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POLYFLUORO-1,2-EPOXY- ALKANES AND -CYCLOALKANES. PART VI. THE SYNTHESIS AND SOME REACTIONS OF 1-TRIFLUOROMETHYLNONAFLUORO-1,2-EPOXYCYCLOHEXANE

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SUMMARY

Aqueous sodium hypochlorite in acetonitrile gave, respectively, 1-trifluoromethylnonafluoro-1,2-epoxycyclohexane (2) from 1-trifluoromethylnonafluorocyclohex-1-ene, and the bis-(1,2):(4,5)-epoxide from 1-trifluoromethylheptafluorocyclohexa-1,4-diene. From epoxide (2) and lithium aluminium hydride, 1*H*,2*H* -2-trifluoromethyloctafluorocyclohexanol was formed, and (2) with potassium fluoride afforded potassium 2-trifluoromethyldecafluorocyclohexanolate (6). The two stereoisomers of 1-methoxy-2-trifluoromethyldecafluorocyclohexane were obtained from alkoxide (6) and dimethyl sulphate: warming of (6) gave 2-trifluoromethylnonafluorocyclohexanone (9). Epoxide (2) with sodium methoxide afforded two acyclic products, methyl decafluoro-6-methoxyhept-5-enoate (10) and methyl nonafluoro-5,6-dimethoxyhept-5-enoate, *via* a sequence which included a ring-opening haloform cleavage stage. Reaction of ketone (9) with sodium methoxide also gave two acyclic esters, (10) and its positional isomer, methyl decafluoro-6-methoxyhept-4-enoate, as an inseparable mixture. Again, ring-opening was by a haloform cleavage.

INTRODUCTION

Earlier parts of this series have described the preparation of epoxides from perfluorocyclohept-enes and -dienes [1], from oligomers of tetrafluoroethene [2], and from polyfluorocyclohexenes [3], using an efficient process

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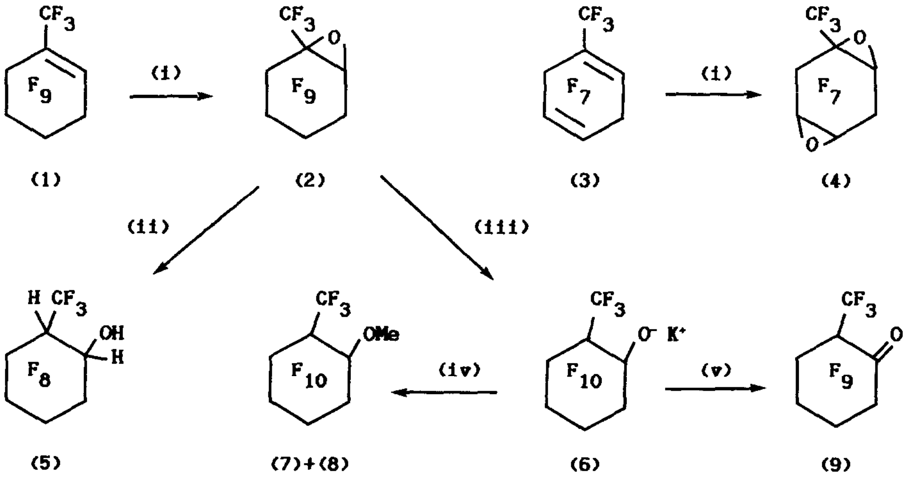
[4] of direct epoxidation by sodium hypochlorite in solution. This paper extends the range of the reaction to cover 1-trifluoromethylnonafluorocyclohex-1-ene (1) [5,6], and 1-trifluoromethylheptafluorocyclohexa-1,4-diene (3) [5] (See Scheme I). Some reactions of the epoxide (2), made from (1), have also been investigated.

RESULTS AND DISCUSSION

Epoxidation of 1-trifluoromethylnonafluorocyclohex-1-ene (1) by aqueous sodium hypochlorite, and acetonitrile as co-solvent, proceeded quite rapidly compared with those of the polyfluorocyclohexenes reported earlier [3]. The reactivity of the double bond towards this reagent was clearly enhanced by the presence of the trifluoromethyl group. The product, 1-trifluoromethylnonafluoro-1,2-epoxycyclohexane (2), obtained in over 90% yield, had the expected nmr (see Table) and ir spectroscopic parameters.



