injector and the extraction cell. Upon dispersal of the co-solvent into the sample matrix, however, the co-solvent/CO_2 ratio is decreased to the point where a single-phase system is formed. Upon the next addition of liquid co-solvent, the process repeats itself. Therefore, the extraction process is very similar to that process when liquid modifying solvent is added directly to the sample matrix in the open extraction cell prior to SFE.

Conclusions

The solvent modification apparatus developed in this work for the SFE system introduced the modifying solvents repeatedly and consistently to the sample matrix. Unlike a high-pressure pump, the extraction system did not have to be depressurized to flush the solvent lines when there were changes of the modifying solvents. With the aid of this modification apparatus, it was possible to investigate a range of modifying co-solvents with repetitive delivery of the modifying solvent at desired intervals.

The addition of polar organic modifying solvents to supercritical CO_2 enhanced the recoveries of the target analytes, carbaryl and the $Cu(acac)_2$ complex. The most critical factor in the SFE process is to decrease the matrix/analyte interaction and increase the partition ratio to the supercritical fluid. The action of the modifying solvent appears to be competition with the analyte for sorption sites on the matrix. Work is under way to investigate means of identifying the optimum solvent or mixture of solvents for any analyte/matrix combination encountered.

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The Synthesis of Trifluoromethylated 1,2-Diphenylvinyl Sulfone and It's Synthetic Utilities

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The treatment of 1,1-bis(phenylthio)-2,2,3,3,3-pentafluoropropylbenzene (**1**) with 2 equiv. of phenyllithium in THF at − 78 °C resulted in the formation of isomeric mixture (70 : 30) of trifluoromethylated 1,2-diphenylvinyl sulfide **2** in 87% yield. The further oxidation of **2** with *m*-chloroperbenzoic acid in methylene chloride afforded isomeric mixture (70 : 30) of trifluoromethylated 1,2-diphenylvinyl sulfone **3** in 87% yield. When **3** was reacted with carbon nucleophiles such as methyllithium, *n*-butyllithium, phenyllithium and lithium octylide, the corresponding addition-elimination adducts **4**, **5**, **6** and **7** were obtained in moderate to good yields. The reaction of **3** with 4 equiv. of tributyltin hydride in benzene at reflux temperature provided isomeric mixture (90 : 10) of trifluoromethylated 1,2-diphenylvinyl stannane **8** in 41% yield. The reaction of **8** with methyllithium in the presence of trimethylsilyl chloride gave isomeric mixtures (90 : 10) of trifluoromethylated 1,2-diphenylvinyl silane **9** in 88% yield. Finally, the treatment of **8** with Br_2 and I_2 resulted in the formation of isomeric mixtures (90 : 10) of trifluoromethylated 1,2-diphenylvinyl bromide **10** and iodide **11** in 72% and 90% yields, respectively.

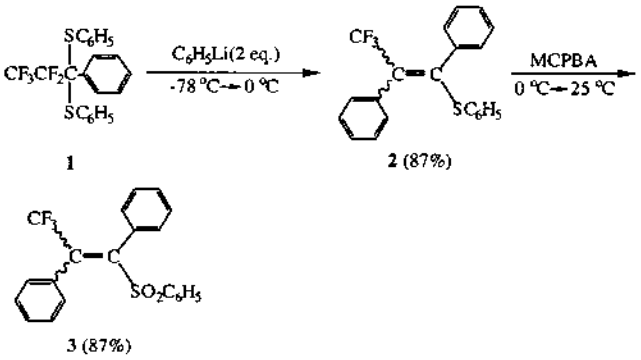
Introduction

Recently, considerable effort has been paid to the development of fluorine-containing synthetic building blocks[1-7] because of their potential to give new synthetic routes to a variety of fluoroorganic compounds, some of which exhibit unique biological properties in the areas of agrochemicals, pharmaceuticals and material science.[8-10] Of particular inter-

