

**RADICAL ADDITION OF DIETHYL CARBONATE TO PENTAFLUOROPROPEN-2-YL BENZOATE**Akihiro HOSOYA<sup>a1</sup>, Tadashi NARITA<sup>a2,\*</sup> and Hiroshi HAMANA<sup>b</sup>

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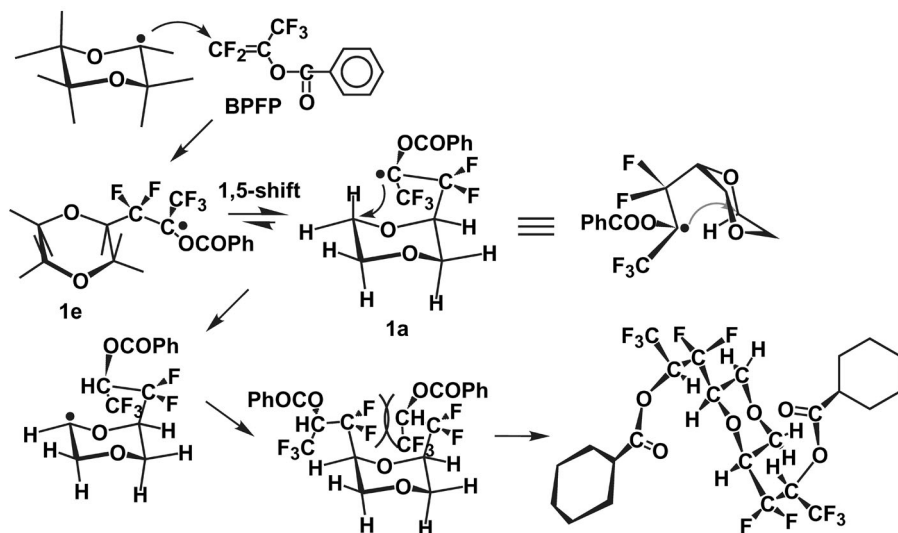
*Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday.*

The reactivity in radical addition of diethyl carbonate to pentafluoropropen-2-yl benzoate [CF<sub>2</sub>=C(CF<sub>3</sub>)OCOC<sub>6</sub>H<sub>5</sub>] (BPPF) was investigated to afford the one-to-one addition product by the carbon-carbon bond formation in the presence of dibenzoyl peroxide at 80 °C. The reaction took place predominantly on the methylene group of diethyl carbonate. The mechanism of the hydrogen abstraction from diethyl carbonate followed by the addition to BPPF was proposed. This might be the first example that shows an addition of an organic compound bearing carbonyl group to a polyfluorinated vinyl compound. The method may be a facile way to prepare pentafluoroalkyl-substituted organic compounds by the formation of carbon-carbon bonds with the aid of fluorine atoms. The radical addition reaction of dipropyl carbonate, ethyl methyl carbonate, dibenzyl carbonate and ethylene carbonate to BPPF showed no peaks assignable to addition products by the analysis of reaction systems with GC-MS.

**Keywords:** Radical additions; Pentafluoropropen-2-yl benzoate; Diethyl carbonate; Fluorinated alkenes; Perfluoroalkenyl building blocks.

The radical additions to pentafluoropropen-2-yl benzoate [CF<sub>2</sub>=C(CF<sub>3</sub>)OCOC<sub>6</sub>H<sub>5</sub>] (BPPF) have previously been reported to be applicable to a wide variety of organic compounds bearing carbon-hydrogen bonds such as tetrahydrofuran<sup>1</sup> (THF), 1,4-dioxane<sup>2</sup> (DOX), 18-crown-6-ether<sup>3</sup>, hexanal<sup>4</sup>, triethylamine<sup>5</sup>, cycloalkane<sup>6</sup> and even hexane<sup>7</sup> (see review<sup>8</sup>). An easy method of the carbon-carbon bond formation was thus demonstrated under mild reaction conditions with the aid of fluorine atoms since no addition reaction has ever taken place with hydrocarbon analogs to organic compounds bear-

ing carbon–hydrogen bonds. A radical shift of the 1,5-transfer mechanism was proposed in the reaction of BFPF with DOX, as shown in Scheme 1<sup>2,9</sup>.



