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DIELS-ALDER REACTIONS OF POLYFLUORO-2-ALKYNOIC ACIDS

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SUMMARY

The Diels-Alder reactions of 4,4,4-trifluoro-2-butynoic acid (1a) and ωH-perfluoro-2-alkynoic acids (1b-d) with 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene, furan, and 1,2,4,5-tetramethylbenzene (durene) were investigated. The F-alkynoic acids (1a-d) reacted easily with the 1,3-butadienes and furan to give the corresponding 1,4-addition products in high yields (71-95%), whereas the Diels-Alder adduct was not obtained in the reaction of 1c with durene.

The mixture of two regioisomers (3a-d and 4a-d) of the adduct was obtained in the reactions of 1a-d with 2-methyl-1,3-butadiene. The structure of the major isomer was discussed based on the FMO theory.

INTRODUCTION

A number of studies on the preparation and reactions of various fluorinated alkynes have been reported [1]. These fluorinated alkynes have been found to be good dienophiles in the Diels-Alder reactions [2]. Krespan and his co-workers reported that bis(polyfluoroalkyl)acetylenes added 1,4 to aromatic rings such as those in durene and naphthalene to form

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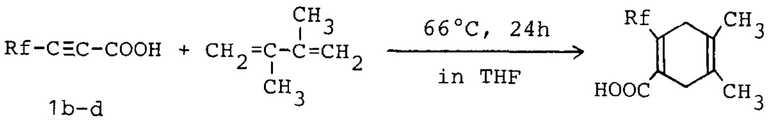
the corresponding bicyclooctatrienes, and they also suggested that the pronounced electrophilic character of these triple bonds was due to the presence of two electronegative polyfluoroalkyl groups [2b]. There are few reports on the alkynes having two different electronegative groups such as a polyfluoroalkyl and a carboxy or an alkoxycarbonyl group attached at both carbons of a triple bond [3]. Recently, Shen and his co-workers obtained fluoroalkylisoxazoles in the 1,3-dipolar cycloadditions of methyl perfluoro-2-alkynoates with aromatic nitrile oxides [4]. However, no Diels-Alder reaction of per- and polyfluoro-2-alkynoic acids or their esters has been reported. In this paper, we report the results of the Diels-Alder reactions of 4,4,4-trifluoro-2-butynoic acid (1a), ωH-perfluoro-2-alkynoic acids (1b-d), and ethyl 4,4-difluoro-2-butynoate (1b-Et) with the 1,3-butadienes, furan, and durene.

RESULTS AND DISCUSSION

ωH-Perfluoro-2-alkynoic acids (1b-d) reacted with 2,3-dimethyl-1,3-butadiene in tetrahydrofuran (THF) at 66°C for 24 hours to give 1-carboxy-2-(ωH-perfluoroalkyl)-4,5-dimethyl-1,4-cyclohexadienes (2b-d) in high yields (86-94%) (Scheme 1 and Table 1). 1,2-Addition products formed in the reaction of fluorinated olefins with 1,3-butadiene were not detected [5].



1b-d

2b-d

Rf; b) HCF_2, c) $HCF_2CF_2CF_2$, d) $HCF_2CF_2CF_2CF_2CF_2$

Scheme 1

The reaction of 4,4,4-trifluoro-2-butynoic acid (1a) with 2-methyl-1,3-butadiene (isoprene:ISP) in THF at 45°C for 72 hours gave two products, which were isolated by evaporation of

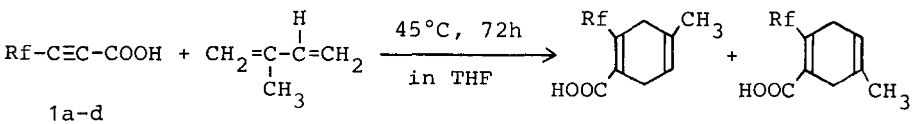
TABLE 1

Reactions of 1 with 1,3-Butadienes[a]

Dienophile	Diene	Reaction Temp(°C)	Reaction Time(h)	Yield(%) 2	Yield(%) 3+4	Isomer Ratio 3/4
1b	DMB[b]	66	24	94	-	-
1c	DMB[b]	66	24	86	-	-
1d	DMB[b]	66	24	91	-	-
1a	ISP[c]	45	72	-	92	2.3
1b	ISP[c]	45	72	-	95	2.7
1c	ISP[c]	45	72	-	83	2.1
1d	ISP[c]	45	72	-	85	1.8
1b-Et	ISP[c]	45	72	-	88[d)]	2.6

[a] In THF. [b] 2,3-Dimethyl-1,3-butadiene.
[c] 2-Methyl-1,3-butadiene. [d] Ethyl ester of 3b and 4b.