ests in this conjunction are trifluoromethylated building blocks for the synthesis of trifluoromethylated 1,2-diphenylethylene derivatives which have been much attention because of their potential mammary tumor inhibiting properties *via* binding to the estrogen receptor.[11] Although the numerous methods for the synthesis of trifluoromethylated compounds have been developed in last two decades,[12,13] there is only one report on the synthesis of trifluoromethylated 1,2-diphenylethylene derivative.[11] However, this method has some limitations such as lack of generality and low yields. As an alternative approach to overcome these synthetic drawbacks, we decided to use trifluoromethylated 1,2-diphenylvinyl sulfone which is a new type of trifluoromethylated building block. In this paper, we wish to describe about the preparation of trifluoromethylated 1,2-diphenylvinyl sulfone and a variety of trifluoromethylated 1,2-diphenylethylene derivatives *via* synthetic transformation of trifluoromethylated 1,2-diphenylvinyl sulfone.

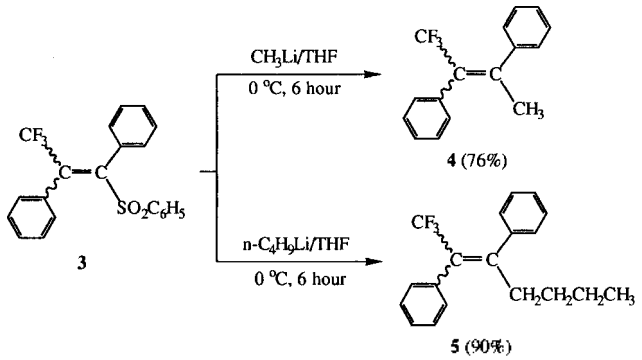
Results and Discussion

In order to prepare trifluoromethylated 1,2-diphenylvinyl sulfone, pentafluoroethylated dithioketal was used as a starting material. Recently, we have developed a general and efficient method for the preparation of perfluorinated dithioketals.[14] Therefore, 1,1-bis(phenylthio)-2,2,3,3,3-pentafluoropropylbenzene (**1**) can be prepared in 60% yield from the reaction of 1 equiv. of pentafluoroethyl phenyl ketone with 2 equiv. of thiophenol in the presence of 1 equiv. $AlCl_3$ at −78 °C for 20 h. The reaction of **1** with 2 equiv. of phenyllithium at −78 °C, followed by warming to 0 °C, afforded the isomeric mixture (70 : 30, E and *Z* can not be determined) of trifluoromethylated diphenylvinyl sulfides **2** in 87% yield. The reaction pathway seems likely that the initial attack on sulfur atom by phenyllithium provides a carbanion bearing the pentafluoroethyl group, which quickly undergoes *β*-defluorination to give *β*-fluoro-*β*-trifluoromethylvinyl sulfide. This reactive vinyl sulfide quickly undergoes the addition-elimination reaction with phenyllithium presented in solution as soon as it was formed. Further oxidation reaction of **2** with *m*-chloroperbenzoic acid provided the isomeric mixture (70 : 30, *E* and *Z* can not be determined) trifluoromethylated 1,2-diphenylvinyl sulfone **3** in 87% yield.

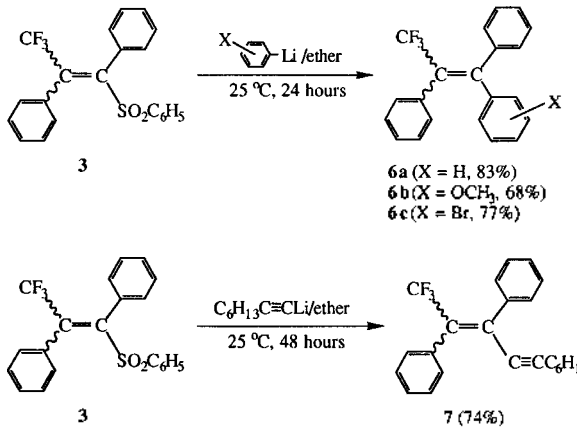


1 2 (87%) 3 (87%)

