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PHOTOCHEMICAL REACTIONS OF PERFLUORODIALKYL PEROXIDES WITH PERFLUOROCYCLOOLEFINS

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SUMMARY

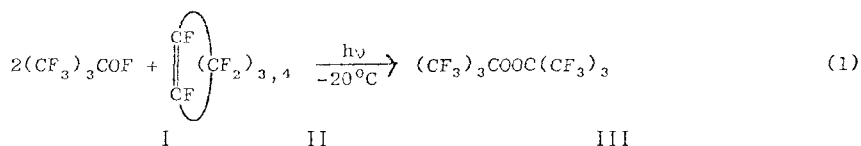
Vicinal perfluorodi-*t*-butoxycycloalkanes and isomers have been prepared in 50 to 70% yields through photochemical reactions of $(\text{CF}_3)_3\text{COOC}(\text{CF}_3)_3$ with perfluorocycloolefins ($\text{c-C}_5\text{F}_8$ and $\text{c-C}_6\text{F}_{10}$) under a 200-watt Hg lamp at -20°C . The two isomers of $\text{vic-C}_5\text{F}_8[\text{OC}(\text{CF}_3)_3]_2$ in 1:4 ratio have been fractionated and identified as *cis*- and *trans*-isomers respectively. The three isomers for $\text{vic-C}_6\text{F}_{10}[\text{OC}(\text{CF}_3)_3]_2$ in 1:4:2 ratio have been fractionated and tentatively identified as equatorial-equatorial, axial-equatorial and axial-axial respectively.

New 2,2'-perfluorodimethoxycycloalkyls have been prepared in 60 to 80% yields through photolysis of CF_3OOCF_3 with perfluorocycloolefins under a 2500-watt Hg-Xe lamp at -20°C . The attempted separations of the rotational isomers have been unsuccessful. The need of a strong ultraviolet source for primary perfluorodialkyl peroxide is discussed and the mechanism and the radical chain sequences are presented.

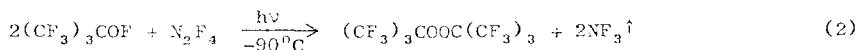
Another new synthesis of bis(perfluoro-*t*-butyl) peroxide $[\text{D}(\text{CF}_3)_3\text{CO-OC}(\text{CF}_3)_3 \approx 34.5 \text{ kcal}]$ from $(\text{CF}_3)_3\text{COF}$ using difluoroamino radicals as the fluoroxy fluorine atoms acceptor is described.

INTRODUCTION

In a previous paper [1] we described the photochemical reactions of perfluoro-*t*-butylhypofluorite (I) with perfluorocycloolefins (II) as fluorine atoms acceptors to yield 50 to 70% of bis(perfluoro-*t*-butyl) peroxide (III) (eq.1). III was first reported by Gould, et. al., through



oxidation of perfluoro-t-butanol with chlorine trifluoride[2]. In this paper we describe another synthesis of $\text{R}_f^t\text{OOR}_f^t$ from the corresponding R_f^tOF using difluoroamino radicals from N_2F_4 ($D_{\text{F}_2\text{N}-\text{NF}_2} = 21.7\text{kcal}$)³ as the fluoroxy fluorine atoms acceptors. Thus the by-product is the inert volatile NF_3 to leave the residue as the pure peroxide (eq. 2). The likely intermediate $(\text{CF}_3)_3\text{CONF}_2$



was not detected. This new synthesis of $(\text{CF}_3)_3\text{COOC}(\text{CF}_3)_3$, which is a colorless inert liquid (dec. at 130°C), facilitates further research of reactions of pure III with perfluorocycloolefins and comparison of the results with reactions of CF_3OOCF_3 .