THF and excess ISP from the reaction mixture, followed by recrystallization (from hexane) of the involatile residue. The mixture of these products proved to be inseparable by fractional recrystallization or column chromatography (silica gel/hexane) and it was therefore analyzed directly. The ^{19}F-NMR spectra of the mixture of these products displayed two singlets of relative intensity 2.3:1. The ^{1}H-NMR (200 MHz, FT-NMR) and mass spectra suggested that the products were the mixture of regioisomers of the substituted 1,4-cyclohexadiene, 1-carboxy-2-(polyfluoroalkyl)-4- and -5-methyl-1,4-cyclohexadiene (3a and 4a) (Scheme 2), but unfortunately, the chemical



1a-d

3a-d

4a-d

Rf; a) CF_3, b) HCF_2, c) $HCF_2CF_2CF_2$, d) $HCF_2CF_2CF_2CF_2CF_2$

Scheme 2

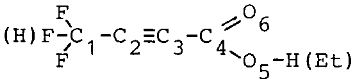
shifts of each proton in the major isomer and in the minor isomer were not sufficiently different to provide a reliable basis for deciding whether 3a or 4a was the major product.

The reactions of the other F-alkynoic acids (1b-d) with ISP under the same conditions afforded the corresponding two regioisomers (3b-d and 4b-d) of the Diels-Alder adducts in high yields (83-95%). Their isomer ratios were determined by the relative intensity of two signals due to the CF_2 group bonded directly to the double bond in ^{19}F-NMR spectra (Table 1). However, the structures of the major isomers were not also decided by their ^1H-NMR spectra, because of the same reasons in 3a and 4a.

The order of the regioselectivity in the reactions of 1 with ISP was as follows; 1b > 1b-Et > 1a > 1c > 1d (Table 1). These observations suggest that the regioselectivity depends on the length of polyfluoroalkyl group and the number of fluorines in 1.

TABLE 2

Frontier Orbitals of 1 Calculated by CNDO/2 Method



$$\text{(H)F}\!-\!C_1(F)_2\!-\!C_2\!\equiv\!C_3\!-\!C_4(=O_6)\!-\!O_5\!-\!\text{H(Et)}$$

1	MO	a_1	a_2	a_3	a_4	a_5	a_6	E
1a	LUMO	0.160	0.496	-0.367	-0.526	0.490	0.180	1.94
1a	HOMO	-0.033	0.327	0.249	-0.309	-0.699	0.472	-15.52
1b	LUMO	0.157	0.491	-0.356	-0.536	0.492	0.182	2.31
1b	HOMO	-0.038	0.399	0.267	-0.308	-0.698	0.454	-15.20
1b-Et	LUMO	0.159	0.492	-0.360	-0.531	0.491	0.177	2.38
1b-Et	HOMO	-0.057	0.412	0.351	-0.272	-0.485	-0.040	-15.82

[a] a_i is the coefficient of atom C_i or O_i in the MO. E is the energy of the MO (eV).

The theoretical predictions of the major regioisomer formed in the Diels-Alder reactions have been discussed on the basis of the FMO theory [6]. The reactions of electron-poor dienophile (low LUMO) with electron-rich diene (high HOMO) and of electron-rich dienophile with electron-poor diene include the $\mathrm{LUMO_{dienophile}}$-$\mathrm{HOMO_{diene}}$ (normal Diels-Alder reaction) and the $\mathrm{LUMO_{diene}}$-$\mathrm{HOMO_{dienophile}}$ interaction (inverse electron demand Diels-Alder reaction) as a major interaction, respectively. The theoretical predictions were in good agreement with the experimental results.