With a convenient route to the trifluoromethylated diphenylethylene derivatives, we decided to examine the possibility of addition-elimination pathway of trifluoromethylated diphenylvinyl sulfones **3** with alkyllithium, phenyllithium and lithium acetylide. Thus, the reaction of trifluoromethylated diphenylvinyl sulfones **3** with methyllithium at 0 °C in THF provided *E* and *Z* isomeric mixtures (*E* : *Z* = 66 : 34) of 1,1,1-trifluoro-2,3-diphenyl-2-butene (**4**) in 76% yield. The chemical shift of CH_3 group in ^{1}H NMR of **4** may assist the geometry assignment, but not the most useful diagnosis. Generally, the CH_3 protons which are arranged to the same side with benzene ring are more shielded than those arranged to the other side.[15] The more useful diagnosis for the analysis of *E* and *Z* isomer of **4** is to use H-F coupling constant between CF_3 and CH_3 group. The *cis* coupling constant is bigger than *trans* coupling constant. Similarly, the treatment of **3** with *n*-butyllithium under the same reaction condition resulted in the formation of *E* and *Z* isomeric mixture (*E* : *Z* = 57 : 43) of 1,1,1-trifluoro-2,3-diphenyl-2-heptene (**5**) in 90% yield.

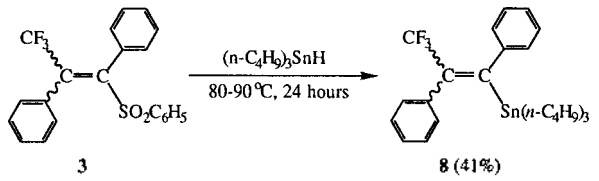


The reactions of **3** with phenyllithium derivatives also provided 3,3,3-trifluoro-1,1,2-triphenylpropene derivatives **6** in good yields. For example, the treatment of **3** with 4-methoxyphenyllithium resulted in the formation of **6b** (*E* : *Z* = 35 : 65) in 68% yield. Assignment of the isomer **6b** was established by the chemical shift of the methoxy group in ^{1}H NMR.[15] When **3** was reacted with lithium octylide at room temperature for 48 h, isomeric mixture (92 : 8, *E* and *Z* can not be determined) of 1,1,1-trifluoro-2,3-diphenyl-2-undecen-4-yne (**7**) in 74% yield.



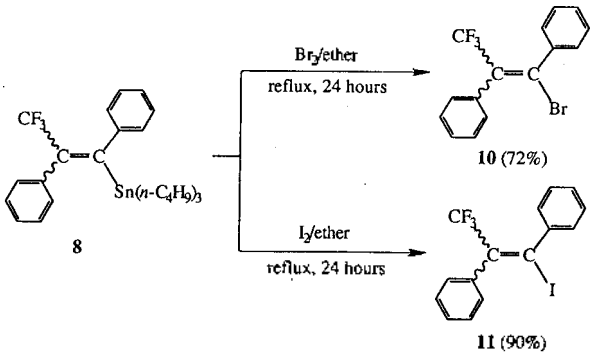
The carbon-carbon bond formation and functionalization at the vinyl carbon *via* addition-elimination reaction of **3** with organolithium reagents has some limitations. Thus, we decided to transform the sulfone group to more easily functionalized group such as stannane functionality. The treatment of **3** with 4 equiv. of tributyltin hydride at 80-90 °C for 24 h resulted in the formation of isomeric mixture (90 : 10, *E* and *Z* can not be determined) of trifluoromethylated 1,

2-diphenylvinylstannane **8** in 41% yield. The reduction product was always obtained in around 30% yield. The variation of dosage of tributyltin hydride in this reaction did not improve the formation of **8**.



3 **8** (41%)

In order to functionalize vinyl stannane compound, **8** was reacted with n-butyllithium at low temperature, followed by the quench with benzaldehyde. However, the desired carbonyl addition product was not observed, but only starting material was recovered. When this reaction was performed with methyllithium instead of n-butyllithium at 0 °C, a small amount of carbonyl addition product was detected in MS spectroscopy. This result indicates that methyllithium is much effective to generate trifluoromethylated 1,2-diphenylvinyl carbanion from **8**. Thus, the reaction of **8** with methyllithium in the presence of trimethylsilyl chloride at 0 °C gave the corresponding vinyl silane **9** (90 : 10, *E* and *Z* can not be determined) in 88% yield. Trifluoromethylated 1, 2-diphenylvinyl carbanion seem to be unstable species at 0 °C.



