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<https://doi.org/10.15017/6661>

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出版情報：九州大学機能物質科学研究所報告. 8 (2), pp.231-243, 1995-03-01. Institute of Advanced  
Material Study Kyushu University

バージョン：

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# Synthesis and Properties of Poly((Perfluoroalkyl) sulfonyl)amides and Methanide Ions as New Types of Anionic Phase-Transfer Catalysts in Azo Coupling Reactions

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A series of lithium salts of bis((perfluoroalkyl) sulfonyl) amides (1) with different chain lengths of perfluoroalkyl group and tris((trifluoromethyl) sulfonyl) methanide (**TTM**) were prepared. The influence of the polyfluoroalkyl chain length of the imide ions on the solubility of their benzyltrimethylammonium salts in water and the partition coefficients ( $\alpha$ ) in dichloromethane/water system were discussed with respect to the applicability of these anions to new types of anionic phase-transfer catalysts. The catalytic activities of these anions were compared with **TFPB** anions in the azo coupling reactions of *p*-nitrobenzenediazonium ions with *N*-ethylcarbazole in dichloromethane/water and dichloromethane/solid two-phase systems.

In many chemical situations where two species are separated by an interface, the lack of activity has been overcome by using the phase transfer catalysis (PTC).<sup>1)</sup> We have developed and investigated the utilities of the anionic PTC reactions promoted by tetrakis (3,5-bis-(trifluoromethyl) phenyl) borate (**TFPB**) ions,<sup>2-3)</sup> in which **TFPB** ions catalyze the transfer of cationic reagents from the aqueous or solid phase to the organic phase. **TFPB** ions have high lipophilicity and chemical stability under acidic and oxidative PTC conditions.<sup>2d)4)</sup> Actually **TFPB** is a first example of effective anionic catalysts which have high lipophilicity and chemical stability under acidic and oxidative two-phase conditions. For example, the diazo coupling reactions of arenediazonium ions with various coupler components in dichloromethane/water two-phase system proceed smoothly in the presence of a catalytic amount of **TFPB** ions (Fig. 1).<sup>2a-2b)</sup>

In the course of our study on the functional organic fluorine compounds, we came to an idea to substitute the well investigated catalyst **TFPB** ions with polyfluorinated organic anions such as bis((perfluoroalkyl) sulfonyl) amides ions (1) and tris((trifluoromethyl)-sulfonyl) methanide ions (**TTM**).

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Received December 7, 1994

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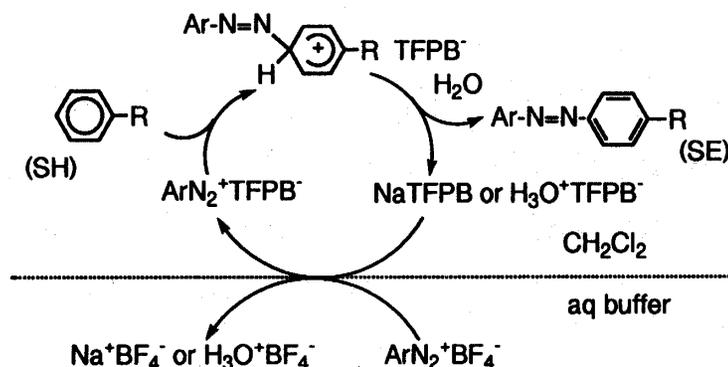
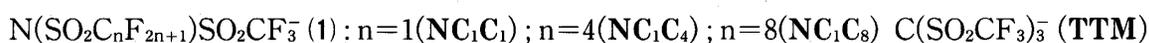


Fig. 1



These amides and methanides highly stabilized by a large number of trifluoromethylsulfonyl(triflyl) groups show characteristic physico-chemical properties, which are different from the corresponding triflates(trifluoromethanesulphonates). In a recent report by I. A. Koppel et al.<sup>5)</sup> on the relative gas phase acidities of perfluoroalkylsulfonyl-substituted carbon (CH), nitrogen(NH), and oxygen(OH) Brønsted acids, the multiple substitutions with triflyl groups in NH<sub>3</sub> and CH<sub>4</sub> have led to a reversal in the intrinsic acidity order, CH < NH < OH; CF<sub>3</sub>SO<sub>2</sub>OH < (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>NH < (CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>CH. The very strong acidity and the remarkable reversal in the intrinsic acidity are due to the intrinsic stability of the highly delocalized electronic structure of poly((perfluoroalkyl)sulfonyl)-substituted amide and methanide ions (Fig. 2).

