

RADICAL ADDITIONS OF HEPTAFLUOROPROPYL TRIFLUOROVINYL ETHERAkihiro HOSOYA^{a1}, Tadashi NARITA^{a2,*} and Hiroshi HAMANA^b

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Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday.

The radical addition reactions of heptafluoropropyl trifluorovinyl ether ($\text{CF}_2=\text{CF}-\text{O}-\text{C}_3\text{F}_7$) with cyclic ethers such as tetrahydrofuran, tetrahydropyran, 1,4-dioxane and 1,3-dioxolane were investigated to afford the corresponding one to one addition products in fairly high yields in the presence of dibenzoyl peroxide at 60 °C. The method provides a facile way to prepare cyclic ethers possessing fluoroalkyl substituents.

Keywords: Additions; Heptafluoropropyl trifluorovinyl ether; Radical reactions; Tetrahydrofuran; Tetrahydropyran; 1,4-Dioxane; 1,3-Dioxolane.

The addition of alcohols, ethers and amines to polyfluorinated vinyl compounds such as tetrafluoroethene, chlorotrifluoroethene or perfluorocyclobutene has been reported by many research groups. It is initiated by radicals or γ -rays irradiation¹ though polymerization of tetrafluoroethene and chlorotrifluoroethene takes place simultaneously. As has been reported previously, the radical addition onto pentafluoropropen-2-yl benzoate ($\text{CF}_2=\text{C}(\text{CF}_3)\text{OCOC}_6\text{H}_5$, BPPF) is applicable to a wide variety of organic compounds bearing carbon-hydrogen bonds such as tetrahydrofuran (THF), 1,4-dioxane (DOX), 18-crown-6, hexanal, triethylamine, cycloalkanes and even hexane². The reaction of BPPF with DOX afforded preferentially the 2,6-disubstituted DOX through 1,5-radical shift mechanism. The hydrolysis of the reaction products of BPPF with cyclic ethers yielded fluorinated alcohols which were subsequently esterified with acryloyl chloride or methacryloyl chloride. These (meth)acrylates afforded polymers possessing cyclic

ether moieties bearing fluoroalkyl groups as side chains under radical polymerization condition³. An easy carbon-carbon bond formation was achieved due to the presence of fluorine atoms.

This paper concerns the addition of cyclic ethers such as THF, tetrahydropyran (THP), DOX and 1,3-dioxolane (DL) to heptafluoropropyl trifluorovinyl ether ($\text{CF}_2=\text{CF}-\text{O}-\text{C}_3\text{F}_7$, PPVE). To our knowledge no addition of cyclic ethers to PPVE has previously been reported, although Paleta and coworkers published the results of photochemical addition of THF⁴, butane-1,4-diol⁵ or DL⁶ to hexafluoropropene and perfluorovinyl ethers. Polymerization of PPVE has been achieved under γ -rays irradiation though polymerization reactivity of trifluorovinyl compounds is generally very low except for tetrafluoroethene and chlorotrifluoroethene⁷.

EXPERIMENTAL

All experiments related to addition reactions were carried out under purified nitrogen in order to preclude oxygen and moisture.

Measurements

GC measurements were carried out with a Hewlett-Packard 6890 with a ZB-1, wide-bore fused silica capillary column (15 m \times 0.53 mm, film thickness: 1.5 μm , Phenomenex) equipped with flame ionization detector. The column temperature was programmed from 60 to 320 $^\circ\text{C}$ at 20 $^\circ\text{C min}^{-1}$. Mass spectra were measured by EI and CI methods on a JEOL JMS-SX102. Isobutane was used as a reagent gas of CIMS. ^1H , ^{13}C and ^{19}F NMR spectra (δ , ppm; J , Hz) were recorded on a JEOL JNM-ECP500 Fourier transform NMR spectrometer at 500 MHz for ^1H {non-decoupled and fluorine-decoupled, [^{19}F (irradiation offset -100 ppm)] condition}, at 125 MHz for ^{13}C {[^1H (5 ppm)], [^1H (5 ppm) and ^{19}F (-100 ppm)]}, and at 470 MHz for ^{19}F [^1H (5 ppm)] NMR with deuterated chloroform as a solvent. Chemical shift of ^{19}F NMR was determined on the basis of absolute magnetic field intensity.

Reagents

PPVE obtained by courtesy of Daikin Industries Ltd. was used as received. THF, THP, DOX and DL were dried by refluxing over calcium hydride and then distilled under purified nitrogen atmosphere. Dibenzoyl peroxide (BPO) was precipitated from chloroform and then recrystallized from methanol at 0 $^\circ\text{C}$.

