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FLUORINATED ALLENES: THE SYNTHESES OF 1-FLUOROPROPADIENE, 1,1-DIFLUOROPROPADIENE AND 1,1-DIFLUORO-3-METHYL-1,2-BUTADIENE

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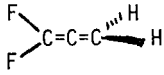
SUMMARY

Improved syntheses of 1-fluoropropadiene and 1,1-difluoropropadiene are presented as is the synthesis of a third reactive allene, 1,1-difluoro-3-methyl-1,2-butadiene. Gram quantities of these highly reactive fluorinated allenes may be prepared conveniently in high yield and purity. All three are reactive dienophiles and cycloadd regiospecifically using their non-fluorine-substituted double bonds.

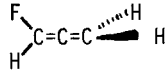
INTRODUCTION

1,1-Difluoropropadiene (DFA) and 1-fluoropropadiene (MFA) have been shown to be very reactive species in cycloaddition reactions, with DFA having significant potential as a mechanistically diagnostic reagent [1,2]. Both DFA and MFA react *regiospecifically* in all of their [2π + 4π] cycloadditions, using exclusively their non-fluorinated double bonds while, in contrast, non-regiospecificity is generally observed in their [2π + 2π] cycloadditions.

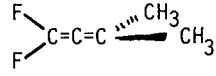
Incorporation of increasing numbers of fluorine substituents on allene makes these species increasingly reactive with the result that DFA and MFA are generally synthesized as required, and if necessary must be stored



DFA



MFA



DDA

in-vacuo at -78° to prevent oligimerization. While both DFA and MFA have been previously synthesized [3,4], neither synthesis was appropriate for

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preparing these allenes in the quantity and purity required for the cycloaddition studies referred to above. In view of the potential utility of these allenes both as synthetic precursors and as mechanistic probes, we wish to report the details of their syntheses at this time.

RESULTS AND DISCUSSION

Our synthesis of DFA is similar to that of Tarrant and Drakesmith [3], with the major modification being in the final step. Gram quantities of high purity DFA may now be readily obtained. The NMR spectra of DFA are characterized by a triplet vinyl proton absorption at δ6.04 (J=3.5Hz) and a

$$CF_3CH{=}CH_2 + Br_2 \longrightarrow CF_3CHBr\text{-}CH_2Br \xrightarrow{KOH} CF_3CBr{=}CH_2$$

$$\xrightarrow{BuLi} CF_3CLi{=}CH_2 \xrightarrow{warm} CF_2{=}C{=}CH_2 + LiF$$

triplet in the ^{19}F spectrum at ϕ106.9 (J=3.5Hz).

The reported synthesis of MFA [4] suffered from a difficult and poor-yield final step. Utilizing the present scheme, it is possible to prepare gram quantities of >97% pure MFA. Its NMR was characterized in the proton spectrum by a one proton doublet of triplets at δ7.1 (J=6Hz, J_{HF}=85 Hz) and a two proton doublet at δ5.5 (J=6Hz) and in the ^{19}F spectrum by a doublet of triplets at ϕ169 (J=85Hz and J=1.1Hz).

$$CHFBr_2 + CH_2{=}CH_2 \xrightarrow[\Delta]{ROOR} BrCH_2CH_2CHBrF \quad (46\%) \xrightarrow[EtOH]{KOH}$$

$$CH_2{=}CHCHBrF + BrCH_2CH{=}CHF \quad (39\%) \xrightarrow{Br_2} BrCH_2CHBrCHBrF$$

$$(82\%) \xrightarrow[EtOH]{KOH} CHF{=}CBrCH_2Br + BrFCHCBr{=}CH_2 \quad (75\%) \xrightarrow[EtOH]{Zn}$$

$$CHF{=}C{=}CH_2 \quad (77\%)$$

A third fluorinated allene was also synthesized in order to test whether the electronic influence of the geminal fluorine substituents of DFA could be overcome by the combined electronic and steric effects of the *gem*-methyl substituents of 1,1-difluoro-3-methyl-1,2-butadiene (DDA).

