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The Synthesis of γ,Δ-Ethylenic Perfluoroalkyl Ketones via Claisen Rearrangement

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SYNTHETIC COMMUNICATIONS, 23(13), 1887-1895 (1993)

THE SYNTHESIS OF γ,δ-ETHYLENIC PERFLUOROALKYL KETONES VIA CLAISEN REARRANGEMENT

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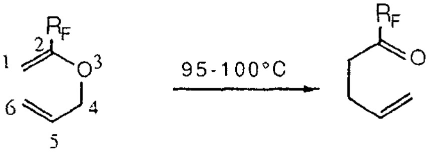
ABSTRACT: γ,δ ethylenic perfluoroalkyl ketones, described for the first time, were prepared through the Claisen rearrangement of allyl F-alkylated vinyl ethers.

The Claisen rearrangement[1] is one of the most widely used methods for preparing fonctionalized carbonyl compounds. In the present work, a new class of hemifluoroalkyl ketones[2] was obtained through the thermal rearrangement of F-alkylated allyl vinyl ethers to γ,δ-unsaturated perfluoroalkyl ketones.



$R_F = C_4F_9, C_6F_{13}, C_8F_{17}$

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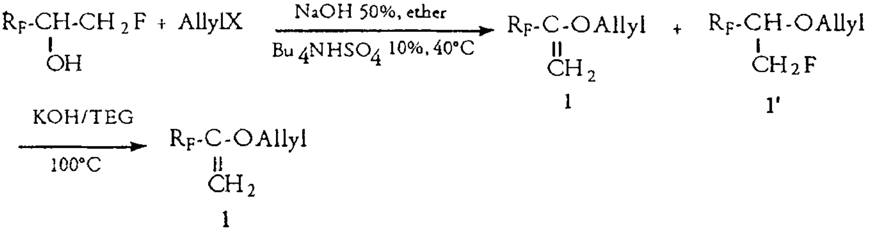
The starting ethers were formed, under phase transfer catalysis in basic medium, from the 0-alkylation reaction between 1-F-alkyl-2-fluoroethanols[3] and allylic halides. As observed when alkylating agents were epichlorohydrin[4] or methylene chloride[5], the dehydrofluorination reaction takes place under these conditions for some of them. As the others, for which this dehydrofluorination reaction was partial or absent, the action of KOH at 100°C in triethyleneglycol (TEG) is needed to prepare the corresponding F-alkylated allyl vinyl ethers.



$$R_F\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_2F + AllylX \xrightarrow[Bu_4NHSO_4\ 10\%,\ 40°C]{NaOH\ 50\%,\ ether} R_F\text{-}\underset{\displaystyle CH_2}{\underset{\|}{C}}\text{-}OAllyl + R_F\text{-}\underset{\displaystyle CH_2F}{\underset{|}{CH}}\text{-}OAllyl$$

1 1'

$$\xrightarrow[100°C]{KOH/TEG} R_F\text{-}\underset{\displaystyle CH_2}{\underset{\|}{C}}\text{-}OAllyl$$

1

The prepared starting material ethers (**1a-i**) are given in table I. The thermal rearrangement of these C-2 perfluoroalkyl allyl vinyl ethers takes place without a solvent nor a catalyst in sealed tube at 95-100°C. The results related to this reaction are given in table II.

These results are in agreement with those known for allyl vinyl ethers substituted on C-2 by electron acceptor or electron donor groups such as F[6], CN[7], CF_3[8] or OCH_3[9]. Recently, it has been shown that the Claisen rearrangement is remarkably accelerated when fluorine atoms are present at C-1 and C-2 position[10]. This is the case for the C-2 F-alkylated ones for which the rearrangement

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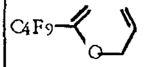
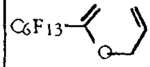
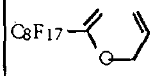
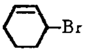
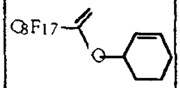
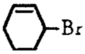
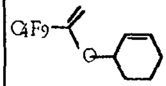
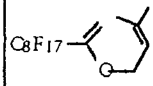
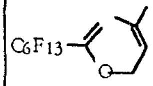
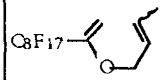
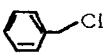
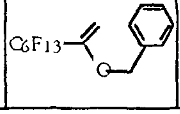
Table I: C-2 perfluoroalkyl allyl vinyl ethers prepared from 1-F-alkyl-2-fluoroethanols R_F-CHOH-CH_2F and allylic halides