Radical Addition of Heptafluoropropyl Trifluorovinyl Ether. General Procedure

Addition reactions to PPVE were carried out by adding 5 equiv. of PPVE and 40 equiv. of cyclic ether in the presence of 2 equiv. of BPO at 60 $^\circ\text{C}$ for 3 days. The conversion of PPVE was quantitative (^{19}F NMR). The product was separated by distillation. Purity of the product was determined by GC.

2-[1,1,2-Trifluoro-2-(heptafluoropropoxy)ethyl]tetrahydrofuran [(C₄H₇O)CF₂CHF-O-CF₂CF₂CF₃]. B.p. 78.3 °C/4.6 kPa, yield 75%. ¹H NMR (CDCl₃): 1.87–2.03 (4-CH₂, 2 H, m); 2.03–2.20 (3-CH₂, 2 H, m); 3.80–3.93 (5-CH₂, 2 H, m); 4.16 and 4.28 (a pair of 2-CH, 1 H, 2 × dddd, ³J_{HH} = 8 and 11, ³J_{HF} = 5.5 and 5.5, ³J_{HF} = 22 and 23, ³J_{HF} = 4 and 3); 6.14 and 6.15 (a pair of CF₂-CHF-O-, 1 H, 2 × dd, ²J_{HF} = 56 and 52, ³J_{HF} = 11 and 12). ¹³C NMR {¹H (5 ppm)}: 24.63 and 24.78 (a pair of 3-CH₂); 25.58 and 25.62 (a pair of 4-CH₂); 69.80 and 69.85 (a pair of 5-CH₂); 75.52 and 75.56 (a pair of 2-CH, 2 × t, ²J_{CF} = 31); 98.61 and 99.97 (a pair of -CHF-O-, 2 × m); 106.70 (-O-CF₂, tt, ¹J_{CF} = 227, ²J_{CF} = 39); 115.89 (-CF₂-CF₃, tm, ¹J_{CF} = 264); 116.31 (-CF₂-CHF-O-, m); 117.21 (CF₂-CF₃, m). ¹⁹F NMR: {¹H (irradiation offset 5 ppm)}: -81.48 and -81.55 (a pair of -CF₂-CF₃, 3 F, 2 × t, ³J_{CF} = 7); -84.86 and -85.11 (a pair of O-CF₂-CF₂, 1 F, 2 × dm, ²J_{FF} = 147); -86.86 and -87.67 (a pair of O-CF₂-CF₂, 1 F, 2 × dm, ²J_{FF} = 147); -129.93 and -129.97 (a pair of -CF₂-CF₂-CF₃, 2 F, 2 × m); -128.85 and -131.95 (a pair of CF₂-CHF, 1 F, 2 × dd, ¹J_{FF} = 267, ³J_{FF} = 10 and 2); -130.57 and -131.12 (a pair of CF₂-CHF, 1 F, 2 × dd, ¹J_{FF} = 265, ³J_{FF} = 12 and 10); -144.31 and -151.87 (a pair of CF₂-CHF, 1 F, 2 × t, ³J_{FF} = 15). MS (EI, *m/z*): 43 (59), 71 (100), 169 (14), 337 (0.4); (CI, *m/z*): 339 [M + H]⁺. HRMS-EI (*m/z*): [M - H]⁺ calculated for C₉H₇F₁₀O₂ 337.0286, found 337.0270.