In order to predict which isomer was major, 3 or 4, in our reactions, we calculated the frontier orbitals of 1a, 1b, 1b-Et, and ISP (cisoid form) by the CNDO/2 method [7]. The results of the calculations are summarized in Table 2 and the frontier orbitals of 1a and ISP are shown in Fig. 1.* It is

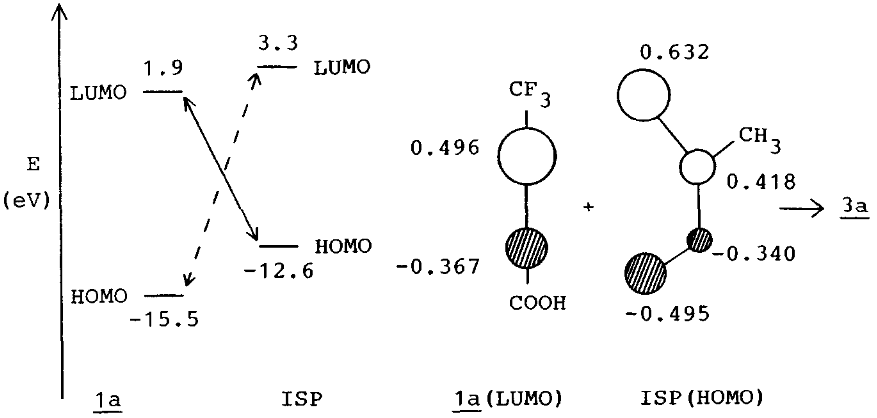


Fig. 1. Frontier orbitals for Diels-Alder reaction of 1a with 2-methyl-1,3-butadiene (ISP).

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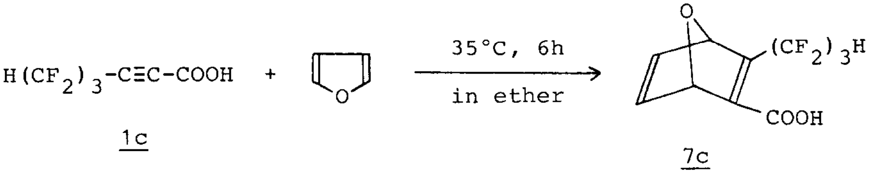
* The FMO energy levels and orbital coefficients calculated by the CNDO/2 method are probably not satisfactory for a quantitative FMO analysis. However, they are sufficient for a qualitative FMO analysis.

apparent from Fig. 1 that the energy separation between $\mathrm{LUMO}_{\underline{1a}}$ and $\mathrm{HOMO}_{\mathrm{ISP}}$ is sufficiently smaller than that between $\mathrm{HOMO}_{\underline{1a}}$ and $\mathrm{LUMO}_{\mathrm{ISP}}$. This suggests that the reaction of 1a with ISP should be the normal. Considering the shapes of the frontier orbitals on the reacting systems, it is predicted that the major product formed in the reaction of 1a with ISP should be 3a. The theoretical prediction was supported by the experimental results.* The same theoretical results were obtained in the cases of 1b and 1b-Et. On the basis of these results and the comparison of the ^{19}F-NMR spectra of the mixture of 3c,d and 4c,d with those of 3a,b and 4a,b, we assumed that 3c,d might be formed preferentially relative to 4c,d in the reactions of 1c,d with ISP.

6H-Perfluoro-2-hexynoic acid (1c) reacted easily with furan in diethyl ether at 35°C for 6 hours to give the Diels-Alder adduct (7c) in 71% yield (Scheme 3). However, 1c reacted with durene in THF at 66°C for 20 hours or in o-dichlorobenzene at 180°C for 3 hours to give no Diels-Alder



Scheme 3

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* The mixture of the cyclohexadienes (3a and 4a) was converted to the mixture of two toluic acids (A and B) containing the trifluoromethyl group in 80% yield. The product ratio (A/B) was almost equal to the isomer ratio (3a/4a) of the starting material. The characterization of the major toluic acid isolated by recrystallization showed that A was p-methyl-o-(polyfluoroalkyl)benzoic acid derived from 3a. The detailed synthetic method and characterization data will be reported by us in this Journal in the near future.

product and to yield 1H,5H-perfluoro-1-pentyne by the decarboxylation of 1c. The reaction of dimethyl acetylenedicarboxylate with furan to give the Diels-Alder adduct in 77% yield requires more vigorous conditions than that of 1c with furan [13]. As cited above, bis(polyfluoroalkyl)acetylenes react with durene to give the adduct [3]. These results show that the reactivity of 1 as dienophile in the Diels-Alder reaction is between those of acetylenedicarboxylate and bis(polyfluoroalkyl)acetylenes.