Reagents: (i) $NaOCl/H_2O/CH_3CN$; (ii) $LiAlH_4/Et_2O$; (iii) KF/CH_3CN
(iv) $(CH_3)_2SO_4/CH_3CN$; (v) Gentle warming.

ALL UNMARKED BONDS ARE TO FLUORINE

SCHEME I.

Epoxidations of octafluorocyclohexadienes using this system had failed, the products being dibasic acids [3]; however, decafluorocycloheptadienes were converted successfully into epoxy-derivatives [1]. It was of interest therefore to find that 1-trifluoromethylheptafluorocyclohexa-1,4-diene (3) reacted smoothly to give a bis-epoxide (4) in about 60% yield (also present were two minor unidentified products). Spectroscopic data suggested that epoxide (4) had the expected structure, 1-trifluoromethylheptafluoro-[(1,2):(4,5)-bis-epoxy]cyclohexane.

The epoxy ring of 1-trifluoromethylnonafluoro-1,2-epoxycyclohexane (2) was cleaved by lithium aluminium hydride in diethyl ether [cf 7] to give an alcohol. ^{19}F nmr showed that the original CF_3 and four CF_2 groups were intact and, by ^{1}H nmr, new groupings CHOH and $CHCF_3$ were now present. Hence, the product was 1*H*,2*H* -2-trifluoromethyloctafluorocyclohexanol (5). The nmr spectra suggested that only one isomer was present, but its stereochemistry was not established: the CF_3 group probably occupies an equatorial position, but that of the hydroxyl is less certain.

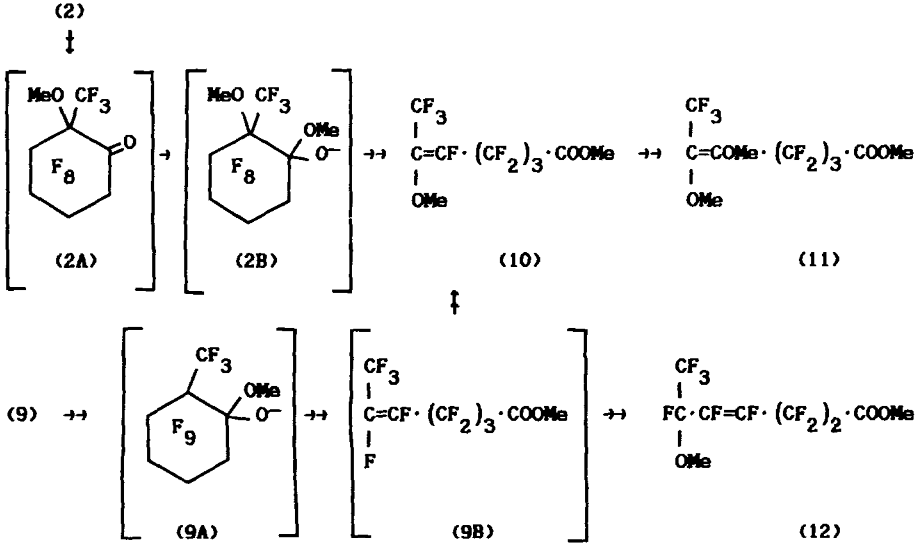
Epoxide (2) and potassium fluoride in acetonitrile afforded the adduct, potassium 2-trifluoromethyldecafluorocyclohexanolate (6). The epoxide ring-opening was carried out at 50 °C, but then an equilibrium appeared to establish [cf 8] between alkoxide (6) and the system KF + ketone (9). After the reaction mixture had been stirred at ca 15 °C for 12 hours, it was treated with dimethyl sulphate. Two components were present in the product and separation by glc gave pure stereoisomers. Both showed appropriate nmr peaks, but the *cis*- isomer, 1-methoxy-2-trifluoromethyl/decafluorocyclohexane (7), had that for the ***F*** -C-OMe position at higher field than was the case for the *trans*- isomer (8) (Φ values 147.0 and 135.2 ppm, respectively). The bulky CF_3 group should preferentially occupy an equatorial position in compounds of this type [cf 9]. At C-1, the *cis* -isomer (7) would then have an equatorial fluorine, and the *trans* -isomer (8) an axial one. Equatorial fluorine in trifluoromethylpolyfluorocyclohexanes normally registers at higher field (by ~ 15 ppm) than does axial fluorine [9].

