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Carbon–carbon bond formation by radical addition of α-trifluoromethylacrylate with cyclic ethers

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Abstract

The radical addition reactivity of *tert*-butyl α-trifluoromethylacrylate (CH_2=$C(CF_3)COOC(CH_3)_3$) (BFMA) with cyclic ethers was investigated in order to compare to that of perfluoroisopropenyl ester. One to one addition compound of BFMA with tetrahydrofuran (THF) was produced in fairy high yields in the presence of 2,2′-azobisisobutyronitrile, benzoyl peroxide or di-*tert*-butyl peroxide to give 2-substituted THF derivative. Time–conversion investigation showed much higher reactivity of BFMA compared to that of 2-benzoxypentafluoropropene [CF_2=$C(CF_3)OCOC_6H_5$]. Radical additions of BFMA with 1,4-dioxane, 1,3-dioxolane and tetrahydropyran were also examined to afford corresponding 1:1 addition products in fairly high yields by achieving carbon–carbon bond formation. It is then concluded that no interconversion of fluoroalkylcarbon radical and hydrocarbon radical may take place in the reaction system of BFMA which possesses two less fluorines in the vinyl group compared to 2-benzoxypentafluoropropene. The method may be a facile way to prepare trifluoromethyl-substituted organic compounds accompanied by the formation of carbon–carbon bonds by the aid of fluorine atoms.

Keywords: Addition reaction; Radical addition; *tert*-Butyl α-trifluoromethylacrylate; Tetrahydrofuran; 1,4-Dioxane; 1,3-Dioxolane; Tetrahydropyran

1. Introduction

The polymerization reactivity of α-trifluoromethylvinyl compounds such as α-trifluoromethylacrylates and α-trifluoromethylstyrenes is extremely low as has been introduced in a review article [1]. The high radical addition reactivity of perfluorovinyl compounds has, on the other hand, been demonstrated by many research groups [2–14]. Radical addition of perfluorovinyl compounds has then been developed as facile methods for preparation of fluorinated organic compounds accompanied by forming carbon–carbon bonds. The carbon–carbon bond formation by the radical addition was also developed to polymer preparation. The radical polyaddition of bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate [CF_2=$C(CF_3)OCOC_6H_4COOC(CF_3)$=$CF_2$] (BFP) affords polymers with 1,4-dioxane (DOX) [15], diformylalkane [16], triethylamine [17] and dialkoxydialkylsilanes [18] and even hexane [19]. The radical polyaddition of perfluoroisopropenyl compounds is summarized in a review article [20]. The radical shift in the reaction intermediate was found to play an important role in the addition of 2-benzoxypentafluoropropene [CF_2=$C(CF_3)OCOC_6H_5$] (BPFP) with DOX, as cited in Scheme 1 [21,22]. The DOX radical generated by the hydrogen abstraction from DOX adds onto BPFP to form a fluoroalkylcarbon radical in the BPFP moiety. The radical abstracts a hydrogen from DOX group by 1,5-radical shift to form hydrocarbon radical followed by the addition of BPFP again. The interconversion of fluoroalkylcarbon radical and hydrocarbon radical by the 1,5-radical shift might then be important in the reaction which induces the exclusive formation of 2:1 addition product of BPFP with DOX. Of particular interest is that BPFP does react exclusively with the DOX radical in preference to other radical species.

The radical additions of ethyl β-fluoroacrylate with tetrahydrofuran (THF) and 1,3-dioxolane (DL) have been reported to afford corresponding addition products achieving carbon–carbon bond formation [23], which demonstrated that β-monofluorinated acrylate achieved the addition onto ethereal compounds.