SCHEME 1  
Mechanism of the reaction of BFPF and 1,4-dioxane

To our knowledge, no radical addition of polyfluorinated vinyl compounds with carbonates has been reported though the addition of alcohols, ethers and amines to polyfluorinated vinyl compounds such as tetrafluoroethylene, chlorotrifluoroethylene and perfluorocyclobutene has been reported by many research groups with radical generators or under  $\gamma$ -rays irradiation<sup>10</sup>. This paper concerns the addition of diethyl carbonate (DEC), dipropyl carbonate, ethyl methyl carbonate, dibenzyl carbonate and ethylene carbonate which possess two types of carbon–hydrogen bonds for radical addition reaction to BFPF. It might be interesting that the 1,7-radical shift mechanism<sup>11</sup> would take place in the case of addition of carbonates to BFPF to yield 1:2 addition products. The fluorinated carbonates might be used as a liquid electrolyte solvent in lithium ion batteries<sup>12,13</sup>.

## EXPERIMENTAL

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

## Analytical Instruments

GC measurements were carried out with a Hewlett-Packard 6890 instrument using a ZB-1 fused silica capillary column (15 m  $\times$  0.53 mm, film thickness 1.5  $\mu$ m, Phenomenex) equipped with a flame ionization detector. The column temperature was programmed from 80 to 320  $^{\circ}$ C at 20  $^{\circ}$ C min $^{-1}$ . Preparative SEC was carried out with an LC-908JAI (Japan Analytical Ind.) instrument with a Gel H1&H2 column series using chloroform as eluent at room temperature (flow rate 3.8 ml min $^{-1}$ ). GC-MS spectrum was measured by electron ionization (EI) and chemical ionization (CI) methods on a JEOL JMS-SX102 instrument. Isobutane was used as a reagent gas of CI. The column used was DB-1, fused silica capillary column (30 m  $\times$  0.25 mm, film thickness 0.25  $\mu$ m, J&W).  $^1$ H,  $^{13}$ C and  $^{19}$ F NMR spectra ( $\delta$ , ppm;  $J$ , Hz) were recorded on a JEOL JNM-ECP500 NMR spectrometer at 500 MHz for  $^1$ H (non-decoupled and F-decoupled [ $^{19}$ F (irradiation offset -100 ppm)], 125 MHz for  $^{13}$ C [{ $^1$ H (5 ppm)], [ $^1$ H (5 ppm) and  $^{19}$ F (-100 ppm)], and 470 MHz for  $^{19}$ F [ $^1$ H (5 ppm)] NMR with deuterated chloroform as a solvent. Chemical shifts of  $^{19}$ F NMR were determined on the basis of absolute magnetic field intensity.

## Reagents

BFPF was synthesized by the reaction of benzoyl chloride with 2 equivalents of the lithium enolate derived from 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) with butyllithium in THF described in refs<sup>14,15</sup>. HFIP (courtesy of Central Glass Co.) was dried by refluxing over calcium hydride and distilled. A commercial butyllithium solution in hexane was used after determination of its concentration by titration. Commercial DEC, dipropyl carbonate and ethyl methyl carbonate were purified by distillation. Dibenzyl carbonate and ethylene carbonate were used as received. Dibenzoyl peroxide (BPO) was precipitated from chloroform and then recrystallized from methanol at 0  $^{\circ}$ C. Di-*tert*-butyl peroxide (DTBP) was used as received.

## Procedures

The addition reactions of DEC, dipropyl carbonate, ethyl methyl carbonate, dibenzyl carbonate and ethylene carbonate to BFPF were carried out in the presence of BPO at 80  $^{\circ}$ C or DTBP at 120  $^{\circ}$ C for 3 days followed by GC analysis.

