January, 1989] *Bull. Chem. Soc. Jpn.*, **62**, *89—95 (1989)*

The Decomposition of Arenediazonium Tetrafluoroborates with Halo- and Azidotrimethylsilanes in Nonaqueous Solvents

Takashi Keumi,* Toshiaki Umeda, Yoshinori Inoue,† and Hidehiko Kitajima
Department of Applied Chemistry, Faculty of Engineering, Fukui University,
Bunkyo, Fukui 910
†Department of Industrial Chemistry, Shiga Prefectural Junior College,
Hassaka-cho, 1900, Hikone 522
(Received June 4, 1988)

The reaction of arenediazonium tetrafluoroborates with chlorotrimethylsilane in a tetrahydrofuran/*N*,*N*-dimethylformamide (DMF) (5v/3v) solution afforded the protodediazotization products in high yields. The reactions of the diazonium salts with halotrimethylsilanes in DMF were found to give the corresponding haloarenes. Among the halodediazotization reactions, the iododediazotization with iodotrimethylsilane proceeded smoothly at room temperature to give the iodoarenes in excellent yields. In a similar manner, a variety of azidoarenes were obtained in consistently high yields by the treatment of arenediazonium tetrafluoroborates with azidotrimethylsilane in a DMF solution.

The reaction of arenediazonium salts is among the first to be studied in organic chemistry, and it has since been extensively studied not only because of its fundamental importance but also because of its industrial importance.1) Arenediazonium halides, which are usually unstable, are prepared in situ by the diazotization of arylamines with sodium nitrite in an aqueous solution containing a mineral acid at a low temperature; subsequent reactions are immediately conducted in the same solution. The reactions carried out in the aqueous solution, however, frequently give rise to some by-products besides the desired products. For the purpose of lowering the amount of undesired products, there has been an attempt to use an isolated arenediazonium tetrafluoroborate salt in a nonaqueous medium. However, most of the tetrafluoroborate salts are too stable to be decomposed, and they are less soluble in organic solvents. Therefore, the decomposition of the diazonium salts has been performed by the addition of a strong base,2) metals such as powdered zinc,3) copper,4) and copper(I) oxide,5) or organometallic compounds, such as rhodium complexes6) and tributyltin hydride.7) Crown ether compounds,4) poly(ethylene glycol),8) or phase-transfer catalysts9) have been used to improve the low solubility of the diazonium salts in organic solvents.

We have found that arenediazonium tetrafluoroborates readily decompose in the presence of halo- and azidotrimethylsilanes in a *N*,*N*-dimethylformamide (DMF) solution to afford the corresponding reduction products or substituted arenes in satisfactory yields. We wish to report herein the protodediazotization and halodediazotization induced by halotrimethylsilanes. The preparation of azidoarenes by the reaction of arenediazonium tetrafluoroborates with azidotrimethylsilane will also be reported.

$$\mathrm{ArN_2BF_4} \xrightarrow[\text{in DMF}]{\mathrm{Me_3SiX}} \mathrm{ArY} \qquad (1)$$

$X = \mathrm{Cl, Br, I, N_3}$
$Y = \mathrm{H, Cl, Br, I, N_3}$

Results and Discussion

The decomposition of 2-fluorenediazonium tetrafluoroborate was attempted in the presence of chlorotrimethylsilane (CTMS) in organic solvents. The results are summarized in Table 1. The diazonium salt was readily decomposed in a tetrahydrofuran (THF) suspension in the presence of an equivalent of CTMS at 60 °C for 10 min to give fluorene in a 69% yield and a trace amount of 2-chlorofluorene. The evolution of nitrogen gas was completed within ten minutes at 60 °C. In contrast, the salt was stable under these conditions in the absence of CTMS. The protodediazotization product was obtained in only a 13% yield, even after the salt has been heated under reflux for 90 min in a THF medium. Therefore, CTMS appears to induce the decomposition of the diazonium tetrafluoroborate. The homogeneous reaction conducted in DMF, which dissolved the salt, did not improve the yield of the protodediazotization product. On using a DMF/THF combined medium, however, the product yield was remarkably increased. In an attempt to apply this procedure as a general method for a reductive dediazotization, some arenediazonium tetrafluoroborates were subjected to a decomposition reaction with CTMS in a solution of THF/DMF (5v/3v) at 60 °C for 1 h. The results are shown in Table 2. Consistently high yields of the reductive dediazotization product were observed in a variety of arenediazonium tetrafluoroborates.

