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New Electrophilic Reaction of Perfluoroalkylethylenes. Synthesis and Some Reactions of 1-Halo-1,1,2-trihydroperfluoroalkenes-2[†]

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Perfluoroalkylethylenes, $R_fCH{=}CH_2$, react with chlorosulfonic acid in the presence of TaF_5 or NbF_5 catalyst to form allyl chlorides, Z-$R_fCF{=}CHCH_2Cl$. These chlorides, or their corresponding bromides, also can be made by the BF_3-catalyzed reaction of $R_fCH{=}CH_2$ with HCl or HBr in anhydrous HF. The allylic chlorine in the newly synthesized compounds Z-$R_fCF{=}CHCH_2Cl$ can be easily replaced by reaction with nucleophiles such as I^-, Br^-, HO^-, or $(CF_3)_2CFO^-$.

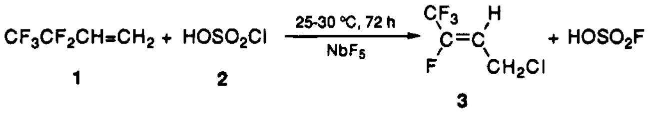
Introduction

The reactions of perfluoroolefins and polyfluoroolefins with electrophiles are important synthetic reactions in organofluorine chemistry,[1] but there are only a few reports on reactions of perfluoroalkylethylenes, $R_fCH{=}CH_2$, with electrophilic reagents. The known reactions of this type are limited to addition of protic acids to CF_3-$CH{=}CH_2$,[2] dimerization of the same olefin in fluorosulfonic acid,[3] alkylation of aromatic compounds with CF_3-$CH{=}CH_2$ in the presence of Lewis acids,[4] and two procedures for preparation of halohydrins by the reaction of $R_fCH{=}CH_2$ with Br_2/CH_3CO_2H in the presence of mercury acetate[5] or with a mixture of halogen with SO_3.[6]

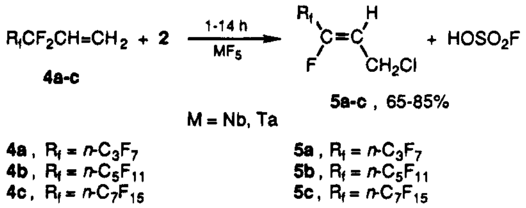
This paper describes new reactions of $R_fCH{=}CH_2$ alkenes with different Bronsted acids to form allylic halides, $R_fCF{=}CHCH_2X$, and some further reactions of these new halides.

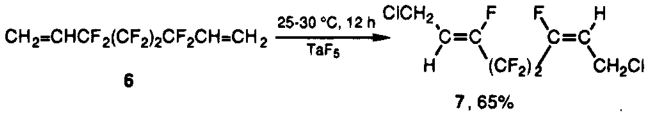
Results and Discussion

Reaction of Perfluoroalkylethylenes with Protic Acids. 3,3,3-Trifluoropropene reacts with chlorosulfonic acid without a catalyst to give 1,1-difluoro-1-(chlorosulfato)-3-chloropropane.[2b] Higher perfluoroalkylethylenes are much less reactive toward $HOSO_2X$ (X = F, Cl, CF_3) and do not react with these acids without a catalyst even at elevated temperature (60−70 °C, 4−5 h). In the presence of a Lewis acid catalyst such as NbF_5, olefin **1** reacts readily with $HOSO_2Cl$ (**2**) at ambient temperature to give equal amounts of allyl chloride **3** and $HOSO_2F$ by ^{19}F NMR. Pure **3** was isolated in 44% yield after washing the crude reaction mixture with ice water and distillation. The structure of **3** was determined by ^1H and ^{19}F NMR, IR, and high-resolution mass spectroscopy.



The reaction with **2** is general to give chlorides **5a−c** in high yields. Both double bonds in diolefin **6** are reactive toward **2**, and the *trans,trans* isomer of dichloro compound **7** is produced in 65% yield.