2-[1,1,2-Trifluoro-2-(heptafluoropropoxy)ethyl]tetrahydropyran [(C₅H₉O)CF₂CHF-O-CF₂CF₂CF₃]. B.p. 76.8 °C/2.4 kPa, yield 79%. ¹H NMR (CDCl₃): 1.45–2.02 (3-, 4-, 5-CH₂, 6 H, m); 3.31–3.48, 3.98–4.06 (6-CH₂, 2 H, m); 3.58 and 3.72 (a pair of 2-CH, 1 H, m); 6.14 and 6.17 (a pair of CF₂-CHF-O-, 1 H, 2 × ddd, ¹J_{HF} = 52 and 56, ³J_{HF} = 12 and 11, ³J_{HF} = 1 and 2). ¹³C NMR {¹H (5 ppm)}: 21.98 (4-CH₂); 22.47 and 22.59 (a pair of 3-CH₂); 25.38 and 25.44 (a pair of 5-CH₂); 68.76 and 68.92 (a pair of 6-CH₂); 74.64 and 75.20 (a pair of 2-CH, 2 × dd, ²J_{CF} = 32, ²J_{CF} = 23 and 24); 97.82 and 99.42 (a pair of -CHF-O-, 2 × m); 106.74 (-O-CF₂, tt, ¹J_{CF} = 277, ²J_{CF} = 37); 115.37 (-CF₂-CHF-O-, m); 115.87 (-CF₂-CF₃, m); 117.26 (CF₂-CF₃, q, ¹J_{CF} = 284). ¹⁹F NMR: {¹H (irradiation offset 5 ppm)}: -81.40 and -81.50 (a pair of -CF₂-CF₃, 3 F, 2 × t, ³J_{FF} = 6 and 7); -84.69 and -88.19 (a pair of O-CF₂-CF₂, 1 F, 2 × d, ²J_{FF} = 148); -85.10 and -86.75 (a pair of O-CF₂-CF₂, 1 F, 2 × d, ²J_{FF} = 147); -129.89 and -130.01 (a pair of -CF₂-CF₂-CF₃, 2 F, 2 × m); -145.38 and -153.92 (a pair of CF₂-CHF, 1 F, 2 × t, ³J_{FF} = 5 and 7); -129.63 and -131.81 (a pair of CF₂-CHF, 1 F, 2 × dd, ¹J_{FF} = 267, ³J_{FF} = 15 and 10); -129.88 and -133.58 (a pair of CF₂-CHF, 1 F, 2 × dd, ¹J_{FF} = 272, ³J_{FF} = 15 and 2). MS (EI, *m/z*): 85 (100), 169 (14), 351 (10), 352 (3); (CI, *m/z*): 353 [M + H]⁺. HRMS-EI (*m/z*): [M]⁺ calculated for C₁₀H₁₀F₁₀O₂ 352.0521, found 352.0512.

2-[1,1,2-Trifluoro-2-(heptafluoropropoxy)ethyl]-1,4-dioxane [(C₄H₇O₂)CF₂CHF-O-CF₂CF₂CF₃]. B.p. 100.0 °C/7.6 kPa, yield 68%. ¹H NMR (CDCl₃): 3.56–3.78 (4-, 5-CH₂, 4 H, m); 3.80–3.96 (3-CH₂, 2 H, m); 4.08 (2-CH, 1 H, dddd, ³J_{HH} = 8 and 6, ³J_{HF} = 22 and 3); 6.12 and 6.14 (a pair of CF₂-CHF, 2 × ddd, ²J_{HF} = 53 and 55, ³J_{HF} = 12 and 10, ³J_{HF} = 3 and 1). ¹³C NMR {¹H (5 ppm)}: 64.00 and 64.09 (a pair of 3-CH₂); 66.25 (6-CH₂); 66.84 and 66.90 (a pair of 5-CH₂); 72.14 and 72.73 (a pair of 2-CH, 2 × dd, ³J_{CF} = 33 and 32, ³J_{CF} = 22 and 23); 106.68 (-O-CF₂-CF₂, tt, ¹J_{CF} = 305, ²J_{CF} = 38); 114.50 (-CH-CF₂-CFH-, m); 115.82 (-CF₂-CF₂-CF₃, tm, ¹J_{CF} = 282); 117.18 (-CF₂-CF₃, q, ¹J_{CF} = 287). ¹⁹F NMR {¹H (5 ppm)}: -81.47 and -81.5 (a pair of -CF₂-CF₃, 3 F, 2 × t, ³J_{FF} = 7); -84.77, -85.23, -86.92 and -88.23 (-O-CF₂-CF₂, 2 F, 4 × d, ²J_{FF} = 146); -129.91 and -130.04 (a pair of -CF₂-CF₃, 2 F, 2 × m); -128.13 and -132.14 (a pair of -CH-CF₂-CHF-, 1 F, 2 × ddd, ²J_{FF} = 273, ³J_{FF} = 20 and 15); -128.32 and -130.12 (a pair of -CH-CF₂-CHF-, 1 F, 2 × ddd, ¹J_{FF} = 269, ³J_{FF} = 15 and 2); -145.17 and -153.58 (a pair of CF₂-CHF, 1 F, 2 × d, ³J_{FF} = 54 and 59). MS (EI, *m/z*): 87 (100), 169 (26), 354 (20); (CI, *m/z*): 355 [M + H]⁺. HRMS-EI (*m/z*): [M]⁺ calculated for C₉H₈F₁₀O₃ 354.0314, found 354.0336.

