PERFLUOROALKYLATION OF CARBANIONS

Teruo UMEMOTO* and Yuriko KURIU Sagami Chemical Research Center Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

A successful perfluoroalkylation of various carbanions by the use of per<u>f</u>luoroalkylphenyliodonium trifluoromethane<u>s</u>ulfonate (FITS) was described. The reactivity of other perfluoroalkyliodonium salts was also examined.

There have been many investigations on perfluoroalkylation.¹⁻³ Conventional methods for the perfluoroalkylation on a carbon site are chiefly referred to the following reactions.

- (1) The reaction of a free radical perfluoroalkyl group $(R_{r}^{,})$.^{1a)}
- (2) The nucleophilic reaction of an anionic perfluoroalkyl group (R_{r}^{-}) .^{1b,2)}
- (3) The coupling reaction of a halide with iodoperfluoroalkane in the presence of copper or with perfluoroalkylcopper.³⁾

On the other hand, the cationic perfluoroalkylation has been rarely reported. Because it has been very difficult to generate a cationic perfluoroalkyl group on the basis of the high electronegativity and bonding ability of a perfluoroalkyl group. An attempt to perfluoroalkylate benzene or anisole with perfluoroalkyl trifluoromethanesulfonate was unsuccessful, which was regarded as the combination of the perfluoroalkyl group and the strongest leaving group.⁴⁾ Recent examination on the reactivity of the trifluoromethanesulfonate with an enamine indicated that the reactive site in the trifluoromethanesulfonate is not the carbon site bonded to the oxygen atom, but the sulfur atom due to easier release of perfluoroalkoxy anion than trifluoromethanesulfonyloxy anion.⁵⁾ We have taken notice of perfluoroalkyliodonium salt as a source of the cationic perfluoroalkyl group. Recently it was reported that perfluoroalkyl-p-tolyliodonium chloride was allowed to react with active aromatic compouds such as aniline derivatives to give p-perfluoroalkylaniline derivatives in low yields.⁶⁾ Since the electronegativity of the perfluoroalkyl group is higher than that of a chlorine atom, 7) the iodonium chloride is not expected as an effective source of the cationic perfluoroalkyl group. In order to create a reactive cationic perfluoroalkylating agent, we have synthesized a series of perfluoroalkylaryliodonium sulfonates as shown in the previous work.⁸⁾ First, we wish to report the reaction with various carbanions. Among the sulfonates, perfluoroalkylphenyliodonium trifluoromethanesulfonate (FITS) was selected as the cationic perfluoroalkylating agent.

We found that FITS was allowed to react with carbanions to give the per-

Table 1. Perfluoroalkylation of carbanions with FITS-m.

Run	(I) ^{a)}	FITS-m	R- _М +ъ)	Solv. ^{c)}	Temp. (°C)	Time (hr)	Yiel (I)	d(%) ^{d)} PhI
1	^{n-C} 8 ^F 17 ^C 8 ^H 17	m = 8	n-C ₈ H ₁₇ MgCl	THF	-78	0.5	65 (47)	83
2	$^{n-C}8^{F}17^{CH}2^{Ph}$	8	PhCH ₂ MgCl	THF	-78 - -45	0.5 - 0.5	36	94
3	11	8	"	n-hexane	0	3	32	100
4	n-C ₃ F7 ^{CH} 2 ^{Ph}	3	11	THF	-110	2	82	100
5	11	3	"	THF	-78	1.5	63	100
6	C ₂ F ₅ CH ₂ -p-Tolyl	. 2	p-TolylCH ₂ MgCl	THF	-110	1	60	80
7	11	2	"	THF	-78	1	58	100
8	n-C8 ^F 17 ^{CH} 2 ^{CH=CH} 2	8	CH2=CHCH2MgC	l THF	0	0.3	51	-
9	11	8	"	n-hexane	0 → r.t.	1 <u>→</u> 0.08	51	_
10	^{n-C} 6 ^F 13 ^{C≡CC} 6 ^H 13	б	n-C6 ^H 13 ^{C≡CLi}	THF	-78	1	70	97
11	^C 2 ^F 5 ^{C≡CC} 6 ^H 13	2	11	n-pentane	0	1	57	85
12	n-C ₃ F7 ^C ≢CPh	3	PhC≝CLi	THF	-110	1	44	100
13	C ₂ F ₅ C≡CPh	2	"	THF	-110	1	57	98
14	n	2	11	THF	- 78	1	56	92
15	II	2	PhC=CMgC1	THF	-78	1	58	100
16	n-C8F17C(CH3)2NO2	8	(CH ₃) ₂ C(NO ₂)N	a DMSO	r.t.	1	(51)	-

a) All products exhibited spectral data(¹H- and ¹⁹F-NMR, IR, and Mass) in accord with the assigned structures or with the literature values. Elementary analyses of new compounds are in good agreement with calculated values.

