

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 perfluoroalkylphenyliodonium trifluoromethanesulfonate (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 ($R_f\cdot$).^{1a)}
- (2) The nucleophilic reaction of an anionic perfluoroalkyl group (R_f^-).^{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 compounds 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.

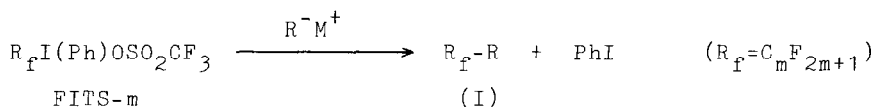
We found that FITS was allowed to react with carbanions to give the per-

Table 1. Perfluoroalkylation of carbanions with FITS-m.

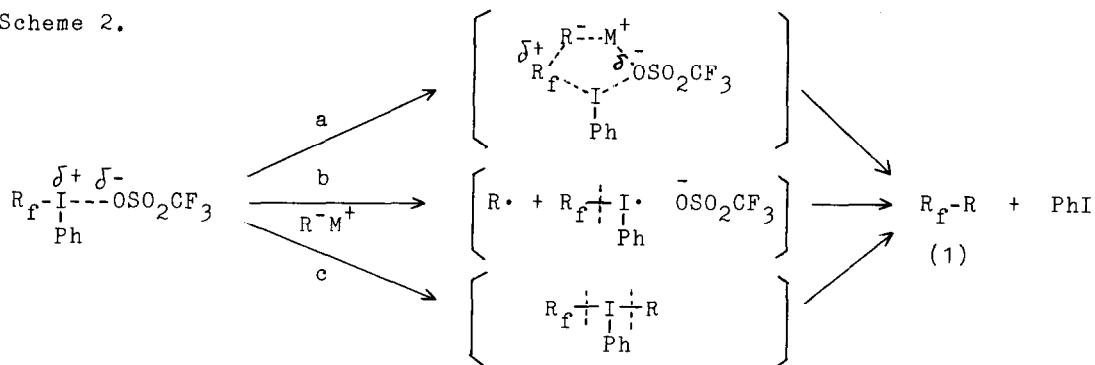
Run	(I) ^{a)}	FITS-m	R ^{-M} + ^{b)}	Solv. ^{c)}	Temp. (°C)	Time (hr)	Yield(%) ^{d)}	
							(I)	PhI
1	n-C ₈ F ₁₇ C ₈ H ₁₇	m=8	n-C ₈ H ₁₇ MgCl	THF	-78	0.5	65 (47)	83
2	n-C ₈ F ₁₇ CH ₂ Ph	8	PhCH ₂ MgCl	THF	-78 → -45	0.5 → 0.5	36	94
3	"	8	"	n-hexane	0	3	32	100
4	n-C ₃ F ₇ CH ₂ Ph	3	"	THF	-110	2	82	100
5	"	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	"	2	"	THF	-78	1	58	100
8	n-C ₈ F ₁₇ CH ₂ CH=CH ₂	8	CH ₂ =CHCH ₂ MgCl	THF	0	0.3	51	-
9	"	8	"	n-hexane	0 → r.t.	1 → 0.08	51	-
10	n-C ₆ F ₁₃ C≡CC ₆ H ₁₃	6	n-C ₆ H ₁₃ C≡CLi	THF	-78	1	70	97
11	C ₂ F ₅ C≡CC ₆ H ₁₃	2	"	n-pentane	0	1	57	85
12	n-C ₃ F ₇ C≡CPh	3	PhC≡CLi	THF	-110	1	44	100
13	C ₂ F ₅ C≡CPh	2	"	THF	-110	1	57	98
14	"	2	"	THF	-78	1	56	92
15	"	2	PhC≡CMgCl	THF	-78	1	58	100
16	n-C ₈ F ₁₇ C(CH ₃) ₂ NO ₂	8	(CH ₃) ₂ C(NO ₂)Na	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.
- b) The organomagnesium compounds were prepared from the chlorides and magnesium in ether by the usual method except for phenylethylnylmagnesium chloride which was prepared by the treatment of phenylacetylene with an 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.



Scheme 2.



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.

References

- 1) a) W.A. Sheppard and C.M. Sharts, "Organic Fluorine Chemistry", W.A. Benjamin, Inc., New York, 1969, p185; b) W.A. Sheppard and C.W. Sharts, *ibid.*, p276.
- 2) J.A. Young, *Fluorine Chemistry Reviews*, **1**, 359 (1967).
- 3) V.C.R. McLoughlin and J. Throwers, *Tetrahedron*, **25**, 5921 (1969); Y. Kobayashi, I. Kumadaki, S. Sato, N. Hara, and E. Chikami, *Chem. Pharm. Bull. Tokyo*, **18**, 2334 (1970); J. Burton, P.L. Coe, C.R. Marsh, and J.C. Tatlow, *J. Chem. Soc. Perkin I*, **1972**, 639; Y. Kobayashi, K. Yamamoto, and I. Kumadaki, *Tetrahedron Lett.*, 4071 (1979).
- 4) G.A. Olah and T. Ohyama, *Synthesis*, 319 (1976).
- 5) Y. Kobayashi, T. Yoshida, and I. Kumadaki, *Tetrahedron Lett.*, 3865 (1979).
- 6) L.M. Yagupolskii, I.I. Maletina, N.V. Kondratenko, and V.V. Orda, *Synthesis*, 835 (1978).
- 7) J.E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).
- 8) T. Umemoto, Y. Kuriu, and H. Shuyama, to be submitted for publication.

(Received in Japan 18 August 1981)