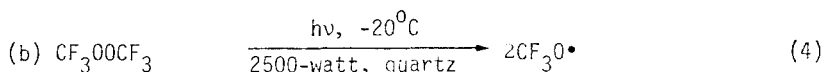
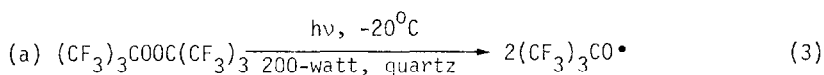
RESULTS AND DISCUSSION

Reactions of primary and tertiary perfluorodialkyl peroxides were carried out in the presence of neat perfluorocycloolefins ($c\text{-C}_5\text{F}_8$ and $c\text{-C}_6\text{F}_{10}$) to give stable colorless liquids. A 200-watt Hg lamp was used for photolysis of III at -20°C for 1 hr, while a 2500-watt Hg-Xe lamp was required for photolysis of CF_3OOCF_3 to react with perfluorocycloolefins at -20°C for 3 hr. The major product of III and perfluorocyclopentene is vicinal perfluorodi-t-butoxycyclopentane ranged from 50 to 70% yields. The ratio of the cis-and trans-isomers of $\text{vic-C}_5\text{F}_8[\text{OC}(\text{CF}_3)_3]_2$ is 1:4 as deduced by ^{19}F NMR, fractionated by gas chromatograph and confirmed by gas chromatograph-mass spectra with identical mass m/e value of 682 (see Experimental). With perfluorocyclohexene, the vicinal perfluorodi-t-butoxycyclohexane (50-70% yields) were prepared, fractionated and identified in the similar manner. The ratio of the three isomers (tentatively identified as equatorial-equatorial, axial-equatorial, axial-axial) of $\text{vic-C}_6\text{F}_{10}[\text{OC}(\text{CF}_3)_3]_2$ is 1:4:2.

The photochemical reactions of CF_3OOCF_3 [4,5] with perfluorocyclopentene and perfluorocyclohexene give inert liquids 2,2'-perfluorodimethoxycyclopentyl and 2,2'-perfluorodimethoxycyclohexyl respectively. Attempted separations of these rotational isomers were unsuccessful by gas chromatograph.

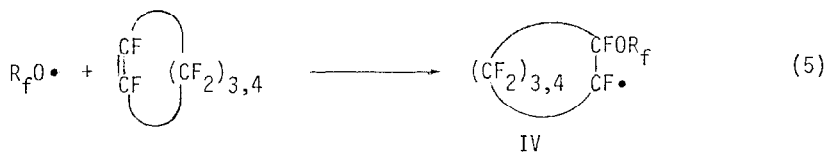
The proposed reaction sequence described below is shown to be consistent with the observed products from the photochemical reactions of perfluorodialkyl peroxides (III and CF_3OOCF_3) with perfluorocycloolefins (II). The mechanism and the radical chain sequences are presented to explain the results.

Initiation



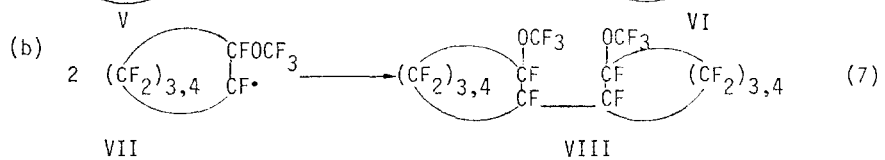
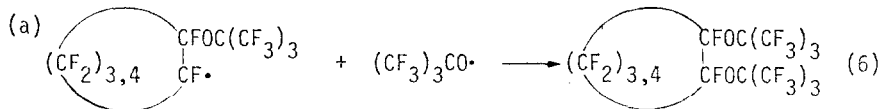
The homolysis of the O-O bond of perfluorodialkyl peroxides initiates the radical chain sequences (eq. 3 and 4). The need of a strong ultraviolet source for CF_3OOCF_3 (eq. 4) suggests the presence of low concentration of trifluoromethoxy radicals under condition of eq. 3 due to fast recombination of $\text{CF}_3\text{O}\cdot$ radicals to reverse to the peroxide CF_3OOCF_3 . The perfluoro-t-butoxy radicals are expected to have longer life time due to the increased bulky groups surrounding the radical center.

Propagation

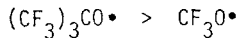


Where $\text{R}_f\text{O}\cdot$ is $(\text{CF}_3)_3\text{CO}\cdot$ and $\text{CF}_3\text{O}\cdot$ radicals. The difference of the reaction products between primary and tertiary perfluorodialkyl peroxides with perfluorocycloolefins (II) is determined by perfluoroalkoxycycloalkyl radical IV (eq. 5) to dimerize or combine with another perfluoroalkoxy radical.