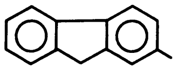
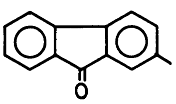
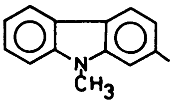
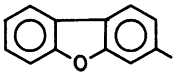
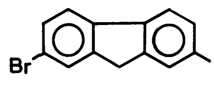
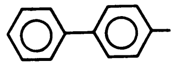
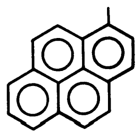
The decomposition of 2-fluorenediazonium tetrafluoroborate with halotrimethylsilanes in DMF or *N*,*N*-dimethylacetamide (DMA) was attempted in the presence of a halogenating reagent. The results are shown in Table 3. Although the reaction of 2-fluorenediazonium tetrafluoroborate with CTMS in DMF afforded only 2% of 2-chlorofluorene, the addition of *N*-chlorosuccinimide (NCS) to the reaction mixture increased the formation of the chloride to a 39% yield. In the reaction carried out in a solution of DMA/car-

Table 1. Protodediazotization of 2-Fluorenediazonium Tetrafluoroborate with Chlorotrimethylsilane (CTMS)[a]

Run	CTMS[c]	Solvent	Time min	Yield of fluorene[b] %
1	None	Tetrahydrofuran (THF)	10	4
2	None	THF	20	6
3	None	THF	90	13
4	1.2	THF	10	69
5	1.2	THF	20	74
6	1.2	THF	60	76
7	1.2	*N,N*-Dimethylformamide (DMF)	60	63
8	1.2	THF/DMF (1v/1v)	60	78
9	1.2	THF/DMF (5v/3v)	60	98

a) Carried out at 60 °C. b) Determined by GLC using dibenzofuran as the internal standard. c) Molar equivalents to the diazonium tetrafluoroborate.

Table 2. Protodediazotization of Arenediazonium Tetrafluoroborates with Chlorotrimethylsilane[a]

Run	Ar (of ArN_2BF_4)	Yield of ArH/%[b]	Mp θ_m/°C Found	Mp θ_m/°C Reported[10]
1		95	114—115	115—116
2		91	79—80	84—85
3		87	86—87	86—87
4		88	82—83	83—84
5		78	112	112—114
6		98	67—68	68—71
7		91	138—141	149—153

a) All the reactions were carried out in a solution of THF/DMF (5v/3v) in the presence of 1.2 equivalents of chlorotrimethylsilane at 60 °C for 1 h. b) Isolated yield.

bon tetrachloride in the presence of NCS, the yield of the chloride was increased to 59%. Similarly, the diazonium salt was decomposed with bromotrimethylsilane in the presence of *N*-bromosuccinimide (NBS) in a DMA solution to give 2-bromofluorene in a 71% yield, while the decomposition without NBS gave the bromide and the reduction products in 41% and 51% yields respectively.

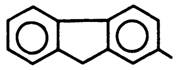
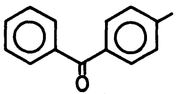
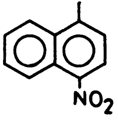
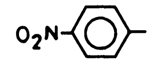
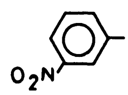
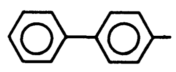
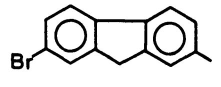
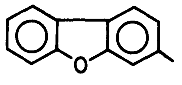
On the other hand, the drop-by-drop addition of iodotrimethylsilane to a solution of 2-fluorenediazonium tetrafluoroborate in DMF violently evolved nitrogen gas at room temperature to give 2-iodofluorene and the reduction product in 55% and 30% yields respectively. The addition of iodomethane into the reaction mixture increased the fomation of 2-iodofluorene. The yield of the iodide increased with an increase in the amount of iodomethane added. Finally, 2-iodofluorene was obtained in a 98% yield in the reaction using a medium of iodomethane mixed with a minimum amount of DMF to dissolve the diazonium salt.