Confirmatory evidence was found in the ir spectra: bands due to equatorial -O-Me stretching are usually [10] at higher frequencies than those from axial -O-Me. Isomer (7) has bands at 980 and 1015 cm^{-1}, whilst those for (8) are at 1000 and 1022 cm^{-1}: (7) thus has an axial -OMe group and (8) an equatorial one, and this is in accord with the nmr evidence.

When the alkoxide was made as described above, and the solvent then evaporated from it *in vacuo*, (6) was isolated as a solid residue, readily decomposed by warming to give 2-trifluoromethylnonafluorocyclohexanone (9).

Reaction of epoxide (2) with methanolic sodium methoxide gave no cyclic products, two open-chain compounds being obtained, after separation by glc. The spectroscopic parameters of each corresponded to an ester structure with a C=C bond; each had a CF_3 and three CF_2 groups, OMe and COOMe functions. The more volatile compound was E-methyl decafluoro-6-methoxyhept-5-enoate (10). The stereochemistry was established by the ^{19}F nmr signal for the CF_3 group, a complex doublet at 65.8, showing coupling to the adjacent vinylic fluorine (J = 23 Hz). This showed that F and CF_3 were arranged cis (normal couplings [11]; J_{cis}~22 Hz, J_{trans}~8 Hz). The ester of lower volatility was methyl nonafluoro-5,6-dimethoxyhept-5-enoate (11): the geometry was less certain here, though only one isomer was present.

The probable route to these products is indicated in Scheme II. Attack by methoxide ion on the epoxide ring of (2), at the carbon carrying the CF_3 group, gives an alkoxide analogous to (6), and this loses fluoride ion to give 2-methoxy-2-trifluoromethyloctafluorocyclohexanone (2A). Further attack



SCHEME II.

by MeO$^-$ on this ketone (2A) would then give rise to a key intermediate, the hemiketal anion (2B).

At this stage a haloform cleavage reaction can occur. This process [12] is a general one for fluorocarbonyl compounds upon treatment with bases:-

$$R\cdot C(=O)\cdot Rf \rightarrow R\cdot COOH + Rf\cdot H \quad :: \quad Rf\cdot C(=O)\cdot Rf \rightarrow Rf\cdot COOH + Rf\cdot H$$

Transfer of the negative charge of hemiketal anion (2B) to the original C-2, and concomitant formation of a carbomethoxy function at the original C-1, as the C1-C2 bond breaks, afford a classical haloform carbanion intermediate (from cyclic substrates, eg (2B), this contains both anion and carbomethoxy functions). Furthermore, this carbanion does not protonate (unlike those in the general examples cited above). The strongly basic medium promotes loss of F$^-$ from the CF_2 at the original C-3 position, leading to formation of the alkene ester (10).

Consideration of the geometry of the anion (2B), suggests that the equatorial F at the original C-3 position can achieve near coplanarity with the C1-C2 bond being broken. The axial F, *cis* to the CF_3 group, will therefore become the vinylic F. This explains the E-geometry of product (10).

Dimethoxy-ester (11), the second product isolated from the reaction of epoxide (2) with sodium methoxide can be plausibly explained as arising *via* addition of methoxide ion to the alkene function of ester (10), followed by loss of F$^-$. The orientation of the addition is the expected one [cf 13].

This explanation of the pathway to the reaction products (10) and (11) was tested by studying the reaction of 2-trifluoromethylnonafluorocyclohexanone (9) with methanolic sodium methoxide. An inseparable mixture of two products was obtained, one being the above ester (10). The second was identified from its nmr spectra as a positional isomer, methyl decafluoro-6-methoxyhept-4-enoate (12) (see Scheme II).

A similar sequence to that postulated above explains this result also. Methoxide attack on ketone (9) affords a hemiketal anion (9A), the haloform cleavage of which would afford the methyl ester (9B). Not found among the products, this would be susceptible to further nucleophilic attack by MeO$^-$, and the formation of a 6-methoxy anionic adduct is plausible. The negative charge on this anion, located at C-5, could be lost as F$^-$ from either C-6 or C-4, giving rise to the alkene esters (10) and (12), actually isolated.

It is to be noted that the products of the reactions of methoxide ion with epoxide (2) and with ketone (9) differ markedly from those arising from its reactions with perfluoro-1,2-epoxycyclo-heptane and -hexane. In the last case [7], the product was 2-methoxynonafluorocyclohexanone (isolated as the hydrate after aqueous work-up), analogous to the proposed ketone intermediate (2A) of Scheme II. The primary product from the cycloheptane epoxide was treated with dimethyl sulphate before work-up [1], being converted into 1,1,2-trimethoxyundecafluorocycloheptane. This methylation was clearly of a hemiketal anion correponding to intermediate (2B) of Scheme II.