Termination



The slower dimerization of radicals V than radicals VII is suggested to be due to the increased bulky group of V adjacent to the radical center. The other factor of importance is that the life-expectancy of the two perfluoroalkoxy radicals at -20°C is as follows [1]:



whose order is just the reverse to the thermal stability of the two radicals [6]. Thus with the availability of $(\text{CF}_3)_3\text{CO}\cdot$ radical to combine with radical V, perfluorodi-*t*-butoxycycloalkane (VI) is formed (eq. 6); whereas the case with low concentration of $\text{CF}_3\text{O}\cdot$ radical further favors the dimerization of the less sterically hindered radicals VII to form 2, 2'-perfluorodimethoxycycloalkyls VIII (eq. 7).

EXPERIMENTAL

Bis(trifluoromethyl) peroxide, perfluoro-*t*-butanol, perfluoro-*n*-pentane, perfluorocyclopentene and perfluorocyclohexene were obtained from PCR and tetrafluorohydrazine from Air Products. These reagents were checked by infrared and ^{19}F NMR spectra.

All compounds were handled in quartz reaction vessels attached to a copper vacuum manifold system as previously described [1]. The IR spectra were measured on a Perkin Elmer 467 spectrometer with a 5-cm Monel gas cell equipped with AgCl windows. The ^{19}F NMR spectra were determined with a Varian XL-100 spectrometer operating at 94.1 Hz, using CFCl_3 as an external reference at 30°C . The gas chromatograph (Hewlett Packard 5712A) used a

3 m x 2 mm glass column packed with 1% SE30 on Gas-Chrom Q and a 6 m x 2 mm glass column packed with 2% OV-210 on Chromosorb W at 50 to 80°C and 3 to 4 atm nitrogen. Mass spectra were obtained from an LKB 9000 mass spectrometer, which has an ionizing potential of 70 eV and a resolving power of 2000. The gas chromatograph-mass spectra were also run on the LKB 9000 instrument, using the similar columns and conditions. The elemental analyses were obtained by a high resolution mass spectrometer (CEC 21-110-B). The molecular weight of the peroxide was determined by a field ionization mass spectrometer.

Preparation of bis(perfluoro-t-butyl)peroxide

Tetrafluorohydrazine (1.2 mmol) was condensed onto an evacuated frozen $n\text{-C}_5\text{F}_{12}$ solution of perfluoro-t-butyl hypofluorite (2.1 mmol), which was prepared from perfluoro-t-butanol as previously described [7], in a quartz reaction vessel at a temperature of -196°C . The solid mixture was warmed to -90°C (in a mixture of methanol and butanol slush bath) to a clear liquid, which was irradiated by a 200-watt high pressure Hg arc lamp for 1 hr and evacuated at -40°C . The volatiles collected in a liquid nitrogen trap, were identified by IR spectra as mainly NF_3 [8] with characteristic absorption at 911 cm^{-1} and a small amounts of CF_3COCF_3 and CF_4 with characteristic absorptions at 1890 and 2200 cm^{-1} , respectively. The residual liquid (60% yield based on perfluoro-t-butyl hypofluorite) was identified as pure $(\text{CF}_3)_3\text{COOC}(\text{CF}_3)_3$ by IR in accordance with the literature [2], by ^{19}F NMR (A singlet at $\delta 69.7$ ppm relative to external standard CFCl_3) and a field ionization mass spectrum of one peak at a mass m/e value of 470.

The thermal decomposition of III occurred at 130°C in the presence of perfluorocyclopentene as the radical scavenger. The ^{19}F NMR was used to follow the concentration of III as a function of time. The O-O bond dissociation energy $D_{(\text{CF}_3)_3\text{CO-OC}(\text{CF}_3)_3}$ was estimated at about 34.5 kcal, while $D_{\text{CF}_3\text{O-OCF}_3}$ was reported as $46.7^{33} \pm 0.8$ kcal [4].

Reactions of bis(perfluoro-t-butyl)peroxide

(a) With perfluorocyclopentene

Perfluorocyclopentene (0.8 mmol) was condensed onto an evacuated frozen bis(perfluoro-t-butyl)peroxide (0.8 mmol) in a quartz reaction vessel at a temperature of -196°C . The solid mixture turned into a clear liquid at -20°C for irradiation by means of a 200-watt high pressure Hg arc lamp

for 1 hr at -20°C . Some white precipitate was observed at -20°C and the mixture was evacuated at -20°C . The stable clear residual liquid 55% yield, based on perfluorocyclopentene at ambient temperature was determined as pure $\text{C}_5\text{F}_8[\text{OC}(\text{CF}_3)_3]_2$ isomers with negligible amount of dimers.