Table 3. Halodediazotization of 2-Fluorenediazonium Tetrafluoroborate with Halotrimethylsilane (X-TMS, X=Halide)[a]

Run	X	Additives (Molar equiv)	Solvent	Temp/°C	Product yield/%[b] 2-X-Fluorene	Fluorene
1	Cl	—	DMF	60	2	63
2	Cl	*N*-Chlorosuccinimide (NCS) (3)	DMF	60	39	41
3	Cl	NCS (3)	DMF/CCl_4 (lv/lv)	60	37	36
4	Cl	NCS (3)	DMA[c]/CCl_4 (lv/lv)	60	59	35
5	Br	—	DMF	60	41	51
6	Br	*N*-Bromosuccinimide (NBS) (1.5)	DMF	60	67	13
7	Br	NBS (3)	DMA	60	71	12
8	I	—	DMF	RT[d]	55	30
9	I	Methyl iodide (MI) (1.5)	DMF	RT	62	23
10	I	MI (3)	DMF	RT	77	13
11	I	MI (3)	DMA	RT	75	11
12	I	MI (33)	DMF	RT	98	Trace

a) Carried out with 1.2 equivalents of halotrimethylsilane. b) Determined by GLC using dibenzofuran as the internal standard. c) *N*,*N*-Dimethylacetamide. d) Room temperature.

Table 4. Iododediazotization of Arenediazonium Tetrafluoroborates with Iodotrimethylsilane[a]

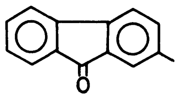
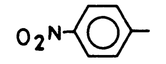
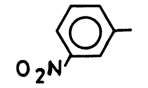
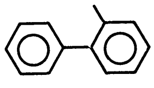
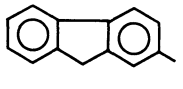
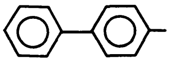
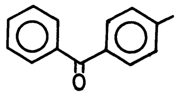
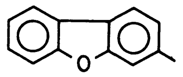
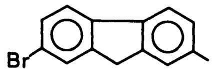
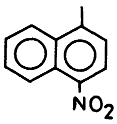
Run	Ar (of ArN_2BF_4)	Yield/%[b]	Mp θ_m/°C Found	Reported
1		95	127—128	128[11]
2		96	99—100	100—101[10]
3		93	122—123	123[10]
4		91	171—172	174[10]
5		96	34—35	39[10]
6		97	112—113	113—114[10]
7		93	177—178	—
8		95	143—145	—

a) All the reactions were carried out in a solution of DMF/CH_3I in the presence of 1.2 equivalents of iodotrimethylsilane at room temperature for 1 h. b) Isolated yields.

This reaction procedure was also applied to the preparation of iodoarenes. Using the optimized conditions defined above, a variety of arenediazonium tetrafluoroborates were converted into the corresponding iodoarenes. The results are summarized in Table 4. 4-Iodobenzophenone, 1-iodo-4-nitronaphthalene, 4-iodo- and 3-iodo-1-nitrobenzenes, 4-iodobiphenyl, 7-bromo-2-iodofluorene, and 3-iododibenzofuran were obtained in excellent yields by this method.

When azidotrimethylsilane dissolved in DMF was

Table 5. Preparation of Azidoarenes by the Reaction of Arenediazonium Tetrafluoroborates with Azidotrimethylsilane[a]

Run	Ar (of ArN_2BF_4)	Yield/%[b]	Mp θ_m/°C	
			Found	Reported
1		99	114—115	117[12]
2		86	70—71	70—71[13]
3		77	53—54	52[13]
4		90	49—50	49—50[14]
5		95	103—104	—
6		99	74—75	—
7		92	70—71	—
8		94	115—116	—
9		91	129—130	—
10		95	96—97	—

a) All the reactions were carried out in a solution of DMF in the presence of 1.2 equivalents of azidotrimethylsilane at room temperature for 1 h. b) Isolated yields.

added to a solution of 2-fluorenediazonium tetrafluoroborate in DMF at room temperature, nitrogen gas was immediately evolved to give 2-azidofluorene in an almost pure form in a 95% yield. No significant amount of the reduction product was observed. A variety of arenediazonium tetrafluoroborates were then reacted with azidotrimethylsilane in the DMF solution at room temperature. The yields and melting points of isolated azidoarenes are summarized in Table 5.