No haloform cleavage occurred in these earlier cases: obviously this C-C bond breaking step is promoted by the ready acceptance onto the carbon carrying the CF_3 group, of the negative charge originally located on the C-1 oxygen of a hemiketal anion such as (2B) or (9A). In the absence of chain branching of this type, the reaction stops at the hemiketal stage.

The reactions of 1-trifluoromethylnonafluoro-1,2-epoxycyclohexane (2), that were studied in this work, clearly involved attack on the epoxy-ring at the carbon carrying the CF_3 group. This directive effect is the same as that established long ago [14] for unsymmetrical perfluoroepoxides such as hexafluoro-1,2-epoxypropane.

EXPERIMENTAL

Synthesis of Epoxides

1-Trifluoromethylnonafluorocyclohex-1-ene (1) [6] (60.0 g) was added during 15 minutes to a vigorously-stirred mixture of acetonitrile (120 cm^3) and aqueous sodium hypochlorite (360 cm^3; 12 % available Cl). The mixture was then stirred at 50 °C for 1 hour. Water (600 cm^3) was added, the lower layer separated, washed with aqueous sodium metabisulphite, and water, dried ($MgSO_4$) and distilled to give 1-trifluoromethylnonafluoro-1,2-epoxycyclohexane (2) (nc); (58.5 g); b.p. 71 °C; (Found: C, 25.7; F, 69.9. $C_7F_{12}O$ requires C, 25.6; F, 69.5 %); there was an ir band at 1470 cm^{-1}.

1-Trifluoromethylheptafluorocyclohexa-1,4-diene (3) [5] (9.7 g) treated with proportional reagent quantities, and the mixture worked up, as above, gave 1-trifluoromethylheptafluoro-[(1,2):(4,5)-bis-epoxy]cyclohexane (4) (nc); (6.3 g); b.p. 77 °C; (Found: C, 27.5. $C_7F_{10}O_2$ requires C, 27.5 %); ir bands were present at 1445 and 1495 cm^{-1}.

Reaction of Epoxide (2) with Lithium Aluminium Hydride

Compound (2) (10.0 g) was added to a stirred suspension of lithium aluminium hydride (1.0 g) in dry diethyl ether (50 cm^3), and the mixture was stirred for 16 hours at 15 °C. Water was then added cautiously, followed by sulphuric acid (50 cm^3; 2M). The combined ether layer and an ether extract of the aqueous phase were dried ($MgSO_4$) and most of the ether distilled off (15 cm column) to leave a crude product (10.2 g). A portion (2.0 g) was separated by semi-preparative glc (Pye Series 104 instrument; glass column 9.1 m x 7 mm int. diam. packed with Silicone gum SE30 on Supasorb (1:9); 95 °C; N_2 flow rate 2 l/hr, retention time 29 min.), to give *1H,2H*-2-trifluoromethyloctafluorocyclohexanol (5) (nc) (1.4 g); b.p. 130-134 °C; (Found: C, 27.2; H, 1.2; F, 67.4. $C_7H_3F_{11}O$ requires C, 26.9; H, 1.0; F, 67.0 %).

Reaction of Epoxide (2) with Potassium Fluoride

Product (2) (10.0 g) was added to a stirred suspension of dry potassium fluoride (1.8 g) in dry acetonitrile (30 cm^3) at 50 °C. After being stirred at 50 °C for 3 hours and then at 15 °C for 12 hours, the mixture was divided into two equal parts.

The solvent was evaporated from the first part *in vacuo* to leave a dry solid residue of potassium 2-trifluoromethyldecafluorocyclohexanolate (6). Gentle heating, finally at 200 °C, gave 2-trifluoromethylnonafluorocyclohexanone (9); (nc); (2.8 g); b.p. 71 °C; (Found: C, 25.6; F, 70.0. $C_7F_{12}O$ requires C, 25.6; F, 69.5 %); ir 1790 cm^{-1} (C=O).