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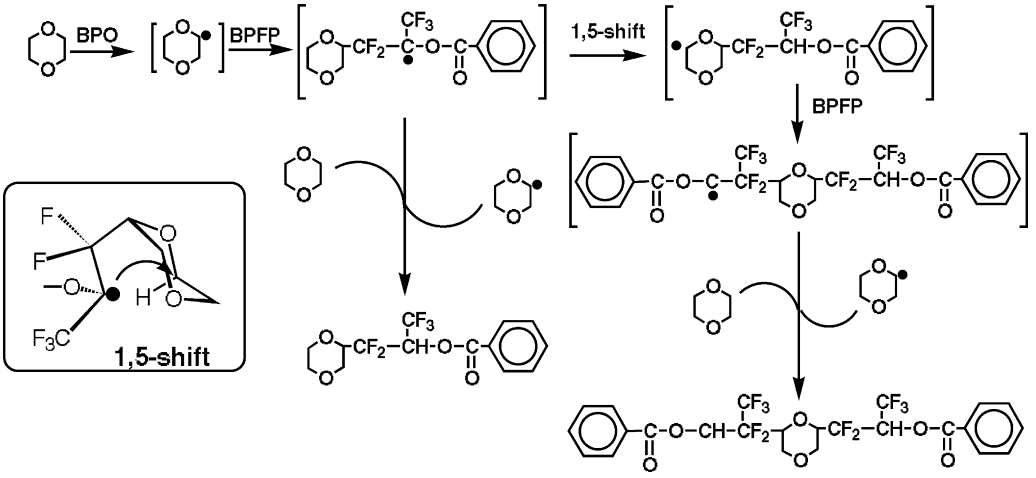


Scheme 1. Radical addition mechanism of BPFP with DOX.

It is interesting how many fluorines should, then, be necessary for interconversion of fluoroalkylcarbon radical and hydrocarbon radical in the reaction intermediates. To investigate the radical addition of α-trifluoromethylacrylate may afford some information on how many fluorines might be needed for radical addition toward ethereal compounds because radical reactions of acrylates and vinyl esters possessing no fluorine atom generally produce polymers instead of addition products. The paper concerns about the addition of *tert*-butyl α-trifluoromethylacrylate [CH_2=$C(CF_3)COOC(CH_3)_3$] (BFMA) with THF, DOX, DL and tetrahydropyran (THP).

2. Results and discussion

The addition reactions of BFMA with cyclic ethers such as THF, DOX, DL and THP in the presence of 2,2′-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO) or di-*tert*-butyl peroxide (DTBP) were carried out and followed by vapor phase chromatographic (GC) analysis.

The reaction of BFMA with THF was carried out by adding 1.5 mmol (5 eq.) of BFMA and 12.0 mmol (40 eq.) of THF in the presence of 0.6 mmol (2 eq.) of AIBN at 60 °C, BPO at 80 °C or DTBP at 120 °C for 3 days. The conversions of BFMA were above 99% by GC measurements of the reaction systems. The product was 2-substituted THF as shown in Eq. (1). The isolated yields of the product were 69% initiated with AIBN, 54% with BPO and 16% with DTBP, respectively, by distillation. THF is mono-functional since no apparent peak assignable to di-addition product of THF was detected in GC. Detailed analyses of the mono-substituted product are described in Section 3. ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC NMR results also indicated that the product was the mixture of diastereoisomers.

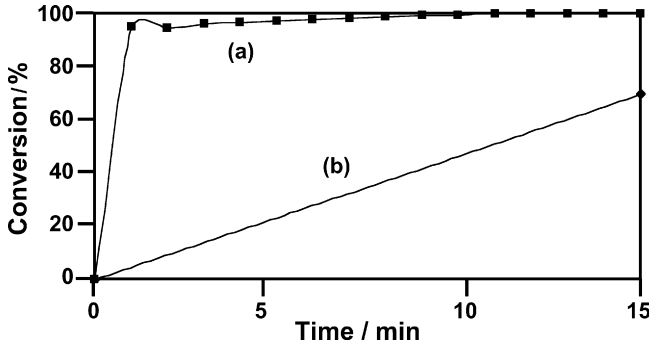
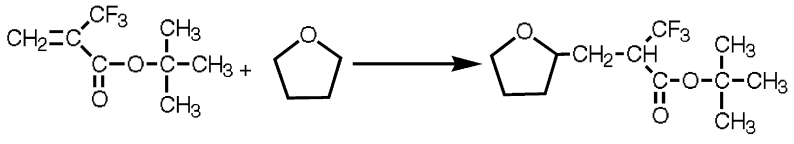


Fig. 1. Time dependency on the conversion of (a) BFMA and (b) BPFP with THF.

