are difficult to form,[30] and they have been detected (by nmr) during productive ketene-forming reactions, such as in the reaction of isobutyryl chloride with Et_3N to form dimethylketene.[25] (No enolate intermediates were observed in this system.) Enolate intermediates were detected, however, during an *in situ* generation of the unstable chloromethylketene.[25] In this case, no acyl ammonium intermediate was observed, nor was the chloromethylketene able to be detected although the yield of its adduct with CPD was excellent.

In an attempt to detect the unstable fluorinated ketenes or their precursors, the reactions of **1 a, b, d,** and **e** with Et_3N were examined by ^{19}F nmr at -40° to +20°C in $CDCl_3$, in the absence of CPD. In each case, including the attempted generation of difluoroketene from **1-b**, absorptions were found (see Table III in the Experimental Section) which were consistent with the formation of both of these types of species (i.e.,**4** and **5**), but in no cases were peaks observed which could be unambiguously assigned to the ketene species.

For example, in the reaction of Et_3N with 2-fluorophenylacetyl chloride (**1-e**) at -40° in $CDCl_3$, three major fluorinated species were observed to appear at the expense of starting material. After 1.08 equivalents of Et_3N had been added, only 6.5% of starting acid chloride remained. A doublet at ϕ184 (J=42 Hz) was assigned to the acyl ammonium species (**4**), while singlets at ϕ108.2 and 110.0 were considered to be derived from the geometrically isomeric enolate species (**5** and **5'**). Upon addition of 1.5 equivalents of Et_3N all starting material



5-c, R = Me

5-e, R = C_6H_5

was gone, and the relative intensity of the above peaks was 2.6:2.5:1.0, respectively. Using C_6F_6 as an internal standard a yield of 67% was determined. The ratios of these intermediates appeared to remain relatively constant during the addition, and they varied only slightly through the whole temperature range examined, although decomposition became rapid at 20°C. Table II summarizes the data obtained for dehydrochlorination of **1-e**. Related data for the 2-fluoroacetyl chloride, 2,2-difluoroacetyl chloride, and 2-fluoropropionyl chloride systems are included in Table III in the Experimental Section.

Some comment is due regarding the nature of the enolate species. Both the methylfluoro- and the phenylfluoroenolates appeared to exist as a *pair* of enolates (with ratios of 2.0 and 2.5, respectively). Most likely

these enolates are *geometric* isomers (such as **5** and **5'**). In the methylfluoro case, starting from **1-c**, the two broad

Table II. Composition of Reaction Mixtures in the Reactions of 2-Phenyl-2-fluoroacetyl chloride with Et_3N

Equiv. of Et_3N used	Temp. °C	Remaining **1-e**(%)	% of Products Formed **4**	**5**	**5'**
0.88	-40°	14.4%	43%	41%	16%
1.08	-40	6.5	46	41	14
	-20	6.9	45	40	14
	0	7.2	42	41	17
1.5	-40	-	43	41	17

quartets observed at ϕ106.3 and 106.6ppm at -40° coalesced to a single broad singlet at 0°, and then resolved to a single broad quartet at +20°, a result which indicates a relatively low energy barrier for interconversion of the two enolate species. In contrast, the singlets at ϕ108.2 and 110.0, due presumably to the isomeric enolates in the phenylfluoro system, did not coalesce within the temperature range examined, although at 20° they were seen to be broadening. From examination of the ^{19}F and ^{1}H nmr spectra of the monofluoro system one could imply the presence of two species, but if so the minor one was detectable in both spectra only as unresolved shoulders on the major enolate's otherwise sharp doublets.

It was also considered whether an intermediate enolate species with $X = N(Et)_3^+$ might be formed, as well as (or instead of) the species with X = Cl. However, it was found that when starting with **1-e** the ratios of enolates (**5/5'**), and of enolates versus acyl ammonium species (**5 + 5'/4**) did not vary significantly with the concentration of Et_3N. (**5/5'** = 2.50, 2.94 and 2.46, and **5+5'/4** = 1.33, 1.19 and 1.35 for 0.88, 1.08 and 1.5 equivalents of Et_3N, respectively, at -40°C in $CDCl_3$.) With 0.88 equiv., 14% of acid chloride remains, with 1.08 equiv. 6.5% remains, while with 1.5 equiv. none remains. Such a result would seem to preclude structures for **5** or **5'** which would have $X = N(Et)_3^+$, since formation of such enolates would require *two* equivalents of Et_3N.

Interestingly, in the case of excess Et_3N, if another, more reactive acid chloride, such as 2,2-dichloroacetyl chloride, was added to the reaction mixture at -40°, starting acid chloride **1-e** was regenerated. This would seem to indicate that formation of **4** and **5** from starting acid chloride is reversible.

