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Preliminary Note

A novel synthesis of α-(perfluoroalkyl) ketones

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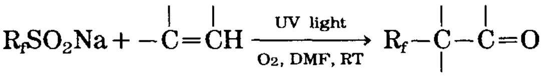
Abstract

Reaction of sodium perhalofluoroalkyl sulfinates with alkenes under UV irradiation and oxygen atmosphere provides α-perhalofluoroalkyl ketones in good yields.

It has been reported that condensation of perfluoroalkyl iodides with enamines gives α-(perfluoroalkyl) carbonyl compounds [1]. Similar condensation of enamines with perhalofluoroalkanes such as CF_2Br_2, CF_2BrCl and CF_2BrCF_2Br has also been described [2]. (Perfluoroalkyl)phenyl-iodonium trifluoromethane sulfonates [$R_fI(Ph))SO_2CF_3$] or sulfates [$R_fI(Ph)OSO_3H$] react with various trimethylsilyl enol ethers or with alkenes under an oxygen atmosphere in the presence of a base to give α-(perfluoroalkyl) carbonyl and γ-(perfluoroalkyl)-α,β-unsaturated carbonyl compounds in moderate to good yields [3, 4].

In previous papers, we reported that sodium perhalofluoroalkyl sulfinates undergo electrophilic displacement, addition or oxidation reaction with various substrates under mild conditions to afford perfluoroalkylated compounds in good yields [5–7]. Here, we report a novel oxy-perfluoroalkylation of alkenes, which provides quite a useful synthetic method for preparing α-perfluoroalkyl ketones.

Sodium perhalofluoroalkyl sulfinates were reacted with alkenes under UV irradiation and an oxygen atmosphere at room temperature in DMF to provide α-perfluoroalkyl ketones in good yields:



$$R_fSO_2Na + -\overset{|}{C}=\overset{|}{C}H \xrightarrow[O_2,\ DMF,\ RT]{UV\ light} R_f-\underset{|}{\overset{|}{C}}-\overset{|}{C}=O$$

($R_f = X(CF_2)_n-$, $X = F$, Cl, $n = 4$, 6, 8)

Examination of the reaction conditions for such oxy-perhalofluoroalkylation definitely showed that both oxygen and UV light were essential. Table 1 summarizes the results of such reactions.

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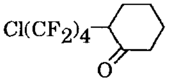
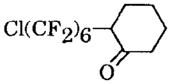
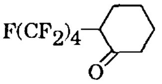
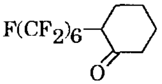
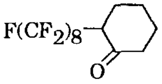
TABLE 1

Oxy-perhalofluoroalkylation of alkenes under UV irradiation and an oxygen atmosphere

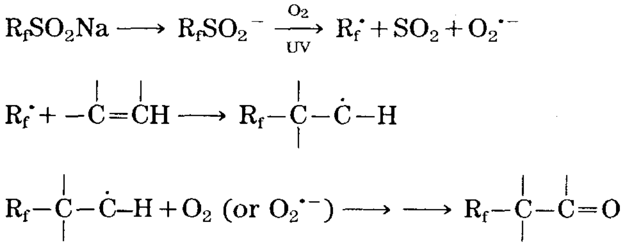
Entry No.	Alkene	R_fSO_2Na	Atm.[a]	Time (h)	Product[b]		Yield(%)[c]
1	1-heptene	$F(CF_2)_8-$	air	4	$F(CF_2)_8CH_2CO(CH_2)_5H$	(**1**)	83
2	1-heptene	$F(CF_2)_6-$	air	6	$F(CF_2)_6CH_2CO(CH_2)_5H$	[8]	84
3	1-hexene	$F(CF_2)_2-$	air	8	$F(CF_2)_2CH_2CO(CH_2)_4H$	(**2**)	75
4	1-hexene	$F(CF_2)_6-$	air	5	$F(CF_2)_6CH_2CO(CH_2)_4H$	(**3**)	85
5	c-hexene	$Cl(CF_2)_4-$	air	6		[9]	77
6	c-hexene	$Cl(CF_2)_6-$	O_2	6		[9]	74
7	c-hexene	$F(CF_2)_4-$	O_2	6		(**4**)	70
8	c-hexene	$F(CF_2)_6-$	O_2	6		[1]	78
9	c-hexene	$F(CF_2)_8-$	O_2	6		(**5**)	70

[a] Under atmospheric pressure.

[b] All products gave satisfactory ^{19}F NMR, ^1H NMR, IR and MS data corresponding to literature values. Compounds **1–5** are new compounds and their data are given below in Table 2.

[c] Isolated yields based on sodium perhalofluoroalkyl sulfinates.