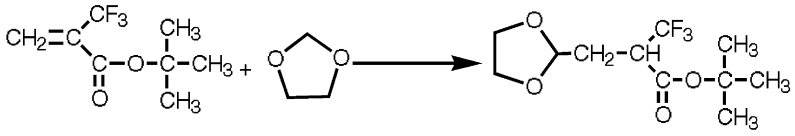
To compare the radical addition reactivity the addition of BFMA and BPFP with THF was examined. The results are shown in Fig. 1. BFMA is found to show much higher reactivity compared to that of BPFP since BFMA is consumed over 90% within 1 min and the conversion of BPFP is about 70% in 15 min.

The reaction of BFMA with DL was carried out by adding 18.0 mmol (5 eq.) of BFMA with 144 mmol (40 eq.) of DL in the presence of 7.2 mmol (2 eq.) of BPO at 80 °C for 3 days followed by GC analyses. The conversion of BFMA was more than 99%. The isolated yield of the product was 63% by distillation. The results of NMR measurements of the product are shown in Fig. 2. The assignment of each absorption is depicted in the figure. The result of ^{1}H–^{13}C HMQC measurement shows the correlation between methylene hydrogens (d and d′) and methylene carbon (D). The result



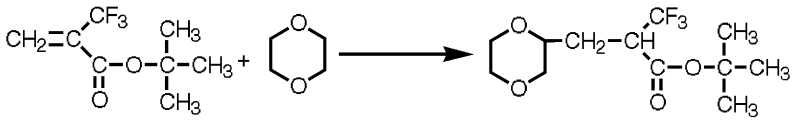
(1)

also supports the conclusion of the stereoisomers. The reaction was then found to take place as shown in Eq. (2).



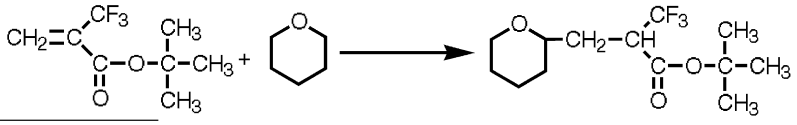
(2)

The reaction of BFMA with DOX was carried out by adding 2.1 mmol (7 eq.) of BFMA with 12.0 mmol (40 eq.) of DOX in the presence of 0.6 mmol (2 eq.) of BPO at 80 °C for 3 days followed by GC analyses. The conversion of BFMA was more than 99%. The isolated yield of the product was 41% separated by distillation and the reaction was found to take place as shown in Eq. (3) by the detailed analyses of the product as described in Section 3. The results of ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC NMR measurements also suggested that the product was the mixture of diastereoisomers. The conclusion might be supported by the results given by the GC analysis which showed two peaks assignable to reaction products and these two products showed the similar mass spectral profiles. It is interesting that no 2,6-disubstituted 1,4-dioxane was detected in GC, though the reaction of BPFP with DOX produces higher yield of 2,6-disubstituted 1,4-dioxane compared to that of mono-substituted one [20], which demonstrated DOX is di-functional. This phenomenon led to the preparation of polymer by BFP with DOX [15]. The 1,5-radical shift mechanism was proposed to comprehend the reaction of BFP with DOX [21,22]. No 1,5-radical shift mechanism might take place in the case of BFMA with DOX, probably because the reactivity of the radical $^{\bullet}C(CF_3)(COO)CH_2$– would be different from that of the radical $^{\bullet}C(CF_3)(OCOC_6H_5)CF_2$–, as the supposed mechanism is shown in Scheme 2, in which no interconversion of fluoroalkylcarbon radical and hydrocarbon radical takes place. It is then concluded DOX is mono-functional in the reaction with BFMA.