In all the cases examined here, the corresponding azidoarenes were obtained in satisfactory yields. The products, 2-azidofluorene, 4-azidobiphenyl, 4-azidobenzophenone, 3-azidodibenzofuran, 2-azido-7-bromofluorene, and 1-azido-4-nitronaphthalene, are new compounds. The IR spectra of these azides show the characteristic absorption peaks at 2180—2270 cm^{-1} due to the azide function. Their ^{1}H NMR spectral data are consistent with the desired structure.

Thus, halotrimethylsilanes (Cl, Br, I as the halide) and azidotrimethylsilane have been found to facilitate the decomposition of arenediazonium tetrafluoroborates to give the protodediazotization products or the corresponding haloarenes and azidoarenes. The acceleration effects of the trimethylsilyl compounds on the decomposition of 2-fluorenediazonium tetrafluoroborate in a DMF solution were in the sequence of: azido->iodo->bromo->chlorotrimethylsilanes. The ratio of halogenation to reduction products in the decomposition with halotrimethylsilanes was increased with the order of: iodo->bromo->chlorotrimethylsilanes. According to the Hard and Soft Acids and Bases (HSAB) principle developed by Pearson,[15] the trimethylsilyl cation belongs to a hard acid group, while the halide ions, Br^- and I^-, and the azide ion, N_3^-, are classified as soft bases, the softness order being; $I^- > N_3^- > Br^- > Cl^-$. On the other hand, the tetrafluoroborate ion seems to be a hard base,[16] accounting for its good affinity to a hard acid, the trimethylsilyl cation. When CTMS is added to a solution of arenediazonium tetrafluoroborate in DMF, the hard acid species, the trimethylsilyl cation, would catch the hard-base anion, BF_4^-, to result in the formation of fluorotrimethylsilane, boron trifluoride, and arenediazonium chloride. This resultant diazonium chloride is usually less stable than the starting diazonium tetrafluoroborates, so it readily decomposes to give the corresponding chloroarenes or reduction products. The decomposition in the presence of the chlorinating reagent NCS increased the formation of chloroarenes. The addition of THF to the reaction medium DMF also remarkably increased the formation of the protodediazotization product. The decomposition appears to proceed by means of a radical mechanism. The decomposition with bromo-, iodo-, and azidotrimethylsilanes would also proceed by means of a process similar to that described above (Eqs. 2 and 3). The formation of fluorotrimethylsilane and boron trifluoride as well as the substituted arene was confirmed by ^{1}H NMR measurements of the reaction mixture of benzenediazonium tetrafluoroborate and azidotrimethylsilane in DMF/deuteriochloroform solutions. The full details of the confirmation will be given in the Experimental section.

$$ArN_2BF_4 + Me_3SiX \longrightarrow ArN_2X + Me_3SiF + BF_3 \quad (2)$$

$$ArN_2X \longrightarrow ArX + N_2 \quad (3)$$

The decompositions with iodo- and azidotrimethylsilanes proceed much more smoothly than that with CTMS. This may be due to the ease of both the exchange of the counter anion and the decomposition of the resultant diazonium salts.

In conclusion, halo- and azidotrimethylsilanes were found to be effective for the decomposition of arenediazonium tetrafluoroborates, which are usually difficult to decompose. Reduction products and haloarenes were obtained in satisfactory yields by the reaction of arenediazonium tetrafluoroborates with halotrimethylsilanes in a DMF solution. Azidoarenes were obtained in excellent yields by the reaction of arenediazonium tetrafluoroborates with azidotrimethylsilane. These reactions can be conducted in a DMF medium under mild conditions. There is no need to use any complex catalysts for the decompositions or any expensive additives to achieve dissolution in organic solvents. Thus, the reaction procedures described here will be useful for the preparation of arenes, haloarenes, and azidoarenes from arenediazonium tetrafluoroborates.

