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TRIETHYLBORANE-INDUCED STEREOSELECTIVE RADICAL ADDITION OF PERFLUOROALKYL IODIDES TO ACETYLENES

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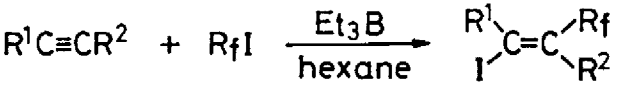
Abstract: Treatment of terminal or internal acetylenes bearing a variety of substituents with perfluoroalkyl iodides in the presence of a catalytic amount of triethylborane provides the corresponding perfluoroalkenes in good to excellent yields. The addition of perfluoroalkyl iodides to olefins is also described.

The addition reaction of perfluoroalkyl iodides to carbon-carbon multiple bond is one of the most efficient and versatile methods for direct introduction of the perfluoroalkyl group to organic molecules.[1] Perfluoroalkylation of acetylenes and olefins has been performed by photolysis,[2] pyrolysis,[3] electrolysis,[4] free radical initiator,[5] or transition-metal catalyst.[6] These methods, however, have some drawbacks and there still exists a need for new methods. In the course of our study on the triethylborane-induced radical addition,[7] we examined the addition of perfluoroalkyl iodides to carbon-carbon multiple bonds and found that triethylborane exhibited good catalytic activity for the reaction.

Triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol)[8] was added to a solution of 1-dodecyne (0.17 g, 1.0 mmol) and tridecafluorohexyl iodide (0.53 g, 1.2 mmol) in hexane (6.0 ml) at 25°C under an argon atmosphere. The resultant mixture was stirred for 5 h at 25°C and concentrated in vacuo. The residual oil was submitted to preparative thin layer chromatography on silica gel to afford (E)-2-iodo-1-tridecafluorohexyl-1-dodecene (**1**, 0.57 g) in 94% yield.

The representative results are summarized in Table 1. The new reaction has the following characteristics. (1) Reaction proceeded with high regio- and stereoselectivities to give (E)-2-iodo-1-perfluoroalkyl-1-alkene (trans-addition product) exclusively. This result is in striking contrast to the results obtained through the previously reported procedure[2-6] which gives the adducts as stereoisomeric mixtures of (E)- and (Z)-2-iodo-1-perfluoroalkyl-1-alkenes. (2) Not only terminal acetylenes but also internal acetylenes reacted easily with perfluoroalkyl iodides under the same conditions

Table 1. Addition of perfluoroalkyl iodides to acetylenes[a]



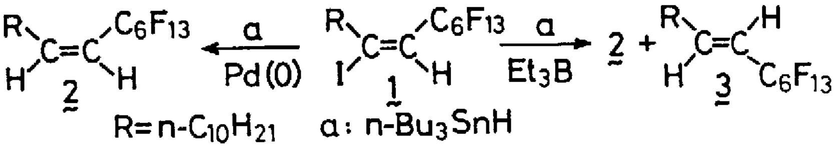
Run	R_fI	Alkyne		Reaction Conditions		Product
		R^1	R^2	Temp(°C)	Time(h)	(%)
1	$C_6F_{13}I$	$n\text{-}C_{10}H_{21}$	H	25	5	94
2		$HOCH_2CH_2CH_2$	H	25	5	71
3		$EtOOC(CH_2)_8$	H	25	5	85
4		$HOOC(CH_2)_8$	H	25	5	75
5		Ph	H	25	5	84
6		$PhCH_2O(CH_2)_4$	H	25	10	73[b]
7		$n\text{-}C_5H_{11}$	$n\text{-}C_5H_{11}$	25	15	60
8	$(CF_3)_2CFI$	$n\text{-}C_{10}H_{21}$	H	25	8	92
9		$HOCH_2CH_2CH_2$	H	25	8	77
10		$EtOOC(CH_2)_8$	H	25	8	82[c]
11		$PhCH_2O(CH_2)_4$	H	25	10	86[d]
12		$n\text{-}C_5H_{11}$	$n\text{-}C_5H_{11}$	25	12	44
13	CF_3I	$n\text{-}C_{10}H_{21}$	H	-24	10	76
14		$HOCH_2CH_2CH_2$	H	-24	10	72
15		$EtOOC(CH_2)_8$	H	-24	10	73
16		$n\text{-}C_5H_{11}$	$n\text{-}C_5H_{11}$	-24	10	46
17	CF_2Br_2	$n\text{-}C_{10}H_{21}$	H	25	8	53

a) Alkyne (1.0 mmol), $C_6F_{13}I$ (or $(CF_3)_2CFI$, 1.2 mmol), and Et_3B (0.1 mmol) were employed (Run 1-12). Alkyne (1.0 mmol), CF_3I (5.0 mmol), and Et_3B (1.0 mmol) were employed (Run 13-16). Alkyne (1.0 mmol), CF_2Br_2 (4.0 mmol), and Et_3B (1.0 mmol) were employed (Run 17). b) Contaminated by Z-isomer (E/Z = 93/7). c) See Ref. 9. d) Contaminated by Z-isomer (E/Z = 95/5).

to give 40-60% yields of the products.[10] (3) Mild reaction conditions enable us to accomplish the effective addition of volatile polyfluoromethanes such as iodotrifluoromethane[11] and dibromodifluoromethane to acetylenes (Run 12-17). (4) The use of hexane as a solvent is critical to the reaction. In other solvents such as benzene, dichloromethane, or tetrahydrofuran, reaction proceeded very slowly and did not complete even after prolonged reaction time. (5) CF_3CH_2I was not so effective as $C_6F_{13}I$. For instance, the reaction of 1-dodecyne with CF_3CH_2I gave $CF_3CH_2CH{=}C(I)C_{10}H_{21}$ (E/Z = 4/1) in 39% yield.