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra (IR) were recorded on a Shimadzu IR-400 infrared spectrometer. ^{1}H-NMR spectra were obtained with a Hitachi R-24B (60 MHz) and/or a Varian XL-200 (200 MHz) spectrometer in $CDCl_3$ solutions with Me_4Si as an internal reference. A Hitachi R-24F (56.466 MHz) and/or a Varian XL-200 (188.220 MHz) spectrometer were used to measure ^{19}F-NMR spectra in $CDCl_3$ with CF_3COOH (TFA) as an external reference. Mass spectra (MS) were taken on a Hitachi M-80B mass spectrometer operating at an ionization potential of 70 eV. All chemicals were of reagent grade. Solvents were purified in the conventional manner. 4,4,4-Trifluoro-2-butynoic acid (1a) and ωH-perfluoro-2-alkynoic acids (1b-d) were prepared according to our previous literature method [9]. All products described below are new.

Reactions of ωH-perfluoro-2-alkynoic acids (1b-d) with 2,3-dimethyl-1,3-butadiene

In a two-necked round-bottomed flask, equipped with a magnetic stirring bar, a thermometer, and a reflux condenser, was placed a mixture of 10 mmol of 1b-d, 50 mmol of 2,3-dimethyl-1,3-butadiene, and 10 ml of THF. The mixture was stirred with refluxing (66°C) for 24 hours and then cooled to room temperature. The excess diene and THF were evaporated from the reaction mixture under reduced pressure. The residue was recrystallized from hexane to give the pure Diels-Alder reaction product (2b-d) as a solid.

1-Carboxy-2-difluoromethyl-4,5-dimethyl-1,4-cyclohexadiene(2b)

94% Yield; Mp 108-110°C; IR (KBr) 1690, 1640 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.79 (6H, s), 2.95 (4H, bs), 7.18 (1H, t, J=54.8 Hz), 8.40 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 41.6 (d, J=54.8 Hz); MS (m/e) 202 (M^+), 157 (M^+-COOH).

1-Carboxy-2-(3H-perfluoropropyl)-4,5-dimethyl-1,4-cyclohexadiene (2c)

86% Yield; Mp 75-77°C; IR (KBr) 1695, 1650 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.66 (6H, s), 2.82 (2H, bs), 2.96 (2H, bs), 6.09 (1H, tt, J= 51.4, 5.7 Hz), 8.61 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 33.1 (2F, m), 50.3 (2F, m), 58.7 (2F, dm, J=51.4 Hz); MS (m/e) 302 (M^+), 257 (M^+-COOH).

1-Carboxy-2-(5H-perfluoropentyl)-4,5-dimethyl-1,4-cyclohexadiene (2d)

91% Yield; Mp 97-99°C; IR (KBr) 1700, 1640 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.66 (6H, s), 2.83 (2H, bs), 3.00 (2H, bs), 6.04 (1H, tt, J= 51.4, 5.2 Hz), 8.58 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 31.3 (2F, m), 41.2 (2F, m), 45.0 (2F, m), 51.2 (2F, m), 58.4 (2F, dm, J=51.4 Hz); MS (m/e) 402 (M^+), 357 (M^+-COOH).

Reactions of polyfluoro-2-alkynoic acids (1a-d) with 2-methyl-1,3-butadiene

A mixture of 10 mmol of 1a-d, 50 mmol of 2-methyl-1,3-butadiene, and 10 ml of THF was stirred with refluxing (45°C) for 72 hours and then cooled to room temperature. The excess diene and THF were evaporated from the reaction mixture under reduced pressure. The residue was recrystallized from hexane to give the mixture of regioisomers (3a-d and 4a-d). The isomer ratios were obtained by the relative intensity of two different signals appeared in the ^{19}F-NMR spectra.