Mass spectroscopic molecular weight (CEC 21-110-B) of $\text{C}_5\text{F}_8[\text{OC}(\text{CF}_3)_3]_2$: Found 681.9477. Calculated for $\text{C}_{13}\text{F}_{26}\text{O}_2$: 681.9483.

TABLE I

Mass Spectra of Vicinal Perfluorodi-t-butoxycycloalkanes and 2,2'-Perfluoro-dimethoxydicycloalkyls

vic- $\text{C}_5\text{F}_8[\text{OC}(\text{CF}_3)_3]_2$ (trans-isomer)	: 682 $\text{C}_{13}\text{F}_{26}\text{O}_2^+$ (1), 663 $\text{C}_{13}\text{F}_{25}\text{O}_2^+$ (13), 563 $\text{C}_{11}\text{F}_{21}\text{O}_2^+$ (15), 435 $\text{C}_8\text{F}_{17}\text{O}^+$ (5), 347 $\text{C}_7\text{F}_{13}\text{O}^+$ (27), 219 C_4F_9^+ (8), 181 C_4F_7^+ (3), 169 C_3F_7^+ (2), 147 $\text{C}_3\text{F}_5\text{O}^+$ (?), 131 C_3F_5^+ (45), 100 C_2F_4^+ (5), 97 $\text{C}_2\text{F}_3\text{O}^+$ (5), 93 C_3F_3^+ (2), 69 CF_3^+ (100).
vic- $\text{C}_6\text{F}_{10}[\text{OC}(\text{CF}_3)_3]_2$ (eq, eq - isomer)	: 732 $\text{C}_{14}\text{F}_{28}\text{O}_2^+$ (0.4), 713 $\text{C}_{14}\text{F}_{27}\text{O}_2^+$ (23), 485 $\text{C}_9\text{F}_{19}\text{O}^+$ (6), 347 $\text{C}_7\text{F}_{13}\text{O}^+$ (14), 285 $\text{C}_5\text{F}_{11}\text{O}^+$ (2), 219 C_4F_9^+ (9), 181 C_4F_7^+ (5), 162 C_4F_6^+ (2), 131 C_3F_5^+ (31), 119 C_2F_5^+ (2), 100 C_2F_4^+ (2), 97 $\text{C}_2\text{F}_3\text{O}^+$ (3), 93 C_3F_3^+ (2), 69 CF_3^+ (100).
$(\text{C}_5\text{F}_8\text{OCF}_3)_2^a$: 594 $\text{C}_{12}\text{F}_{22}\text{O}_2^+$ (10), 506 $\text{C}_{11}\text{F}_{18}\text{O}_2^+$ (2.3), 444 $\text{C}_9\text{F}_{16}\text{O}_2^+$ (3.8), 421 $\text{C}_{10}\text{F}_{15}\text{O}^+$ (5.7), 409 $\text{C}_9\text{F}_{15}\text{O}^+$ (8.3), 393 $\text{C}_9\text{F}_{15}^+$ (6.0), 378 $\text{C}_8\text{F}_{14}\text{O}^+$ (2.0), 371 $\text{C}_9\text{F}_{13}\text{O}^+$ (0.8), 356 $\text{C}_8\text{F}_{12}\text{O}_2^+$ (1.5), 343 $\text{C}_8\text{F}_{13}^+$ (2.2), 340 $\text{C}_8\text{F}_{12}\text{O}^+$ (0.8), 321 $\text{C}_8\text{F}_{11}\text{O}^+$ (1.7), 305 $\text{C}_8\text{F}_{11}^+$ (0.8), 293 $\text{C}_7\text{F}_{11}^+$ (8.0), 290 $\text{C}_7\text{F}_{10}\text{O}^+$ (1.0), 262 $\text{C}_6\text{F}_{10}^+$ (1.7), 243 C_6F_9^+ (7.3), 231 C_5F_9^+ (0.8), 221 $\text{C}_6\text{F}_7\text{O}^+$ (3.0), 205 C_6F_7^+ (1.7), 193 C_5F_7^+ (7.0), 181 C_4F_7^+ (2.3), 162 C_4F_6^+ (2.5), 159 $\text{C}_4\text{F}_5\text{O}^+$ (2.0), 155 C_5F_5^+ (2.2), 131 C_3F_5^+ (17.0), 100 C_2F_4^+ (6.3), 93 C_3F_3^+ (1.0), 69 CF_3^+ (100.0).