Experimental

Materials and Measurements. The melting points are uncorrected. The IR spectra were recorded on a Hitachi EPI-S2 model infrared spectrophotometer. The ^{1}H NMR spectra were recorded on a JEOL-FX 270 FT-NMR spectrometer in deuteriochloroform solutions, with teramethylsilane as the internal standard. GLC analysis was carried out on a Hitachi GC Model 163 gas chromatograph equipped with a hydrogen-flame ionization detector and a stainless steel column (length 3 m, i.d. 3 mm) packed with 3% Dexil 300 GC on Chromosorb W.

Preparation of Arenediazonium Tetrafluoroborates. All the diazonium salts were prepared by standard techniques (Ref. 17). The following salts have not been found in the above references. The yields, decomposition temperatures, and IR data for them are as follows.

1-Pyrenediazonium Tetrafluoroborate: 100% yield; mp 135—137 °C (decomp); IR (KBr) 2200, 1620, 1470, and 851 cm^{-1}.

9-Methyl-2-carbazolediazonium Tetrafluoroborate: 88% yield; mp 161—163 °C (decomp); IR (KBr) 2210, 1578, 1452, and 750 cm^{-1}.

3-Dibenzofurandiazonium Tetrafluoroborate: 69% yield; mp 160—163 °C (decomp); IR (KBr) 2260, 1626, 1432, 1200, and 750 cm^{-1}.

9-Oxo-2-fluorenediazonium Tetrafluoroborate: 89% yield; mp 159—162 °C (decomp); IR (KBr) 2275, 1723, 1608, 1590, and 765 cm^{-1}.

7-Bromo-2-fluorenediazonium Tetrafluoroborate: 90% yield; mp 139—140 °C (decomp); IR (KBr) 2230, 1591, 1170, and 818 cm^{-1}.

Protodediazotization Reactions. One procedure for the protodediazotization of 2-fluorenediazonium tetrafluoroborate is described as typical. Into a solution of 2-fluorenediazonium tetrafluoroborate (0.200 g; 0.714 mmol) in DMF (3 mL) cooled in an ice water bath, we added portion by portion a solution of CTMS (0.093 g; 0.857 mmol) in THF (5 mL) with stirring. After the mixture has then been heated at 60 °C with stirring for 1 h, it was poured into water. The resulting solid was filtered and washed with water to give fluorene (0.117 g; 98% yield; mp 104—107 °C). The recrystallization of the solid from ethanol gave a product with the mp of 114—115 °C (lit,[10] mp 115—116 °C).

Halodediazotization Reactions. The iododediazotization of 2-fluorenediazonium tetrafluoroborate will be described as a typical method. To a solution of iodotrimethylsilane (0.171 g; 0.857 mmol) and iodomethane (1.5 mL), we added drop by drop a solution of 2-fluorenediazonium tetrafluoroborate (0.200 g; 0.714 mmol) in DMF (1.5 mL) at room temperature under a nitrogen stream. After this addition, the mixture was stirred for 1 h at room temperature, poured into ice water, and then extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous sodium sulfate. After the evaporation of the solvent, crude 2-iodofluorene was obtained (0.198 g; 95% yield; mp 126—127 °C). The recrystallization of the product from 80% ethanol gave a product with the mp of 127—128 °C (lit,[11] mp 128 °C). In a similar manner, the following iodoarenes were prepared.

3-Iododibenzofuran: 95% yield; mp 143—144 °C (from 90% EtOH); IR (KBr) 1453, 1440, 1183, 868, 810, and 748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.32—7.70 (m, 5H) and 7.90—9.93 (m, 2H).

Found: C, 48.85; H, 2.38%. Calcd for $C_{12}H_7OI$: C, 49.01; H, 2.40%.

7-Bromo-2-iodofluorene: 93% yield; mp 177—178 °C (from EtOH); IR (KBr) 1452, 1393, 1003, and 802 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.85 (s, 2H, CH_2) and 7.47—7.87 (m, 6H).

Found: C, 41.83; H, 2.17%. Calcd for $C_{13}H_8BrI$: C, 42.09; H, 2.17%.

