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1,2-Migration of Fluorine Atom in CH_2FCF_2 Radical Produced by the Addition of a Hydrogen Atom to Trifluoroethylene

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The reaction of hydrogen atoms with trifluoroethylene has been studied at room temperature by using the mercury photosensitized decomposition of hydrogen as the source of hydrogen atoms. Product analyses using gas chromatography and ^1H and ^{19}F NMR spectroscopy confirmed the 1,2-migration of a fluorine atom in the $CH_2F\dot{C}F_2$ radical produced by the addition of a hydrogen atom to trifluoroethylene. The rate constant of the migration was estimated to be $2\times10^{10}\,s^{-1}$ from the pressure dependence of the five kinds of hexafluorobutanes produced. NMR parameters for these fluorinated compounds were determined.

When we consider the addition reaction of a free atom to the olefinic double bond of an organic compound in the gas phase, there arise two naive questions: One is which side of the double bond is attacked by the free atom, and the other is how the radical produced behaves before being thermalized.

In the case of a hydrogen atom-addition reaction to olefinic hydrocarbons, it has been established that a hydrogen atom is added to the less substituted carbon atom in the double bond and that no 1,2-migration of a hydrogen atom occurs in the radical produced.[1,2]

For the last few years, Rowland and his colaborators studied the reactions of radioactive ^{38}Cl atoms with a series of halogenated olefines,[3–5] and found that chlorine and bromine atoms in the produced radical often undergo a 1,2-migration in the radical produced by the addition of a ^{38}Cl atom to the olefin. In fact, the 1,2-migration of chlorine and bromine atoms has been reported even in the liquid phase reaction of complex organic compounds.[6]

In the case of a fluorine atom, however, no 1,2-migration has been reported in liquid phase reactions as far as we are aware. Siefert et al. have recently studied the reactions of recoiled tritium atoms with fluorinated olefins, using $^3He(n,p)T$ as the source of tritium atoms.[7] In a reaction with 1,2-difluoroethylene they found the formation of tritiated 1,1-difluoroethylene as one of the main products and suggested that the 1,2-migration of a fluorine atom occurs in the 1,2-difluoroethyl radical produced by the addition of a tritium atom to 1,2-difluoroethylene. Very recently, our laboratory has also studied the rèactions of hot tritium atoms with fluorinated ethylenes ($CFH{=}CH_2$, $CF_2{=}CH_2$, and $CF_2{=}CFH$)[8] and found evidence for the 1,2-migration of a fluorine atom; however, in hot tritium atom reactions so many fragmental products were formed that evidence for the 1,2-migration could not be obtained straightforwardly. We, therefore, looked for a precise method to establish the 1,2-migration of a fluorine atom.

The reaction of hydrogen atoms with hydrocarbon olefins is a prototype subject for chemical kinetics and has been extensively studied.[9] The reaction with fluorinated olefins, however, has not been fully investigated, probably because of the difficulty to identify multi-fluorinated hydrocarbons. Most of these compounds are not commercially available. Scott and Jennings studied the reactions of hydrogen atoms with fluoroethylenes using the mercury photosensitized decomposition of hydrogen as the source of hydrogen atoms.[10] They used gas chromatography and mass spectroscopy for the analysis of products; however, the identification of several fluorinated hydrocarbons was not successful. Consequently, they did not propose a reaction mechanism for the formation of products in the reaction of hydrogen atoms with trifluoroethylene. They derived only the relative rate constants for the addition reactions.

Using this old technique, the mercury photosensitized decomposition of hydrogen as the source of hydrogen atoms, we have reinvestigated the reactions of hydrogen atoms with trifluoroethylene. For an analysis of products, ^1H and ^{19}F NMR spectroscopy were used along with gas chromatography and mass spectroscopy. As a result, we could confirm the 1,2-migration of fluorine atoms in a 1,1,2-trifluoroethyl radical as well as various interesting results.

Experimental

Trifluoroethylene was kindly supplied by Professor Ishikawa of this Institute and was used as received. Other fluorinated compounds used for the identification of products were CH_2FCHF_2 (PCR) and CF_3CH_3 supplied by Central Glass Co. Bottled hydrogen (Showa Denko Co.) and helium (Japan Helium Center), used as a reactant and a carrier gas in a gas chromatograph, respectively, were passed through liquid nitrogen traps before use.