TABLE I (continued)

$(C_6F_{10}OCF_3)_2^b$: 694 $C_{14}F_{26}O_2^+(0.06)$, 606 $C_{13}F_{22}O_2^+(0.28)$, 578 $C_{12}F_{22}O^+(0.35)$, 543 $C_{12}F_{21}^+(0.87)$, 521 $C_{12}F_{19}O^+(0.80)$, 499 $C_{12}F_{17}O_2^+(0.17)$, 493 $C_{11}F_{19}^+(1.15)$, 490 $C_{11}F_{18}O^+(0.41)$, 471 $C_{11}F_{17}O^+(0.17)$, 459 $C_{10}F_{17}O^+(0.67)$, 437 $C_{10}F_{15}O_2^+(0.28)$, 393 $C_9F_{15}^+(0.33)$, 371 $C_9F_{13}O^+(0.83)$, 343 $C_8F_{13}^+(3.33)$, 293 $C_7F_{11}^+(1.15)$, 281 $C_6F_{11}^+(0.61)$, 259 $C_6F_9O^+(0.43)$, 255 $C_7F_9^+(0.57)$, 243 $C_6F_9^+(0.76)$, 231 $C_5F_9^+(0.6)$, 205 $C_6F_7^+(0.33)$, 193 $C_5F_7^+(0.77)$, 181 $C_4F_7^+(1.08)$, 169 $C_3F_7^+(0.7)$, 162 $C_4F_6^+(0.85)$, 159 $C_4F_5O^+(0.6)$, 155 $C_5F_5^+(0.4)$, 143 $C_4F_5^+(0.67)$, 135 $C_2F_5O^+(0.52)$, 131 $C_3F_5^+(25.0)$, 112 $C_3F_4^+(0.20)$, 109 $C_3F_3O^+(0.65)$, 100 $C_2F_4^+(2.0)$, 93 $C_3F_3^+(1.05)$, 69 $CF_3^+(100.0)$, 50 $CF_2^+(0.18)$, 43 $C_2F^+(0.78)$, 31 $CF^+(0.41)$.

a 2,2'-Perfluorodimethoxydicyclopentyl

b 2,2'-Perfluorodimethoxydicyclohexyl

The ^{19}F NMR spectrum identified the liquid residue as a mixture of cis- and trans-isomers of vic- $C_5F_8[OC(CF_3)_3]_2$ at a 1:4 ratio in accord to the literature [7]. The isomers were separated by gas chromatograph (Hewlett Packard 5712A) using a 3 m x 2 mm glass column packed with 1% SE30 on Gas-Chrom Q at 50°C and 3 atm nitrogen. The order of increasing elution time is from trans- to cis-isomer and the relative peak area as 4:1 ratio, which is in agreement of the deduced isomers ratio from ^{19}F NMR spectrum. The trans- and cis-isomers were further analyzed by gas chromatograph-mass spectrograph using the identical column and conditions. Table I shows the mass spectrum (LKB 9000) of trans-isomer of vic- $C_5F_8[OC(CF_3)_3]_2$. The cis-isomer at a later elution time shows identical mass value of the parent ion and with minor difference in mass cracking patterns.

(b) With perfluorocyclohexene

The reaction of perfluorocyclohexene (0.59 mmol) and bis(perfluoro-t-butyl)peroxide (1.15 mmol) was carried out in the same manner as the above procedure. The stable clear residual liquid (63% yield based on perfluorocyclohexene) at ambient temperature was identified as pure $C_6F_{10}[OC(CF_3)_3]_2$ isomers.

Mass spectroscopic molecular weight (CEC21-110-B) of $C_6F_{10}[OC(CF_3)_3]_2$:
 Found: 731.9497. Calculated for $C_{14}F_{28}O_2$: 731.9451.

