PERFLUOROALKYLATION OF ALKYNES WITH RfI(Ph)OSO2CF3

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Perfluoroalkylation of alkynes with $RfI(Ph)OSO_2CF_3$ is described. This offers the first example of electrophilic perfluoroalkylation of alkynes.

Many reports appeared on the reactions of alkynes with perfluoroalkyl free radical species thermo- or photochemically generated from iodoperfluoroalkanes or perfluoroalkylcoppers, but none of ionic perfluoroalkylations of alkynes has been reported.^{1a-d)} In the previous paper.²⁾ we have described the successful electrophilic perfluoroalkylation of alkenes and alkadienes with (perfluoroalkyl)-phenyliodonium trifluoromethanesulfonates (FITS-m), RfI(Ph)OSO₂CF₃(Rf=n-C_mF_{2m+1}). We now wish to report on the electrophilic perfluoroalkylation of alkynes with FITS.

Phenylacetylene reacted with FITS in methylene chloride in the presence of a base to afford displacement product (1), adduct (2), and ketone (3) in 47%, 36%, and 4% yields. respectively, and iodobenzene as another product in a quantitative yield (Run 1 in Table 1). These products suggested strongly the presence of a cationic species as a reaction intermediate. We carried out the reaction in several conditions and showed the results in Table 1. Polar solvents such as dimethylformamide and methanol afforded (1) exclusively, while formic acid gave selectively (3) in a high yield. As (2) could not be converted to (3) under such reaction conditions, (2) is not an intermediate for (3). When FITS reacted phenylacetylene in formic acid in the presence of pyridine, vinyl formate (4) could

FITS	5-2 + HCECPh -	Base 1h	RfC=CPh + (1)	RfCH=C(Ph)OSO ₂ (2)	CF3 + F	fCH₂COPh (3)
T a ble ´	1. Reaction of	FITS-2 with	phenylacety	lene		
Run	Base	Solv.	Temp.(°C)	(1)(%)	(2)(%)	(3)(%)
1	Pyridine(1eq)	CH2Cl2	Reflux	47	36	4
2	No base	**	11	15	31	0
3	11	DMF	50	45	0	0
4	11	СН зОН	50	100	0	0
5	n	НСООН	50	4	0	86

3580

FITS-2 + HCECPh
$$\xrightarrow{\text{Base}}$$
 RfCH=C(OCHO)Ph^{3a)} \longrightarrow RfCH₂COPh
rt in HCOOH (4) Isolated. (3)

be isolated, which was slowly hydrolysed to (3) under the conditions. It was strange that adduct (5) was not formed by the reaction in methanol. Probably the solvent effect is a dominant factor. In fact, the reaction was carried out in acetonitrile in the presence of methanol to yield (5) along with (1) and (2).

FITS-2 + HCECPh
$$\xrightarrow{CH_3OH/Pyridine}$$
 RfCH=C(OCH₃)Ph^{3a)} + (1) + (2)
50°C, 2h in CH₃CN (5) 8% 36% 8%

The reaction of FITS-m with 1-octyne was examined as shown in Table 2. It is interesting that (perfluoroalkyl)alkene (7) was obtained besides displacement product (6). While phenylacetylene gave the alkyne (1) as a sole product with polar solvents such as DMF or methanol, 1-octyne afforded the alkene (7) as a sole or a main one. The adduct could not be isolated even in the use of formic acid as a solvent.

FITS-m + HCECR (R=n-C₆H₁₃)
$$\xrightarrow{\text{Base}}$$
 RfCECR + RfCH=CHR^{3b}
(6) (7)

Table 2. Reaction of FITS-m with 1-octyne

Run	FITS-m	Base	Solv.	Temp.(°C)	Time(h)	(6)(%)	(7)(%)
1	m = 8	Pyridine	CH ₂ Cl ₂	Reflux	2	10	21
2	8	No base	CH ₂ Cl ₂	17	2	16	27
3	8	**	DMF	80	2	0	41
4	8	11	СН₃ОН	60	5	2	28
5	2	17	нсоон	60	3	28	28

4-Octyne produced (perfluoroalkyl)alkene (8).

FITS-6 + RCECR
$$\xrightarrow{\text{Pyridine, rt}}$$
 RfRC=CHR^{3c)} (R=n-C₃H₇)
overnight in CH₂Cl₂ (8) 44%

Since both ir spectra of (7) and (8) isolated by means of column-chromatography on silica gel showed a weak absorption band at 1980 cm⁻¹ characteristic of allenes besides 1680 cm⁻¹ (vc=c), (7) and (8) are probably contaminated with a small amount of each corresponding allene. Attempts to isolate the allenes were unsuccessful.