$$2(CH_3)_2CHMgBr + CF_3CO_2Et \xrightarrow[(59\%)]{Et_2O} CF_3CH(OH)CH(CH_3)_2 \xrightarrow[(93\%)]{AcCl}$$

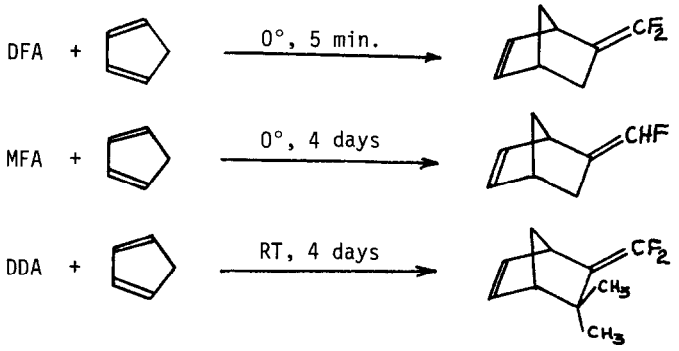
$$CF_3CH(OAc)CH(CH_3)_2 \xrightarrow[(75\%)]{\Delta 500^\circ} CF_3CH{=}C(CH_3)_2 \xrightarrow[(79\%)]{Br_2}$$

$$CF_3CHBrCBr(CH_3)_2 \xrightarrow[(74\%)]{KOH\Delta} CF_3CBr{=}C(CH_3)_2 \xrightarrow[(28\%)]{BuLi,heptane,-85^\circ}$$

$$CH_2{=}C{=}C(CF_3)_2$$

Its NMR spectra were characterized by a triplet in the ^{1}H spectrum at δ1.97 (J=5.1Hz) and a septet in the ^{19}F spectrum at ϕ102.2 (J=5.1Hz).

Typical [2 + 4] cycloadditions of each of these three allenic species are given below.



Numerous additional examples of such reactions with DFA and MFA may be found in our earlier communications. As can be seen, the fluorine substituents do indeed exert a dominating influence upon the regiochemistry of these concerted cycloadditions. The effects of fluorine substituents on the molecular orbitals of allene along with the resultant consequences of such perturbations on their cycloaddition reactions have also been discussed earlier [5].

EXPERIMENTAL

1,3-Dibromo-1-fluoropropane

A 250 ml steel bomb containing 5.60 g (0.0231 mol) benzoyl peroxide 396 g (2.06 mol) degassed dibromofluoromethane and 14.0 g (0.500 mol) ethylene was heated at 120° for 6 hours in a rocking autoclave. After recovery of excess dibromofluoromethane by fractional distillation, the product was distilled at reduced pressure. A yield of 51 g (46%) 1,3-dibromo-1-fluoropropane was obtained: bp 46-54° at 19mm (lit. [4] bp 62°, 86mm); ^{1}H NMR, 6.5 (CHBrF, d of t, 1H, J=5.2, J=50Hz), 3.4 (CH_2Br, t, 2H, J=6.4Hz), 3.0-2.3 (CH_2, m, 2H).

3-Bromo-1-fluoropropene and 3-Bromo-3-fluoropropene

To a 250 ml, round-bottom flask containing 40.6 g (0.185 mol) dibromofluoropropane was added a solution of 13.0 g (0.197 mol) KOH pellets in 60 ml 95% ethanol over a period of 15 minutes. After stirring for 1 hour, the white mixture was poured into 120 ml water. The organic layer was washed with four 5-ml portions water and dried over anhydrous $CaCl_2$.

Fractional distillation gave 10.1 g (39%) bromofluoropropenes, bp 60-82°. The crude mixture was used in the next step. ^1H NMR, δ6.8 (CHBrF, d of d, 1H, J=5.4Hz, J_{FH}=50Hz), 6.3-5.0 (vinylic, complex m, 2.6H), 3.9 (CH_2Br, complex t, J=7Hz).