(3)

The reaction of BFMA with THP was carried out by adding 16.8 mmol (5 eq.) of BFMA with 133 mmol (40 eq.) of THP in the presence of 6.6 mmol (2 eq.) of BPO at 80 °C for 3 days. The conversion of BFMA was above 99% by the GC measurement. The isolated yield of the product was as low as 2% since the isolation of the product was difficult by distillation or chromatography because of by-products whose structures were not identified. The reaction was found to take place as shown in Eq. (4) by the analyses of the product as described in Section 3. ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC NMR results also suggested that the product was the mixture of diastereoisomers.



(4)

3. Experimental

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

3.1. Reagents

BFMA presented by courtesy of TOSOH F-TECH INC. was used after distillation with calcium hydride; 64.0 °C/66 mmHg. BPO and AIBN were precipitated from chloroform and then recrystallized in methanol at 0 °C. DTBP was used as received. THF, DOX, DL and THP were purified by the usual methods followed by distillation under purified nitrogen atmosphere. BPFP was synthesized by the reaction of benzoyl chloride with lithium enolate derived from hexafluoroisopropanol (HFIP) with 2 eq. of butyllithium in THF described in the literature [24]. Benzoyl chloride was used as received. A hexane solution of butyllithium was used after determination of the concentration by titration. HFIP presented by the courtesy of Central Glass Co. Ltd was purified by refluxing over calcium hydride followed by distillation.

3.2. Measurements

Measurement of GC was carried out with a Hewlett-Packard 6890 with a ZB-1, wide-bore fused silica capillary column (15 m × 0.53 mm, film thickness: 1.5 μm, Phenomenex)

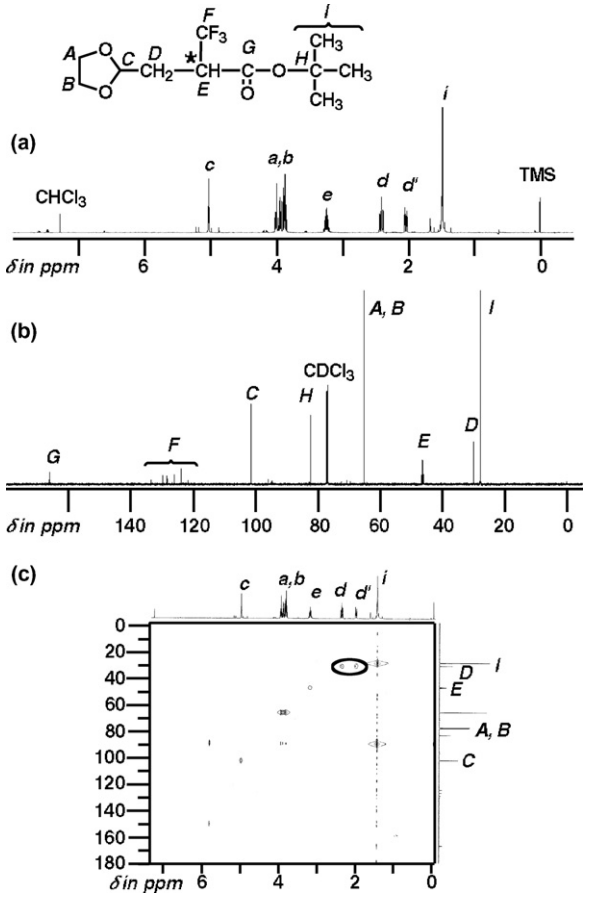


Fig. 2. ^{1}H NMR (a), ^{13}C NMR (b) and ^{1}H–^{13}C HMQC (c) spectra of the product of BFMA with 1,3-dioxolane.

