REACTIONS OF R, I (Ph)OSO₂CF₃ WITH ALKENES AND ALKADIENES

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A successful cationic perfluoroalkylation of alkenes and alkadienes with $R_{\rm r}I(\rm Ph)OSO_2 CF_3$ was described. The reactivity of $R_{\rm f}I(\rm Ph)OSO_3 H$ was also examined.

There have been many investigations on the reactions of free-radical perfluoroalkyl species (R_f .) with alkenes.¹⁾ Anionic perfluoroalkylation of perfluoroalkenes has been observed in the oligomerization of tetrafluoroethylene or hexafluoropropene by the action of a fluoride anion.²⁾ On the other hand, no cationic perfluoroalkylation of alkenes has been reported. We now wish to report the cationic perfluoroalkylation of alkenes and alkadienes with perfluoroalkylphenyliodonium trifluoromethanesulfonates (FITS), $R_fI(Ph)OSO_2CF_3$. Our previous studies have shown that FITS can act upon carbanions, arenes, and thiols as cationic perfluoroalkylating agents.³⁾

First, styrene was heated under reflux with FITS in methylene chloride for 0.5 h in the presence of an equivalent amount of pyridine as a base to give trans- β -(perfluoroalkyl)styrene in a good yield and iodobenzene was liberated in a quantitative yield (Scheme 1). It is preferable to use the base in order Scheme 1.

 $\begin{array}{c} CH_2=CHPh \ + \ R_f I(Ph)OSO_2 CF_3 \\ FITS-m^{4} \\ (R_f=n-C_m F_{2m+1}) \end{array} \xrightarrow{\begin{array}{c} Pyridine \\ reflux, \ 0.5 \ h \\ in \ CH_2 Cl_2 \end{array}} \xrightarrow{\begin{array}{c} R_f \\ CH=CH \\ m=8 \ 73 \ \% \end{array} Quant.}$

to neutralize trifluoromethanesufonic acid released from FITS. The reactions with a series of alkenes and alkadienes were carried out under the same conditions. The results are shown in Table 1. Alkenes and alkadienes possessing allylic hydrogen atoms afforded the (perfluoroalkyl)alkenes and -alkadienes with the rearrangement of double bonds as main products except for propene which gave the adduct as a major component. Perfluoroalkylphenyliodonium sulfates (FIS-m), $R_{\rm f}I({\rm Ph})OSO_{3}{\rm H}$ ($R_{\rm f}$ =n-C $_{\rm m}F_{2m+1}$), ³⁾ reacted with styrene at elevated temperature (reflux in CHCl₃) to give the same product in a 40 % yield.

Interestingly, the introduction of ethylene or butadiene gas into a solution of FITS and pyridine in methylene chloride at room temperature led to the ready formation of the pyridinium salts (Schme 2). Accordingly the examination for the addition reaction with other nucleophiles showed the easy formation of the addition products with nucleophiles such as water, formic acid,

Run	Alkene or Alkadiene	FITS-m	Product ^a)	Yield(%) ^{b)}
1	CH ₂ =CH-n-C ₅ H ₁₁	m = 7	R _f CH ₂ CH=CHC ₄ H ₉ C)	71
2	CH2=CHCH3	8	R _r ch ₂ ch(ch ₃)oso ₂ cF ₃	(54)
	~)		R CH=CHCH3	(20)
			R _f CH ₂ CH=CH ₂	(7)
3	CH ₂ =C(CH ₃)Ph	8	R _f CH=C(CH ₃)Ph	(8)
	~)		$R_{f}CH_{2}C(=CH_{2})Ph$	(42)
4	cyclopentene	8	$3-R_{f}$ -cyclopentene	46
5	CH2=CHCH=CHCH3	.8	R _r CH=CHCH=CHCH ₃	(7)
	~)		R _F CH ₂ CH=CHCH=CH ₂	(45)
6	1,3-cyclooctadiene	2	5-R _f -1, 3-cyclooctadiene	25(37)

Table 1. Reactions of FITS-m with alkenes and alkadienes

a) Spectral data of all products are in good agreement with assigned structures. b) Isolated yields. Values in parentheses are GLC yields.

c) A mixture of stereoisomers (3 : 1 = trans : cis).

acetic acid, methanol, and sodium halides. FIS were also found to undergo the same reaction. Table 2 summerizes the results.

Scheme 2.

$$CH_{2} \neq CH-CH \Rightarrow CH_{2} + FITS-m \xrightarrow{Pyridine}_{at rt, 1 h} R_{f}CH_{2} + (CH=CH) + CH_{2} +$$

+ /----

Table 2. Reactions of FITS-m or FIS-m with alkenes and alkadienes in the presence of nucleophiles

Run	Alkene or Alkadiene	FITS-m or FIS-m	Nucleophile	Base	Product ^{a)}	Yield(%) ^{b)}
1	CH2=CH2	FITS-8	СН 30Н	Na ₂ CO ₃	R _f CH ₂ CH ₂ OCH ₃	27(50)
2	~~~~~ 11	11	но	~	R CH CH CH OH	38(42)
3	n	FIS-8	нсоон	NaHCO ₃	R _f CH ₂ CH ₂ OCHO	(26)
4	CH2=CHPh	FITS-2	NaCl	-	R _f CH ₂ CHClPh	(25)
5	CH2=CHCH3	FITS-8	СНЗОН	Ру	R _f CH ₂ CH(OCH ₃)CH ₃	28(33)
6	~)	11	H ₂ Ó	NaHCO ₃	R _f CH ₂ CH(OH)CH ₃	32(43)
7	CH2=CHCH=CH2	11	ii ii	11	R _f CH ₂ CH=CHCH ₂ OH	47
8	~ 11	FIS-8	FT	Ħ	1	59
9	**	FITS-8	CH ₃ COONa	-	R _f CH ₂ CH=CHCH ₂ OCOCH ₃	30
10	11	FIS-8	нсоон	NaHCO3	R _f CH ₂ CH=CHCH ₂ OCHO	79(100)

a) b) See below Table 1.