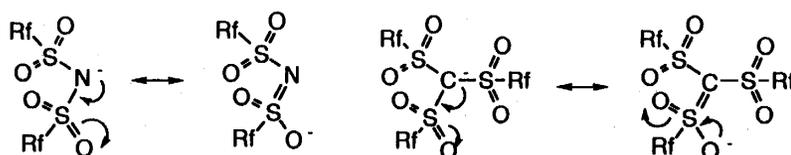


Fig. 2

Furthermore our studies on the Diels-Alder reactions catalyzed by the metal salts of the amides (1), and the methanide (**TTM**) revealed that the metal salts were highly soluble in dichloromethane compared to the corresponding metal triflate and the metal amides and methanide showed the remarkable Lewis acidities as shown in Fig. 3.<sup>6)</sup>

With special regard to a possible usage of the amides (1) and the methanide (**TTM**) ions as catalysts in the anionic PTC we investigated the effect of polyfluoroalkyl chain length of these amides on the solubility of their benzyltrimethylammonium salts in water and the partition coefficient ( $\alpha$ ) in dichloromethane/water two-phase system. On the basis of PTC

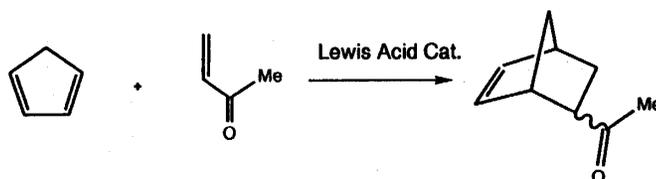


Fig. 3

**Table 1.** The Solubilities of Benzyltrimethylammonium Amides in Water at 25 °C.

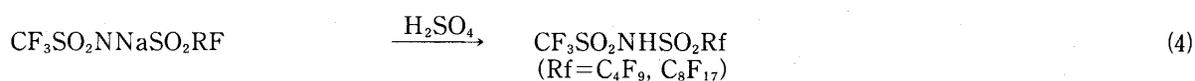
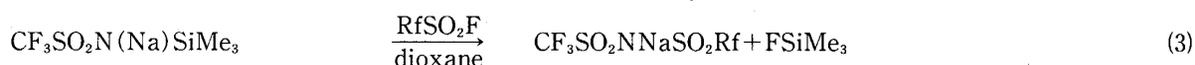
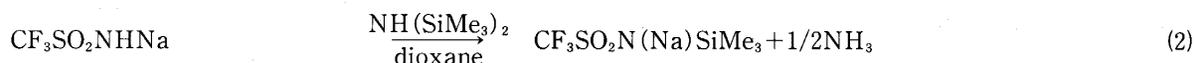
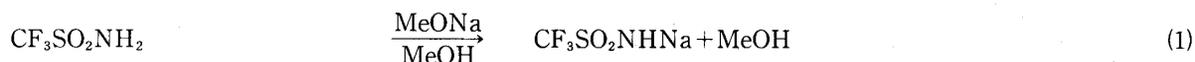
Amides (Tf=SO <sub>2</sub> CF <sub>3</sub> )	$\lambda$ max /nm	Absorb.	Conc. $\times 10^3/\text{mol l}^{-1}$	Conc. (average) $\times 10^3/\text{mol l}^{-1}$
NTf <sub>2</sub> (NC <sub>1</sub> C <sub>1</sub> )	268	2.886	9.6	
	262	3.82	9.6	9.6
	257	3.196	9.7	
NTfSO <sub>2</sub> C <sub>4</sub> F <sub>9</sub> (NC <sub>1</sub> C <sub>4</sub> )	268	0.437	1.5	
	262	0.567	1.4	1.4
	257	0.477	1.4	
NTfSO <sub>2</sub> C <sub>8</sub> F <sub>17</sub> (NC <sub>1</sub> C <sub>8</sub> )	268	0.037	0.12	
	262	0.049	0.12	0.12
	257	0.005	0.16	