*4-(Benzoyloxy)-3,3,5,5,5-pentafluoropent-2-ylethyl carbonate* [C<sub>6</sub>H<sub>5</sub>COOCH(CF<sub>3</sub>)CF<sub>2</sub>CH(CH<sub>3</sub>)OCOOCH<sub>2</sub>CH<sub>3</sub>]. Yield 15.5% (preparative SEC). The product was pale yellow liquid.  $^1$ H NMR (in CDCl<sub>3</sub>): 1.28, 1.29 (a pair of CH<sub>2</sub>CH<sub>3</sub>, t,  $J$  = 7.0, 3 H); 1.44, 1.45 (a pair of CHCH<sub>3</sub>, d,  $J$  = 6.5, 3 H); 4.131, 4.151, 4.190, 4.194 (two pairs of diastereotopic CH<sub>2</sub>CH<sub>3</sub>, q,  $J$  = 7.0, 2 H); 5.03, 5.13 (a pair of CF<sub>2</sub>CH(CH<sub>3</sub>), ddq,  $J_{\text{HH}}$  = 6.4,  $J_{\text{HF}}$  = 2.8, 20.6,  $J_{\text{HH}}$  = 6.4,  $J_{\text{HF}}$  = 0.1, 22.5, 1 H); 6.02, 6.06 (a pair of CF<sub>2</sub>CH(CF<sub>3</sub>), m, 1 H); 7.50, 7.51 (a pair of *o*-CH, t,  $J$  = 7.8, 2 H); 7.65, 7.66 (a pair of *p*-CH, t,  $J$  = 7.8, 1 H); 8.08, 8.13 (a pair of *m*-CH, d,  $J$  = 7.8, 2 H).  $^{13}$ C{ $^1$ H (irradiation offset 5 ppm)} NMR: 12.0, 13.0 (a pair of CH<sub>3</sub>CHCF<sub>2</sub>, dd,  $^3J_{\text{CF}}$  = 3.6, 4.8,  $^3J_{\text{CF}}$  = 2.6, 4.6); 14.05, 14.07 (a pair of CH<sub>3</sub>CH<sub>2</sub>); 64.9, 65.0 (a pair of CH<sub>2</sub>CH<sub>3</sub>); 66.2, 67.6 (a pair of CF<sub>2</sub>CH(CF<sub>3</sub>), m); 70.3, 71.9 (a pair of CF<sub>2</sub>CH(CH<sub>3</sub>), dd,  $^3J_{\text{CF}}$  = 24, 37,  $^3J_{\text{CF}}$  = 24, 33); 116.8, 117.7 (a pair of CF<sub>2</sub>, t,  $^2J_{\text{CF}}$  = 250, 254); 120.5, 120.8 (a pair of CF<sub>3</sub>, q,  $^2J_{\text{CF}}$  = 283); 127.46, 127.53 (a pair of aromatic carbon); 128.8 (*m*-C); 130.37, 130.48 (a pair of *o*-C); 134.5 (*p*-C); 153.69, 153.71 (a pair of O-CO-O); 163.66, 163.84 (a pair of C<sub>6</sub>H<sub>5</sub>CO).  $^{19}$ F{ $^1$ H (5 ppm)} NMR: -71.4, -72.0 (a pair of CF<sub>3</sub>, t,  $^4J_{\text{FF}}$  = 11, 8, 3 F); -116.7, -119.5 and -119.7, -122.3 (two pairs of diastereotopic CF<sub>2</sub>, dq,  $^2J_{\text{FF}}$  = 272,  $^4J_{\text{FF}}$  = 11,  $^2J_{\text{FF}}$  = 272,  $^4J_{\text{FF}}$  = 11

and  $^2J_{\text{FF}} = 272$ ,  $^4J_{\text{FF}} = 8$ ,  $^2J_{\text{FF}} = 272$ ,  $^4J_{\text{FF}} = 12$ , 2 F). EI-MS ( $m/z$ ): 370 [M]<sup>+</sup>, 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>, 105 [C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup>, 122 [C<sub>6</sub>H<sub>5</sub>COO]<sup>+</sup>, 281 [C<sub>6</sub>H<sub>5</sub>COOCH(CF<sub>3</sub>)CF<sub>2</sub>CH(CH<sub>3</sub>)]<sup>+</sup>. CI-MS ( $m/z$ ): 370 [M]<sup>+</sup>, 371 [M + H]<sup>+</sup>.