1-Fluoro-1,2,3-tribromo-propane

To a 100 ml flask containing 10.2 g (0.0734 mol) bromofluoropropenes in 20 ml CCl_4, cooled in an ice-water bath, was added 11.7 g (0.0732 mol) Br_2 in 10 ml CCl_4 over a period of 20 minutes. The reaction was irradiated periodically and the addition rate was adjusted so that the temperature remained below 20°.

After concentration by rotary evaporation, fractional distillation at reduced pressure yielded 18.0 g (82%) fluorotribromopropane: bp 83-93° at 18 mm; ^1H NMR, δ6.7 (CHBrF, complex d, 1H, J_{FH}=48Hz), 4.7-4.2 (CHBr, complex m, 1H), 3.8 (CH_2Br, t, 2H).

2,3-Dibromo-1-fluoropropene and 2,3-Dibromo-3-fluoropropene

To a 100 ml flask equipped with addition funnel and containing 17.7 g (0.0592 mol) fluorotribromopropane in 10 ml ethanol was added a solution of 4.00 g (0.0606 mol) KOH pellets in 30 ml ethanol over a period of 5 minutes. After stirring 2.5 hours, the white mixture was poured into 90 ml water. The organic layer was separated to give 9.6 g (75%) dibromofluoropropene mixture, which was used directly in the next step. ^1H NMR, δ7.3 (=CHF, d, 1H, J =78Hz), 6.85 (CHBrF, d, 2H, J_{FH}=48Hz), 6.2 and 5.7 ($=CH_2$, m, 4H), 4.2 (CH_2Br, m, 3H).

1-Fluoro-1,2-propadiene (MFA) [4]

A 100 ml, 3-necked, round-bottom flask was equipped with magnetic stirrer, pressure-equalizing addition funnel with nitrogen inlet, and coil

reflux condenser leading to a trap in a Dewar of ice water, then to a trap in a Dewar of dry ice/isopropanol. To a mixture of 18.0 g (0.275 mol) zinc dust and 18 ml 95% ethanol at reflux was added 9.54 g (0.0438 mol) dibromofluoropropenes in 15 ml ethanol by way of the addition funnel. After 15 minutes, addition was completed and the mixture was stirred at reflux for 30 minutes with a slow flow of nitrogen through the system. A total of 1.96 g (77%) MFA was obtained from the trap at dry-ice temperature. The purity was 97% by glpc analysis. The IR was identical to previous reports [4]; ^{1}H NMR, δ7.1 (=CHF, d of t, 1H, J=6, J_{FH}=84 Hz), 5.5 (=CH_2, d, 2H, J=6Hz); ^{19}F NMR, ϕ169 (d of t, 1F, J_{FH}=85, J_{FH}=1.1 Hz); MS gave M^+ 58.02520, Calcd. for C_3H_3F: 58.02188, dev. = 0.0033 (57 ppm), other major fragments, 58 (base), 39.

2,3-Dibromo-1,1,1-trifluoropropane [7]

A 250 ml, 3-necked, round-bottom flask was equipped with magnetic stirrer, dry-ice condenser, thermometer, and gas dispersion tube. After flushing the system with nitrogen, 343 g (2.14 mol) bromine were added and the flask was cooled in an ice-water bath.

Commercial 1,1,1-trifluoropropene was added through the dispersion tube at such a rate that the temperature remained below 25°. Periodic irradiation with a sun lamp facilitated the reaction. After 1.5 hours, a clear, yellow solution was obtained. Simple distillation gave 525 g (96%) dibromotrifluoropropane : bp 115-120° (lit. [7] bp 115-117°); IR, 2990 (w), 1340, 1275, 1250, 1180, 1110, 910, 895 cm^{-1}; ^{1}H NMR, δ4.6-4.2 (CHBr, m, 1H), 4.1-3.5 (CH Br, m, 2H); ^{19}F NMR, ϕ86.3 (d, 3F); MS gave M^+ 253.85506, Calcd. for $C_3H_3Br_2F_3$: 253.85520, dev. = 0.00014 (0.55 ppm); other major fragments, 177, 175 (base), 113, 111, 69, 28.