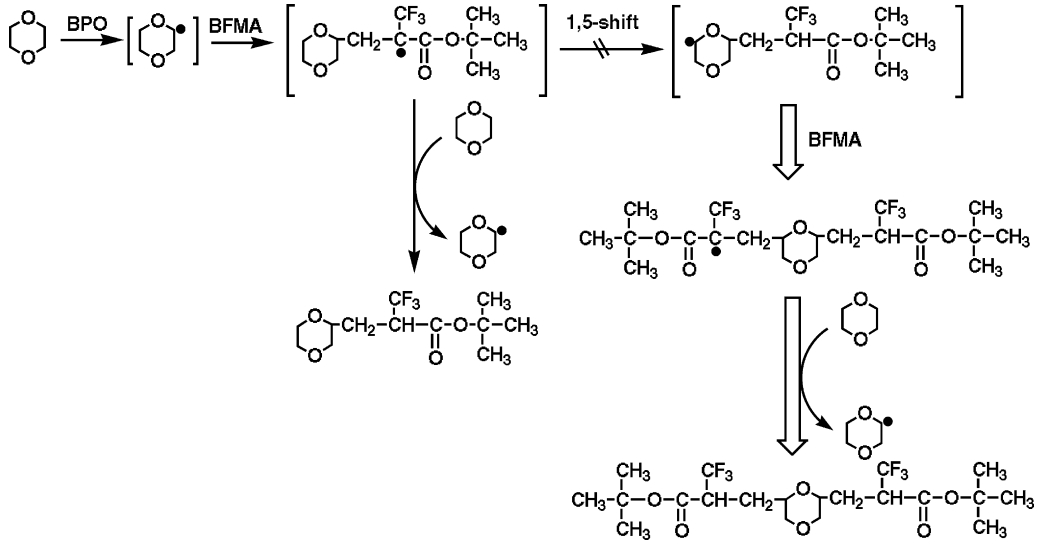
equipped with flame ionization detection. The column temperature was programmed from 80 to 320 °C at 20 °C min^{-1}. Mass spectrum was measured by electron impact method (EIMS) and chemical ionization method (CIMS) on a JEOL JMS-SX102. Isobutane was used as a reagent gas of CIMS. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a JEOL JNM-ECP500 Fourier transform NMR spectrometer at 500 MHz for ^{1}H {non-decoupled and fluorine decoupled [^{19}F (irradiation offset: −100 ppm)]} condition, 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 shift of ^{19}F NMR was determined on the basis of absolute magnetic field intensity.

3.3. Procedures

The addition reactions of BFMA with cyclic ethers such as THF, DOX, DL and THP were carried out in the presence of AIBN at 60 °C, BPO at 80 °C or DTBP at 120 °C for 3 days followed by GC analysis.

The reaction of BFMA with THF was carried out by adding 1.5 mmol (5.0 eq.) of BFMA and 12.0 mmol (40 eq.) of THF with 0.6 mmol (2.0 eq.) of radical generator into a glass ampule. The conversion of BFMA was above 99% by the measurement of GC of the reaction system. Benzoic acid produced by the decomposition of BPO was removed by washing with a saturated sodium hydrogencarbonate solution. The product was separated by distillation.

2-(2-*tert*-Butoxycarbonyl-3,3,3-trifluoropropyl)tetrahydrofuran (addition product of BFMA with THF): bp: 88.4 °C/3 mmHg. Yield: 69% by AIBN; 54% by BPO and 16% by DTBP. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.47 and 1.48 ppm (a pair of s, 9H, –C(C**H**$_3$)$_3$), 1.51–2.16 (m, 6H, –C**H**$_2$–C**H**$_2$–CH<, –C**H**$_2$–CH(CF$_3$)–), 3.12 and 3.29 (a pair of ddq, ^{3}J = 9.7, 4 Hz, $^{3}J_{HF}$ = 8.5 Hz and ^{3}J = 11.7, 2.9 Hz, $^{3}J_{HF}$ = 8.5 Hz, 1H, –C**H**(CF$_3$)–), 3.69–3.98 (m, 3H, –C**H**$_2$–O–C**H**<). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 25.7 and 25.8 (–**C**H$_2$–CH–O–), 27.9 and 28.0 (–C(**C**H$_3$)$_3$), 31.6 (–**C**H$_2$–CH$_2$–CH<), 32.1 and 32.3 (–**C**H$_2$–CH(CF$_3$)–), 48.7 and 49.7 (q, $^{2}J_{CF}$ = 27.6 Hz, –**C**H(CF$_3$)–), 67.7 and 68.0 (–CH$_2$–O–CH<), 75.7 and 77.0 (–O–CH<), 82.5 and 82.8 (–**C**(CH$_3$)$_3$), 125.3 (q, $^{1}J_{CF}$ = 278 Hz, –CF$_3$), 166.8 and 166.9 (q, $^{3}J_{CF}$ = 3.1, >**C**=O). ^{19}F NMR ($CDCl_3$, 470 MHz): δ = −68.3 and −68.4 (a pair of d,