The ^{19}F NMR spectrum identified the liquid residue as a mixture of three isomers. The two bulky groups at the 1,2-positions of perfluorocyclohexane ring [9] make fluorine assignment of the different isomers difficult. The three types of absorptions are: (1) perfluoro-t-butoxy of three different types at δ +70, where one is a quintet with $J = 7$ Hz and the other two couplings are unresolved, (2) difluoromethylene at δ +120 to 135, AB type, $J_{AB} = 300$ Hz and (3) tertiary fluorine as $F-C \begin{matrix} \diagup C \\ \diagdown C \end{matrix}$ at δ +140 with unresolved coupling, in the ratio of 9:4:1 [1]. The relative peak areas from gas chromatograph (Hewlett Packard 5712A) using an identical column as above but at $80^\circ C$ were recorded in the order of increasing elution time of the three isomers as 1:4:2 ratio, which agrees with the deduced three isomers ratio 1:4:2 (tentatively identified by ^{19}F NMR as equatorial-equatorial, axial-equatorial and axial-axial) respectively. The three isomers were further analyzed by gas chromatograph-mass spectrograph using an identical column at $80^\circ C$ and conditions. Table 1 shows the mass spectrum (LKB 9000) of the first eluted isomer (eq, eq) of vic- $C_6F_{10}[OC(CF_3)_3]_2$. The other two isomers (tentatively identified as ax, eq and ax, ax) at two later elution times respectively show identical mass values of parent ions and only minor variations in mass cracking patterns.

Reactions of bis(trifluoromethyl)peroxide

(a) With perfluorocyclopentene

The reaction of perfluorocyclopentene (5.9 mmol) and bis(trifluoromethyl)peroxide (5.9 mmol) was carried out in the same manner as above except a 2500-watt Hg-Xe lamp was used for 3 hr. Fractionation of the products used a 6 m x 2 mm glass column packed with 2% OV-210 on Chromosorb W at $70^\circ C$ with 4 atm nitrogen carrier gas pressure led to the isolation and identification of 2,2'-perfluorodimethoxydicyclopentyl (vapor pressure is about 4 mm at $25^\circ C$). The yield is 60% based on perfluorocyclopentene with a small amount of vicinal perfluorodimethoxycyclopentane (< 5% yield).

Mass spectroscopic molecular weight (CEC21-110-B) of $(C_5F_8OCF_3)_2$:
 Found, 593.9537. Calculated for $C_{12}F_{22}O_2$, 593.9547.
 Attempted separation of the rotational isomers of 2,2'-perfluorodimethoxydicyclopentyl was unsuccessful. The ^{19}F NMR of perfluorodimethoxydicyclopentyl

isomers are: ϕ 53 to 55 ppm (relative peak 6.2, 6F, $2\text{CF}_3\text{O}$), ϕ 117 to 144 ppm (relative peak area 15.4, 14F, 6CF_2 and $2\text{F}-\text{C}(\text{CF}_3)_2$), ϕ 164 to 176 ppm (relative peak area 2.2, 2F, $2\text{F}-\text{C}-\text{C}$). The mass spectrum was shown in Table I. The IR spectrum has strong absorptions at 1230, 1140, 1020, 970, 885 and 740 cm^{-1} .

(b) With perfluorocyclohexene

The reaction of perfluorocyclohexene (6.1 mmol) and bis(trifluoromethyl) peroxide (6.0 mmol) was carried out, fractionated and identified in the same manner as the reaction of perfluorocyclopentene and CF_3OOCF_3 . Yield of 2,2'-perfluorodimethoxycyclohexyl liquid was 77% based on perfluorocyclohexene.

Mass spectroscopic molecular weight (CEC21-110-B) of $(\text{C}_6\text{F}_{10}\text{OCF}_3)_2$:
Found: 693.9547. Calculated for $\text{C}_{14}\text{F}_{26}\text{O}_2$: 693.9547.

The ^{19}F NMR of 2,2'-perfluorodimethoxycyclohexyl are: ϕ 52 to 54 ppm (relative peak area 6.8, 6F, $2\text{CF}_3\text{O}$), ϕ 126 to 142 ppm (relative peak area 17.2, 18F, 8CF_2 , $2\text{F}-\text{C}(\text{OCF}_3)_2$), ϕ 160 to 175 ppm (relative peak area 2.2, 2F, $2\text{F}-\text{C}-\text{C}$). The mass spectrum was shown in Table I. The IR spectrum has strong absorptions at 1235, 1130, 1015, 965, 870 and 720 cm^{-1} .

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