Entry	AllylX	R_F	Time (h)	Ration[a] 1:1'	AVE[b]	Yield[c] (%)
1a		C_4F_9	4	100 : 0		61
1b		C_6F_{13}	8	100 : 0		52
1c		C_8F_{17}	6	100 : 0		74
1d		C_8F_{17}	24	100 : 0		45
1e		C_4F_9	24	55 : 45		46
1f		C_8F_{17}	24	0 : 100		50
1g		C_6F_{13}	24	0 : 100		62
1h		C_8F_{17}	24	0 : 100		40
1i		C_6F_{13}	6	100 : 0		40

a. Ratio of allyl vinyl ether and ß -fluoroallyl ether obtained from 1-F-alkyl-2-fluoroethanol and allylic halide under phase transfer catalysis condition.
b. AVE: Allyl vinyl ether
c. Yield of isolated pure AVE

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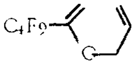
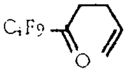
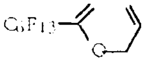
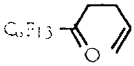
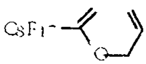
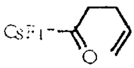
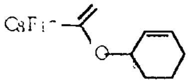
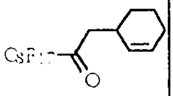
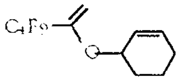
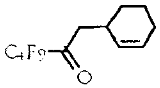
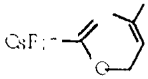
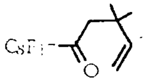
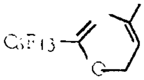
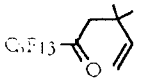
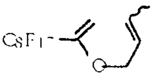
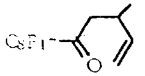
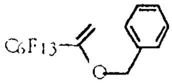
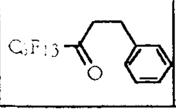
Table II: the Claisen rearrangement of C-2 perfluoroalkyl allyl vinyl ethers.

Entry	AVE	Temp (°C)	Time (h)	Product	Yield (%)
2a		95	24		100
2b		95	24		100
2c		95	24		100
2d		100	48		90
2e		100	48		90
2f		95	24		90
2g		95	24		90
2h		95	24		90
2i		250[a]	216		45

a. The reaction is carried out in monoglyme

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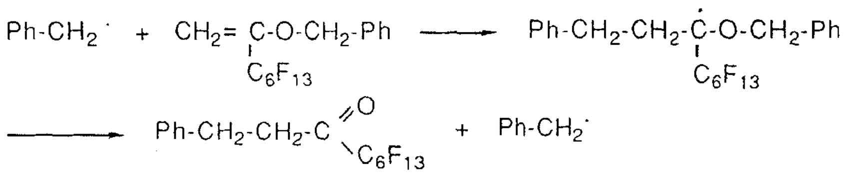
began on storage in a refrigerator and was achieved easily and quantitatively at 95-100°C.

When the alkylating agent is the benzyl chloride, the rearrangement of the corresponding benzyl ether (**1i**) doesn't take place. As for the other vinyl benzyl ethers[11], the starting material is regenerated after 48 H at 170°C. In the monoglyme at higher temperatures (250°C) for 9 days, the C-2 F-alkylated vinyl benzyl ether (**1i**) was transformed into ketone identified as $C_6F_{13}\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}Ph$ (**2i**). This compound appear to arise by a free radical chain process which is highly probable in these conditions[12].



$$Ph\text{-}CH_2^{\cdot} + CH_2{=}\underset{C_6F_{13}}{C}\text{-}O\text{-}CH_2\text{-}Ph \longrightarrow Ph\text{-}CH_2\text{-}CH_2\text{-}\underset{C_6F_{13}}{\overset{\cdot}{C}}\text{-}O\text{-}CH_2\text{-}Ph \longrightarrow Ph\text{-}CH_2\text{-}CH_2\text{-}C(=O)C_6F_{13} + Ph\text{-}CH_2^{\cdot}$$