Conditions, ratio of reactants, and yields for reaction of **4a−c** and **6** are summarized in Table 1. As expected, TaF_5 is a more active catalyst for this process than NbF_5 wherein, under similar conditions, reactions catalyzed by TaF_5 are clearly faster (see entries 3, 6, and 8 in Table 1). Surprisingly, antimony pentafluoride *is not active* in this reaction at all (entry 4, Table 1), probably because of side reactions with chlorosulfonic acid that deactivate the catalyst.

Olefin stereochemistry was assigned by the NMR signal of the vinyl hydrogen in $R_fCF{=}CHCH_2X$ which appeared as a doublet of triplets at 5.75−6.00 ppm. The coupling constant to vinyl fluorine was 29−34 Hz, indicating *trans* arrangement for vinyl hydrogen and fluorine.[7] *Cis* isomers were never observed.

In sharp contrast to the results for alkylethylenes with **2**, the reactions of **4a** with either fluorosulfonic or trifluoromethansulfonic acid in the presence of a catalytic NbF_5 or SbF_5 lead only to a mixture of dimers of **4a** (the structure was not determined), having formula $C_{12}H_6F_{18}$ and $C_{12}H_5F_{17}$ (by high-resolution GC−MS). This agrees with the previously reported results for the reaction of 3,3,3-trifluoropropene with fluorosulfonic acid.[3] A similar result was obtained in the reaction of **4a** with HF in the presence of BF_3 as a catalyst. After 18 h at 50 °C, 75% of **4a** was converted to its dimers, along with about 25% of $C_4F_9CH_2CH_2F$ (by MS and ^1H NMR).

Compound **5a** was the main product from the reaction of **4a** with equimolar amounts of HCl in anhydrous HF

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

(1) Chambers, R. D. *Fluorine in Organic Chemistry;* Wiley: New York, 1973; pp 170−172,.

(2) (a) Henne, A. L.; Kaye, S. *J. Am. Chem. Soc.* **1950**, *72*, 3369. (b) Myhre, P. C.; Andrews, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 7596.

(3) Myhre, P. C.; Andrews, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 7595.

(4) Kobayashi, Y.; Nagai, T.; Kumadaki, I.; Takahashi, M.; Yamauchi, T. *Chem. Pharm. Bull.* **1984**, *32*, 4382.

(5) Coudures, C.; Pastor, R.; Cambon, A. *J. Fluorine Chem.* **1984**, *24*, 93.

(6) Krespan, C. G. U.S. Pat. 5,185,477, 1993.

(7) Feiring, A. E.; Hovey, M. C.; Arthur, S. D. *J. Fluorine Chem.* **1984**, *26*, 161.

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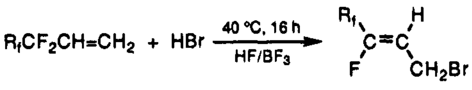
solvent and catalytic BF_3. The crude product contained 8% starting material, 9% $C_4F_9CH_2CH_2F$, 78% **5a** and 5% unidentified, higher boiling point materials by GC and ^{19}F NMR.

$$\mathbf{4a} + HCl \xrightarrow[HF/BF_3]{50\ °C,\ 16\ h} \mathbf{5a},\ 53.3\%$$

The reaction of olefins **4a,b** with HBr in the HF/BF_3 system is a convenient route to allyl bromides **8a,b**, since the instability of bromosulfonic acid precludes its use in an analogous manner to chlorosulfonic acid.



