PERFLUOROALKYL-SELENATION OF OLEFINS

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Summary; Perfluoroalkyl-selenation of olefins has been performed by the reaction of diphenyl diselenide with sodium borohydride followed with perfluoroalkyl halides (RfX) and olefins where one electron transfer from phenylseleno anion to RfX occurs, generating perfluoroalkyl and phenylseleno radicals.

Monofluoro-selenation of olefins has been studied quite recently for the preparation of monofluorinated olefins, 1) while no study on perfluoroalkyl-selenation of olefins has appeared so far in contrast to extensive studies on perfluoroalkyl halogenations.^{2),3)} Because perfluoroalkyl phenyl selenides are too stable to undergo the desired perfluoroalkyl-selenation in contrast to phenylselenenyl halides with excellent electrophilicity to olefins,⁴⁾ generation of both phenylseleno (PhSe•) and perfluoroalkyl radicals (Rf•), or both phenylseleno cation and perfluoroalkyl carbanion must be incorporated for the purpose. Phenylseleno anion is highly reductive and nucleophilic and thus in principle would transfer one electron^{5),6)} to perfluoroalkyl halide, inducing generation of both Rf• and PhSe• radicals.

Here we describe perfluoroalkyl-selenation of olefins in a PhSeNa - RfX system.



Into a suspension of sodium phenylselenide prepared from (PhSe)₂ (0.3 mmol) and NaBH₄ (1.5 mmol) dissolved in dry ethanol (0.3 ml) at 0 °C for 15 min, isobutyl vinyl ether (6 mmol) and CgF₁₇I (0.9 mmol) were added under N₂. The mixture was stirred at room temperature for 2 h. The usual workup and chromatography (SiO₂, hexane-benzene) gave 2 (86%)⁷) and perfluoroalkyl phenyl selenide 3 (Rf = CgF₁₇, 7.4%).

The results of the perfluoroalkyl-selenation are summarized in Table 1. Most of the terminal olefins can trap perfluoroalkyl radicals smoothly, affording the desired compounds 2 in reasonable yields. The electron donating substituents of olefins enhance a trapping efficiency of the highly electrophilic Rf• radicals. (Entry 1, 2) The ratio of perfluoroalkyl phenyl selenides 3 to 2 increased as the olefin is less reactive from the electronic and steric points of view. (Entry 5, 6) The relative reactivity of $C_nF_{2n+1}I$ was found to be almost same so far as examined (n=4, 6 and 8). Trifluoromethyl bromide does react although the yield is moderate, and trifluoromethyl phenyl selenide which seems to be an $S_{RN}1$ product, becomes one of the major products.

The perfluoroalkyl radicals add to carbon-carbon double bond regioselectively so as to form more stable (Markownikoff type) carbon radicals, which may be trapped with PhSe• radicals or with PhSe⁻ anion. In the latter case, anion radicals $[2]^-$ would further transfer one electron to RfI to propagate a chain reaction.⁸,9)

The intramolecular five membered ring formation (exo addition) followed by trapping the terminal radicals with PhSe- radicals or PhSe⁻ anion was found to be a major pathway for diallyl ether (4, 53%).¹⁰) The present perfluoroalkyl-selenation is not stereoselective since a mixture of *trans* and *cis* adducts was obtained for both cyclohexene **5a** (75:25) and dihydropyran **5b** (73:27).



Oxidative deselenation (H₂O₂ in CH₂Cl₂) of **2a** proceeds regioselectively to give a *trans* 7-hexadecene **6** rather than the corresponding 6-hexadecene in a quantitative yield, presumably due to the higher acidity of the perfluoroalkylated methylene protons. Likewise, **2b** provided 7 quantitatively.



Entry	RfX	Olefin	2	Yield (%) ^{b)} 3 (RfSePh)	(PhSe) ₂
1	C ₈ F ₁₇ I	<i>~~~</i> ~	86	7	trace
2		∕s	66	trace	30
3		$\sim\sim$	59	19	21
4		\sim	63	25	15
5		\bigcirc	39	42	9
6		\bigcirc	15	60	17
7	C ₆ F ₁₃ I	<i>∽</i> ₀~	84	6	trace
8		$\sim\sim\sim$	47	22	16
9		\sim	53	27	8
10	C₄F ₉ I	<i>∽</i> ₀~	78	2	11
11		$\sim\sim\sim$	57	17	13
12		\sim	55	20	19
13	CF₃Br	<i>∽</i> ₀∕	38	32 ^{c)}	20
14		$\sim\sim\sim$	26	3 4 ^{c)}	31

Table 1. Perfluoroalkyl-selenation of Olefins^{a)}

a) Entry1~12: $(PhSe)_2$ (0.3 mmol), NaBH₄ (1.5 mmol), dry EtOH (0.3 ml), Olefin (6 mmol), RfI (0.9 mmol), r.t., 2h; Entry13,14: $(PhSe)_2$ (0.5 mmol), NaBH₄ (1.5 mmol), dry EtOH (0.5 ml), Olefin (10 mmol), dry DME (1 ml), r.t., 6h, under CF₃Br gas atmosphere (a rubber baloon fitted with CF₃Br was settled with a reaction flask.)

b) Isolated yield based on PhSeNa

c) G.C. yield based on PhSeNa

References and Notes

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- 7) Structures of 2 were determined by IR, ¹H and ¹⁹F-NMR and MS spectral analyses.
- 8) A small amount of the corresponding perfluorooctyl-iodinated adduct (8) from 1-octene was observed in vpc analysis. The iodide 8 prepared by known method was subjected to the same reaction conditions for perfluoroalkyl-selenation, revealing that only 4.8% of 2 was obtained, 91% of 8 was recovered. This result suggests that a major part of the selenide 2 does not form via 8 in the present perfluoroalkyl-selenation conditions.
- 9) The perfluoroalkylated radical intermediate of olefins generated by 2-AIBN-Bu₃SnH-Benzene system in the presence of sodium p-methoxyphenylselenide (9) traps 9, providing the corresponding perfluoroalkylated aryl selenide (2).
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