reactions under two-phase system in Fig. 1, the high partition coefficient ( $\alpha$ ) of the catalysts is essentially important for the efficacy of the PTC system.<sup>2g)</sup> Similarly the influential effect of alkyl chain length is well known in the cases of the the partition coefficients of polyalkylammonium and phosphonium ions.<sup>1)</sup> Furthermore in comparison with **TFPB** ions we report here first attempts of the diazo coupling reaction of *p*-nitrobenzenediazonium fluoroborate with *N*-ethylcarbazol under liquid/liquid and liquid/solid two-phase systems in the presence of catalytic amounts of lithium salts of these amides (1) and **TTM**.

## Results and Discussion

### Synthesis of Lithium and Benzyltrimethylammonium Salts of Poly((perfluoroalkyl)sulfonyl)-substituted Amides (1) and Lithium TTM

The amides (NC<sub>1</sub>C<sub>4</sub>) and (NC<sub>1</sub>C<sub>8</sub>) were first prepared by J. N. Meußdoerfer and H. Niederprüm.<sup>7)</sup> However, since the details of the synthetic procedures for the amides (NC<sub>1</sub>C<sub>4</sub>) and (NC<sub>1</sub>C<sub>8</sub>) were not described, we prepared the amides (NC<sub>1</sub>C<sub>4</sub>) and (NC<sub>1</sub>C<sub>8</sub>) by modifying the reported method for the amide (NC<sub>1</sub>C<sub>1</sub>)<sup>8)</sup> according to Scheme 1. The lithium salts of the amides (NC<sub>1</sub>C<sub>4</sub>) and (NC<sub>1</sub>C<sub>8</sub>) were newly prepared almost quantitatively by neutralizing the corresponding acids with lithium carbonate in water. Details of the synthetic procedure were shown in Experimental.



Scheme 1

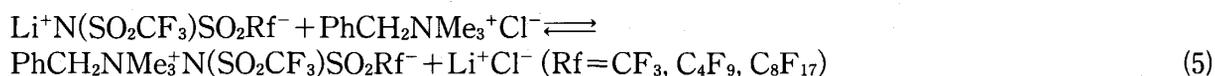
Lithium **TTM** was prepared by exchanging potassium ions of potassium **TTM**<sup>10-11)</sup> with lithium ions by using an excess amount of LiCl in water.

Benzyltrimethylammonium amides (NC<sub>1</sub>C<sub>1</sub>), ((NC<sub>1</sub>C<sub>4</sub>), and (NC<sub>1</sub>C<sub>8</sub>) were prepared by

**Table 2.** The Partition Coefficients ( $\alpha$ ) of Benzyltrimethylammonium Amides ( $\text{NC}_1\text{C}_1$ ) and ( $\text{NC}_1\text{C}_4$ ) in Dichloromethane/Water System at 25 °C.

Amides (Tf=SO <sub>2</sub> CF <sub>3</sub> )	Phase	$\lambda_{\text{max}}$ /nm	Absorb.	Conc. $\times 10^3/\text{mol l}^{-1}$	$\alpha$
NTf <sub>2</sub> ( $\text{NC}_1\text{C}_1$ )	H <sub>2</sub> O	268	0.504	1.7	4.6
		262	0.655	1.6	
		257	0.542	1.6	
	CH <sub>2</sub> Cl <sub>2</sub>	270	2.719	7.6	
		263	3.447	7.5	
		258	2.815	7.4	
NTfSO <sub>2</sub> C <sub>4</sub> F <sub>9</sub> ( $\text{NC}_1\text{C}_4$ )	H <sub>2</sub> O	268	0.102	0.34	5.1
		262	0.133	0.33	
		257	0.119	0.36	
	CH <sub>2</sub> Cl <sub>2</sub>	270	0.646	1.8	
		263	0.793	1.7	
		258	0.668	1.8	

the following exchange reaction (Eq. 5) (see Experimental):