4a-c **8a-c**, 47-90%

4a, $R_f = n\text{-}C_3F_7$
4b, $R_f = n\text{-}C_5F_{11}$
4c, $R_f = n\text{-}C_7F_{15}$

8a, $R_f = n\text{-}C_3F_7$
8b, $R_f = n\text{-}C_5F_{11}$
8c, $R_f = n\text{-}C_7F_{15}$

Olefin conversions were typically 80–90% under these conditions, and the crude products always contained 10–13% of the corresponding alkanes $R_fCH_2CH_2F$, which were not isolated but identified by ^1H NMR. Conditions, ratio of reactants, and yields for reaction of **4a–c** with HBr in HF are summarized in Table 1. Olefin **4a** does not react with such a weak π-base as tetrafluoroethylene (TFE) in the HF/BF_3 system. At 50 °C the reaction leads to formation of dimers of **4a** only. However, the reaction between **4a** and benzene proceeds already at 25 °C and produces alkylbenzene **9** along with small amounts of alkenylbenzene **10** and dialkylbenzene **11**.

$$\mathbf{4a} + C_6H_6 \xrightarrow[HF/BF_3]{25\ °C,\ 16\ h} \underset{\mathbf{9}}{C_4F_9CH_2CH_2C_6H_5} + \underset{\mathbf{10}}{C_3F_7CF{=}CHCH_2C_6H_5} + \underset{\mathbf{11}}{(C_4F_9CH_2CH_2)_2C_6H_4}$$

Compound **9**, containing 10% of **10**, was isolated by distillation. Notably, the amount of **9** and **10** formed in this reaction is temperature dependent: at 50 °C the ratio of **9**, **10**, and **11** in the crude product was 55:20:25 vs 78:9:12 of **9, 10**, and **11** at 25 °C. The reaction of monochlorobenzene with **4a** is slower (conversion of **4a** after 16 h at 25 °C is about 40%) and, surprisingly, produces only unsaturated product **12** (mixture of all three isomers) along with small amounts (<3%) of polyalkenylbenzenes.

$$\mathbf{4a} + C_6H_5Cl \xrightarrow[HF/BF_3]{25\ °C,\ 16\ h} \underset{\mathbf{12},\ 35\%}{C_3F_7CF{=}CHCH_2C_6H_4Cl}$$

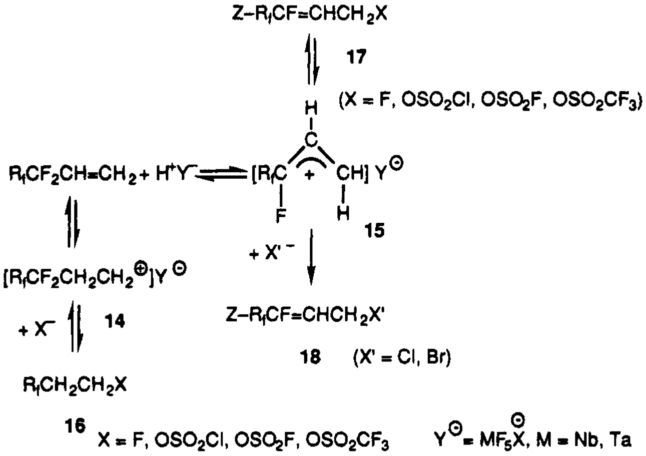
Mechanistic Considerations. The formation of compounds **3**, **5a–c**, **7**, and **8a–c** in reaction of corresponding olefins with chlorosulfonic acid or HX in hydrogen fluoride, along with results on reaction **4a** with aromatics and dimerization of **4a** in acidic media, may be explained by the mechanism in Scheme 1.

Table 1. Reaction of Compounds 1, 4a–c, and 6 with Different Acids and Aromatic Compounds[a]