2-[1,1,2-Trifluoro-2-(heptafluoropropoxy)ethyl]-1,3-dioxolane [(C₃H₅O)CF₂CHF-O-CF₂CF₂CF₃]. B.p. 81.2 °C/5.1 kPa, yield 57%. ¹H NMR (CDCl₃): 3.90–4.12 (4-, 5-CH₂, 4 H, m); 5.22 (2-CH, 1 H, t, ³J_{HF} = 8); 6.07 (CF₂-CHF, 1 H, dt, ²J_{HF} = 49, ³J_{HF} = 6). ¹³C NMR {¹H (5 ppm)}: 66.21 (4-CH₂ and 5-CH₂); 98.62 (2-CH, t, ²J_{CF} = 26); 99.44 (-CF₂-CHF-, dt, ¹J_{CF} = 242, ²J_{CF} = 33); 106.65 (-O-CF₂-CF₂-, tt, ¹J_{CF} = 270, ²J_{CF} = 39); 113.40 and 113.47 (diastereotopic -CF₂-CHF-, 2 × td, ¹J_{CF} = 256, ²J_{CF} = 25); 115.87 (-CF₂-CF₃, tm, ¹J_{CF} = 276); 117.23 (-CF₂-CF₃, q, ¹J_{CF} = 287). ¹⁹F NMR {¹H (5 ppm)}: -81.6 (CF₂-CF₃, 3 F, t, ³J_{FF} = 39); -85.0 and -87.5 (a pair of -O-CF₂-CF₂-, 2 F, 2 × dt, ²J_{FF} = 150 and 147, ³J_{FF} = 8); -130.01 (-CF₂-CF₃, 2 F, s); -133.14 and -133.41 (diastereotopic CF₂-CHF-, 2 F, 2 × dd, ¹J_{FF} = 270, ³J_{FF} = 5 and 10); -147.33 (CH-CF₂-CHF, 1 F, m). MS (EI, *m/z*): 45 (68), 73 (100), 125 (29), 339 (2); (CI, *m/z*): 341 [M + H]⁺. HRMS-EI (*m/z*): [M - H]⁺ calculated for C₈H₅F₁₀O₃ 339.0079, found 339.0103.

RESULTS AND DISCUSSION

The addition reactions of cyclic ethers such as THF, THP, DOX or DL on PPVE were carried out by adding 5 equiv. of PPVE and 40 equiv. of cyclic ether in the presence of 2 equiv. of BPO at 60 °C for 3 days. The conversions of PPVE were quantitative (¹⁹F NMR). The reactivity of PPVE is, then, as high as that of BPPF since the conversions of BPPF was also quantitative in the reaction of THF and DOX². Typical GC chart of the PPVE-THF reaction system is shown in Fig. 1. GC-MS measurements indicated that the compounds appearing at ca. 3.8 min (retention time) were 1:1 addition products of PPVE with THF. A trace amount of the 2:1 adduct appears at ca. 5.0 min in GC, which was confirmed by GC-MS. Thus, THF behaves monofunctional compound. Broad peaks around 7.0 min were assigned to benzoic acid formed by decomposition of BPO. The isolated yield of the 1:1 addition product is 75% as a 1:1 mixture of diastereomers as determined by the data described in Experimental. The structure analyses by ¹H, ¹³C and ¹⁹F NMR show that the addition reaction takes place at position 2 of THF as depicted in Eq. (1).