Scheme 2. Supposed mechanism of BFMA with DOX.

$^3J_{FH}$ = 8.5 Hz and $^3J_{FH}$ = 8.5 Hz, –C**F**$_3$). EIMS: *m*/*z* = 211 (70), 195 (100), 71 (60), 57 (35), CIMS: *m*/*z* = 269 (M^++1, 20).

To compare the radical addition reactivity, the reaction was carried out by adding 6.24 mmol of BFMA, 50 mmol of THF and 2.50 mmol of BPO and keeping at 80 °C. The reaction was analyzed by GC after taking out a portion of the reaction mixture by appropriate time intervals. The reaction of BPFP with THF was under the same condition and the measurement.

The reaction of BFMA with DL was carried out by adding 18.0 mmol (5.0 eq.) of BFMA and 144 mmol (40 eq.) of DL with 7.2 mmol (2.0 eq.) of radical generator into a glass ampule. The conversion of BFMA was above 99% by the measurement of GC of the reaction system. The product was separated by distillation after the reaction mixture was washed by a saturated sodium hydrogencarbonate solution to remove benzoic acid when BPO was used.

2-(2-*tert*-Butoxycarbonyl-3,3,3-trifluoropropyl)-1,3-dioxolane (addition product of BFMA with DL): bp: 78.0 °C/1 mmHg. Yield: 63% by BPO. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.48 ppm (s, 9H, –C(C**H**$_3$)$_3$), 2.03 and 2.40 (diastereotopic methylene proton, ddd, ^3J = 14, 3.6, 2.6 Hz and ^3J = 14, 11, 3.6 Hz, 2H, –C**H**$_2$–CH(CF_3)–), 3.23 (ddq, ^3J = 11, 2.6, $^3J_{HF}$ = 8.7 Hz, 1H, –C**H**(CF_3)–), 3.83–4.02 (m, 4H, –C**H**$_2$–C**H**$_2$–), 5.02 (t, ^3J = 3.6 Hz, 1H, –O–C**H**<). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.7 (–C(**C**H_3)$_3$), 30.0 (q, $^3J_{CF}$ = 1.9 Hz, –**C**H_2–CH(CF_3)–), 46.3 (q, $^2J_{CF}$ = 27.7 Hz, –**C**H(CF_3)–), 65.2 (–**C**H_2–**C**H_2–), 82.4 (–**C**(CH_3)$_3$), 101.4 (–O–**C**H<), 125.1 (q, $^1J_{CF}$ = 279 Hz, –**C**F_3), 166.2 (q, $^3J_{CF}$ = 2.9 Hz, **C**=O). ^{19}F NMR ($CDCl_3$, 470 MHz): δ = −68.6 (d, $^3J_{FH}$ = 8.7 Hz, –C**F**$_3$). EIMS: *m*/*z* = 255 (5), 213 (40), 197 (100), 73 (80), 57 (38), CIMS: *m*/*z* = 271 (M^++1, 20), 215 (100).

The reaction of BFMA with DOX was carried out by adding 2.1 mmol (7.0 eq.) of BFMA and 12.0 mmol (40 eq.) of DOX with 0.6 mmol (2.0 eq.) of radical generator into a glass ampule. The conversion of BFMA was above 99% by the measurement of GC of the reaction system. The product was separated by distillation after the reaction mixture was washed with a saturated sodium hydrogencarbonate solution when BPO was used.