entry	olefin (mol)	HX (mol)	HF (g)	catalyst (mmol)	temp (°C)	time (h)	product (yield, %)
1	**1** (0.2)	HSO_3Cl (0.2)		NbF_5 (5.3)	25	72	**3** (44)
2	**4a** (0.1)	HSO_3Cl (0.1)		NbF_5 (4.2)	25–30	16	**5a** (75.3)
3	**4a** (0.5)	HSO_3Cl (0.51)		TaF_5 (11)	25–30	5	**5a** (76)
4	**4a** (0.1)	HSO_3Cl (0.1)		SbF_5 (10)	25	16	**5a** (0)
5	**4b** (0.1)	HSO_3Cl (0.1)		NbF_5 (8)	100	24	**5b** (66)
6	**4b** (0.1)	HSO_3Cl (0.2)		TaF_5 (2.2)	50–60	2	**5b** (88.2)
7	**4c** (0.1)	HSO_3Cl (0.11)		TaF_5 (5.4)	50–60	1	**5c** (86)
8	**6** (0.1)	HSO_3Cl (0.22)		TaF_5 (2.1)	25–30	12	**7** (65.1)
9	**4a** (0.2)	HCl (0.21)	100	BF_3 (103)	50	16	**5a** (53.5)
10	**4a** (0.2)	HBr (0.22)	100	BF_3 (103)	40	16	**8a** (89.7)
11	**4b** (0.13)	HBr (0.11)	100	BF_3 (103)	40	16	**8b** (63)
12	**4c** (0.1)	HBr (0.11)	100	BF_3 (103)	40	16	**8c** (47)
13	**4a** (0.2)	C_6H_6 (0.2)	100	BF_3 (103)	25	16	**9*** (67)
10	**4a** (0.2)	C_6H_5Cl (0.2)	100	BF_3 (103)	25	18	**12**** (25)

[a] * = isolated product contained 10% of **10**. ** = mixture of *o*-, *m*-, and *p*-isomers; the ratio was not determined.

Scheme 1



Protonation of alkylethylene can form two different electrophilic species: saturated carbocation **14** by protonation of the C=C bond or allyl cation **15** by protonation and abstraction of fluoride from the CF_2 group. Formation of fluoroalkyl[8] and polyfluorinated allyl cations[9] under action of Bronsted and Lewis acids is well documented, and many of these species have lifetimes long enough to be characterized by NMR spectroscopy. Stabilization of cations **14** and **15** by reaction with counteranion or solvent (HF, $HOSO_2X$) produces either alkane **16** or unsaturated compound **17** or **18**. Compounds **16** and **17** having a "basic" fragment, such as a fluorine or $\text{-}OSO_2X$ group, can be protonated with generation of cations **14** and **15**. In other words, under reaction conditions, **16** and **17** are in equilibrium with starting alkylethylene. However, formation of compounds **18** by reaction of allyl cation **15** with HCl (chlorosulfonic acid at room temperature is in equilibrium with HCl and SO_3[10]) or HBr under reaction conditions is likely irreversible, and it shifts all equilibria toward formation of **18**. Fluorosulfonic acid is produced in

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(8) Olah, G. A.; Mo, Y. K. *Adv. Fluorine Chem.* **1967**, *7*, 69.

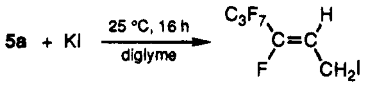
(9) Bakhmutov, V. I.; Galakhov, M. V. *Russ. Chem. Rev.* **1988**, *57* (9), 839.

reactions of olefins with $HOSO_2Cl$ by the reaction of HF and SO_3 derived from the equilibrium $HSO_3Cl \rightleftharpoons SO_3^{+}$-HCl.[10] The formation of dimers of **4a** in $HOSO_2F$ or $HOSO_2CF_3$ also can be explained by the same mechanism where the irreversible step instead is the reaction of **15** with another molecule of olefin.

The presence of $R_fCH_2CH_2F$ as a byproduct in all reactions carried out in HF solvent, and saturated compound **9** in the reaction of **4a** with benzene, probably indicates that the cation **14** is an intermediate in this reaction. Preferential formation of saturated product in the case of the reaction of **4a** with benzene vs almost exclusive formation of unsaturated product in the reaction of **4a** with chlorobenzene can be explained by the much lower electrophilicity of carbocation **14** vs allyl cation **15**.