2-Bromo-3,3,3-trifluoropropane [3,7]

According to the published procedure, 491 g (1.92 mol) dibromotrifluoropropane and 500 g (7.57 mol) KOH pellets yielded 200 g (60%) pure bromotrifluoropropene : bp 32.5-34.5° (lit. [8] bp 33.5-34.5°); IR, 1640 (w), 1285, 1185, 1090 cm^{-1}; ^{1}H NMR, δ6.4 (m, 1H), 6.0 (m, 1H).

1,1-Difluoropropadiene (DFA) [3]

A 1000 ml, 3-necked, round-bottom flask was equipped with magnetic stirrer, pressure-equalizing addition funnel with nitrogen inlet, low temperature thermometer, and a Friedrich condenser with nitrogen outlet. The outlet was attached to two traps in series. The first was cooled in a Dewar of salt-ice water (-15°) and the second in a Dewar of dry ice/isopropanol (-78°).

To the flask was added 50.0 g (0.286 mol) 2-bromo-3,3,3-trifluoropropene and 250 ml hexane. To the addition funnel was added 190 ml (0.304 mol) of a 1.6M solution of commercial n-BuLi in hexane.

The flask was cooled with a hexane slush bath by addition of liquid nitrogen until the temperature of the solution inside the flask was -85°. Then the n-BuLi solution was added over a period of 25 minutes at such a rate that the temperature remained below -80°.

The slightly cloudy, yellowish solution was allowed to stir an additional 10 minutes. Then the hexane slush bath was removed. Upon reaching -30°, a gelatinous precipitate formed and the temperature rapidly rose to 28°.

The volatile product was removed from solution by heating the mixture at reflux for 30 minutes with a slow flow of nitrogen through the system. A total of 21 g (97%) DFA was obtained from the dry-ice-temperature trap. The IR was identical to that previously reported [8]; ^{1}H NMR, δ6.04 (t, J=3.5 Hz); ^{19}F NMR ϕ106.9 (t, J=3.5Hz).

3-Methyl-1,1,1-trifluorobutan-2-ol [9]

A 5-1, 3-necked, round-bottom flask was equipped with magnetic stirrer, nitrogen inlet, addition funnel and Friedrich condenser. Isopropyl magnesium bromide was prepared in the usual manner from 120 g (4.95 mol) Mg turnings, 609 g (4.95 mol) isopropyl bromide and 2300 ml dry ether.

The flask containing the Grignard solution was cooled in an ice-water bath and 284 g (2.00 mol) ethyltrifluoroacetate in an equal volume of ether was added over a period of 50 minutes. After removal of the ice bath, the dark brown solution was stirred for one hour, as propene was evolved. Stirring was continued overnight for 15 hours.

After careful acidification with 1500 ml dilute HCl, the ether layer was separated. The aqueous layer was extracted with five 300 ml portions of ether. The combined ether layers were dried over anhydrous Na_2SO_4. After

removal of the ether by fractional distillation, 168.4 g (59%) methyltrifluorobutanol were collected from 95-100°. Distillation of the product from CaH_2 gave bp 97-101.5°; IR, 3420 (broad), 2980, 1480, 1280, 1175, 1150, 1080, 1030, cm^{-1}; ^1H NMR, δ4.0-3.5 (complex m, 1H), 3.3 (OH, s, 1H), 2.4-1.7 (complex m, 1H), 1.1 (CH_3, d, 6H, J=7Hz); ^{19}F NMR, ϕ76.4 (CF_3, d, 3F, J_{FH}=5.1 Hz); MS gave 141 (M^+-1), 125, 122, 80, 79, 73, 55, 43 (base), 41.

