NOVEL OXY-PERFLUOROALKYLATION

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(Perfluoroalkyl)phenyliodonium sulfonates underwent novel oxy-perfluoroalkylation with alkenes under oxygen atmosphere in the presence of a base.

We wish to report novel oxy-perfluoroalkylation of alkenes. In the previous papers, we have described that (perfluoroalkyl)phenyliodonium sulfonates undergo electrophilic displacement or addition reactions with many kinds of nucleophiles under mild conditions to afford perfluoroalkylated compounds in good yields.¹⁻⁶⁾

Surprisingly, we found that the iodonium salts were allowed to react with alkenes under oxygen atmosphere at room temperature in the presence of pyridine as a base to produce α -(perfluoroalkyl) carbonyl or γ -(perfluoroalkyl)- α , β -unsaturated carbonyl compounds in moderate or good yields and iodobenzene as another product in a quantitative yield.

The examination of reaction conditions for the oxy-perfluoroalkylation definitely showed that both oxygen and a base were essential for the reaction. Table 1 summarizes the results of the reaction of the iodonium salts with some alkenes.

Ethylene did not undergo the oxy-perfluoroalkylation, but propene did that. Acyclic vinyl ethers with enhanced π -electron density underwent the reaction even under air atmosphere to give the corresponding esters in good yields. π -Electron density higher than that of ethylene is necessary for the reaction. Interestingly, with a cyclic vinyl ether, another type of oxy-perfluoroalkylation occurred, though the major was the displacement product (Run 9). Whereas the iodonium salts reacted with butadiene and pyridine in the absence of oxygen to give exclusively the corresponding pyridinium salts as shown in a previous paper,⁵⁾ oxygen atmosphere completely depressed the formation of the pyridinium salts. Oxygen inhibited such an electrophilic perfluoroalkylation.

An oxygen isotope experiment was performed to prove the participation of molecular oxygen. Oxygen containing ^{18}O in about 50 atom % content, and then buta-

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Run	Alkene ^{a)}		FITS/ FIS-m	Atm. ^{b)}	Base ^C) Solv.	Time (h)	Product ^{d)}	Yield ^{e)} (%)
1	$CH_2 = CHCH_3 (3.1)$	5)	FITS-8	O 2	4	CH ₂ Cl ₂	2	RfCH 2COCH 3	30
2	$CH_2 = CHCH = CH_2 (excess)$		u	"	п		1	$RfCH_{2}CH=CHCHO^{f}$	47
3	$CH_2 = CHCH = CHCH_3 (1.2)$		н	п	1		2	RfCH ₂ CH=CHCOCH ₃	$E) \begin{pmatrix} (53) \\ 30 \end{pmatrix}$
4	$CH_2 = CHO_1 - C_8 H_{17} (2)$		FIS-2	11	2.2	CH ₃CN	3	RfCH ₂ COO1-C ₈ H ₁	7 39
5	11	(")	FITS-2	Aır	4	DMF	24	"	45
6	$CH_2 = CHO_1 - C_4H_9$ (1.2)		FITS-8	н	10	CH_2Cl_2	21	RfCH ₂ COO1-C ₄ H ₉	43
7	IF	(3)	"	11	"	"	8	н	73
8		(")	FITS-7	"	и	0	6	11	71
9	\bigcirc	(")	FITS-8	O 2	u	n	4	CORF OCHO (1:5)	Rf(67)

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Table 1. Oxy-perfluoroalkylation of alkenes

a) Values in parentheses are molar equivalent amounts to FITS or FIS b) At atmospheric pressure c) Pyridine was used as a base Values are molar equivalent amounts to FITS or FIS d) All the products showed spectral data (¹H- and ¹⁹F-NMR, IR, and Mass) in accord with the assigned structures. e) Isolated yields except for Run 1 (NMR yield) Parenthese show GLC yields f) trans-Isomers

diene were introduced to a solution of FITS-8 and pyridine in methylene chloride (not degassed). The mass spectral analysis showed that the product contained the oxygen isotope with about 20 atom % content. However the detailed mechanism of the oxy-perfluoroalkylation is not clear at the present stage.

The oxy-perfluoroalkylation provided quite a new synthetic method to prepare α -(perfluoroalky1) carbonyl or γ -(perfluoroalky1)- α , β -unsaturated carbonyl compounds which were important intermediates for the preparation of interesting fluorinated compounds as exemplified below, directly from alkenes.

RfCH₂COOR
$$\xrightarrow{\text{Et}_3\text{N}/\text{SlO}_2 \text{ in CCl}_4}$$
 $\xrightarrow{\text{Rf'}}_F \xrightarrow{\text{COOR}} (\text{Rf'=CF}_3)$

References and Notes

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 7) FITS=(perfluoroalky1)pheny1iodonium trifluoromethanesulfonates FIS=(perfluoroalky1)pheny1iodonium sulfates The letter m means the number of carbons in the perfluoroalkyl groups

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