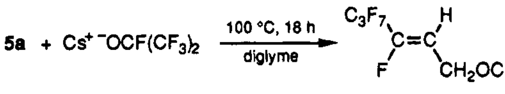
Some Reactions of R_f CF=CH CH_2X. Reaction of 5a with Nucleophiles. Nucleophilic replacement of chlorine in perfluoroallyl chloride,[11] or fluorosulfonyl group in polyfluorinated allyl sulfates,[12,13] is well documented. Despite its uncertain mechanism, this substitution reaction is widely used for the functionalization of unsaturated fluorocarbons. Allyl chlorides prepared in this work were quite reactive toward various nucleophiles. All reactions were demonstrated with only **5a**, but they should be general for **5a**–**c**.

Dry potassium iodide reacts with **5a** at room temperature in diglyme to give iodide **19** in nearly quantitative yield.



19, 95.4%

The perfluoro isopropoxy anion (generated from CsF and hexafluoroacetone) reacts more slowly even at 100 °C to afford allyl ether **20**.

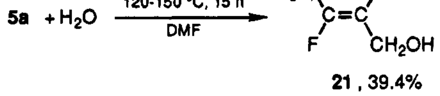


20, 58%

Allyl bromide **8a** is obtained in high yield from NaBr and **5a**.

$$\mathbf{5a} + \text{NaBr} \xrightarrow[\text{sulfolane}]{120\text{-}130\ ^\circ\text{C}} \mathbf{8a}\text{, 82\%}$$

Allyl chloride **5a** is converted into unsaturated alcohol **21** by reaction with wet dimethylformamide. This procedure has been used before to hydrolyze partially fluorinated iodides $R_fCH_2CH_2I$ (**22**).[14]



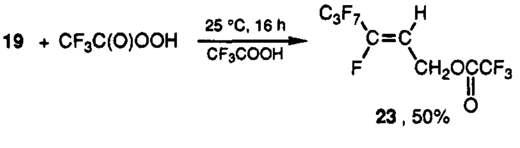
21, 39.4%

Notably, all the allylic substitution reactions described above are stereospecific. On the basis of NMR data, compounds **8a** and **19**–**21** have the same *trans* configuration as the starting allyl chloride **5a**.

Oxidation of Allyl Iodide 19. The compounds R_f-CF=$CHCH_2X$ may be derivatized by processes other than nucleophilic displacements. Trifluoroacetate **23**, for example, was prepared in 50% yield by an oxidative reaction with $CF_3C(O)OOH$, an approach which has been used to convert iodides **22** into their corresponding trifluoroacetates.[15] Interestingly, however, oxidation of R_fCH_2I by $CF_3C(O)OOH$ is reported to give $R_fCH_2I(OC(O)CCF_3)_2$ in contrast to the above results.[16]

Table 2. Reaction of 5a with Nucleophiles

entry	amount of **5a** (mmol)	reagent (mmol)	solvent (mL)	temp (°C)	time (h)	product (yield, %)
1	236	KI (265)	diglyme (20)	25	2	**19** (95.4)
2	40	$(CF_3)_2CFO^-Cs^+$ (50)	diglyme (50)	100	18	**20** (58)
3	40	KBr (50)	sulfolane (50)	120–130	4	**8a** (82)
4	325	H_2O (10 g)	DMF (200)	120–150	15	**21** (39.4)



23, 50%

Experimental Section

^{19}F and ^1H NMR spectra were recorded on a QE-300 (General Electric) instrument using $CFCl_3$ as an internal standard and $CDCl_3$ as a lock solvent. IR spectra were recorded on a Perkin-Elmer Model 983G spectrometer in the gas phase or in a liquid film. All reagents were commercial and used without further purification. KI and NaBr were kept in vacuum at 100–120 °C (2 h) to remove water and used immediately after drying.