One Torr (133.322 Pa) of trifluoroethylene and about 100 to 750 Torr of hydrogen were introduced into a reaction vessel (359 ml) made of fused quartz, into which a drop of mercury was present, and mixed by means of a glass-covered magnetic fan which could be rotated from outside using a magnet. This reactant mixture was irradiated by a mercury lamp (Sankyo GL6) for a certain time interval. The light intensity absorbed by mercury atoms was found to be 4.8×10^{15} photons/s (estimated by the mercury photosensitized decomposition of N_2O (110 Torr) in the presence of a small amount of butene-1 (5 Torr) on the assumption that the quantum yield of nitrogen is unity).[1] Irradiated samples were slowly pumped out through two long spiral glass traps cooled with liquid nitrogen. Condensed compounds were analyzed with a gas chromatograph equipped with a thermal conductivity detector (Shimadzu GC-6AM) using two columns (one contained dibutyl phthalate (8 m), and the other Porapak-S (4 m)) as well as a temperature-programed operation during chromatography (30 to 80 °C with the dibutyl phthalate column and 70 to 150 °C with Porapak-S column). Reaction products of eleven compounds were found, out of which seven could be identified by using ^1H and ^{19}F NMR spectra obtained with a JEOL FX-90Q spectrometer. Each sample analyzed was the accumulation of 10 to 20 runs of the photochemical reaction.

Results

Identification of Products. The eleven peaks observed with a gas chromatograph of dibutyl phthalate column were named alphabetically from A to K in the order of their retention times (Fig. 1a). When using a Porapak-S column (Fig. 1b), peak A was clearly separated into two peaks; the one named T was a reactant, trifluoroethylene, and the other named A′ was later identified as CF_3CH_3. Since with this column compounds D, F, H, I, J, and K (later identified as mainly fluorinated C_4 compounds with retention times longer than 15 min) were clearly separated from compounds T, A′, B, C, and E (with retention times shorter than 15 min), quantitative gas chromatograms could be obtained by increasing the column temperature from 70 to 150 °C between these two groups of compounds. No authentic samples, except for A′ and E, were available. The relative response of the peak area against the absolute amount was assumed to be 1 to 2 for the C_2 compounds group to the C_4 compounds group, since with this column, the relative sensitivities of C_2—C_4 hydrocarbons for the thermal conductivity detector were found to be proportional to the molecular weight.[11]

Table 1 summarizes the identified products. In the Appendix, their experimental NMR parameters are described. Peaks B and C were too small to be identified. Two compounds corresponding to F and G were also too small and were found to be secondary products (as shown later).

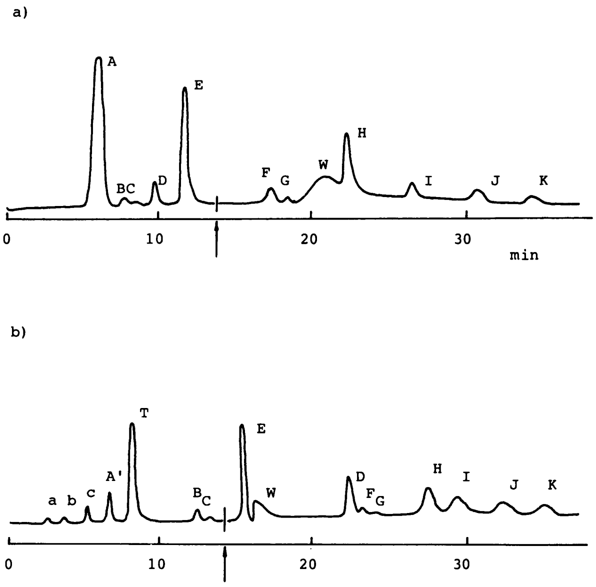

Fig. 1. (a) A typical gas chromatogram obtained with the dibutyl phthalate column. The arrow indicates the start of temperature programed operation from 30 to 80 °C with the rate of 15° min^{-1}. W: Water trapped from the carrier gas. (b) A gas chromatogram obtained with the Porapak S column. The arrow indicates the start of temperature programed operation from 70 to 150 °C with the rate of 5° min^{-1}. a—c were not identified.