## RESULTS AND DISCUSSION

The reaction of DEC with BFPF was carried out by reacting 107.8 mmol of DEC, 13.5 mmol of BFPF and 5.4 mmol of BPO at 80 °C or of DTBP at 120 °C for 3 days. The conversions of BFPF was 53% for BPO (GC) and the yield 15.5 % (preparative SEC). The reactivity of DEC is, hence, lower compared to those of THF or DOX since the conversions of BFPF were quantitative in these reaction systems<sup>1,2</sup>. The GC-MS measurements of the compounds showed that the two peaks at the GC retention times 8.7 min (peak A) and 9.0 min (peak B) in Fig. 1a were 1:1 addition products of DEC to BFPF since the protonated molecular ion peaks ( $m/z = 371$ ) appeared in CI-MS measurement. These compounds are purified by preparative SEC as the result is shown in Fig. 1b. The compounds were impossible to be separated by preparative SEC.

EI-MS spectra depicted in Fig. 2 point out that the fragment patterns of these two compounds are almost same, which implies that the compounds possess the same chemical structure. The peak at  $m/z = 77$  should be assigned to phenyl group, 105 to benzoxy group and 281 to the C<sub>6</sub>H<sub>5</sub>COO-CH(CF<sub>3</sub>)CF<sub>2</sub>CH(CH<sub>3</sub>) fragment, respectively.

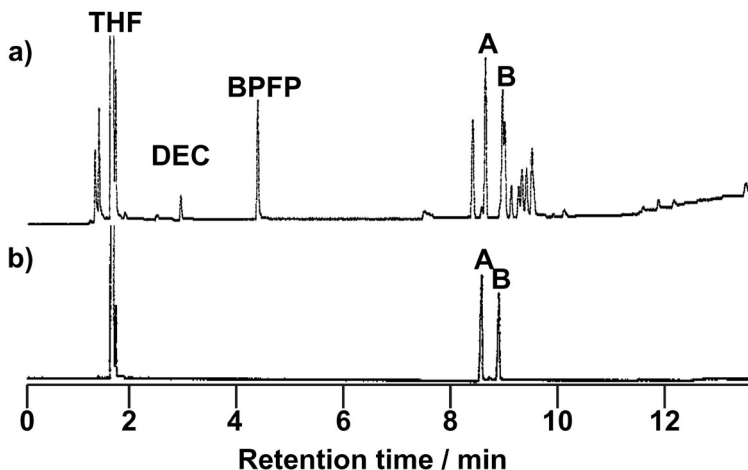


FIG. 1

GC of DEC to BFPF reaction system (a) and after purification by preparative SEC (b)