### The Influence of the Chain Length of Benzyltrimethylammonium Bis((perfluoroalkyl)sulfonyl)amides on the Solubility in Water and the Partition Coefficient in Dichloromethane/Water System

The bis((perfluoroalkyl)sulfonyl)amides with different chain lengths ( $\text{NC}_1\text{C}_1$ ), ( $\text{NC}_1\text{C}_4$ ), and ( $\text{NC}_1\text{C}_8$ ) were prepared to know how the length of perfluoroalkyl group affects the physicochemical properties of the anions. In order to get some quantitative information about these properties, we examined to measure the solubilities of the benzyltrimethylammonium amides in water and the partition coefficients ( $\alpha$ ) in dichloromethane/water two-phase system.

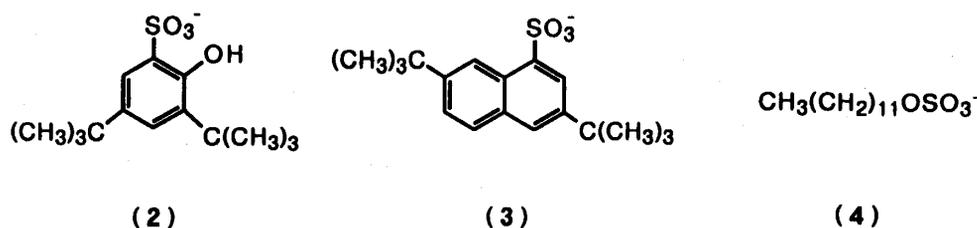
**The Solubility in Water:** The solubilities of the benzyltrimethylammonium amides in water were determined as shown in Table 1. The relative solubilities of benzyltrimethylammonium amides are as follows:

$$[\text{NC}_1\text{C}_1]/[\text{NC}_1\text{C}_4]/[\text{NC}_1\text{C}_8]=9.6/1.4/0.12=80/12/1$$

The hydrophilicity of the amides decreased by increasing the chain length of the perfluoroalkyl group; the hydrophilicity of the shortest CF<sub>3</sub> group is 80 times of that of C<sub>8</sub>F<sub>17</sub> group.

All of these benzyltrimethylammonium amides were highly soluble in dichloromethane and the solubilities in ether were less than 10<sup>-4</sup> mol l<sup>-1</sup>, then the solubilities data in organic solvents of these amides were not determined in our experiments.

**The Partition Coefficient in Dichloromethane/Water System:** The partition of diazonium ions between an aqueous phase and an organic phase can be formulated with a partition coefficient ( $\alpha$ ). In the case of an arenediazonium tetrafluoroborate in the presence of an anionic catalyst,  $\alpha$  is shown by the ratio of the concentrations of the diazonium ion in both phases (Eq. 6).



**Table 3.** Partition Coefficient ( $\alpha$ ) for *p*-Methoxybenzenediazonium Ions in Dichloromethane/Water System at 20 °C<sup>a)</sup>

Catalyst	$\alpha$	$[\text{ArN}_2^+\text{BF}_4^-]_{\text{org}}$ (mol l <sup>-1</sup> )	$[\text{ArN}_2^+\text{Cat}^-]_{\text{org}}$ (mol l <sup>-1</sup> )
none	$4.77 \times 10^{-3}$	$1.98 \times 10^{-7}$	0
<b>2</b>	$2.25 \times 10^{-2}$	$1.98 \times 10^{-7}$	$6.87 \times 10^{-7}$
<b>3</b>	$6.67 \times 10^{-2}$	$1.98 \times 10^{-7}$	$2.31 \times 10^{-6}$
<b>4</b>	$8.36 \times 10^{-2}$	$1.98 \times 10^{-7}$	$2.84 \times 10^{-6}$
<b>TFPB</b>	$3.82 \times 10^1$	$1.98 \times 10^{-7}$	$3.81 \times 10^{-5}$

a) Taken from Ref. 2g.