By means of a similar procedure, chlorodediazotization and bromodediazotization reactions of 2-fluorenediazonium tetrafluoroborates with CTMS and bromotrimethylsilane were carried out in the presence of NCS and NBS respectively.

Preparation of Azidoarenes. Into a solution of 2-fluorenediazonium tetrafluoroborate (0.200 g; 0.714 mmol) in DMF (1.5 mL), we dropped a solution of azidotrimethylsilane (0.099 g; 0.857 mmol) in DMF (1.5 mL) at room temperature. After the mixture has then been stirred for 1 h at that temperature, it was poured into ice water (about 100 mL). The resulting precipitate was filtered, washed with water, and dried to give 2-azidofluorene (0.14 g; 95% yield; mp 102—104 °C). The recrystallization of the solid from 80% ethanol gave a product with the mp of 103—104 °C; IR (KBr) 2200, 1580, 1450, 1289, and 761 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.88 (s, 2H, CH_2), 7.03 (d, J=3.0 Hz, 1H), 7.20 (s, 1H), 7.25—7.40 (m, 2H), 7.52 (d, J=8 Hz, 1H), and 7.72 (d, J=3 Hz, 2H).

Found: C, 75.54; H, 4.08; N, 20.19%. Calcd for $C_{13}H_9N_3$: C, 75.35; H, 4.38; N, 20.28%.

By a similar procedure, the following azidoarenes were prepared.

4-Azidobenzophenone: 92% yield; mp 70—71 °C (70% EtOH); IR (KBr) 2200, 1645, 1598, 1280, and 713 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.12 (d, J=3 Hz, 2H), 7.46—7.60 (m, 3H), 7.77 (d, J=3 Hz, 2H), and 7.85 (d, J=3 Hz, 2H).

Found: C, 69.95; H, 4.17; N, 18.51%. Calcd for $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82%.

1-Azido-4-nitronaphthalene: 95% yield; mp 96—97 °C (80% EtOH); IR (KBr) 2270, 1573, 1285, and 761 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.27 (d, J=3 Hz, 1H), 7.63 (t, J=3 Hz, 1H), 7.78 (t, J=3 Hz, 1H), 8.23 (d, J=3 Hz, 1H), 8.34 (d, J=3 Hz, 1H), and 8.68 (d, J=3 Hz, 1H).

Found: C, 56.42; H, 2.64; N, 25.85%. Calcd for $C_{10}H_6N_4O_2$: C, 56.08; H, 2.82; N, 26.16%.

4-Azidobiphenyl: 99% yield; mp 74—75 °C (80% MeOH); IR (KBr) 2200, 1485, 1290, 833, and 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.09 (d, J=3 Hz, 2H), 7.31—7.45 (m, 3H), and 7.54—7.59 (m, 4H).

Found: C, 73.60; H, 4.77; N, 21.37%. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52%.

3-Azidodibenzofuran: 94% yield; mp 115—116 °C (70% EtOH); IR (KBr) 2200, 1602, 1453, 1288, and 779 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.03 (dd, J=3, 0.7 Hz, 1H), 7.23 (d, J=0.7 Hz, 1H), 7.34 (td, J=3, 0.4 Hz, 1H), 7.44 (td, J=3, 0.5 Hz, 1H), 7.55 (d, J=3 Hz, 1H), and 7.89 (d, J=3 Hz, 2H).

Found: C, 69.21; H, 3.52; N, 20.00%. Calcd for $C_{12}H_7N_3O$: C, 68.89; H, 3.37; N, 20.09%.

2-Azido-7-bromofluorene: 91% yield; mp 129—130 °C (80% EtOH); IR (KBr) 2200, 1613, 1457, 1293, and 798 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.85 (s, 2H, CH_2), 7.03 (dd, J=3, 0.7 Hz, 1H), 7.18 (s, 1H), and 7.47—7.70 (m, 4H).

Found: C, 54.45; H, 2.53; N, 14.54%. Calcd for $C_{13}H_8BrN_3$: C, 54.57; H, 2.83; N, 14.69%.