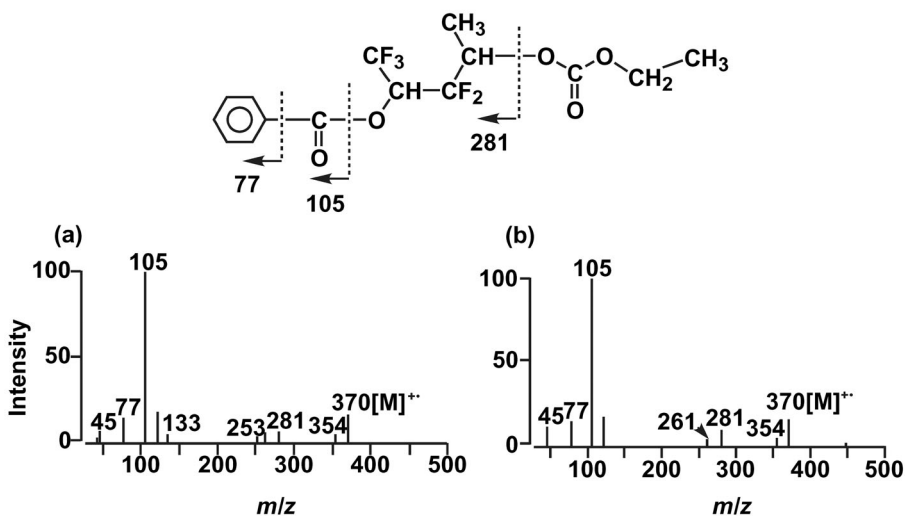
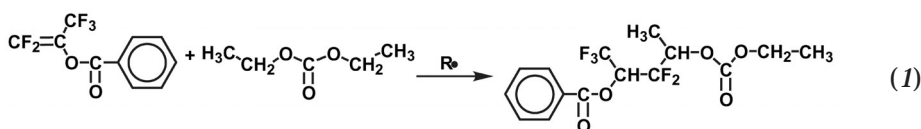


FIG. 2  
EI-MS of the 1:1 addition product of DEC to BFPF appearing at 8.7 (a) and 9.0 min (b) in GC

The results of NMR measurements are shown in Fig. 3. Detailed assignment is depicted in Fig. 3 and Experimental. The peaks at ca. 6.1 ppm (Fig. 3a) is assigned to methine hydrogen *e* attached to the trifluoromethyl group because the two singlet peaks appeared under F-decoupled condition (Fig. 3b). The peak at ca. 5.2 ppm is assigned to hydrogen *c* since a pair of quartet peaks are observed under non-decoupled condition (Fig. 3a). No reaction with methyl group of DEC took place since the area ratio of two methyl groups of the product was 1.0:0.98 ( $^1\text{H}$  NMR) which is within an experimental error. The result is supported by the fact that no GC peaks assignable to addition products other than those observed by the reaction of the methylene carbon of DEC were found. The addition reaction of DEC to BFPF takes place at methylene carbon of DEC (Eq. (1)). The reaction product possesses two asymmetric carbon atoms and hence consists of two diastereomers. The area ratio of two peaks at ca. 6.1 ppm in Fig. 3b is 1.0:0.9, which indeed corresponds to nearly equimolar diastereomer mixture in agreement with the GC results of reaction system (Fig. 1b).



DEC is monofunctional similarly to THF though DOX behaves predominantly as difunctional. Polyaddition of DOX to bis(pentafluoropropen-2-yl) terephthalate took also place affording polymers of MW  $9.9 \times 10^3$  (ref.<sup>2</sup>). The results mentioned above indicate that the reaction takes place without the 1,7-radical shift mechanism, as shown in Scheme 2, which is similar to that of the reaction of BPFPP with THF<sup>1</sup>.

The conversion of radical reaction of BPFPP with dipropyl carbonate was quantitative. However, many products were detected by GC analyses. The yield of addition product of BPFPP to DEC (initiated by DTBP) was not ob-