Table 1. Identification of Reaction Products

A′	CF_3CH_3
E	CH_2FCHF_2
D	$CF_3CH_2CH_2CF_3$
H	$CF_3CH_2CF_2CH_2F$
I	$CF_3CH_2CHFCHF_2$
J	$CH_2FCF_2CF_2CH_2F$
K	$CH_2FCF_2CHFCHF_2$

Irradiation Time and Pressure Dependence of Products. Figure 2 shows the irradiation time dependence of the products. The relative yield of 1.0 corresponds to 0.20 μmol. All products, except F and G, were found to be linearly dependent upon the irradiation time. Table 2 summarizes the relative amounts of each product obtained as a function of the hydrogen pressure. The pressure of trifluoroethylene was 1 Torr and the irradiation time was 6 min.

Discussion

At very low hydrogen pressures (lower than 50 Torr), the formation of fragmental products such as $CF_2{=}CH_2$ and probably $CF{\equiv}CH$ has been found; however, we ignore them in the present discussion because it is well-known that most of the 253.7-nm resonance line is absorbed within a zone of 1 cm from the window of the reaction vessel and the radicals primarily produced, including hydrogen atoms,

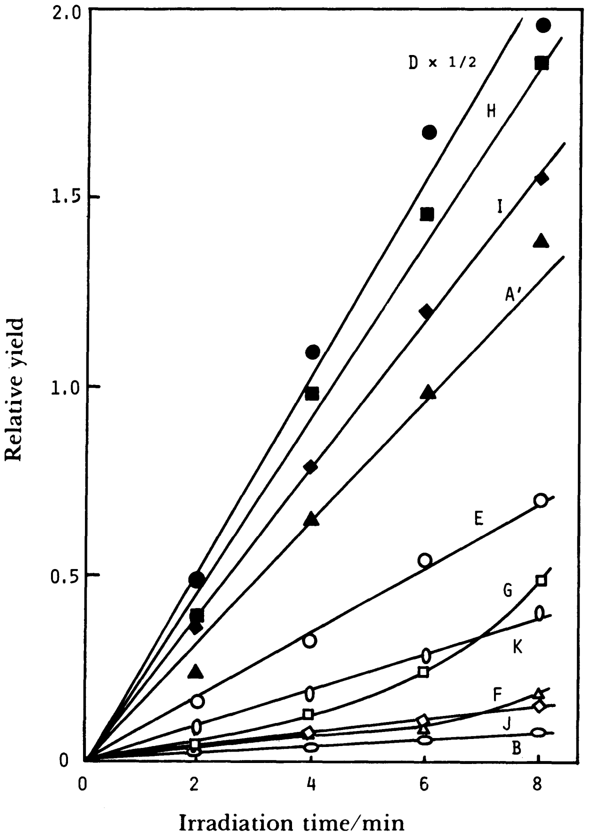

Fig. 2. Irradiation time dependence of the amounts of products. Initial hydrogen pressure is 109.5 Torr and trifluoroethylene is 1 Torr. Relative yield 1.0 corresponds to 0.20 μmol.

Table 2. Hydrogen Pressure Dependence of the Relative Amounts of Products.[a] Trifluoroethylene Pressure is 1 Torr and Irradiation Time is 6 min.

Hydrogen pressure (Torr) Product	19.1	59.1	109.5	516.0	754.9
A′	0.484	0.840	0.976	1.264	1.200
D	2.18	3.23	3.36	1.44	1.14
E	n.d.[b]	0.464	0.524	0.984	1.12
H	1.37	1.59	1.46	1.88	1.98
I	0.808	1.14	1.20	0.624	0.592
J	0.020	0.032	0.113	0.380	0.722
K	0.086	0.130	0.288	0.396	0.596

a) Relative yield 1.0 corresponds to 0.20 μmol. b) Not determined.

diffuse to the quartz surface and react differently from a gas-phase reaction.

Initial reactions may be described as follows:

$$Hg(^1S_0) + h\nu \longrightarrow Hg(^3P_1) \quad (1)$$

$$Hg(^3P_1) + H_2 \longrightarrow Hg(^1S_0) + 2H \quad (2)$$

$$H + CF_2 = CFH \longrightarrow \dot{C}F_2CFH_2 \quad \alpha \quad (3)$$

$$\longrightarrow CF_2H\dot{C}FH \quad 1-\alpha. \quad (4)$$

Here, α and $1-\alpha$ denote the fractions of the Markovnikov and anti-Markovnikov additions, respectively. No other reactions such as the formation of HF are considered, since the formation of fragmental products has not been observed at hydrogen pressures higher than 50 Torr.