The reactions with propargyl alcohol and its derivatives presented interesting results (Table 3 and 4). (Perfluoroalkyl)acrolein (13a) or vinyl ketone (13b) was formed besides (11a,b) and (12a,b). The ratios varied with the polarity of solvents. The use of DMSO as a high polar solvent led to a decrease of (11) and an increase of (13). On the other hand, 3-hydroxy-3-methyl-1-butyne.

FIT	S-8 + H	C≡CCHROH (10a,b)	Pyridine	RfC≡CCHROH (11a,b)	H + RfCH=CHC (12a,b)	HROH ^{3d)} + F	RfCH=CHCOR ^{3e)} (13a,b)
Table	3. Reac	tion of H	TITS-8 with	propargyl	alcohol and i	ts derivativ	<i>v</i> e
Run	(10a/b)	Solv.	Temp.(°C)	Time(h)	(11a/b)(%)	(12a/b)(%)	(13a/b)(%)
1	R =H	CH ₂ Cl ₂	25	Overnight	42	13	7
2	Н	DMF	25	*1	Trace	36	11
3	Н	DMSO	25	1	**	11	25
4	R=CH ₃	CH ₂ Cl ₂	40	2	38	13	0
5	СН з	DMF	40	2	0	45	11
6	СН з	DMSO	40	2	0	8	32
FITS-8 + HC=CC(CH ₃) ₂ OH $\xrightarrow{\text{Pyridine}}$ RfC=CC(CH ₃) ₂ OH + RfCH=CHC(CH ₃) ₂ OH ^{3e}) (14) (15)							
Table	4. Reac	tion of H	FITS-8 with	3-hydroxy-	-3-methyl-1-bu	tyne	
Run	Sol	v.]	ſemp.(°C)	Time(h)) (14)	(%)	(15)(%)

1 CH ₂ Cl ₂ 25 2 34 11 2 DMF 25 2 1 73	
2 DMF 25 2 1 73	-
3 DMSO 25 2 14 52	

where there is no α -proton, gave perfluoroalkylated alkyne (14) and alkene (15). It is in contrast to the fact that the reaction of a perfluoroalkylcopper with the hydroxymethylbutyne yielded 1-(perfluoroalkyl)-3-methyl-1,2-butadiene.^{1d})

1-Butyn-4-ol also afforded perfluoroalkylated alkyne (16) and alkene (17).

FITS-8	+	HC=C(CH ₂) ₂ OH	Pyridine	RfC∓C(CH₂)₂OH	+	$RfCH=CH(CH_2)_2OH^{3f}$
			40°C, 2h	(16)		(17)
			in CH ₂ Cl ₂	33%		42%
			in DMF	2%		64%

The following mechanism was proposed to account for the above results. The formation of the displacement products (1), (6), (11), (14), and (16) or the allenes, and the adducts or the ketones (2), (3), (4), and (5) can be explained by the elimination of protons from the cationic intermediates, and the attack of some nucleophiles to them, respectively. Which path the reaction proceeds by is greatly dependent on the effects of solvents. The formation of (13a,b) in the case of propargyl alcohols results from the hydride shift in the intermediates, giving more stable α -hydroxyallyl cations, followed by the elimination of protons from the reaction of perfluoroalkyl radical species with alkynes gave perfluoroalkylated alkenes only, ^{1d} it is reasonable to consider that (perfluoroalkyl)alkenes (7), (8), (12), (15), and (17) are formed by the hydrogen abstraction of the radical intermediates which are perhaps formed by





the electron exchange with the iodine atoms. However the abstraction of hydrides by the cationic intermediates as another route is not quite excluded. There is no formation of β -(perfluoroalkyl)styrene in the case of phenylacetylene, indicating that the reaction is exclusively via the vinyl cation stabilized by the neiboring phenyl group. Since there is not such a neiboring stabilizing effect in the case of alkylacetylenes, the reaction is accompanied with the radical process to yield the (perfluoroalkyl)alkenes along with the displacement products. In this way, the complexity of the reaction of FITS with alkynes compared to that with alkenes is due to the difficulty in the formation of the alkenyl cations relative to the alkyl cations.

The electrophilic perfluoroalkylation using FITS-2 followed by dehydrofluorination easily afforded β-fluoro-β-trifluoromethyl-α,β-unsaturated carbonyl compounds which are versatile intermediates⁴⁾ for the preparation of the compounds containing the biologically important trifluoromethyl groups.⁵⁾ So it is expected that FITS serve as useful reagents for the preparation of various kinds of perfluoroalkylated compounds.



References and Notes

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