It was further observed that when CPD was added to such a reaction mixture at -20°, and cycloaddition began to occur, the ratio of enolates did not vary (2.14 versus 2.19), while the ratio of enolates to acyl ammonium salt increased (from 1.36 to 1.62). Since reaction with CPD would serve to deplete the concentration of ketene (which is too small to be observable), which should then consequently give rise to a depletion of the concentration of its precursor, the relative lowering of concentration of **4** would would point toward the acyl ammonium species **4** being the precursor of the ketene. In the presence of CPD and at -30°C, the three intermediate peaks were found to decrease at approximately the same rates, with the peak due to the ketene-CPD adduct appearing concomitantly. In addition, the rate of formation of adduct was found to be dependent upon the CPD concentration, but the order was less than first order (i. e., $k = 9.7\ (\pm 0.6) \times 10^{-5}$ for 2.5 fold excess of CPD, while k

= 2.4 (±0.2) x 10^{-4} for a 10-fold excess).

When all of the above observations are taken into consideration, it seems apparent that under the conditions of these *in situ* ketene reactions, *all* species (i. e. acid chloride, acyl ammonium salt, enolates and ketene) are in dynamic equilibrium, with the ketenes being implied as the reactive species in cycloadditions, while unfortunately being at such low concentration that they are not able to be unambiguously observed. A word of caution should probably be added here in as much as in the absence of direct observation of ketenes in these reactions, one cannot explicitly rule out the possibility that a ketene precursor, such as **4**, might actually be the species which undergoes cycloaddition.

Conclusions. In conclusion, our study of the generation and trapping of a series of fluorine-substituted ketenes led to stereochemical results which are consistent with the currently accepted steric-based mechanistic rationale for stereochemical determination in ketene cycloadditions. The ketenes could not be detected under the reaction conditions, although low temperature nmr observations were consistent with the existence of acyl ammonium and enolate species as intermediates, with the former acting as the probable immediate precursor to the elusive ketene which appears to be only reactive enough in [2 + 2] cycloadditions to undergo reaction with cyclopentadiene.

Experimental Section

Sodium fluoroacetate was purchased from Aldrich Chemical Co. The ^{1}H nmr and ^{19}F nmr spectra were recorded in $CDCl_3$ on VXR 200 and VXR 300 spectrometers. Chemical shifts were recorded in δ (ppm downfield from TMS) and in φ (ppm upfield from $CFCl_3$) for H and F nmr spectra, respectively. Preparative glpc was carried out on a 20', 1/4" 20% SE-30 column. GCMS analyses were performed on a Finnigan 4000 GC/MS, and high resolution mass spectra were measured with an AEI MS30 instrument. Melting points are uncorrected.

Fluoroacetyl chloride (1-a) was prepared by reacting 25 g (0.25 mol) of sodium fluoroacetate and 60.2 g (0.29 mol) of PCl_5 by the method of Truce[28]: **1-a** (yield: 77%); bp 70°C; ^{1}H nmr δ5.2 (d, J=48 Hz); ^{19}F nmr φ213.3 (t, J=48 Hz).

Difluoroacetyl chloride (1-b) was prepared by reacting 5g (52.1 mmol0 of difluoroacetic acid with 12g (57.6 mmol) of PCl_5 using the standard method[29]: **1-b** (yield: 62%); bp 32°C; ^{19}F nmr φ122.8 (d, J=54.2 Hz).

2-Fluoropropionic acid was prepared from 12.5g (0.14 mol) of d,l-alanine via diazotization in 70% polyhydrogen fluoride/pyridine reagent by the method of Olah and Welch[26]: (Yield: 54%); ^{1}H nmr δ10.4 (s, 1H), 5.8-4.5 (d of q, 1H, J=48 and 7 Hz), 1.9-1.2 (d of d, 3H, J=24 and 7 Hz); ^{19}F nmr φ186.8 (m).

2-Fluoropropionyl chloride (1-c) was prepared by reacting 7 g (76.1 mmol) of 2-fluorolpropionic acid with 16g (76.8 mmol) of PCl_5 using the standard method[29]: **1-c** (yield: 69%); bp 72°C; ^{1}H nmr δ5.8-4.6 (d of q, 1H, J=48 and 7 Hz), 2.0-1.4 (d of d, 3H, J=24 and 7 Hz); ^{19}F nmr φ175.5 (m).

2-Fluoro-2-phenylacetic acid was prepared from 20.2g of d,l-phenylglycine by the method of Olah and Welch.[26] Crude product was purified by disolving in 20% aq KOH, followed by acidification with conc HCl and recrystallization: (yield: 58%); mp 155°C; ^{1}H nmr δ9.7 (s, 1H), 7.6-7.0 (m, 5H), 5.8 (d, 1H, J=47.5 Hz); ^{19}F nmr φ180.8 (d, J=47.4 Hz).