From two kinds of radicals, $\dot{C}F_2CFH_2$ and $CF_2H\dot{C}FH$, we can expect the formation of following products as the result of radical reactions, if no 1,2-migration of F or H atom is considered.

$$\dot{C}F_2CFH_2 + \dot{C}F_2CFH_2 \longrightarrow CFH_2CF_2CF_2CFH_2 \text{ (J)} \quad (5)$$

$$\longrightarrow CF_2{=}CFH \text{ (T)} + CF_2HCFH_2 \text{ (E)}$$

$$\dot{C}F_2CFH_2 + CF_2H\dot{C}FH \longrightarrow CFH_2CF_2CFHCF_2H \text{ (K)} \quad (6)$$

$$\longrightarrow CF_2{=}CFH \text{ (T)} + CF_2HCFH_2 \text{ (E)}$$

$$CF_2H\dot{C}FH + CF_2H\dot{C}FH \longrightarrow CF_2HCFHCFHCF_2H \text{ (L)} \quad (7)$$

$$\longrightarrow CF_2{=}CFH \text{ (T)} + CF_2HCFH_2 \text{ (E)}$$

Here, the disproportionation reaction accompanied by a fluorine-atom transfer is not taken into consideration, since the expected products have not been observed. Compound L appearing in Reaction 7 has not been observed in the experiments. Judging from the retention times of other products, Compound L probably has a very long retention time and the amount produced may be smaller than other C_4 compounds (discussed later).

Obviously, Reactions 5 to 7 cannot explain the formation of products A′, D, H, and I. We, thus, propose the following 1,2-migration of a fluorine atom in the 1,1,2-trifluoroethyl radical:

$$\underset{1-\beta}{\dot{C}F_2CFH_2} \longrightarrow \underset{\beta}{CF_3\dot{C}H_2}. \quad (8)$$

Here, β denotes the fraction of the radicals which undergo a 1,2-migration and proceed to the following radical reactions:

$$CF_3\dot{C}H_2 + CF_3\dot{C}H_2 \longrightarrow CF_3CH_2CH_2CF_3 \text{ (D)} \quad (9)$$

$$CF_3\dot{C}H_2 + \dot{C}F_2CFH_2 \longrightarrow CF_3CH_2CF_2CFH_2 \text{ (H)} \quad (10)$$

$$\longrightarrow CF_3CH_3\text{(A}'\text{)} + CF_2{=}CFH \text{ (T)}$$

$$CF_3\dot{C}H_2 + CF_2H\dot{C}FH \longrightarrow CF_3CH_2CFHCF_2H \text{ (I)} \quad (11)$$

$$\longrightarrow CF_3CH_3\text{(A}'\text{)} + CF_2{=}CFH \text{ (T)}.$$

In order to estimate α and β, we assume that all radical Reactions 5—7 and 9—11 occur proportionally to the collision number of radicals and let R1, R2, and R3 denote $\dot{C}F_2CFH_2$, $CF_3\dot{C}H_2$ and $CF_2H\dot{C}FH$ radicals, respectively; then, we can obtain the following equations:

$$[R1] : [R2] : [R3] = \alpha(1-\beta) : \alpha\beta : 1-\alpha, \quad (I)$$

$$a \times [R1] = 2[J] + [H] + [K] + 2N_1 [E] + M_1[A'], \quad (II)$$

$$a \times [\mathrm{R2}] = [\mathrm{H}] + 2[\mathrm{D}] + [\mathrm{I}] + [\mathrm{A'}], \qquad \text{(III)}$$

$$a \times [\mathrm{R3}] = [\mathrm{K}] + [\mathrm{I}] + 2[\mathrm{L}] + 2N_2[\mathrm{E}] + M_2[\mathrm{A'}], \qquad \text{(IV)}$$

and $N_1 + N_2 = 1$ and $M_1 + M_2 = 1$.