General Procedure (Reactions of 1, 4a–c, and 6 with chlorosulfonic acid (2)). The catalyst was charged in a flask inside a glovebox. Chlorosulfonic acid was added slowly dropwise with stirring. A slight exotherm and gas evolution were observed. The perfluoroalkylethylene was then added immediately, and the reaction mixture (two layers) was vigorously stirred at 25–100 °C for 1–24 h. The resulting homogeneous reaction mixture was carefully poured onto crushed ice, and the lower layer was separated, dried over $MgSO_4$, and distilled. The specific reaction conditions, yields, and properties of all new compounds are summarized in Tables 1 and 3.

General Procedure (Reactions of 4a–c with HCl, HBr, C_6H_6, and ClC_6H_5 in hydrogen fluoride). A 400-mL Hastelloy shaker tube was charged with olefin (or mixture of olefin and C_6H_6 or ClC_6H_5), cooled to −78 °C, evacuated, and loaded with HF, HCl, or HBr and BF_3. The reactor was shaken at 25–50 °C for 16 h. The reactor then was cooled to room temperature, and 200 mL of H_2O was slowly injected. The lower organic layer was separated, washed with water, dried over P_2O_5, and distilled. The reaction conditions, yields, and properties of all new compounds are summarized in Tables 1 and 3.

General Procedure (Reactions of 5a with nucleophiles). A mixture of **5a** with the nucleophilic reagent in an appropriate solvent was stirred in a glass flask protected from atmospheric moisture at 25–150 °C for 2–18 h. The resulting reaction mixture was diluted with water, and the lower organic layer was separated, washed, dried over P_2O_5, and distilled. The reaction with hexafluoroacetone was carried out in a 100-mL stainless steel cylinder. The reaction conditions, yields, and properties of the new compounds are summarized in Tables 2 and 3.

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(10) Woods, J. T.; Bank, H. N. *Anal. Chem.* **1950**, *22*, 549.

(11) Miller, W. T.; Fainberg, A. H. *J. Am. Chem. Soc.* **1957**, *79*, 4164.

(12) Krespan, C. G.; England, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 5598.

(13) Cherstkov, V. F.; Sterlin, S. R.; German, L. S. *Izv. AN SSSR Ser. Khim.* **1982**, 2791.

(14) Brace, N. O. *J. Fluorine Chem.* **1986**, *31*, 151.

Table 3. Properties of New Compounds[a]