2-Fluoro-2-phenylacetyl chloride (1-e) was prepared by reacting 7g (45.2 mmol) of the acid with 10.4g (50.0 mmol) of PCl_5 using the standard method[29]: **1-e** (yield: 64%); bp 59°C; ^{1}H nmr δ7.6-7.3 (m, 5H), 5.9 (d, 1H, J=47.5 Hz); ^{19}F nmr φ164.6 (d, J=47.5 Hz).

2,3,3,3-Tetrafluoropropionyl chloride (1-d) was prepared by reacting 19.4g (0.11 mol) of 1,1,2,3,3,3-hexafluoropropyl ether[27] with 24.8g (0.21 mol) of chlorosulfonic acid by the method of Cheburkov[21]: **1-d** (yield: 98%); bp 47°C; ^{1}H nmr δ5.2 (d of q, 1H, J=50 and 6 Hz); ^{19}F nmr φ76.0 (d of d, 3F, J=14 and 6 Hz), 194 (d of q, 1F, J=50 and 12 Hz).

General procedure for ketene-cyclopentadiene cycloadditions. To a soln of 20 mmol of triethylamine and 91 mmol of freshly distd cyclopentadiene (CPD) in 30 ml of dry ether, 18.1 mmol of the acid chloride was added dropwise at -78°C, with stirring. After the addn was completed, the reaction mixture was slowly warmed to 0°C over a 2 hr period. The reaction mixture was then placed in the refrigerator (4°C) for 15 hrs. The precipitated amine HCl was filtered off and washed 3 times with 10 ml portions of ether. The combined ether solutions were dried ($MgSO_4$), concentrated, and the products isolated by preparative glpc. The isomer distributions and yields were determined by ^{19}F nmr of the crude product with α,α,α-trifluorotoluene as the internal standard.

The fluoroketene-CPD cycloaddition led to adducts being formed in a total of 32% yield, with a 10:1 endo/exo ratio: *exo-7-fluorobicyclo[3.2.0]hept-2-en-6-one* (**2-a**): (yield: 3%); ^{1}H nmr δ6.0-5.8 (m, 2H), 4.96 (d,d,d, 1H, J=54.1, 2.9, and 2.2 Hz), 4.15-3.95 (m, 1H), 3.75-3.55 (m, 1H), 2.8-2.45 (m, 2H); ^{19}F nmr ϕ178.5 (d,d, J=54.6 and 15.3 Hz); ^{13}C nmr δ180.8 (s), 134.8 (d, J=2.2 Hz), 127.9 (d, J=5.9 Hz), 102.6 (d, J=223.5 Hz), 59.8 (d, 4.9 Hz), 47.1 (d, J=20.9 Hz), 35.5 (s); gcms m/e (%rel int) 127 (0.16), 126 (0.89), 125 (7.96), 98 (50), 97 (100), 79 (45), 78 (17), 77 (28). *endo-7-fluorobicyclo[3.2.0]hept-2-ene-6-one* (**3-a**): (yield: 29%); ^{1}H nmr δ6.0-5.9 (m, 1H), 5.8-5.65 (m, 1H), 5.5-5.4 (m, 1H), 4.0-3.8 (m, 1H), 3.6-3.4 (m, 1H), 2.85-2.45 (m, 2H); ^{19}F nmr ϕ 185.8 (d, J=53.4 Hz); ^{13}C nmr δ180.8 (s), 136.2 (s), 126.4 (d, J=3.6 Hz), 96.8 (d, J=239.5 Hz), 53.1 (d, J=12.2 Hz), 46.2 (d, J=18.9 Hz), 35.4 (s).

The fluoromethylketene-CPD cycloaddition led to one adduct being formed in 23% yield: *exo-7-fluoro-endo-7-methylbicyclo[3.2.0]hept-2-en-6-one* (**2-c**): ^{1}H nmr δ 6.0-5.9 (m, 1H), 5.75-5.65 (m,1H), 4.15-4.05 (m, 1H), 3.7-3.55 (m, 1H), 2.75-2.4 (m, 2H), 1.3 (d, 3H, J=24.0 Hz); ^{19}F nmr ϕ144.8 (d of q, J=24.4 and 24.1 Hz); ^{13}C nmr δ208.3 (s), 135.7 (d, J=2.5 Hz), 127.1 (d, J=6.8 Hz), 109.8 (d, J=204.4 Hz), 59.8 (s), 51.7 (d, J=23.6 Hz), 34.8 ((s), 14.2 (d, J=24.9 Hz); gcms m/e (% rel int) 141 (0.84), 140 (8.4), 125 (13), 112 (24), 111 (11), 109 (12), 97 (100), 93 (44), 91 (18), 86 (11), 77 (24), 66 (69), 65 (19), 51 (10); High Resolution ms, calcd for C_8H_9OF 140.06374, found 140.06305.