Here a is a proportional constant. N_1 and N_2 are the relative amounts of product E produced through Reactions 6 and 7, respectively. Similarly, M_1 and M_2 are the relative amounts of product A′ produced through Reactions 10 and 11, respectively. These relative values may be expressed as follows:

$$N_1/N_2 = (1-\beta)/(1-\alpha)[\alpha^2(1-\beta) + 4\alpha(1-\alpha)]/[1-\alpha+4(1-\beta)], \text{ and} \qquad \text{(V)}$$

$$M_1/M_2 = \alpha(1-\beta)/(1-\alpha). \qquad \text{(VI)}$$

When two radicals, X and Y, are recombined at random, the relative amounts of products X_2, XY, and Y_2 can be expressed as $[XY]^2=4[X_2][Y_2]$. The amount of Compound L may be estimated by using the following equation from the amounts of Compounds J and K:

$$[\mathrm{L}] = [\mathrm{K}]^2/4[\mathrm{J}]. \qquad \text{(VII)}$$

Figure 3 shows the values of α and β calculated by using Eqs. I to VII as a function of the hydrogen pressure. Obviously, the α value was found to be 0.84, independent of the pressure (as it should be), while the β value was found to be pressure dependent (0.79 at 50 Torr and 0.50 at 750 Torr). This dependence may be explained by the competition between 1,2-fluorine-atom migration in the energy rich radical produced by a hydrogen atom addition reaction and a deactivation of this radical by a collision with a third body, mainly hydrogen molecules in the present system. Reactions 3 and 8 may be rewritten as follows:

$$\mathrm{H} + \mathrm{CF_2{=}CFH} \longrightarrow \dot{\mathrm{C}}\mathrm{F_2CFH_2}^*, \qquad (3')$$

$$\dot{\mathrm{C}}\mathrm{F_2CFH_2}^* \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftarrows}} \mathrm{CF_3}\dot{\mathrm{C}}\mathrm{H_2}^*, \qquad (8')$$

$$\dot{\mathrm{C}}\mathrm{F_2CFH_2}^* \xrightarrow{+\mathrm{M}} \dot{\mathrm{C}}\mathrm{F_2CFH_2}, \qquad (12)$$

$$\text{and } \mathrm{CF_3}\dot{\mathrm{C}}\mathrm{H_2}^* \xrightarrow{+\mathrm{M}} \mathrm{CF_3}\dot{\mathrm{C}}\mathrm{H_2}. \qquad (13)$$

Here, k_f and k_b are the rate constants of the forward and reverse isomerization reactions, and M denotes the third body.

A steady state treatment gives

$$(1-\beta)/\beta = k_\mathrm{f}/k_\mathrm{b} + (z/k_\mathrm{f})[\mathrm{M}]. \qquad \text{(VIII)}$$

Here, z is the collision number between a radical and a third body; $z=k_{12}=k_{13}$ is assumed. The value of z can be calculated from the collision diameters of the radical and a hydrogen molecule; σ(radical)≈σ(ethane)=3.54 A and (H_2)=2.57 A.[12] Figure 4 shows plots of $(1-\beta)/\beta$ as a function of the hydrogen pressure. Although the expected linearity is not so good, we can estimate $k_\mathrm{f}=2\times10^{10}\ \mathrm{s}^{-1}$ from the slope and $k_\mathrm{b}/k_\mathrm{f}$ to be 0.2 from the intercept; this corresponds to the equilibrium constant between two energy rich radicals, $\dot{\mathrm{C}}\mathrm{F_2CFH_2}^*$ and $\mathrm{CF_3}\dot{\mathrm{C}}\mathrm{H_2}^*$.

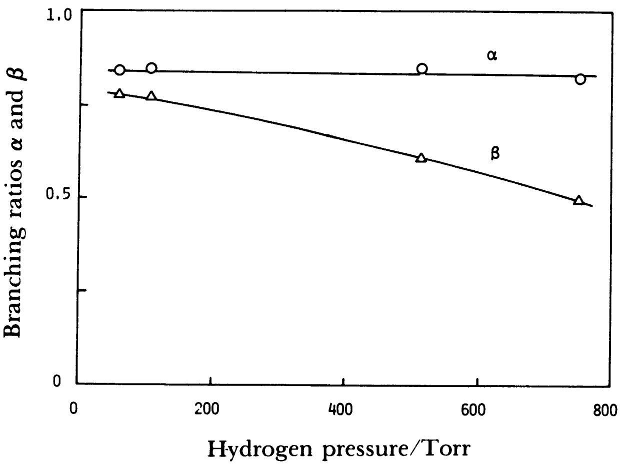

Fig. 3. The branching ratios α and β as functions of hydrogen pressure.