$$\alpha = \frac{[\text{ArN}_2^+]_{\text{org}}}{[\text{ArN}_2^+]_{\text{aq}}} = \frac{([\text{ArN}_2^+\text{BF}_4^-]_{\text{org}} + [\text{ArN}_2^+\text{Cat}^-]_{\text{org}})}{([\text{ArN}_2^+\text{BF}_4^-]_{\text{aq}} + [\text{ArN}_2^+\text{Cat}^-]_{\text{aq}})} \quad (6)$$

Since we did not isolate *p*-nitrobenzenediazonium bis((perfluoroalkyl)sulfonyl) amides (**1**) and methanide (**TTM**), the partition coefficients ( $\alpha$ ) for the diazonium salts under dichloromethane/water system were not determined. Instead we used the benzyltrimethylammonium amides to determine  $\alpha$ . Benzyltrimethylammonium amide (**NC<sub>1</sub>C<sub>1</sub>**) was used as a standard to determine the molar extinction coefficient ( $\epsilon$ ) of benzyltrimethylammonium ion in dichloromethane at 25 °C:  $\lambda_{\text{max}} = 270 \text{ nm}$  ( $\epsilon = 360 \text{ l mol}^{-1} \text{ cm}$ ); 263 nm ( $\epsilon = 460$ ); 258 nm ( $\epsilon = 380$ ). Similarly by using the correlation of the absorbance of benzyltrimethylammonium ion with the concentration of the cation in water and in dichloromethane (see Experimental),  $\alpha$  of the benzyltrimethylammonium amides (**NC<sub>1</sub>C<sub>1</sub>**) and (**NC<sub>1</sub>C<sub>4</sub>**) in dichloromethane/water two-phase system were determined as shown in Table 2.

We can see the relatively large experimental variation (40%) in the absorption values in the case of **NC<sub>1</sub>C<sub>4</sub>**. This variation might be due to the high volatility of dichloromethane and the very low molar extinction coefficient ( $\epsilon$ ) of benzyltrimethylammonium ion. Therefore the similar experiment for  $\text{PhCH}_2\text{NMe}_3\text{NTfSO}_2\text{C}_8\text{F}_{17}$  was not done.

Table 2 shows that the partition coefficients ( $\alpha$ ) of the benzyltrimethylammonium amides (**NC<sub>1</sub>C<sub>1</sub>**) ( $\alpha = 4.6$ ) and (**NC<sub>1</sub>C<sub>4</sub>**) ( $\alpha = 5.1$ ) are quite low and similar. This means that the influence of the chain lengths between  $\text{CF}_3$  and  $\text{C}_4\text{F}_9$  on the partition coefficient is negligible. The structural feature of benzyltrimethylammonium ions, a well-known cationic PTC catalyst, whose positive charge is formally localized on nitrogen atom shielded by four lipophilic alkyl groups in a tetrahedral way, makes a strong contrast to that of benzenediazonium ions, whose cationic nitrogen atoms are exposed to the surrounding media and provide strongly hydrophilic nature. Therefore the partition coefficients of *p*-nitrobenzenediazonium bis((perfluoroalkyl)sulfonyl) amides in dichloromethane/water system might be much smaller than those of the benzyltrimethylammonium amides (see below).