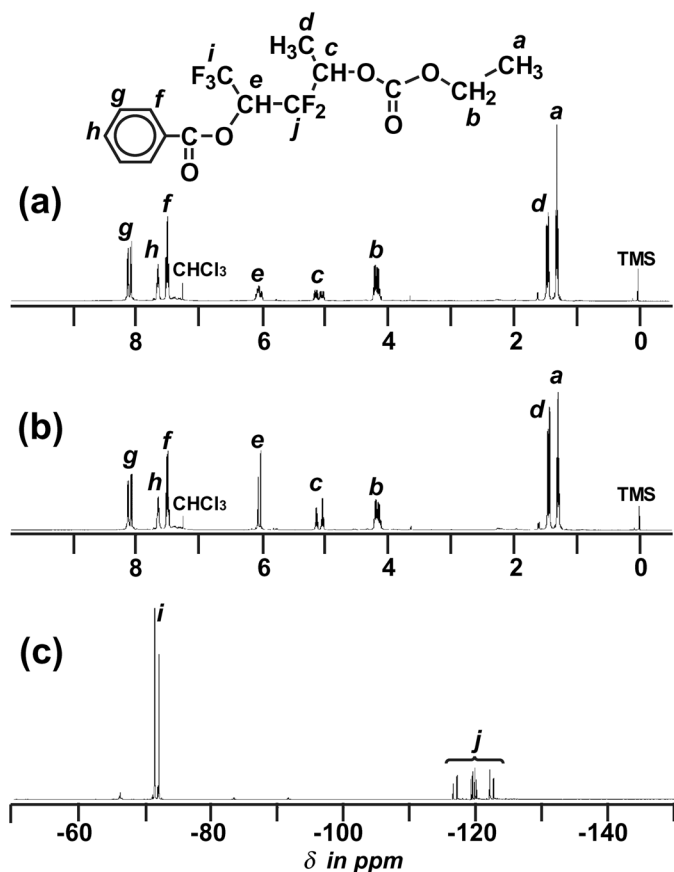
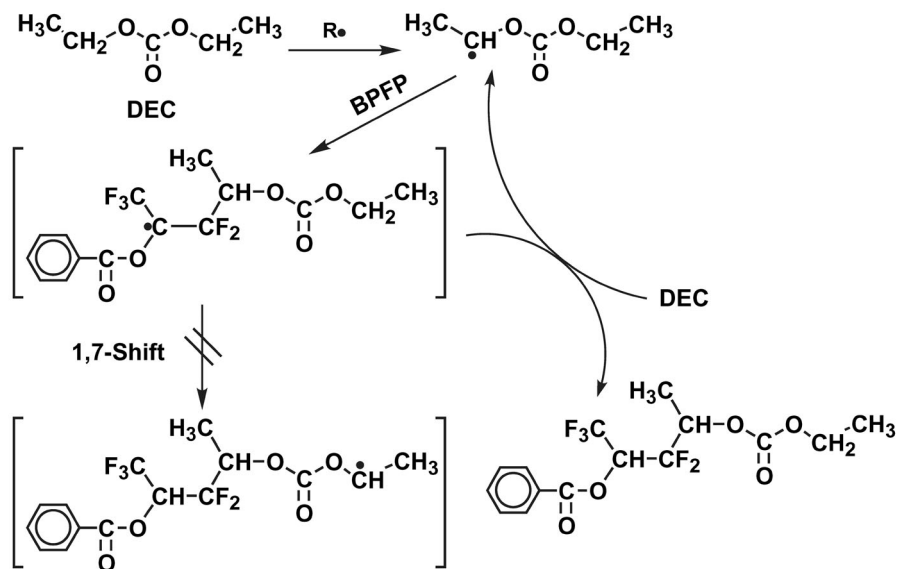


FIG. 3

$^1\text{H}$  (a), F-decoupled  $^1\text{H}$  (b) and  $^{19}\text{F}$  NMR (c) of the 1:1 addition product of DEC to BPFPP

tained because a complex mixture was formed. The reactions with ethyl methyl carbonate, dibenzyl carbonate and ethylene carbonate hardly took place because only a slight decrease of BPPF concentration was detected by GC.



SCHEME 2  
Mechanism of the reaction of BPPF and DEC

## CONCLUSIONS

The reactivity in radical addition of diethyl carbonate to pentafluoropropen-2-yl benzoate [ $\text{CF}_2=\text{C}(\text{CF}_3)\text{OCOC}_6\text{H}_5$ ] was investigated affording one-to-one addition product in fair yield. The addition took place predominantly on methylene group of diethyl carbonate to give diastereomer mixture. The mechanism that the hydrogen abstraction from diethyl carbonate is followed by the addition to BPPF was proposed. To our knowledge, this might be the first example which undergoes an addition of polyfluorinated vinyl compounds onto an organic compound bearing carbonyl group.

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