Mixture of 1-carboxy-2-trifluoromethyl-4-methyl-1,4-cyclohexadiene (3a) and 1-carboxy-2-trifluoromethyl-5-methyl-1,4-cyclohexadiene (4a)

92% Yield; Isomer ratio (3a/4a) : 2.3; (Mp 100-102°C); IR (KBr) 1720, 1670 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.72 (3H, s), 2.73-3.05 (4H, m), 5.39 (1H, bs), 10.5 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ -12.4 (s, 3a), -12.7 (s, 4a); MS (m/e) 206 (M^+), 161 (M^+-COOH).

Mixture of 1-carboxy-2-difluoromethyl-4-methyl-1,4-cyclohexadiene (3b) and 1-carboxy-2-difluoromethyl-5-methyl-1,4-cyclohexadiene (4b)

95% Yield; Isomer ratio (3b/4b) : 2.7; (Mp 112-114°C); IR (KBr) 1690, 1640 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.74 (3H, s), 2.85-3.14 (4H, m), 5.42 (1H, bs), 7.18 (1H, t, J=55.7 Hz), 10.6 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 41.8 (d, J=55.7 Hz, 3b), 41.5 (d, J=55.7 Hz, 4b); MS (m/e) 188 (M^+), 143 (M^+-COOH).

Mixture of 1-carboxy-2-(3H-perfluoropropyl)-4-methyl-1,4-cyclohexadiene (3c) and 1-carboxy-2-(3H-perfluoropropyl)-5-methyl-1,4-cyclo-hexadiene (4c)

83% Yield; Isomer ratio (3c/4c) : 2.1; (Mp 56-58°C); IR (KBr) 1695, 1650 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.73 (3H, s), 2.73-3.16 (4H, m), 5.40 (1H, bs), 6.11 (1H, tt, J=52.8, 5.7 Hz), 11.3 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 33.4 (m, 3c), 33.1 (m, 4c), 50.3 (m, 3c+4c), 58.9 (dm, J=52.8 Hz, 3c+4c); MS (m/e) 288 (M^+), 243 (M^+-COOH).

Mixture of 1-carboxy-2-(5H-perfluoropentyl)-4-methyl-1,4-cyclohexadiene (3d) and 1-carboxy-2-(5H-perfluoropentyl)-5-methyl-1,4-cyclohexadiene (4d)

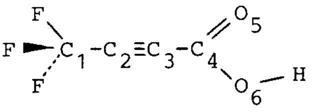
85% Yield; Isomer ratio (3d/4d) : 1.8; (Mp 66-68°C); IR (KBr) 1690, 1650 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.73 (3H, s), 2.74-3.19 (4H, m), 5.44 (1H, bs), 6.05 (1H, tt, J=52.3, 5.1 Hz), 10.8 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 31.7 (m, 3d), 31.5 (m, 4d), 41.4 (m, 3d+4d), 45.2 (m, 3d+4d), 51.5 (m, 3d+4d), 58.9 (dm, J=52.3 Hz, 3d+4d); MS (m/e) 388 (M^+), 343 (M^+-COOH).

Mixture of 1-ethoxycarbonyl-2-difluoromethyl-4-methyl-1,4-cyclohexadiene (3b-Et) and 1-ethoxycarboxy-2-difluoromethyl-5-methyl-1,4-cyclohexadiene (4b-Et)

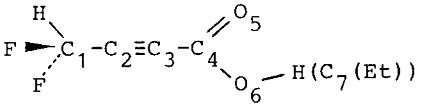
88% Yield; Isomer ratio (3b-Et/4b-Et) : 2.6; (Oil); IR (film) 1720, 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.29 (3H, t, J=7.1 Hz), 1.69 (3H, s), 2.74-3.02 (4H, m), 4.20 (2H, q, J=7.1 Hz), 5.35 (1H, bs), 7.06 (1H, t, J=55.8 Hz); ^{19}F-NMR ($CDCl_3$, TFA) δ 42.2 (d, J=55.8 Hz, 3b-Et), 41.7 (d, J=55.8 Hz, 4b-Et); MS (m/e) 216 (M^+), 171 ($M^+-OCH_2CH_3$), 143 ($M^+-COOCH_2CH_3$).