8

The halogenation reactions of **8** with Br_2 and I_2 in ether at reflux temperature for 24 h afforded 1-bromo-3,3,3-trifluoro-1,2-diphenyl-1-propene (**10**) and 1-iodo-3,3,3-trifluoro-1,2-diphenyl-1-propene (**11**) in 72% and 90% yields, respectively. Although the stereochemistry could not be determined in these reactions, the isomeric ratio was not changed.

Experimental

General. ^1H NMR spectra were recorded on a 100 MHz Bruker AC-100F NMR Spectrometer with tetramethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were recorded on a 100 MHz Bruker AC-100F NMR spectrometer. $CFCl_3$ was used as an internal standard and chemical shifts are reported in parts per million. Infrared spectra were determined on a Mattson Genesis series FT High Resolution Spectrophotometer. Mass spectra were obtained on Hewlett-Packard 5890 GC/5970B MSD (EI, 70 eV). Melting points were determined in open capillary tubes and are uncorrected.

Commercially available reagents were purchased from Aldrich, PCR and Tokyo Kasei. All solvents were dried by general purification method.

1,1-Bis(phenylthio)-2,2,3,3,3-pentafluoropropylbenzene (1). A 500 mL 3-neck round bottom flask equipped with a septum, a solid addition tube filled with $AlCl_3$ (2.67 g, 0.02 mol), a magnetic stir bar and a nitrogen tee connected to a source of nitrogen was charged with pentafluoroethyl phenyl ketone (4.48 g, 0.02 mol), thiophenol (4.40 g, 0.04 mol) and 200 mL dry CH_2Cl_2. The reaction mixture was cooled to −78 °C by using dry-ice/isopropanol slush and $AlCl_3$ was added in several portions *via* a solid addition tube. After stirring at −78 °C for 20 h, the reaction mixture was quenched with water at −78 °C. The mixture was poured into 150 mL of water and extracted with CH_2Cl_2 (300 mL×2). After washing with saturated NaCl water solution, CH_2Cl_2 layer was dried with anhydrous Na_2CO_3. Column chromatography (hexane) provided 5.11 g (60% yield) of **1**: mp 60-61 °C; ^1H NMR ($CDCl_3$) δ 7.80-7.18 (m, 15H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −74.85 (s, 3F), −103.62 (s, 2F); MS, m/z (relative intensity) 426 (M^+, 2), 317 (100), 165 (15), 71 (17), 58 (41); IR (KBr) 3010, 1210, 1170, 750, 690 cm^{-1}.

3,3,3-Trifluoro-1,2-diphenyl-1-phenylthiopropene (2). A 100 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with **1** (4.26 g, 0.01 mol) and 30 mL dry THF. The reaction mixture was cooled to −78 °C and then phenyllithium 11.5 mL (0.02 mol, 1.8 M solution in cyclohexane-ether) was added dropwise at −78 °C. The reaction mixture was allowed to warm to 0 °C and then quenched with 5% HCl solution. After extraction with ether (30 mL×2) and drying with anhydrous $MgSO_4$, column chromatography (hexane) provided 3.10 g (87% yield) of **2** (isomeric ratio = 70 : 30): oil; ^1H NMR ($CDCl_3$) δ 7.52-7.32 (m, 5H), 7.29-6.91 (m, 10H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −55.49 (s, 3F, one isomer), −56.21 (s, 3F, other isomer); MS, m/z (relative intensity) 356 (M^+, 100), 287 (15), 247 (74), 227 (97), 178 (24), 121 (22); IR (neat) 3058, 1605, 1583, 1309, 1238, 1159, 1114, 750, 707 cm^{-1}.