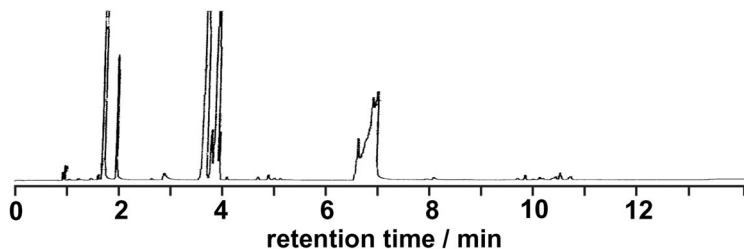
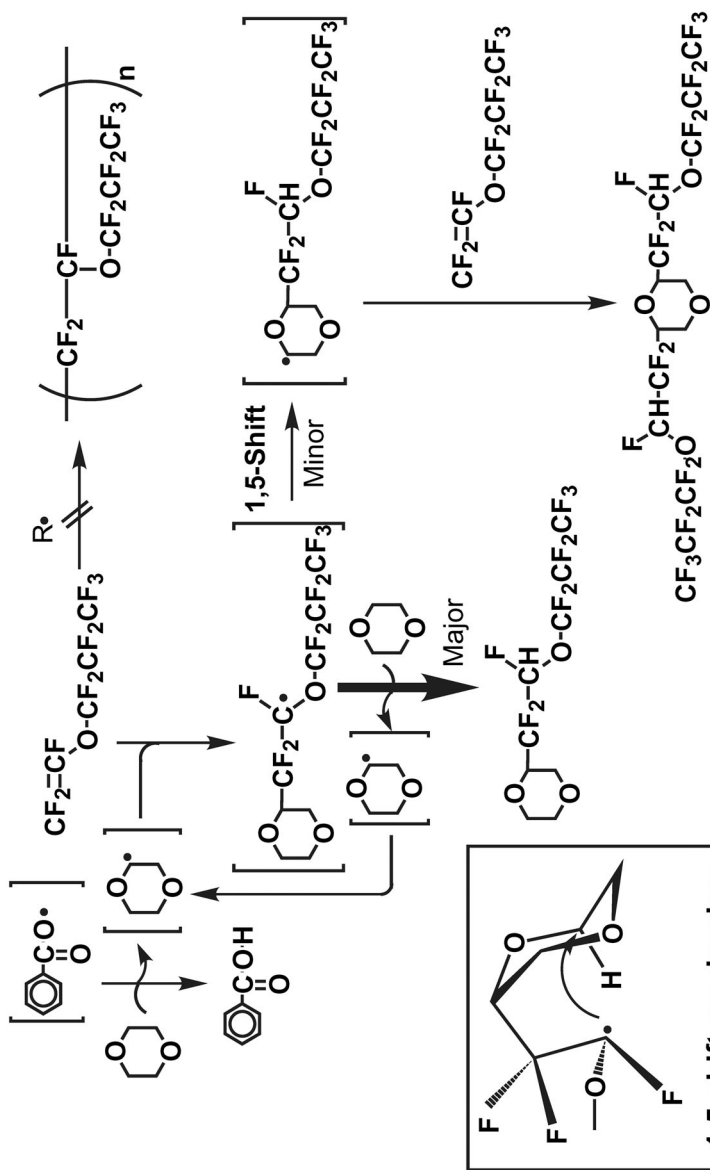


FIG. 1
GC of PPVE-THF reaction mixture

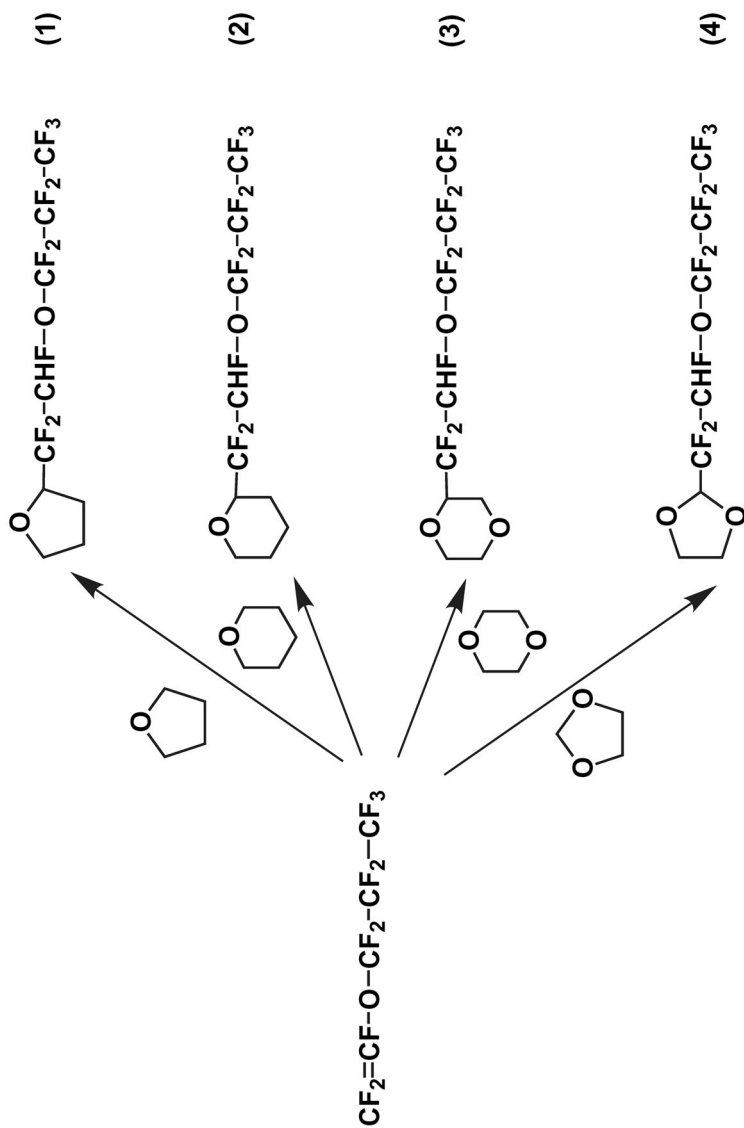
The reaction of PPVE with THP showed a similar GC pattern compared with that of the THF reaction system. No peaks assignable to the 2:1 adduct of PPVE and THP were observed in GC and GC-MS. Hence, THP also behaves as monofunctional. The isolated yield of the 1:1 addition product is 79% as a 1:1 mixture of the diastereomers with trace amount of regioisomer. The structure analyses of the main product demonstrate that the addition reaction takes place at position 2 of THP as depicted in Eq. (2). The regioisomers could not be isolated because their boiling points were almost the same and their structure was presumed to be $\text{CHF}_2\text{CF}(\text{C}_5\text{H}_9\text{O})\text{-O-CF}_2\text{CF}_2\text{CF}_3$.