3-Methyl-1,1,1-trifluorobutane-2-ol acetate (n.c)

Into a 1000 ml flask equipped with magnetic stirrer and Friedrich condenser was added 224.8 g (1.58 mol) methyltrifluorobutanol and 310 g (3.95 mol) acetyl chloride. The vigorous evolution of HCl was controlled by cooling with an ice-water bath. After 4 hours at reflux, the solution was stirred overnight (15 hours) at room temperature.

The solution was carefully poured into 600 ml water. Separation of the organic layer yielded 270 g (93%) of crude ester which was dried over anhydrous $MgSo_4$ and purified by fractional distillation to give 228 g methyltrifluorobutane acetate, bp 111-121°. IR, 2980, 1770, 1475, 1375, 1280, 1225, 1170, 1125, 1090, 1050 cm^{-1}, ^1H NMR δ5.1 (d of q, 1H, J=5.5, J_{FH}=7.2), 2.1 (m, 4H), 1.0 (CH_3, d, 6H, J=6Hz); ^{19}F NMR, ϕ74.1 (CF_3, d, 3F, J_{FH}=7.0 Hz); MS gave 185 (M^+ + 1), 169, 164, 142, 122, 104, 43 (base).

2-Methyl-4,4,4-trifluoro-2-butene (n.c)

A vertical pyrolysis tube (40 cm x 2 cm) packed with glass wool was equipped with pressure-equalizing addition funnel with nitrogen inlet at the top and a flask at the bottom with nitrogen outlet. Over a period of 12 hours, 228 g (1.24 mol) methyltrifluorobutyl acetate were passed through the tube at 500° (2 drops/sec, 12 ml/min N_2).

The brown pyrolysate collected in the ice-chilled flask was poured into 450 ml water. The amber organic layer was separated, treated with K_2CO_3 and purified by fractional distillation to yield 115 g (75%) methyltrifluorobutene: bp 48-51°; IR, 2990, 2960, 2925, 1685, 1385, 1355, 1275, 1230, 1110 cm^{-1}; ^1H NMR, δ5.4 (complex q, 1H, J_{FH}=8.4Hz), 1.9 (CH_3, s, 6H); MS gave M^+ (base) 124.0505, Calcd. for $C_5H_7F_3$: 124.0500, dev. = 0.0005 (4.0 ppm), other major fragments 109, 105, 89, 77, 59, 55, 39.

2,3-Dibromo-2-methyl-4,4,4-trifluorobutane (n.c)

A 500 ml, 3-necked flask was equipped with magnetic stirrer, thermometer, and addition funnel. To the flask was added 109 g (0.881 mol) methyltrifluorobutene. To the stirred, cooled solution (10°, salt-ice bath) was added 140 g (0.88 mol) Br_2 over a period of 50 minutes. Periodic irradiation with a sun lamp produced a pale yellow solution which was treated with K_2CO_3. Purification by fractional distillation at reduced pressure gave 198 g (79%) dibromomethyltrifluorobutane : bp 64-65° at 36 mm; IR, 2990, 1460 (w), 1255, 1185, 1110 cm^{-1}; ^1H NMR δ4.5 (q, 1H, J_{FH}=7.2 Hz), 2.0 (CH_3, s, 6H); ^{19}F NMR, ϕ63.7 (CF_3, d, 3F, J_{FH}=7.5Hz); MS gave 285, 283, 281, 203 (base), 123, 103, 77, 59, 39. Analysis gave %C 21.39, %H 2.61, %F 19.82, Calcd. for $C_5H_6Br_2F_3$ %C 21.15, %H 2.48, %F 20.07.

3-Bromo-2-methyl-4,4,4-trifluoro-2-butene (n.c.)

A 1000 ml, 3-necked flask was equipped with magnetic stirrer, pressure-equalizing addition funnel and fractional distillation apparatus with vacuum adapter. To the flask was added 200 g (3.03 mol) KOH pellets and to the funnel was added 197.7 g (0.696 mol) dibromomethyltrifluorobutane.