2-(2-*tert*-Butoxycarbonyl-3,3,3-trifluoropropyl)-1,4-dioxane (addition product of BFMA with DOX): bp: 75.5 °C/1 mmHg. Yield: 41% by BPO. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.47 and 1.49 ppm (a pair of s, 9H, C(C**H**$_3$)$_3$), 1.71, 1.92 and 1.75, 2.01 (two pair of diastereotopic methylene protons, ddd, ^3J = 13.9, 10.5, 2.8 Hz, ^3J = 13.9, 11.8, 2.8 Hz, and ^3J = 14.3, 4.9, 3.7 Hz, ^3J = 14.3, 9.5, 8.9 Hz, 2H, >CH–C**H**$_2$–CH(CF_3)–), 3.16 and 3.36 (a pair of ddq, ^3J = 8.8, 4.9 Hz, $^3J_{HF}$ = 8.8 Hz and ^3J = 11.8, 2.8 Hz, $^3J_{HF}$ = 8.8 Hz, 1H, –C**H**(CF_3)–), 3.28 and 3.29 (a pair of dd, ^3J = 11.4, 9.7 Hz and ^3J = 11.5, 9.8 Hz, 1H, >CH–O–C**H**$_{ax}$–), 3.49–3.79 (m, 6H, –O–C**H**$_2$–). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.8 and 27.9 (a pair of C(**C**H_3)$_3$), 28.0 (q, $^3J_{CF}$ = 1.9 Hz, –**C**H_2–CH(CF_3)–), 46.9 and 48.1 (a pair of q, $^2J_{CF}$ = 27.1 Hz, –**C**H(CF_3)–), 66.37 and 66.42 (a pair of O–**C**H_2–), 66.51 and 66.70 (a pair of O–C**H**$_2$–), 70.7 and 70.9 (a pair of O–**C**H_2–CH<), 71.8 and 73.3 (a pair of O–CH_2–**C**H<), 82.5 and 82.8 (a pair of **C**(CH_3)$_3$), 124.95 and 125.00 (a pair of q, $^1J_{CF}$ = 278.5 Hz, **C**F_3), 166.15 and 166.32 (a pair of q, $^3J_{CH}$ = 3.6 Hz, **C**=O). ^{19}F NMR ($CDCl_3$, 470 MHz): δ = −68.4 and −68.7 (a pair of d, $^3J_{FH}$ = 8.8 Hz, –C**F**$_3$), EIMS: *m*/*z* = 227 (48), 211 (100), 185 (46), 167 (47), 57 (88), CIMS: *m*/*z* = 285 (M^++1, 3).

The reaction of BFMA with THP was carried out by adding 16.8 mmol (5.0 eq.) of BFMA and 133 mmol (40 eq.) of THP with 6.6 mmol (2.0 eq.) of radical generator into a glass ampule. The conversion of BFMA was above 99% by the measurement of GC of the reaction system. The product was separated by distillation after the reaction mixture was washed by a saturated sodium hydrogen carbonate solution when BPO was used.