3,3,3-Trifluoro-1,2-diphenyl-1-phenylsulfonylpropene (3). A 50 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with **2** (1.07 g, 0.003 mol) and 10 mL dry CH_2Cl_2. The reaction mixture was cooled to 0 °C and then *m*-chloroperoxybenzoic acid (2.07 g, 0.006 mol, 50% technical grade) was added at 0 °C. The reaction mixture was stirred at 0 °C for 5 hours and then washed with saturated $NaHCO_3$ and 10% $NaHSO_3$. After extraction with CH_2Cl_2 (30 mL×2) and drying with anhydrous $MgSO_4$, column chromatography (hexane : ethyl acetate = 4 : 1) provided 1.02 g (87% yield) of **3** (isomeric ratio = 70 : 30): mp 149-150 °C; ^1H NMR ($CDCl_3$) δ 7.68-7.26 (m, 10H), 7.15-6.71 (m, 5H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −53.01 (s, 3F, one isomer), −54.05 (s, 3F, other isomer); MS, m/z (relative intensity) 388 (M^+, 3), 263 (23), 247 (100), 227 (56), 178 (18); IR (KBr) 3058, 1490, 1444, 1302, 1252, 1167, 1124, 1087, 1052, 978, 748, 703 cm^{-1}.

1,1,1-Trifluoro-2,3-diphenyl-2-butene (4). A 25 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with **3** (0.10 g, 0.26 mmol) and 5 mL dry THF. The reaction mixture was cooled to 0 °C and then methyllithium (0.52 mL, 0.78 mmol, 1.5 M

solution/LiBr) was added at 0 °C. After the reaction mixture was stirred at 0 °C for 6 hours, the mixture was extracted with ether (30 mL×2) and dried with anhydrous $MgSO_4$. Column chromatography (hexane) provided 0.052 g (76% yield) of **4** (*E* : *Z* = 66 : 34): oil; ^{1}H NMR ($CDCl_3$) δ 7.39-7.19 (m, 10H, one isomer), 7.10-6.82 (m, 10H, other isomer), 2.31 (q, *J*=2.3 Hz, 3H, E isomer), 1.80 (q, *J*=2.2 Hz, 3H, Z isomer); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −56.28 (s, 3F, *Z* isomer), −56.69 (s, 3F, *E* isomer); MS, m/z (relative intensity) 262 (M^+, 100), 247 (41), 227 (42), 193 (62), 178 (83), 165 (15), 115 (48), 91 (16), 77 (23), 51 (19).

1,1,1-Trifluoro-2,3-diphenyl-2-heptene (5). A 25 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with **3** (0.10 g, 0.26 mmol) and 5 mL dry THF. The reaction mixture was cooled to 0 °C and then n-butyllithium (0.31 mL, 0.78 mmol, 2.5 M solution) was added at 0 °C. After the reaction mixture was stirred at 0 °C for 6 hours, the mixture was extracted with ether (30 mL×2) and dried with anhydrous $MgSO_4$. Column chromatography (hexane) provided 0.071 g (90% yield) of **5** (*E* : *Z* = 57 : 43): oil; ^{1}H NMR ($CDCl_3$) δ 7.44-7.25 (m, 10H, one isomer), 7.14-6.87 (m, 10H, other isomer), 2.75-2.65 (m, 2H, *E* isomer), 2.15-2.08 (m, 2H, *Z* isomer), 1.43-1.26 (m, 4H, *E* isomer), 1.20-1.01 (m, 4H, *Z* isomer), 0.92 (t, *J*=7.1 Hz, 3H, *E* isomer), 0.65 (t, *J*=7.1 Hz, 3H, *Z* isomer); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −55.99 (s, 3F, *E* isomer), −56.22 (s, 3F, *Z* isomer); MS, m/z (relative intensity) 304 (M^+, 37), 261 (21), 248 (9), 221 (9), 191 (18), 183 (100), 133 (14), 115 (15), 91 (31), 77 (13), 41 (13).

3,3,3-Trifluoro-1-(4'-methoxyphenyl)-1,2-diphenylpropene (6b). To a ether (5 mL) solution of 4-iodoanisole (0.702 g, 3.0 mmol) was added *n*-BuLi (2.5 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 30 min. under argon atmosphere. The solution of **3** (0.194 g, 0.5 mmol) dissolved in ether (1 mL) was added and then the reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was treated with aqueous HCl solution (3%) and extracted with ether twice. The ether solution was dried and chromatographed on SiO_2 column. Elution with hexane provided 0.60 g (68% yield) of **6b** (*E* : *Z* = 35 : 65): mp 97-99 °C; ^{1}H NMR ($CDCl_3$) δ 7.32-6.49 (m, 14H), 3.70 (s, 3H, *Z* isomer), 3.63 (s, 3H, *E* isomer); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −55.86 (s, 3F, *E* isomer), −56.15 (s, 3F, *Z* isomer); MS, m/z (relative intensity) 354 (M^+, 100), 285 (12), 270 (17), 253 (16), 195 (19), 165 (14), 157 (12), 119 (12); IR (KBr) 3097, 2956, 1737, 1606, 1505, 1487, 1305, 1250, 1200, 1171, 1100, 1020, 810, 750, 690 cm^{-1}.