After lowering the pressure to 100 mm, the flask was heated to 90° and the dibromide was added over a period of 2 hours. The product distilled with a head temperature of 48-50° (100 mm). The crude product was dried over molecular sieves and purified by fractional distillation at ambient pressure to give 104.8 g (74%) bromomethyltrifluorobutene : bp 106-108°; IR, 2940, 1645 (m), 1375 (m), 1355 (w), 1285, 1220, 1165, 1130, 920 cm^{-1}; ^1H NMR, δ2.2-2.0 (CH_3, m, 6H); ^{19}F NMR, ϕ57.4 (CF_3, broad s, 3F); MS gave 204, 202, 189, 183, 123, 103 (base), 77, 59, 53, 43, 39. Analysis gave, %C 29.39, %H 3.13, %F 29.22, Calcd. for $C_5H_6BrF_3$: %C 29.58, %H 2.98, %F 28.08.

1,1-Difluoro-3-methyl-1,2-butadiene (n.c) (DDA)

A solution of n-BuLi in heptane was prepared from commercial n-BuLi by flash vacuum distillation of the hexane followed by addition of an equal volume of dry heptane (distilled from P_2O_5 under nitrogen).

A 250 ml, 3-necked, flask was equipped with magnetic stirrer, pressure-equalizing addition funnel with nitrogen inlet, low temperature thermometer, and coil reflux condenser with nitrogen outlet. After flame drying the apparatus, the outlet was connected first to a spiral trap in a Dewar of

water, then to a trap in a Dewar of dry ice/isopropanol. To the flask was added 16.5 g (0.0813 mol) bromomethyltrifluorobutene and 75 ml dry heptane. To the funnel was added 35 ml (0.0514 mol) of 1.47M n-BuLi in heptane.

After the flask was cooled with a hexane slush bath to -85°, the n-BuLi solution was added over a period of 5 minutes. The colorless, slightly cloudy solution was allowed to stir an additional 10 minutes, then warm to room temperature.

After replacing the funnel and thermometer with stoppers, a vacuum system was attached to the dry-ice temperature trap and the pressure was lowered to 180 mm. The flask was heated at reflux (180 mm) for one hour. A total of 3.9 g crude product was collected in the dry-ice-temperature trap.

Purification by prep. glpc using a 10' x 1/4" 10% Dinonylphthalate column at 50°, 24 ml/min He, gave 1.49 g (28%) pure DDA : bp 52-53°; IR (gas phase) 3000, 2930, 2410 (w), 2010, 1500, 1430, 1370 (w), 1210, 1085, 905 cm^{-1}; ^{1}H NMR δ1.97 (t, 6H, J_{FH}=5.1 Hz); ^{19}F NMR ϕ102.2 (septet, 2F, J_{FH}=5.05); MS gave M^{+} 104.0367, Calcd. for $C_5H_6F_2$: 104.04376, dev. = 0.00009 (0.9 ppm) other major fragments; 104 (base), 89, 85, 83, 77, 69, 65, 59, 53, 39.

5-(Difluoromethylene)-6,6-dimethylbicyclo[2.2.1]-hept-2-ene (n.c)

To a 5-ml flask was added 1.00 g (15 mmol) cyclopentadiene and 172 mg (1.65 mmol) DDA. After 4 days stirring at room temperature the product was isolated from unreacted difluorodimethylallene, cyclopentadiene, and dicyclopentadiene by prep glpc using a 10' by 1/4" 10% DNP column at 140° (24ml/min He). A total of 106 mg (38%) difluoromethylenedimethylbicycloheptene were obtained : bp 149-152°; IR, 2980, 1765, 1460 (m), 1230, 1030, 735 cm^{-1}; ^{1}H NMR, δ6.2 (complex m, 2H, olefinic), 3.4 (broad s, 1H, di-allylic CH), 2.5 (broad s, 1H, allylic CH), 1.8 and 1.5 (two d, 2H, CH_2), 1.3 (s, 3H, CH_3), 1.03 (s, 3H, CH_3); ^{19}F NMR, ϕ96.6 (d, 1F, J=74 Hz), 93.0 (d, 1F, J=74 Hz); MS gave M^{+} 170.09103, Calcd. for $C_{16}H_{12}F_2$: 170.09071, dev. = 0.00032 (1.3 ppm), other major fragments, 155, 135, 127, 91, 66 (base).