GC of the reaction mixture of PPVE with DOX showed high peaks assignable to the 1:1 adduct and small peaks assigned to the 2:1 adduct. The area ratio of these two peaks was about 8:2. Analytical data of the 1:1 addition product are shown in Experimental. The 2:1 adduct was identified by GC-MS which showed the peak at $m/z = 621$ assignable to $[\text{M} + \text{H}]^+$. The reaction scheme might be different compared to that of BFPF and DOX which predominantly formed 2:1 addition product as has been reported previously^{2,5}. The isolated yield of the 1:1 addition product purified by distillation was 68% as a 1:1 mixture of the diastereomers. The 2:1 adduct could not be separated due to the small amount produced. The structure analyses described in Experimental show that the reaction takes place as shown in Eq. (3).

The radical addition mechanism is proposed in Scheme 1 by referring to that of BFPF with DOX^{2,8}, wherein benzoyloxy radical generated from BPO abstracts a hydrogen at position 2 of DOX followed by the addition onto PPVE to form the radical at the α -position of the PPVE moiety. The 80% of the radical abstracts a hydrogen from DOX to yield radical at position 2 of DOX again to afford the 1:1 addition product since the area ratio of the 1:1 adduct to the 2:1 adduct was about 8:2 in GC. The 20% of the residual radicals might migrate intramolecularly by a 1,5-shift mechanism to position 6 of the DOX moiety and the radical adds onto PPVE again to form the radical at the α -position of the PPVE moiety to yield 1,6-disubstituted DOX. The structure of 2:1 addition product of PPVE with DOX could not be unequivocally confirmed as shown in Experimental. The mechanism might easily be inferred to that of the reaction of BFPF with DOX. The reaction of BFPF with DOX, as has been mentioned in the beginning, afforded preferentially the 2,6-disubstituted DOX via 1,5-radical shift mechanism². It is suggested that the effect of trifluoromethyl-substituted carbon radical yielded by the reaction of BFPF with DOX might be different from that of monofluorocarbon radical produced by the reaction of PPVE with DOX.



SCHEME 1
Mechanism of the reaction of PPVE with DOX



The reaction of PPVE with DL showed a similar GC pattern compared to that of PPVE with THP. No peaks assignable to the 2:1 addition product of PPVE with DL was shown in GC and GC-MS. DL thus behaves as mono-functional compound. The isolated yield of the 1:1 adduct is 57% and contains trace amount of regioisomers. The structure analyses demonstrate that the addition reaction takes place at position 2 of DL as depicted in Eq. (4).

CONCLUSIONS

The radical reactivity in the additions of cyclic ethers such as tetrahydrofuran, tetrahydropyran, 1,4-dioxane and 1,3-dioxolane on heptafluoropropyl trifluorovinyl ether ($\text{CF}_2=\text{CF}-\text{O}-\text{C}_3\text{F}_7$) was investigated to afford the corresponding 1:1 addition products in fairly high yields. A trace amount of the 2:1 addition product was obtained in the reaction of PPVE with THF, and the reaction of PPVE with DOX produced 1:1 and 2:1 adducts in ca. 8:2 ratio. The method represents a facile method of preparation of cyclic ethers possessing fluoroalkyl substituents.

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