To the second part of the original mixture, was added dimethyl sulphate (2.0 g). After being stirred (15 °C; 2 hours), water (100 cm^3) was added, the organic layer was separated, washed with dilute KOH (50 cm^3; 4M), water, and dried ($MgSO_4$). Analytical glc showed 2 components, and separation by preparative glc (copper tube, 4.8 m x 35 mm int. diam.; packing, dinonyl phthalate/Chromosorb P 30-60 (1:5); katharometer detector; 85 °C; N_2 flow rate 12 l/hr) afforded:- (i) 1-methoxy-2-trifluoromethyl/decafluorocyclohexane (*cis*) (7) (nc); (0.9 g); b.p. 113 °C; (Found: C, 26.5; H, 1.0; F, 68.3. $C_8H_3F_{13}O$ requires C, 26.5; H, 0.8; F, 68.2 %): (ii) mixture (0.9 g): (iii) 1-methoxy/-2-trifluoromethyldecafluorocyclohexane (*trans*) (8) (nc); (0.8 g); b.p. 118 °C; (Found: C, 26.8; H, 0.7; F, 68.2 %).

Reactions with Sodium Methoxide

(a) 1-Trifluoromethylnonafluoro-1,2-epoxycyclohexane (2)

This (10.0 g), added slowly to a solution of sodium (2.0 g) in dry methanol 40 cm^3) and ether (10 cm^3), gave an exothermic reaction. After having been stirred at 15 °C for 12 hours, the mixture was acidified (H_2SO_4; 100^3cm; 2M) and extracted with ether (3 x 50 cm^3). The extracts were dried ($MgSO_4$), concentrated, washed with water to remove methanol, and redried ($MgSO_4$). Of the resultant filtrate (3 components by glc), ca. half (3.0 g) was separated (Pye 104 as above; packing, polyethylene glycol adipate/Chromosorb P 30-60 (1:6); 160 °C; N_2 flow rate 3 l/hr) to give:- (i) after 16 min., E-methyl decafluoro-6-methoxyhept-5-eneoate (10) (nc); (1.4 g); b.p. 170-171 °C; (Found: C, 31.0; H, 1.6; F, 54.2. $C_9H_6F_{10}O_3$ requires C, 30.7; H, 1.7; F, 54.0 %); ir 1780 cm^{-1} (broad): (ii) after 31 min., unidentified (0.1 g): (iii) after 45 min., methyl nonafluoro-5,6-dimethoxyhept-5-enoate (11) (nc); (1.1 g); b.p. 213-215 °C; (Found: C, 32.9; H, 2.2; F, 46.7. $C_{10}H_9F_9O_4$ requires C, 33.0; H, 2.5; F, 47.0 %); ir 1780 cm^{-1} (broad).

(b) 2-Trifluoromethylnonafluorocyclohexanone (9)

This (3.0 g) in dry methanol (5 cm^3) was added to a stirred solution of sodium (0.6 g) in methanol (30 cm^3); stirring was continued for 12 hours at 15 °C. Isolation as in case (a) gave:- (i) after 6.5 min., recovered (9) (0.3 g; correct ir): (ii) after 12 min., unidentified (0.1 g): (iii) after 17 min., a mixture (1.4 g) of 57 % of fraction (a)(i) above, (compound (10)) together with 43 % of methyl decafluoro-6-methoxyhept-4-enoate (12) (Found: C, 30.6; H, 1.5 %); ir 1780 cm^{-1} (broad).

Spectroscopy

(a) Infrared spectra were measured as liquid films on a Perkin-Elmer 257 machine. Peaks of particular significance are noted; other peaks were at the positions expected for these types of compounds.

(b) Nmr spectra were measured by a Perkin-Elmer R12B spectrometer, using solutions in deuterochloroform (10-20 % w/v), unless otherwise stated. ^1H data were recorded at 60 MHz, chemical shift values being in δ units (ppm to low field of the internal reference, tetramethylsilane) and ^{19}F at 56.4 MHz; values being quoted in Φ units (ppm to high field of the internal reference, trichlorofluoromethane). Peak descriptions:- b = broad; c = complex; d = doublet; m = multiplet; q = quintet; s = singlet; t = triplet.