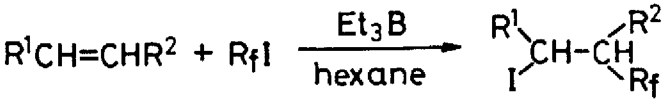
Trans-addition was confirmed as follows. Treatment of 1, derived from

1-dodecyne and tridecafluorohexyl iodide, with tributyltin hydride in the presence of $Pd(PPh_3)_4$ gave (Z)-tridecafluoroalkene **2** exclusively. On the other hand, triethylborane-induced hydrodehalogenation[12] of **1** afforded a mixture of **2** and its stereoisomer **3** (**2**/**3** = 1/1).



The new technique provided us with a convenient and effective method for the addition of perfluoroalkyl iodides to alkenes (Table 2).[13,14]

Table 2. Addition of perfluoroalkyl iodides to alkenes[a]



Run	R_fI	Alkene R^1	R^2	Reaction Conditions Temp(°C)	Time(h)	Product (%)
1	$C_6F_{13}I$	$n\text{-}C_{10}H_{21}$	H	25	3.5	93
2		$MeOOC(CH_2)_8$	H	25	3.0	90
3		$CH_3C(O)CH_2CH_2$	H	25	3.5	96
4		$n\text{-}C_5H_{11}$	$n\text{-}C_5H_{11}$	25	10	67[b]
5	$(CF_3)_2CFI$	$n\text{-}C_{10}H_{21}$	H	25	3.0	87
6		$MeOOC(CH_2)_8$	H	25	3.0	84
7		$HOCH_2CH_2CH_2$	H	25	2.0	76
8	CF_3I	$n\text{-}C_{10}H_{21}$	H	-24	5.0	78
9		$MeOOC(CH_2)_8$	H	-24	3.5	86
10		$HOCH_2CH_2CH_2$	H	-24	10	73
11		$CH_3C(O)CH_2CH_2$	H	-24	3.5	64
12		$n\text{-}C_5H_{11}$	$n\text{-}C_5H_{11}$	-24	4.0	61[b]
13	CF_2Br_2	$n\text{-}C_{10}H_{21}$	H	25	10	89[c]
14		$MeOOC(CH_2)_8$	H	25	10	90[d]

a) Alkene (1.0 mmol), $C_6F_{13}I$ (or $(CF_3)_2CFI$, 1.2 mmol), and Et_3B (0.1 mmol) were employed (Run 1-7). Alkene (1.0 mmol), CF_3I (5.0 mmol), and Et_3B (1.0 mmol) were employed (Run 8-12). Alkene (1.0 mmol), CF_2Br_2 (4.0 mmol), and Et_3B (1.0 mmol) were employed (Run 13 and 14). b) Erythro/threo = 1/1. c) Product was $n\text{-}C_{10}H_{21}CH(Br)\text{-}CH_2CF_2Br$. d) Product was $MeOOC(CH_2)_8CH(Br)\text{-}CH_2CF_2Br$.

References and Notes

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8. We appreciate Toyo Stauffer Chemical Company for the gift of Et_3B.
9. Bp 110°C (bath temp)/1.0 Torr; IR (neat) 2976, 2928, 2854, 1737, 1635, 1466, 1459, 1302, 1278, 1229, 1181, 1044, 980, 710 cm^{-1}; ^1H-NMR ($CDCl_3$) δ1.25 (t, *J* = 7.0 Hz, 3H), 1.27-1.42 (m, 8H), 1.45-1.75 (m, 4H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 4.15 (q, *J* = 7.0 Hz, 2H), 6.19 (d, *J* = 29.5 Hz, 1H). Found: C, 38.34; H, 4.49%. Calcd for $C_{16}H_{22}F_7O_2I$: C, 37.96; H, 4.38%.
10. Single isomer (by ^{13}C-NMR and ^{19}F-NMR) was obtained in Run 7, 12 or 16, and tentatively assigned as (E) stereoisomer.
11. Gaseous CF_3I (5.0 mmol) was introduced and condensed in a 25 ml reaction flask at -78°C under argon. To this were added, successively, hexane (5 ml), 1-dodecyne (0.17 g, 1.0 mmol), and a hexane solution of Et_3B (1.0 M, 1.0 ml, 1.0 mmol) at -24°C. The resultant mixture was maintained at -24°C for 10 h (or 0°C for 5 h) and concentrated in vacuo. The product was purified by preparative thin layer chromatography on silica gel to give (E)-1-trifluoromethyl-2-iodo-1-dodecene (0.28 g) in 76% yield: Bp 67°C (bath temp)/1 Torr; IR (neat) 2922, 2852, 1637, 1466, 1459, 1338, 1315, 1260, 1129 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.8-1.0 (m, 3H), 1.15-1.40 (m, 14H), 1.40-1.70 (m, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 6.40 (q, *J* = 7.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ14.11, 22.70, 28.32, 29.29, 29.45, 29.55, 29.60, 31.90, 40.72, 119.19, 121.11 (q, *J* = 6.2 Hz), 124.7, 128.9 (q, *J* = 34.5 Hz). Found: C, 43.18; H, 6.09%. Calcd for $C_{13}H_{22}F_3I$: C, 43.11; H, 6.12%. We thank Asahi Glass Co., Ltd. for the gift of CF_3I.
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13. The relative reactivities for alkynes and alkenes to the addition of $C_6F_{13}I$ in competitive reaction conditions were as follows: 1-Octyne$\approx$1-octene (1.0)>cyclooctene (0.3)>3-hexyne$\approx$4-octene (0.1).
14. Financial support by the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Scientific Research #63740047) is acknowledged.

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