The reaction works well with primary and secondary alkenes. However, in the absence of alkenes, sodium perhalofluoroalkyl sulfinates react with oxygen under UV irradiation giving the corresponding perhalofluoroalkyl carboxylic acids exclusively, as shown in a previous paper [6]. A mechanism for such oxy-perhalofluoroalkylation is tentatively proposed as follows:



$$R_fSO_2Na \longrightarrow R_fSO_2^- \xrightarrow[UV]{O_2} R_f^{\bullet} + SO_2 + O_2^{\bullet -}$$

$$R_f^{\bullet} + -\overset{|}{C}=\overset{|}{C}H \longrightarrow R_f-\underset{|}{\overset{|}{C}}-\dot{C}-H$$

$$R_f-\underset{|}{\overset{|}{C}}-\dot{C}-H + O_2\ (\text{or } O_2^{\bullet -}) \longrightarrow \longrightarrow R_f-\underset{|}{\overset{|}{C}}-\overset{|}{C}=O$$

The typical procedure was as follows. A two-necked quartz tube fitted with a condenser and an air (or oxygen) inlet tube was charged with 2.5 g (5 mmol) sodium n-perfluorooctyl sulfinate, 0.7 g (7 mmol) 1-heptene and 20 ml *N*,*N*-dimethylformamide. The reaction mixture was irradiated under

TABLE 2

Spectroscopic and analytical data for compounds **1–5**

Compound **1**: M.p., 40.0–41.5 °C. ^{19}F NMR δ: 5.3 (3F); 37.0 (2F); 46.1 (8F); 48.0 (2F); 50.4 (2F) ppm. ^{1}H NMR δ: 0.85 (t, 3H); 1.2–1.6 (m, 6H); 2.60 (t, 2H); 3.41 (t, 2H) ppm. MS *m/z*: 534 ($M^+ + 1$); 533; 517 (100); 513; 133; 99; 71; 57; 43. IR (cm^{-1}): 2920; 2850; 1730. Anal.: Calc. for $C_{15}H_{13}F_{17}O$: C, 33.85; H, 2.46; F, 60.88%. Found: C, 33.58; H, 2.44; F, 61.02%.

Compound **2**: B.p., 71–72 °C/15 mmHg. ^{19}F NMR δ: 5.5 (3F); 41.3 (2F) ppm. ^{1}H NMR δ: 0.86 (t, 3H); 1.2–1.6 (m, 4H); 2.60 (t, 2H); 3.41 (t, 2H) ppm. MS *m/z*: 218 (M^+); 202 (100); 198; 99; 85; 57; 43. IR (cm^{-1}): 2925; 2850; 1725. Anal.: Calc. for $C_8H_{11}F_5O$: C, 44.04; H, 5.08: F, 43.54%. Found: C, 43.85; H, 5.23; F, 43.37%.

Compound **3**: B.p., 76–78 °C/0.5 mmHg. ^{19}F NMR δ: 5.3 (3F); 37.0 (2F); 45.9 (2F); 46.8 (2F); 47.4 (2F); 50.4 (2F) ppm. ^{1}H NMR δ: 0.88 (t, 3H); 1.2–1.6 (m, 4H); 2.65 (t, 2H); 3.45 (t, 2H) ppm. MS *m/z*: 419 ($M^+ + 1$); 417; 403 (100); 397; 383; 99; 85; 57; 43. IR (cm^{-1}): 2950; 2850; 1725. Anal.: Calc. for $C_{12}H_{11}F_{13}O$: C, 34.47; H, 2.65; F, 59.06%. Found: C, 34.31; H, 2.80; F, 59.24%.

Compound **4**: B.p., 60–62 °C/1 mmHg. ^{19}F NMR δ: 5.6 (3F); 37.4 (2F); 44.4 (4F) ppm. ^{1}H NMR δ: 1.3–3.0 (m, 8H); 4.05 (m, 1H) ppm. MS *m/z*: 316 (M^+); 300; 298; 97; 75 (100). IR (cm^{-1}): 2950; 2850; 1730. Anal.: Calc. for $C_{10}H_9F_9O$: C, 37.99: H, 2.87; F, 54.08%. Found: C, 38.42; H, 2.61; F, 53.7%.

Compound **5**: B.p., 88–90 °C/0.5 mmHg. ^{19}F NMR δ: 5.5 (3F); 37.3 (2F); 46.4 (8F); 47.3 (2F); 51.0 (2F) ppm. ^{1}H NMR δ: 1.3–2.8 (m, 8H); 3.85 (m, 1H) ppm. MS *m/z*: 517 ($M^+ + 1$); 516; 501; 497; 481; 97; 75 (100). Anal.: Calc. for $C_{14}H_9F_{17}O$: C, 32.58; H, 1.76; F, 62.57%. Found: C, 32.99; H, 1.42; F, 62.91%.

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a 400 W Hg lamp with continuous bubbling of air or oxygen for 4 h. Then the reaction mixture was poured into 20 ml water and extracted with ether (2 × 50 ml). The combined extract was washed with 50 ml of aqueous Na_2CO_3 solution, water (4 × 50 ml) and then dried over $MgSO_4$. After the removal of solvent, the residue was purified by chromatography on silica gel [petroleum ether (60–90)/ethyl acetate, 8:2] to yield 2.2 g (83%) of the product, $F(CF_2)_8CH_2CO(CH_2)_5H$.

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