compd	bp, °C (mmHg)	^{1}H NMR, δ, ppm	^{19}F NMR ($CFCl_3$), ppm	IR (C=C), cm^{-1}	anal. or MS, found (calcd)
3	65	4.28 (d, 2H) 5.75 (1H, dt)	−73.66 (3F, d) −131.39 (1F, dq)	1720	C, 29.60 (29.56) H, 1.99 (1.85) F 46.31 (46.76)
5a	101−102	4.18 (dq, 2H) 5.84 (1H, dt)	−81.88 (3F, t) −120.33 (2F, q) −127.45 (1F, dm) −128.43 (2F, d)	1709	C, 26.46 (27.45) H, 1.32 (1.52) F, 58.27 (57.90) *m/e*, 261.9791 (261.9795)
5b	94−95 (158)	4.22 (dq, 2H) 5.86 (dt, 1H)	−81.29 (3F, t) −118.70 (2F, dm) −123.50 (4F, m)	1709	C, 26.50 (26.50) H, 0.81 (0.83) F, 62.34 (62.89)
5c	92−94 (40)	4.23 (dq, 2H) 5.89 (dt, 1H)	−79.90 (3F, t) −117.22 (2F, m) −120.88 (4F, m) −121.94 (4F, m) −125.00 (3F, m)	1708	C, 25.63 (25.96) F, 67.70 (65.71)
6	50−52 (0.15)	4.21 (d, 2H) 5.80 (dt, 1H)	−119.36 (4F, g) −125.64 (dm, 2H)	1708	C, 33.85 (33.47) F, 39.71 (40.00) H, 2.11 (2.13)
8a	119−120	4.11 (dq, 2H) 6.00 (dt, 1H)	−79.85 (3F, t) −118.32 (2F, m) −125.72 (1F, m) −126.40 (2F, m)	1705	C, 23.61 (23.47) F, 49.30 (49.51) H, 0.95 (0.97)
8b	140−142	4.08 (dq, 2H) 5.98 (dt, 1H)	−79.94 (3F, t) −118.26 (2F, m) −123.46 (4F, m) −126.54 (2F, m) −126.86 (1F, m)	1705	C, 23.38 (21.59) F, 59.77 (59.74) H, 0.79 (0.68)
8c	81−83 (15)	4.05 (dq, 2H) 5.94 (dt, 1H)	−81.38 (3F, m) −118.74 (2F, m) −122.48 (4F, m) −123.36 (4F, m) −126.84 (2F, m) −127.00 (1F, m)	1704	C, 23.57 (23.68) F, 59.81 (59.95) H, 0.76 (0.60)
9	35−36 (0.1)	2.42 (m, 2H) 2.94 (m, 2H) 7.1−7.3 (m, 4H)	−80.20 (3F, t) −114.08 (2F, m) −123.56 (2F, m) −125.13 (2F, m)		*m/e*, 324.0519* (324.0561)
10**		3.60 (dq, 2H) 5.85 (dt, 1H)	79.91 (3F, t) 113.20 (2F, m) 125.00 (2F, m)	1708	*m/e* 324.0414* (324.0498)
12	99 (65)	3.74 (dm, 2H) 5.82 (dt, 2H) 7.26 (m, 4H)	−81.00 ÷ −81.50 (3F) −115 ÷ −120 (2F) −126 ÷ −128 (2F) −131 ÷ −133 (1F)	1708	
19	94 (180)	3.94 (dq, 2H) 6.00 (dt, 1H)	−81.09 (3F, t) −119.47 (2F, dt) −127.64 (2F, d) −128.12 (1F, m)	1699	C, 20.12 (20.35) F, 43.46 (42.94) H, 0.85 (0.98)
20	68−69	4.75 (dq, 2H) 5.83 (dt, 1H)	−78.36 (6F, d) −81.33 (3F, t) −119.82 (2F, m) −127.03 (1F, m) −127.88 (2F, m) −142.58 (1F, m)	1710	C, 26.28 (26.23) F, 68.87 (69.16) H, 0.83 (0.73)
21	35−40 (0.5)	2.54 (br s, OH) 4.42 (dq, 2H) 5.82 (dt, 1H)	−80.92 (3F, t) −118.98 (2F, m) −127.45 (2F, d) −128.47 (1F, m)	1711	C, 29.46 (29.51) F, 62.29 (61.94) H, 1.64 (1.66)
23	122−124	5.08 (dq, 2H) 5.75 (dt, 1H)	−73.99 (3F, s) −80.91 (3F, m) −119.01 (2F, m) −127.46 (2F, d) −128.34 (1F, m)	1717 (1796, C=O)	C, 28.19 (28.25) F, 61.07 (61.45) H, 0.80 (0.88)

[a] * = GC/MS data. ** = Compound **10** was characterized in the mixture with **9**.

Oxidation of 19 with CF_3COOOH. To 150 mL of trifluoroacetic anhydride at 10 °C in a 300-mL glass flask protected against atmospheric moisture was added dropwise 10 mL of 30% H_2O_2 followed by dropwise addition of 35 g (0.1 mol) of **19** over a 10-min period. The reaction mixture was brought to 25 °C and held at this temperature for 16 h. The precipitated I_2 was filtered off, the collected filtrate was poured onto crushed ice, and the lower organic layer was separated, dried over P_2O_5, and distilled to give 17 g (50%) of **23:** bp 122−124 °C. Additional properties of **23** are given in Table 3.

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(15) Konrad, W. German Pat. DE 30 35 641, 1982.

(16) Umemoto, T.; Goto, Yo. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3307.