Calculations of the frontier orbitals of 1a, 1b, 1b-Et, and ISP

The computer program produced by Kikuchi was used for these calculations [10]. The computation was carried out by NEC ACOS system 850/10 at the Data Processing Center of Kyoto Institute of Technology. The coordinates of each atom in 1a, 1b, and 1b-Et, input data for the computer program, were calculated using the bond length and angle, which were chosen from the literature values where possible [11]. In the cases of no literature values such as the bond length of $CF_3-C\equiv$ and $CHF_2-C\equiv$ (C_1-C_2) and the angle of $F-C_1-F$, $F-C_1-C_2$, $H-C_1-F$, and $H-C_1-C_2$, the values of common hydrocarbons such as $CH_3-C\equiv$ length and sp^3 carbon atom angle were used. The values employed are shown below.



1a ,



1b , 1b-Et

Bond length (Å)

$F-C_1$; 1.38, C_3-C_4 ; 1.45,
$H-C_1$; 1.11, $C_4=O_5$; 1.21,
C_1-C_2 ; 1.46, O_6-H ; 0.97,
C_2-C_3 ; 1.21, O_6-C_7 ; 1.44,
$C_4-O_6(-H)$; 1.36,
$C_4-O_6(-C_7)$; 1.33

Bond angle (deg)

$F-C_1-F = F-C_1-C_2 = H-C_1-F = H-C_1-C_2$; 109.5,
$C_1-C_2-C_3 = C_2-C_3-C_4$; 180,
$C_3-C_4-O_5$; 127,
$C_3-C_4-O_6$; 110,
C_4-O_6-H ; 107,
$C_4-O_6-C_7$; 115

The calculation of the frontier orbitals of 1a using another value of C_1-C_2 (1.40 Å) and/or F-C_1-C_2 (100 deg), however, gave no result which reversed the regioselectivity of the reaction of 1a with ISP.

The frontier orbitals of ISP (cisoid form) were also calculated by the same computer program. The results were in good agreement with the literature values [6c].

Reaction of 6H-perfluoro-2-hexynoic acid (1c) with furan

In a round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was placed a mixture of 2.20 g (10 mmol) of 1c, 2.10 g (30 mmol) of furan, and 10 ml of ether. The mixture was stirred with refluxing (35°C) for 6 hours and then cooled to room temperature. The excess furan and ether were evaporated from the reaction mixture under reduced pressure. The involatile residue was recrystallized from hexane to give the pure product (7c) (2.04 g, 71%). 7c: Mp 66-68°C; ^{1}H-NMR ($CDCl_3$) δ 5.68-5.72 (2H, m), 6.08 (1H, tt, J=52.5, 5.6 Hz), 7.18 (1H, m), 7.28 (1H, m), 9.70 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 3.15 (1F, d, J=277 Hz), 3.63 (1F, d, J=277 Hz), 51.5 (2F, m), 58.3 (2F, dm, J=52.5 Hz) (The two doublets at δ 31.5 and 36.3 appear as an AB-type band system [12].); MS (m/e) 288 (M^+), 271, 262, 187, 161, 141, 68.

Reaction of 6H-perfluoro-2-hexynoic acid (1c) with 1,2,4,5-tetramethylbenzene

In a two-necked round-bottomed flask, equipped with a magnetic stirring bar, a thermometer, and a reflux condenser, was placed a mixture of 2.20 g (10 mmol) of 1c, 4.00 g (30 mmol) of 1,2,4,5-tetramethylbenzene, and 10 ml of o-dichlorobenzene. The mixture was stirred with refluxing (180°C) for 3 hours and then cooled to room temperature. ^{19}F-NMR spectra of the reaction mixture showed the disappearance of 1c and the existence of only one kind of product. The product isolated by distillation of the reaction mixture was 1H,5H-perfluoro-1-pentyne (8c). 8c: ^{1}H-NMR ($CDCl_3$) δ 3.07 (1H, t, J=5.6 Hz), 5.97 (1H, tt, J=52.0, 5.2 Hz); ^{19}F-NMR ($CDCl_3$, TFA) δ 23.2 (2F, m), 52.9 (2F, m), 59.0 (2F, dm, J=52.0); MS (m/e) 176 (M^+), 75.

A mixture of 2.20 g (10 mmol) of 1c, 4.00 g (30 mmol) of 1,2,4,5- tetramethylbenzene, and 10 ml of THF was stirred with refluxing (66°C) for 20 hours. ^{19}F-NMR spectra of the reaction mixture showed only the existence of 1c (92%) and 8c (8%).

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