The fluorotrifluoromethylketene-CPD cycloaddition led to one adduct in 10% yield: *exo-7-fluoro-endo-7-trifluoromethylbicyclo[3.2.0]hept-2-en-6-one* (**2-d**): ^{1}H nmr δ6.1-6.0 (m,1H), 5.8-5.65 (m,1H), 4.35-4.2 (m,1H), 3.95-3.7 (m,1H), 2.95-2.5 (m,2H); ^{19}F nmr ϕ74.8 (d,3F, J=9.2 Hz), 164.9 (d,q, 1F, J=19 and 9 Hz); ^{13}C nmr δ180.9 (s), 137.4 (s), 123.9 (d, J=6.1 Hz), 120.0 (d of q, J=220 and 32 Hz), 104.2 (d of q), 61.3 (s), 49.2 (d, J=23 Hz), 35.7 (s); gcms m/e (rel int), 194 (0.11), 193 (0.57), 174 (1.2), 147 (8), 145 (6), 127 (33), 98 (6), 97 (100), 96 (11), 95 (12), 77 (30), 75 (7), 69 (13), 66 (22), 65 (10), 57 (7), 55 (10).

The fluorophenylketene-CPD cycloaddition was carried out by reacting a soln of 2g (11.6 mmol) of acid chloride **1-e** in 10 ml of ether with a soln of 1.40g (13.9 mmol) of TEA and 3.8g (57.6 mmol) of CPD in 30 ml of ether as described in the general procedure. A 38% yield of a single adduct was obtained: *exo-7-fluoro-endo-7-phenylbicyclo[3.2.0]hept-2-en-6-one* (**2-e**): bp 61°C/0.04mmHg; ^{1}H nmr δ7.4-7.3 (m,5H), 5.9-5.7 (m,1H), 5.4-5.2 (m,1H), 4.4-4.1 (m,1H), 4.1-3.85 (m,1H), 2.9-2.7 (m,1H), 2.65-2.4 (m, 1H); ^{19}F nmr ϕ138.0 (d, J=17.4 Hz); ^{13}C nmr δ206.8 (d,J=17.4 Hz), 135.8 (d,J=2.4 Hz), 134.4 (d,J=135.5 Hz), 129.1 (d, J=2.7 Hz), 128.2 (s), 127.3 (d, J=6.2 Hz), 126.5 (d, J=6.4 Hz), 110.1 (d, J=203.6 Hz), 60.3 (s), 53.3 (d, J=26.4 Hz), 35.3 (s); gcms m/e (rel int), 203 (2.3), 202 (19.1), 174 (55(), 173 (18), 159 (22), 155 (65), 154 (17), 153 (23), 152 (15), 147 (18), 146 (24), 136 (30), 133 (27), 128 (11), 115 (14), 109 (94), 108 (100), 107 (31), 91 (11), 77 (12), 66 (14), 63 (13), 51 (17); high resolution ms, calc for $C_{13}H_{11}FO$, 202.07939, found 202.07979.

When this reaction was carried out in $CHCl_3$, the yield of the adduct improved to 69%, while using THF as solvent lowered the yield to 16%.

General procedure for the low temperature nmr studies. To a soln of 0.2 mmol of Et_3N in 0.6 ml of $CDCl_3$ in an nmr tube, 0.2 mmol of the acid chloride was added dropwise using a syringe at -78°C. After the addition of the acid chloride was completed, the reaction was mixed well by shaking, and the spectra were obtained at the appropriate temperatures, beginning at the lowest temperatures and working up. The assigned ^{19}F nmr chemical shifts and coupling constants for the putative acyl ammonium salts and the enolates from each of the acid chlorides are given in Table III.

Table III. Nmr data for the Acyl Ammonium and Enolate Salt Intermediates.

Ketene	Acyl Ammonium Salt (4)		Enolate Salts (5)		Ratios	
Substs	ϕ (ppm)	J_{HF} (Hz)	ϕ (ppm)	J_{HF} (Hz)	5/4	5/5'
F, H	231.5(t)[a]	45.9	139.2(d)[b]	67.8	1.4	
F, F	123.7(d)	53.3	83.6(d), 88.5(d)	45.1, 43.4	0.28	
F, Me	185.3(d,q)	46.8, 23.5	106.3(q), 106.6(q)	18.3, 18.3	1.3	2.0
F, Ph	184 (d)	42	108.2 (s), 110.0 (s)		1.3	2.5

[a] ^{1}H nmr δ5.24 (d, J = 45.6 Hz); [b] ^{1}H nmr δ8.75 (d, J = 67.9 Hz)

In the kinetic studies, appropriate amounts of CPD were also added along with internal standard C_6F_6, and the

temperature raised to -30°C. The approximate rates of loss of intermediates and formation of cycloadduct were determined by nmr integration of these peaks versus the internal standard at various time increments.

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