1,1,1-Trifluoro-2,3-diphenyl-2-undecen-4-yne (7). A 25 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with 1-octyne (0.15 g, 1.30 mmol) and 5 mL dry ether. The reaction mixture was cooled to 0 °C and then n-butyllithium (0.52 mL, 1.30 mmol, 2.5 M solution) was added at 0 °C, followed by stirring for 30 min. The THF solution (1 mL) of **3** (0.10 g, 0.26 mmol) was added to the reaction mixture. After the reaction mixture was stirred at room temperature for 48 hours, the mixture was quenched with water, extracted with ether (30 mL×2) and dried with anhydrous $MgSO_4$. Column chromatography (hexane) provided 0.068 g (74% yield) of **7** (isomeric ratio = 92 : 8): oil; ^{1}H NMR ($CDCl_3$) δ 7.37-7.32 (m, 10H, one isomer), 7.18-6.97 (m, 10H, other isomer), 2.38 (t, *J*=6.1 Hz, 2H, one isomer), 1.47-1.04 (m, 8H, one isomer), 0.82 (t, *J*=6.1 Hz, 3H, one isomer); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −55.67 (s, 3F, one isomer), −59.64 (s, 3F, other isomer); MS, m/z (relative intensity) 356 (M^+, 21), 285 (43), 272 (53), 265 (29), 217 (39), 215 (100), 202 (50), 189 (12), 165 (7), 127 (8), 97 (18), 91 (22), 115 (15), 55 (40), 41 (33).

1-Tributyltin-3,3,3-trifluoro-1,2-diphenylpropene (8). A 25 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with **3** (0.388 g, 1.00 mmol), tributyltin hydride (1.165 g, 4 mmol), AIBN (10 mol%) and 10 mL dry benzene. The reaction mixture was heated to 80-90 °C for 24 h. After the reaction mixture was cooled to room temperature, benzene was removed. Column chromatography (hexane) provided 0.20 g (41% yield) of **8** (isomeric ratio = 90 : 10): oil; ^{1}H NMR ($CDCl_3$) δ 7.35-6.60 (m, 10H), 1.67-1.16 (m, 27H, one isomer), 1.00-0.52 (m, 27H, other isomer); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −56.04 (s, 3F, one isomer), −62.03 (s, 3F, other isomer); MS, m/z (relative intensity) 481 (M^+-56, 13), 461 (35), 347 (13), 227 (16), 209 (100), 177 (14), 41 (20); IR (neat) 3025, 2985, 1300, 1133, 1107, 697 cm^{-1}.

3,3,3-Trifluoro-1-trimethylsilyl-1,2-diphenylpropene (9). A 25 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with **8** (0.200 g, 0.37 mmol), trimethylsilyl chloride (0.109 g, 1.0 mmol) and 5 mL dry THF. The reaction mixture was cooled to 0 °C and then methyllithium (0.4 mL, 0.60 mmol). After the reaction mixture was stirred at 0 °C for 30 min., the mixture was quenched with water, extracted with ether (10 mL×2) and dried with anhydrous $MgSO_4$. Column chromatography (hexane) provided 0.104 g (88% yield) of **9** (isomeric ratio = 90 : 10): oil; ^{1}H NMR ($CDCl_3$) δ 7.39-6.66 (m, 10H), 0.15-0.07 (m, 9H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.90 (s, 3F, one isomer), −66.38 (s, 3F, other isomer); MS, m/z (relative intensity) 320 (M^+, 22), 305 (19), 227 (100), 209 (59), 178 (48), 152 (10), 127 (8), 77 (41), 73 (35); IR (neat) 3024, 2957, 2924, 1488, 1443, 1307, 1254, 1160, 1116, 992, 863, 756, 701 cm^{-1}.