Surprisingly, when the reactions of FITS or FIS with alkenes and alkadienes were run in a moist amide solvent such as dimethylformamide (DMF), dimethylacetamide (DMAC), and formamide (FA), the following formates and acetate could be isolated (Table 3).

On the other hand, alkenes with nucleophilic functional groups such as hydroxy and carboxy in the same molecules gave the intramolecular addition products in good yields under the similar conditions as shown in Scheme 3. It

Run	Alkene or Alkadiene	FITS-m or FIS-m	Amide/H ₂ 0	Product	Yield (%)
1	CH2=CH2	FITS-8	DMF	R.CH_CH_OCHO	73
2	х х II	FIS-8	"	1 & 2 11	46(73)
3	11	FITS-8	DMAC	R _r CH ₂ CH ₂ OCOCH ₃	50(64)
4	tf.	11	FA	R _r CH ₂ CH ₂ OCHO	26(38)
5	CH2=CHPh	FIS-3	DMF	R _r CH ₂ CH(Ph)OCHO	56
6	CH2=CHCH=CH2	FITS-8	"	R _f CH ₂ CH=CHCH ₂ OCHO	92
7	~ " ~	FIS-8	11	±~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	56
8	CH2=CHCH=CHCH3	FITS-8	tı	R _f CH ₂ CH=CHCH(CH ₃)OCHC) 47

Table 3. Reactions of FITS-m or FIS-m with alkenes and alkadienes in moist amide solutions

a) b) See below Table 1.

is interesting that allyl alcohol or its derivatives afforded the carbonyl compounds or the ketal along with the intramolecular adducts. The ratios of the products vary with the polarity of solvents used.

Scheme 3.
$$CH_{2}=CHCH_{2}CH_{2}COOH \xrightarrow{FITS-8/Py}_{rt, 1 h} R_{f}CH_{2}$$

Scheme 4 is proposed as a reaction mechanism. In the reaction of FITS with propene, the adduct (triflate) could be isolated. Although the triflate is thought to be an intermediate for the other products, the idea can be excluded because the triflate do not react appreciably with pyridine or methanol under the similar conditions. These facts are in favor of the mechanism containing a cationic intermediate as seen in the scheme. The cationic intermediate is probably formed through the four-ring transition state (the six-ring transition state in the case of alkadienes) from the π -complex of FITS with



alkenes. The transition state might consist of the one-electron transfer mechanism A or the two-electron transfer mechanism B, or both. At the present stage, it is not clear which mechanism is predomi-



nant. The formation of the carbonyl compounds and the ketal from allyl alcohol and its derivatives can be explained by a hydride shift from the cationic intermediate. The fact that the proportion of the carbonyl compounds increases with the polarity of solvents is in support of the hydride shift mechanism.

To our knowledge, FITS are the first to make it possible to undergo the successful cationic perfluoroalkylation of alkenes and alkadienes. In this way, under the mild conditions FITS can easily afford the compounds, the preparation of which is difficult or requires multiple steps in the conventional methods. Since the perfluoroalkyl group has unique properties⁵⁾ - high electronegativity, stability, lipophilicity, and interfacial activity, it is also expected that FITS serve as useful reagents for the preparation of a wide range of interesting perfluoroalkyl compounds among organic chemists.

References and Note

1) W.A.Sheppard and C.M.Sharts, "Organic Fluorine Chemistry", W.A.Benjamin, Inc., New York, 1969, p185. 2) a) J.A.Young, Fluorine Chemistry Reviews, <u>1</u>, 359 (1967); b) N.Ishikawa and A.Sekiya, Nippon Kagaku Kaishi, <u>1972</u>, 2214. 3) a) T.Umemoto, Y.Kuriu, H.Shuyama, O.Miyano, and S.Nakayama. Abstracts, 7th Symposium on Fluorine Chemistry of Japan, Oct., 1981. p4 and 6; b) T.Umemoto and Y.Kuriu, Tetrahedron Lett., in press; c) T.Umemoto, Y.Kuriu, and H.Shuyama, Chemistry Lett., in press; d) T.Umemoto and Y.Kuriu, submitted. 4) The letter m means the number of carbons in the perfluoroalkyl group. 5) a) W.A. Sheppard and C.M.Sharts, "Organic Fluorine Chemistry", W.A.Benjamin, Inc., New York, 1969, p18; b) R.Filler, CHEMTECH, Dec. 752 (1974): c) J.C.Tatlow, Chemistry and Industry, Jul. 522 (1978): d) N.Ishikawa, Yu Kagaku, <u>26</u>, 613 (1977).

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