2-(2-*tert*-Butoxycarbonyl-3,3,3-trifluoropropyl)tetrahydropyran (addition product of BFMA with THP). bp: 64.0 °C/1 mmHg. Yield: 2% by BPO. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.26–1.34 (m, 1H, >CH–C**H**$_2$–), 1.46 and 1.49 ppm (a pair of s, 9H, C(C**H**$_3$)$_3$), 1.46–1.60 (m, 3H, >CH–CH_2–C**H**$_{ax}$–, –O–C**H**$_2$–CH_2–), 1,52–1.62 (m, 1H, >CH–C**H**$_2$–), 1.79, 1.99 and 2.07 (diastereotopic methylene protons, ddd, ^3J = 13.9, 10.2, 2.8 Hz, ^3J = 13.9, 11.5, 2.8 Hz, and ^3J = 14.2, 8.9, 8.9 Hz, 1.5H, >CH–C**H**$_2$–CH(CF_3)–), 1.80–1.86 (m, 1.5H, >CH–CH_2–C**H**$_{eq}$–, >CH–C**H**$_2$–CH(CF_3)–), 3.13 and 3.37 (a pair of ddq, ^3J = 8.9, 5.1 Hz, $^3J_{HF}$ = 8.7 Hz and ^3J = 11.5, 2.8 Hz, $^3J_{HF}$ = 8.7 Hz, 1H, –C**H**(CF_3)–), 3.19 and 3.29 (a pair of tt, ^3J = 10.6, 3 Hz and ^3J = 10.1, 3 Hz, 1H, >C**H**–CH_2–CH(CF_3)–), 3.32 and 3.33 (a pair of dd, ^3J = 11.9, 1.8 Hz, 1H, >CH–O–C**H**$_{ax}$–), 3.93 and 3.97 (a pair of ddd, ^3J = 11.2, 4.6, 2.4 Hz, 1H, >CH–O–C**H**$_{eq}$–). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 23.33 and 23.37 (a pair of >CH–CH_2–**C**H_2–), 25.8 and 25.9 (a pair of O–CH_2–**C**H_2–), 27.8 and 27.9 (a pair of C(**C**H_3)$_3$), 31.8 and 32.0 (a pair of >CH–**C**H_2–CH_2–), 32.7 and 32.9 (a pair of >CH–**C**H_2–CH(CF_3)–), 47.4 and 48.7 (a pair of q, $^2J_{CF}$ = 26.7 Hz, –**C**H(CF_3)–), 68.3 and 68.5 (a pair of O–**C**H_2–), 74.1 and 75.7 (a pair of –O–**C**H<), 82.2 and 82.4 (a pair of –**C**(CH_3)$_3$), 125.2 and 125.3 (a pair of q, $^1J_{CF}$ = 278.5 Hz, **C**F_3), 166.7 and 166.8 (a pair of q, $^3J_{CF}$ = 3.1 Hz, **C** = O). ^{19}F NMR ($CDCl_3$, 470 MHz): δ = −68.4 and −68.6 (a pair of d, $^3J_{FH}$ = 8.7 and $^3J_{FH}$ = 8.7 Hz, –C**F**$_3$). EIMS: *m*/*z* = 225 (100), 209 (94), 98 (64), 57 (38), CIMS: *m*/*z* = 283 (M^++1, 3).

4. Conclusion

The radical addition reactivity of *tert*-butyl α-trifluoromethylacrylate (CH_2=C(CF_3)COOC(CH_3)$_3$) was investigated with cyclic ethers such as tetrahydrofuran, 1,3-dioxolane, 1,4-dioxane and tetrahydropyran to afford corresponding 1:1 addition products in fairy high yields. These cyclic ethers are concluded to be mono-functional. No 1,5-radical shift mechanism proposed in the reaction of 2-benzoxypentafluoropropene (CF_2=C(CF_3)OCOC$_6H_5$) with 1,4-dioxane might take place in the case of *tert*-butyl α-trifluoromethylacrylate with 1,4-dioxane, probably because the reactivity of the radical $^{\bullet}$C(CF_3)(COO)CH_2– would be different from that of the radical $^{\bullet}$C(CF_3)(OCO)CF_2–. It is then concluded that interconversion of fluoroalkylcarbon radical and hydrocarbon radical may not take place in the reaction intermediate of *tert*-butyl α-trifluoromethylacrylate which possesses two less fluorines

compared to 2-benzoxypentafluoropropene though the radical reaction of α-fluoroacrylate was reported to yield polymers [1]. The method may be a facile way to form carbon–carbon bonds by the aid of trifluoromethyl group in the field of fluorinated organic syntheses because radical reactions of acrylates and vinyl esters possessing no fluorine atom generally produce polymers instead of addition products.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2007.09.002.

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