1-Bromo-3,3,3-trifluoro-1,2-diphenylpropene (10). A 25 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with **10** (0.100 g, 0.19 mmol), bromine (0.127 g, 0.76 mmol) and 5 mL dry ether. The reaction mixture was heated to reflux for 12 hours. After the reaction mixture was cooled to room temperature, the remained bromine was removed with $NaHSO_3$ solution, extracted with ether, and dried with anhydrous $MgSO_4$. Column chromatography (hexane) provided 0.044 g (72% yield) of **10** (isomeric ratio = 90 : 10): oil; ^{1}H NMR ($CDCl_3$) δ 7.43-7.10 (m, 10H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −56.68 (s, 3F, one isomer), −59.48 (s, 3F, other isomer); IR (neat) 3062, 2925, 1616, 1488, 1444, 1306, 1246, 1162, 1129, 750, 707 cm^{-1}.

3,3,3-Trifluoro-1-iodo-1,2-diphenylpropene (11). A 25 mL round bottom flask equipped with a rubber septum, stir bar and nitrogen tee was charged with **10** (0.100 g, 0.19 mmol), iodine (0.190 g, 0.76 mmol) and 5 mL dry ether. The reaction mixture was heated to reflux for 12 hours. After the reaction mixture was cooled to room temperature,

the remained iodine was removed with $NaHSO_3$ solution, extracted with ether, and dried with anhydrous $MgSO_4$. Column chromatography (hexane) provided 0.063 g (90% yield) of **11** (isomeric ratio = 90 : 10): oil; ^1H NMR ($CDCl_3$) δ 7.47-7.05 (m, 10H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −56.28 (s, 3F, one isomer), −60.03 (s, 3F, other isomer); MS, m/z (relative intensity) 374 (M^+, 34), 247 (100), 227 (67), 178 (17); IR (neat) 3059, 3029, 1607, 1487, 1443, 1301, 1232, 1166, 1444, 1126, 747, 702 cm^{-1}.

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Characteristics of the Low Frequency Sequence Bands Observed in the Vibronic Emission Spectra of the Jet Cooled *p*-Fluorobenzyl Radical in the $D_1 \rightarrow D_0$ Transition

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The *p*-fluorobenzyl radical was generated from the *p*-fluorotoluene and vibronically excited in a corona excited supersonic expansion with inert buffer gases. The vibronic emission spectra of the jet cooled *p*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition have been observed in the visible region. The spectra exhibit several low frequency sequence bands in the vicinity of the every strong vibronic band. The characteristics of the sequence bands have been examined by varying the experimental conditions such as carrier gas and nozzle size to identify the origin of the transition in the spectra.

Introduction

The identification of the transition states of the bands in the spectrum experimentally observed provides an important information on the molecular structure and motions.[1,2] Since the properties of the potential energy surface along the rotational and vibrational potential coordinate often largely change upon electronic excitation, it is very difficult to assign the correct quantum numbers to the weak transitions of large molecule from the spectra obtained in the visible/uv region. In order to solve this difficulty, many spectroscopists have often employed supersonic cooling which has played a critical role in simplifying the otherwise congested spectra that would result from the population of low energy levels.[3] For the better assignments of the transitions, on the other hand, reliable theoretical calculations may be carried out on such molecules. These calculations provides valuable information about potential energy surfaces in both ground and electronically excited states.[4]

Bindley *et al.*[5] obtained for the first time the vibronic emission spectra of *p*-fluorobenzyl radicals generated from the electric discharge of p-fluorotoluene and identified the origin band in the visible region. Also, Cossart-Magos and Cossart have made the provisional assignments on the low frequency sequence bands observed with the origin band in the gas phase discharge emission spectra of *p*-fluorobenzyl.[6] The first low resolution excitation spectrum of *p*-fluorobenzyl radical in the visible region was reported by Charlton and Thrush.[7] Although Fukushima and Obi[8] have recently observed many bands from the excitation spectra of *p*-fluorobenzyl radical at very low temperature, they could assign only strong vibronic bands, leaving many bands

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