TABLE

NMR spectra of compounds 2-12

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
2	F	67.0	3	CF_3	cm
		124.0	2	CF_2	cAB; $J = 288; \Delta\gamma = 908$
		128.7	2	CF_2	cAB; $J = 276; \Delta\gamma = 1053$
		133.5	2	CF_2	cAB; $J = 288; \Delta\gamma = 769$
		{ 121.4	1 }	CF_2	cm
		{ 132.7	1 }		
		162.4	1	F-C-O-	cm
4	F	66.6	3	CF_3	cm
		118.1	2	CF_2	cAB; $J = 288; \Delta\gamma = 767$
		122.0	2	CF_2	cm
		163.4	1	F-C-O-(C2)	cm
		169.9	1	F-C-O-	cm
		171.0	1	F-C-O-	cm
5	H	3.16	1	$\mathrm{C}\mathit{H}\,\mathrm{OH}$	bm
		3.30	1	OH; lost on shaking with D_2O	bm
		4.66	1	$CHCF_3$	bm
	F	61.8	3	CF_3	q; $J_q = 10$
		118.5	2	CF_2	cm
		125.6	2	CF_2	cAB; $J = 282; \Delta\gamma = 798$
		130.5	2	CF_2	cAB; $J = 288; \Delta\gamma = 1210$
		131.4	2	CF_2	cAB; $J = 288: \Delta\gamma = 943$
7	H	3.77	-	CH_3O	d of m; $J_d = 5$
	F	69.4	3	CF_3	cq; $J_q = 11$
		123.9	2	CF_2	cAB; $J = 282; \Delta\gamma = 1041$
		128.7	2	CF_2	cAB; $J = 276; \Delta\gamma = 916$
		128.9	2	CF_2	cAB; $J = 276; \Delta\gamma = 1204$
		132.5	2	CF_2	cAB; $J = 288; \Delta\gamma = 1066$
		147.0	1	$\mathrm{MeOC}\text{-}\mathit{F}$	cm
		187.4	1	$\mathrm{CF_3C}\text{-}\mathit{F}$	cm
8	H	3.47	-	CH_3O	cdd; $J = 4$; $J = 1$
	F	68.5	3	CF_3	cm
		127.2	4	CF_2	cAB; $J = 288; \Delta\gamma = 770$
		129.9	2	CF_2	cAB; $J = 276; \Delta\gamma = 1192$

(Continued)

TABLE (cont.)

TABLE OF NMR SPECTRA OF COMPOUNDS 8 (cont.), 9-12

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
/continued					
8	F	131.4	2	$\mathrm{CF_2}$	cAB; $J = 282$; $\Delta\gamma = 1194$
		135.2	1	$\mathrm{MeOC}\text{-}F$	cm
		186.1	1	$\mathrm{CF_3C}\text{-}F$	cm
9	F	72.1	3	$\mathrm{CF_3}$	cm
		123.6	2	$\mathrm{CF_2}$	cAB; $J = 282$; $\Delta\gamma = 1026$
		129.4	2	$\mathrm{CF_2}$	cm
		129.9	2	$\mathrm{CF_2}$	cAB; $J = 276$; $\Delta\gamma = 1034$
		133.1	2	$\mathrm{CF_2}$	cAB; $J = 276$; $\Delta\gamma = 1012$
		179.3	1	$\mathrm{CF_3C}\text{-}F$	cm
10	H	3.70	1	$\mathrm{CH_3O}$	bs
		3.97	1	$\mathrm{CH_3O{\cdot}CO}$	s
	F	65.8	3	$\mathrm{CF_3}$	cd; $J = 23$
		117.4	2	$\mathrm{CF_2(C3)}$	cm
		119.1	2	$\mathrm{CF_2(C4)}$	cdt; $J = 3$, $J = 10$
		124.6	2	$\mathrm{CF_2(C2)}$	cd; $J = 6$
		177.0	1	$\mathrm{-CF=}$	bm
11 (neat)	H	3.47	1	$\mathrm{CH_3O}$	bs
		3.50	1	$\mathrm{CH_3O}$	bs
		3.67	1	$\mathrm{CH_3O{\cdot}CO}$	s
	F	66.9	3	$\mathrm{CF_3}$	s
		114.9	2	$\mathrm{CF_2(C3)}$	cm
		120.6	2	$\mathrm{CF_2(C4)}$	ct; $J = 11$
		125.1	2	$\mathrm{CF_2(C2)}$	bs
12	H	3.67	1	$\mathrm{CH_3O}$	bs
		3.97	1	$\mathrm{CH_3O{\cdot}CO}$	s
	F	84.0	3	$\mathrm{CF_3}$	q; $J = 3$
		119.5	2	$\mathrm{CF_2}$	cm
		120.9	2	$\mathrm{CF_2}$	cm
		136.2	1	$\mathrm{CF(C6)}$	cd; $J = 31$
		153.5	2	$\mathrm{FC{=}CF}$	cAB; $J = 138$; $\Delta\gamma = 368$

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