The organomagnesium compounds were prepared from the chlorides and mag-nesium in ether by the usual method except for phenylethynylmagnesium chloride which was prepared by the treatment of phenylacetylene with an etheraced solution of benyletraneoium chloride in TWF. b) ethereal solution of benzylmagnesium chloride in THF. The sodium salt of 2-nitropropane was in situ prepared by the treatment of 2-nitropropane with sodium methylsulfinyl methide in DMSO.
c) FITS was mixed with THF below 0°C.
d) Yields were determined by GLC. Values in parentheses are isolated yields

Scheme 1.

$$R_{f}^{R}(Ph)OSO_{2}CF_{3} \xrightarrow{R^{-}M^{+}} R_{f}^{-}R^{+}PhI \qquad (R_{f}^{-}C_{m}F_{2m+1})$$

FITS-m (I)

fluoroalkyl-compounds (I) in moderate yields and iodobenzene was liberated in an almost quantitative yield (Scheme 1). Accordingly the reaction with various carbanions was examined. Table 1 shows the results and reaction conditions. As a result, it was found that FITS reacted with carbanions such as alkyl, allyl, benzyl, α -nitroalkyl, and alkynyl anions to afford the perfluoroalkylcompounds in moderate to good yields.

The typical experimental procedure is as follows. An ethereal solution (1.2 ml) of n-octylmagnesium chloride (1.3 mmol) was added into a mixture of FITS (0.5 g, 0.65 mmol) and dried tetrahydrofuran.(2.5 ml) at -78° C with stirring under an argon atmosphere. After stirring for 1 hr, the reaction mixture was quenched by aqueous ammonium chloride followed by extraction with diethyl ether. The ethereal extract was washed with water and dried on magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel using pentane as an eluent to give 1-(n-heptadecafluorooctyl)octane in 47% yield (GLC yield 65%).

Similarly perfluoroalkylphenyliodonium sodium sulfate derived from perfluoroalkylphenyliodonium sulfate (FIS) by the use of sodium hydride reacted with sodium salt of 2-nitropropane at room temperature to afford 2-(perfluoroalkyl)-2-nitropropane in 30% isolated yield. The yield is lower than that in FITS (51% isolated yield).

$$\begin{array}{c} R_{f}I(Ph)OSO_{3}H \xrightarrow{\text{NaH}} R_{f}I(Ph)OSO_{3}Na \xrightarrow{\text{NaC(CH}_{3})_{2}NO_{2}} R_{f}^{-C(CH_{3})_{2}NO_{2}} \\ (FIS-8) & 30\%(R_{f}^{-n-C_{8}F_{17}}) \end{array}$$

We also found that perfluoroalkyl-p-tolyliodonium chloride prepared by L.M.Yagupolskii et al. was treated with carbanions such as benzylmagnesium chloride to afford the corresponding perfluoroalkyl-compounds. On the other hand, the reaction with 1-octynyl anion gave the product in a low yield compared to that of FITS (70%) and that with n-octyl anion resulted in no formation of the perfluoroalkyl-compound under the same conditions.

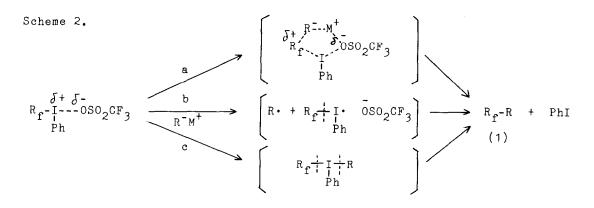
$$R_{f}I(p-Tolyl)Cl + PhCH_{2}MgCl \xrightarrow{R_{f}=n-C_{3}F_{7}}_{-78°C in THF} R_{f}-CH_{2}Ph + p-Tolyl-I \\ 58\% \qquad 80\%(GLC)$$

$$" + n-C_{6}H_{13}C=CLi \xrightarrow{R_{f}=n-C_{6}F_{13}}_{-30\%(GLC)} R_{f}-C=CC_{6}H_{13} \\ 30\%(GLC)$$

$$" + n-C_{8}H_{17}MgCl \xrightarrow{R_{f}=n-C_{8}F_{17}}_{-78°F_{17}} R_{f}-C_{8}H_{17}$$

From the above findings, it is understandable that FITS is the reactive cationic perfluoroalkylating agent. The high reactivity of FITS is attributed to the strongest leaving ability of trifluoromethanesulfonyloxy proup.

Although the participation of the cationic perfluoroalkyl, perhaps, through the ring transition state as seen in Scheme 2a is first anticipated as the reaction mechanism, the following other routes (Scheme 2b and 2c) can also be considered. Scheme 2b and 2c consist of the cleavage of R_f -I bond by the



electron transfer from the carbanion to the iodine atom and the decomposition of the trivalent iodine compound derived from the attack of the carbanion to the iodine atom, respectively. At the present stage, none of three routes can be neglected.

In any event, FITS can react with various carbanions to give the perfluoroalkyl-compounds. To our knowledge, FITS is the first to make it possible to perfluoroalkylate the carbanions. Since a wide variety of carbanions can easily be prepared by the advanced synthetic methods, it is expected that FITS is used extensively as the cationic perfluoroalkylating agent.

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