EXPERIMENTAL

^1H NMR spectra were obtained on a Jeol NM-PMX apparatus (60 MHz) using $CDCl_3$ as solvent and ^{19}F NMR spectra on a Bruker AC 200 (188,3 MHz) using $CDCl_3$ as solvent and $CFCl_3$ as reference. Mass spectra were obtained on a Nermag R10-10C spectrometer. Infrared Spectra were recorded on a Perkin-Elmer 681 instrument. 3-Bromocyclohexene was prepared by a reported procedure[13].

Synthesis of F-alkylated allyl vinyl ethers

General procedure: To a vigorously stirred mixture of 50% w/w aqueous sodium hydroxide (6 ml), diethyl ether (5 ml) and tetrabutylammonium hydrogen sulfate 0,17g (5.10^{-4} mol), a solution of 1-F-alkyl-2-fluoroethanol[3] (5.10^{-3} mol) and freshly

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distilled allylic halide ($5,5.10^{-3}$ mol) in 5 ml of diethyl ether is added dropwise at room temperature. After addition, the mixture is maintained at 40°C during 4 to 24 H. The reaction mixture is poured on ice/water (20 ml). The aqueous phase is extracted with diethyl ether. The organic layer is dried over anydrous $MgSO_4$, the solvent evaporated and the residue distilled. Ethers (**1e-h**), for which the dehydrofluorination reaction was partial or absent: to a solution of 1,12 g (2.10^{-2} mol) of KOH in 10ml of triethyleneglycol 4.10^{-3} mol of R_F-CH(OAllyl)-CH_2F is added at room temperature. The reaction mixture was stirred at 100°C for 15 mn. After cooling, 20ml of water was added. The aqueous phase is extracted with diethyl ether. The organic layer is dried over $MgSO_4$, the solvent evaporated and the residue distilled.

Synthesis of γ,δ-ethylenic perfluoroalkyl ketones

General procedure: perfluoroalkyl allyl vinyl ether was sealed in pyrex tube and heated to 95-100°C for 24 to 48 hours. On cooling, the contents of the tube distilled.

Nonafluorobutyl but-3-enyl ketone (**2a**):

B.P:64°C/65 torr. IR ($CHCl_3$): ν= 1760cm^{-1} (C=O). ^1H NMR (δ ppm): 2,50 (t, 2H, J= 6,0 Hz); 2,86 (m, 2H); 4,80-5,30 (m, 2H); 5,50-6,20 (m,, 1H). ^{19}F NMR (δ ppm): -81,5 (3F, CF_3); -121,1 (2F,$CF_2\alpha$); -123,8 (2F, $CF_2\beta$); -126,3 (2F, $CF_2\omega$). Mass m/z(%): 83(52); 69(22); 55(100); 41(28).

Tridecafluorohexyl but-3-enyl ketone (**2b**):

B.P: 82°C/45 torr. IR ($CHCl_3$): ν= 1760 cm^{-1} (C=O). ^1H NMR (δ ppm):

2,50 (t, 2H, J= 6,0 Hz); 2,86 (m, 2H); 4,80-5,30 (m, 2H); 5,50-6,20 (m, 1H). ^{19}F NMR (δ ppm): -81,6 (3F, CF_3); -121,1 (2F,$CF_2\alpha$); -122,8 (2F, $CF_2\beta$); -122,9 (2F, $CF_2\gamma$); -123,5 (2F, $CF_2\delta$); -126,9 (2F, $CF_2\omega$). Mass m/z(%): 83(48); 69(17); 56(15); 55(100); 53(19); 41(33).

Heptadecafluorooctyl but-3-enyl ketone (**2c**):
B.P: 84°C/17 torr. IR ($CHCl_3$): ν= 1760 cm^{-1} (C=O). ^{1}H NMR (δ ppm): 2,50 (t, 2H, J= 6,0 Hz); 2,86 (m, 2H); 4,80-5,30 (m, 2H); 5,50-6,20 (m, 1H). ^{19}F NMR (δ ppm): -81,4 (3F, CF_3); -120,8 (2F,$CF_2\alpha$); -121,8 (2F, $CF_2\beta$); -122,4 (6F, $(CF_2)_3\gamma$); -123,2 (2F, $CF_2\delta$); -126,7 (2F, $CF_2\omega$).