Confirmation of the Formation of Fluorotrimethylsilane and Boron Trifluoride. To a solution of benzenediazonium tetrafluoroborate (0.003 g) in DMF/deuteriochloroform (2v/8v) (1 mL) containing tetramethylsilane, we added a few drops of azidotrimethylsilane at 0—5 °C. After gas evolution had ceased, the mixture was subjected to ^{1}H NMR measurement at 27 °C. The NMR spectrum showed singlet peaks at 8.28, 3.36, 3.17, and 0.068 ppm in addition to the peaks due to DMF [7.99 (s, 1H), 2.96 (s, 3H), 2.85 (s, 3H)], azidobenzene [7.36 (t, 2H, J=7.3 Hz), 7.14 (t, 1H, J=7.3 Hz), 7.03 (d, 2H, J=8.3 Hz)], and azidotrimethylsilane [0.27 (s)]. The former three singlets (in a relative intensity of 1:3:3) were identified with those due to the DMF–boron trifluoride complex by comparing them with those observed in the ^{1}H NMR spectrum of a mixture of DMF and ethyl ehter-boron trifluoride (1/1) in deuteriochloroform. The later singlet was identified as the peak due to fluorotrimethylsilane by being in accord with the chemical shift of that prepared from azidotrimethylsilane and KF in DMF/deuteriochloroform (2v/8v) solutions.

We wish to thank Fukui Chemical Industry Co. for its financial support of this work.

References

1) H. Zollinger, *Acc. Chem. Res.*, **6**, 335 (1973); H. Zollinger, *Angew. Chem., Int. Ed. Engl.*, **17**, 141 (1979); H. B. Ambroz and T. J. Kemp, *Chem. Soc. Rev.*, **8**, 353 (1979); Y. Hashida and S. Sekiguchi, *Yuki Gosei Kagaku Kyokai Shi*, **40**, 752 (1982).

2) P. R. Singh, B. Jayaraman, and H. K. Sing, *Chem. Ind.*, **1977**, 311.

3) A. Roe and J. R. Graham, *J. Am. Chem. Soc.*, **74**, 6297 (1952).

4) G. D. Hartman and S. E. Biffar, *J. Org. Chem.*, **42**, 1468 (1977).

5) A. H. Lewin and T. Cohen, *J. Org. Chem.*, **32**, 3844 (1967); S. H. Korzeniowski, L. Blum, and G. W. Gokel, *J. Org. Chem.*, **42**, 1469 (1977).

6) L. Toniolo and R. Eisenberg, *J. Chem. Soc., Chem. Commun.*, **1971**, 455; G. S. Max, *J. Org. Chem.*, **36**, 1725 (1971).

7) J. Nakayama, M. Yoshida, and O. Shimamura, *Tetrahedron*, **26**, 4609 (1970).

8) N. Suzuki, Y. Kaneko, T. Nomoto, and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, **1984**, 1523.

9) S. H. Korzeniowski, L. Blum, and G. W. Gokel, *Tetrahedron Lett.*, **1977**, 1871.

10) H. Heibron, "Dictionary of Organic Compounds," Maruzen, Tokyo (1965).

11) A. Korczynski, G. Karlowska, and L. Kierzek, *Bull. Soc. Chim.*, **41**, 65 (1927).

12) A. Korczynski and St. Namylsloniski, *Bull. Soc. Chim.*, **35**, 1186 (1924).

13) H. O. Spauschus and J. M. Scott, *J. Am. Chem. Soc.*,

73, 210 (1956).

14) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2438 (1951).

15) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963); T. L. Ho, "Hard and Soft Acids and Bases Principle in Organic Chemistry," Academic Press, New York (1977), p. 5.

16) The negative charge of the tetrafluoroborate ion seems to be located on the fluorine atom according to the electroneutrality principle of the central atom of complex ions (L. Pauling, "The Nature of the Chemical Bond," Cornell University Press (1960), p. 172). Therefore, the ion is classified as a hard-base group, like the perchlorate ion.

17) N. Kornblum, *Org. React.*, **2**, 262 (1944); A. Roe, *ibid.*, **5**, 193 (1949); M. P. Doyle and W. J. Bryker, *J. Org. Chem.*, **44**, 1572 (1979).