Alkoxyperfluoroalkylation of Enol Ethers Catalysed by Iron Complexes

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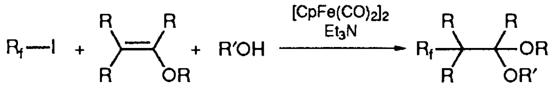
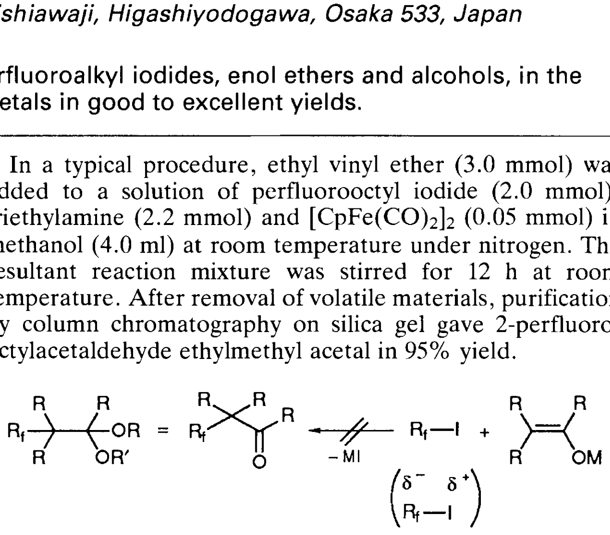
The iron-catalysed coupling reaction of three components, perfluoroalkyl iodides, enol ethers and alcohols, in the presence of a base gives directly perfluoroalkyl-substituted acetals in good to excellent yields.

Organofluorine compounds and their synthesis[1] have attracted much attention in the field of biologically active compounds and material science. Recently transition-metal complexes and metalloids have proved to be effective in perfluoroalkylation of carbon–carbon multiple bonds,[2] however, the substrates have been limited to alkenes and alkynes bearing no functional groups. There are few reports of the direct perfluoroalkylation of enol ethers by perfluoroalkyl halides.[3] Here, we describe a novel 'alkoxyperfluoroalkylation' of enol ethers catalysed by iron complexes, Scheme 1.



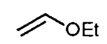
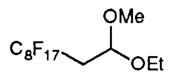
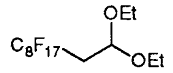
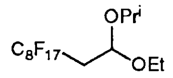
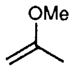
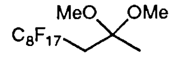
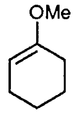
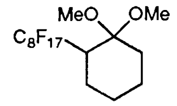
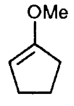
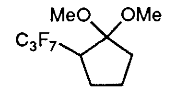
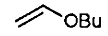
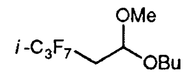
Scheme 1

In a typical procedure, ethyl vinyl ether (3.0 mmol) was added to a solution of perfluorooctyl iodide (2.0 mmol), triethylamine (2.2 mmol) and $[CpFe(CO)_2]_2$ (0.05 mmol) in methanol (4.0 ml) at room temperature under nitrogen. The resultant reaction mixture was stirred for 12 h at room temperature. After removal of volatile materials, purification by column chromatography on silica gel gave 2-perfluorooctylacetaldehyde ethylmethyl acetal in 95% yield.



Scheme 2

Table 1 Alkoxyperfluoroalkylation of enol ethers catalysed by $[CpFe(CO)_2]_2$[a]

Run	R_fI	Enol ether	Mol equiv.	R'OH	Time/h	Product[b]	Yield (%)[c]
1	$C_8F_{17}I$		1.5	MeOH	12		95
2			2.0	EtOH	24		69
3			2.0	Pr^{i}OH	38		75
4			1.5	MeOH	12		93
5			1.5		18		81[d]
6	C_3F_7I		1.5		18		68
7	i-C_3F_7I		4.0		12		63[d]

[a] Unless noted, all reactions were carried out in the presence of 2.5 mol% of $[CpFe(CO)_2]_2$ and 1.1 equiv. of Et_3N at room temperature. [b] All new compounds gave satisfactory spectral data (^1H NMR, ^{19}F NMR, IR, EIMS) and elemental analysis. [c] Isolated yields. [d] 5 mol% of $[CpFe(CO)_2]_2$ was used.

Representative results are summarized in Table 1. The present reaction is characteristic of a three-component coupling in which alkoxy and perfluoroalkyl groups are incorporated into the α- and β-carbon positions, respectively, of enol ethers. Terminal double bonds as well as internal ones in enol ethers react readily with perfluoroalkyl iodides and alcohols under mild conditions to give perfluoroalkyl-substituted acetals in good to excellent yields.

We examined the catalytic activity of several iron complexes toward the alkoxyperfluoroalkylation of 2-methoxypropene and found that cyclopentadienyldicarbonyliron complex, $[CpFe(CO)_2]_2$, is the best choice for the present reaction. A principal role of triethylamine is in trapping the hydrogen iodide produced during the reaction. The addition of p-dinitrobenzene (0.2 equiv.) as a radical scavenger completely inhibited the reaction, suggesting that the present reaction may involve some radical character.

Perfluoroalkyl-substituted acetals obtained here are masked carbonyl compounds bearing an α-perfluoroalkyl group. These are promising building blocks incorporating perfluoroalkyl groups, which are not prepared readily using ionic reactions[4] because of the inverse polarity in perfluoroalkyl halides compared with that in ordinary hydrocarbon analogues (Scheme 2). The present alkoxyperfluoroalkylation of enol ethers may provide an effective route to such useful compounds.

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