Heptadecafluorooctyl (cyclohex-2-enyl) methyl ketone (**2d**):
B.P: 86°C/0,1 torr. IR ($CHCl_3$): ν= 1760 cm^{-1} (C=O). ^{1}H NMR (δ ppm): 1,00-2,20 (m, 6H); 2,70 (s, 2H); 2,33-3,00 (m, 1H); 5,30-6,00 (m, 2H). ^{19}F NMR (δ ppm): -81,5 (3F, CF_3); -120,9 (2F,$CF_2\alpha$); -121,0 (2F, $CF_2\beta$); -122,6 (6F, $(CF_2)_3\gamma$); -123,4 (2F, $CF_2\delta$); -126,8 (2F, $CF_2\omega$). Mass m/z(%): 542(22, $M^{+\cdot}$); 124(15); 123(63); 96(14); 95(65); 81(94); 80(92); 79(60); 77(15); 69(26); 67(37); 55(25); 54(18); 53(46); 52(10); 51(15); 43(9); 42(24);;41(100).

Nonafluorobutyl(cyclohex-2-enyl) methyl ketone (**2e**):
B.P: 80°C/15 torr. IR ($CHCl_3$): ν= 1760 cm^{-1} (C=O). ^{1}H NMR (δ ppm): 1,00-2,20 (m, 6H); 2,70 (s, 2H); 2,33-3,00 (m, 1H); 5,30-6,00 (m, 2H).

Heptadecafluorooctyl 2,2-dimethylbut-3-enyl ketone (**2f**):
B.P: 102°C/17 torr. IR ($CHCl_3$): ν= 1760 cm^{-1} (C=O). ^{1}H NMR (δ ppm): 1,15 (s, 6H); 2,70 (s, 2H); 4,75-5,15 (m, 2H); 5,63-6,16 (m, 1H).

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Tridecafluorohexyl 2,2-dimethylbut-3-enyl ketone (**2g**):
B.P: 83°C/25 torr. IR ($CHCl_3$): ν= 1760 cm^{-1} (C=O). ^1H NMR (δ ppm): 1,15 (s, 6H); 2,70 (s, 2H); 4,75-5,15 (m, 2H); 5,63-6,16 (m, 1H).
^{19}F NMR (δ ppm): -81,6 (3F, CF_3); -120,9 (2F,$CF_2\alpha$); -122,2 (2F, $CF_2\beta$); -122,8 (2F, $CF_2\gamma$); -123,5 (2F, $CF_2\delta$); -126,9 (2F, $CF_2\omega$).

Heptadecafluooctyl 2-methylbut-3-enyl ketone (**2h**):
B.P: 90°C/17 torr. IR ($CHCl_3$): ν= 1760 cm^{-1} (C=O). ^1H NMR (δ ppm): 1,10(d, 3H, J= 6,0Hz); 1,70 (m, 1H); 2,76 (m, 2H); 4,83-5,26 (m, 2H), 5,50-5,83 (m, 1H).

Tridecafluorohexyl phenylethyl ketone (**2i**):
A sealed tube containing 2 g of 1-tridecafluorohexyl vinyl benzyl ether and 1ml of monoglyme was heated to 250°C for 9 days. On cooling, the contents of the tube distilled.
B.P.: 74°C/ 0,15 torr. IR ($CHCl_3$): ν= 1760 cm^{-1} (C=O). ^1H NMR (δ ppm): 3,00(s, 4H); 7,23 (s, 5H). ^{19}F NMR (δ ppm): -81,7 (3F, CF_3); -120,9 (2F,$CF_2\alpha$); -122,2 (4F, $(CF_2)_2\beta$); -123,5 (2F, $CF_2\gamma$);-126,9 (2F, $CF_2\omega$). Mass m/z(%): 133(40); 106(6); 105(68); 91(100); 77(12); 69(13).

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