(E)-and(Z)-5-(Fluoromethylene)bicyclo[2.2.1]hept-2-ene

Into a thick-walled, glass tube was condensed 1.50 g (0.0227 mol) cyclopentadiene and 117 mg (2.02 mmol) MFA. After sealing under vacuum, the tube was kept in an ice-water bath for 101 hours.

The two isomeric products were separated from cyclopentadiene and dicyclopentadiene by prep glpc using a 10' by 3/8" 10% SE-30 column at 140° (23 ml/min He).

The two isomers, present in 1:1 ratio, were isolated using a 20' by 1/4" 15% ODPN column at 60° (133 ml/min He).

The first eluted compound was (Z)-5-(fluoro-methylene)-bicyclo[2.2.1]-hept-2-ene: IR, 2980, 1700, 1340, 1110, 1060, 1020, 810 cm^{-1}; ^1H NMR, δ6.37 (d, 1H, =CHF J_{FH}=87Hz, $J_{HH} \leq$ 1.5Hz), 6.12 (m, 2H, olefinic), 3.76 (m, 1H, diallylic CH), 3.05 (m, 1H, allylic CH), 2.24 (d, 1H, 6-exo-H, J=14Hz), 1.69 (d, 1H, 6-endo-H, J=14Hz), 1.58 and 1.25 (two d, 2H, J=8Hz); ^{19}F NMR, φ136.8 (d of d, 1F, J_{FH}=87, J_{FH}=3.5Hz); MS gave M^+ 124.06844, Calcd. for C_9H_9F: 124.06883, dev. = 0.00039 (3 ppm), other major fragments 123, 109 (base), 103, 97, 96, 91, 78, 77, 66, 51, 39.

The second eluted compound was (E)-5-(fluoromethylene)-bicyclo[2.2.1]-hept-2-ene: IR, 2980, 1700, 1260, 1060, 1020, 815 cm^{-1}; ^1H NMR, δ6.68 (d, 1H, =CHF, J_{FH}=87Hz, J_{HH}=2Hz), 6.08 (m, 2H, olefinic), 3.18 (m, 1H, diallylic CH), 3.03 (m, 1H, allylic CH), 2.37 (d, 1H, 6-exo-H, J=15Hz), 1.85 (d, 1H, 6-endo-H, J=15Hz), 1.47 and 1.24 (two d, 2H, 7-CH_2, J=7Hz); ^{19}F NMR, φ138.9 (broad d, 1F, J_{FH}=87Hz); MS gave M^+ 124.06833, Calcd. for C_9H_9F: 124.06883, dev. = 0.0005 (4 ppm), other major fragments, 123, 109 (base), 103, 97, 96, 91, 78, 77, 66.

Glpc yield using octane as an internal standard was 89%.

5-(Difluoromethylene)bicyclo[2.2.1]hept-2-ene [10]

This adduct was prepared as in the preceding procedure, except DFA was used and the reaction was complete after a few minutes: bp 115-117°; IR, 2990 (m), 1775, 1240, 1045, 835 cm^{-1}; ^1H NMR, δ6.08 (m, 2H, olefinic), 3.42 (s, 1H, diallylic CH), 3.03 (s, 1H, allylic CH), 2.31 (d of q, 1H, 6-exo-H), 1.86-1.26 (m, 3H, 6-endo-H and 7-CH_2); ^{19}F NMR, φ94.9 (d, 1F, J=71Hz), 93.3 (d, 1F, J=71Hz); MS gave M^+ 142.0585, Calcd. for $C_8H_8F_2$: 142.0593, dev. = 0.0008 (5.6 ppm).

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