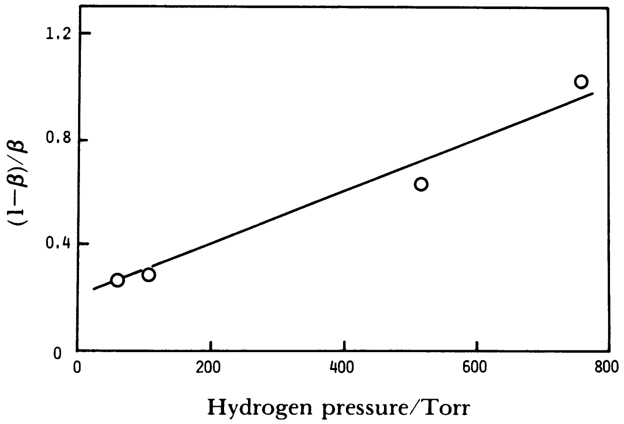

Fig. 4. The plots of $(1-\beta)/\beta$ as a function of hydrogen pressure.

In the above treatment, we ignored the reactions between radicals and the reactant olefin since if R1, R2, and R3 radicals have the same reactivity to the olefin, the above treatment for obtaining the relative ratios, α and β, are not affected by these reactions. Moreover, in this series of experiments, we did not observe the deposition of polymers on the wall of the reaction vessel. This suggests that the reactions leading to the formation of C_6 and/or heavier compounds may be ignored in the present system.

In this report, the 1,2-migration of a fluorine atom in the energy rich trifluoroethyl radical has been phenomenologically proved; however, as described in the Introduction, it is known that the 1,2-migration of a hydrogen atom in an ethyl radical does not occur under similar conditions, in spite of the fact that the binding energy of the C–F bond is usually larger than that of the C–H bond. We, therefore, carried out INDO molecular orbital calculations for these 1,2-migrations. The preliminary results showed that the fluorine atom migration is much easier than the hydrogen atom migration in partially fluorinated ethyl radicals.[8)] More extensive calculations are being undertaken.

Appendix

Molecule	Chemical shift[a)]	Coupling constant
	ppm	Hz
$C\overset{1}{F}_3C\overset{2}{H}_2CH_2CF_3$	(1) −86.7 (2) 2.4	
$C\overset{1}{F}_3C\overset{2}{H}_2C\overset{3}{F}_2C\overset{4}{H}_2\overset{5}{F}$	(1) −91.7 (2) 2.8 (3) −112.5 (4) 4.5 (5) −197.5	(1-2) 9.8 (2-3) 14.3 (1-3A) 8.79 (2-5) 2.1 (1-3B) 8.35 (3-4) 11.8 (1-5) 2.20 (3-5) 15.38 (4-5) 46.1
$C\overset{1}{F}_3C\overset{2}{H}_2C\overset{3}{H}\overset{4}{F}C\overset{5}{H}\overset{6}{F}_2$	(1) −90.2 (2) 2.5 (3) 4.8 (4) −171.8 (5) 5.8 (6A) −136.2 (6B) −130.8	(1A-4) 7.03 (4-6B) 13.2 (1B-4) 6.58 (5-6) 54 (3-4) 55 (6A-6B) 280 (4-6A) 12.3
$C\overset{1}{H}_2\overset{2}{F}C\overset{3}{F}_2CF_2CH_2F$	(1) 4.6 (2) −212 (3) −115.6	(1-2) 46.4 (1-3) 12.1
$C\overset{1}{H}_2\overset{2}{F}C\overset{3}{F}_2C\overset{4}{H}\overset{5}{F}C\overset{6}{H}\overset{7}{F}_2$	(1) 4.5 (2) −194 (3A) −115 (4) 4.7 (3B) −122 (5) −172.9 (6) 6.0 (7) −131.4	(3A-3B) 286 (4-5) 46 (6-7) 54.6

a) Compounds used as standard for ^{19}F and ^{1}H atoms are trifluoroacetic acid and TMS, respectively. The solvent is $CDCl_3$.

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