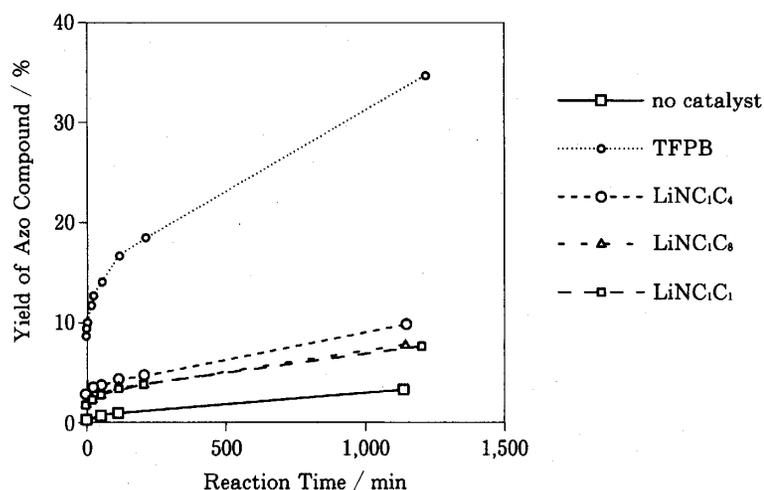
#### Azo Coupling Reaction under Dichloromethane/Water System

We chose the coupling reaction of *p*-nitrobenzenediazonium ions with *N*-ethylcarbazole

**Table 4.** Rate Constants and Yields of Azo Coupling Reactions of *p*-Nitrobenzediazonium Fluoroborate with *N*-Ethylcarbazole under Dichloromethane/Solid PTC Conditions.

Catalyst	Yield of Azo Compd after 20 h/%	$k_{obs}^a$ /s <sup>-1</sup>
none	3.3±0.1	$(6.0±0.5) \times 10^{-5}$
LiNC <sub>1</sub> C <sub>1</sub>	7.7±0.8	$(6.0±0.4) \times 10^{-4}$
LiNC <sub>1</sub> C <sub>8</sub>	7.5±0.7	$(6.0±0.3) \times 10^{-4}$
LiNC <sub>1</sub> C <sub>4</sub>	10±1	$(6.0±0.5) \times 10^{-4}$
<b>TFPB</b>	33±1	$(2.5±0.3) \times 10^{-3}$

a) Average Values of Three Experiments with Each Catalyst.

**Fig. 4** Time Course of Formation of Azo Compound in Dichloromethane/Solid PTC system.

under PTC conditions to examine the applicability of the poly((perfluoroalkyl)sulfonyl)-amides (**1**) and methanide (**TTM**) ions in anionic PTC reaction. This PTC reaction was first demonstrated by Ellwood et al.<sup>12)</sup> with a catalytic amount of sodium dodecylbenzenesulfonate (**NaDBS**). We have also used this reaction for dichloromethane/water PTC systems with catalytic **TFPB** ions.<sup>2a, 2b)</sup> A dichloromethane solution of *N*-ethylcarbazole ( $2.0 \times 10^{-4}$  mol l<sup>-1</sup>) and 33 mol % of sodium **TFPB** ( $6.5 \times 10^{-5}$  mol l<sup>-1</sup>) was vigorously stirred for 20 min at 25 °C with an aqueous solution of *p*-nitrobenzediazonium fluoroborate ( $2.0 \times 10^{-3}$  mol l<sup>-1</sup>) at PH=7 buffered with NaHPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>. *N*-Ethylcarbazole (70%) was coupled to give *N*-ethyl-3-(*p*-nitrophenylazo)carbazole under these reaction conditions. The pseudo-first order rate constant ( $k_{obs}$ ) was  $(8.0 \pm 0.5) \times 10^{-4}$  s<sup>-1</sup>. These rate constant and yield were similar to those obtained in our previous experiments of the same reaction system.<sup>13)</sup>

On the other hand, the attempted PTC azo coupling reaction did not proceed at all in the presence of the lithium amides (**1**) (NC<sub>1</sub>C<sub>1</sub>), (NC<sub>1</sub>C<sub>4</sub>), and (NC<sub>1</sub>C<sub>8</sub>) and the methanide (**TTM**). Prolonged vigorous stirring of the reaction mixture with or without the lithium amides resulted in the decomposition of ca. 20% of the diazonium ions to give unidentified complex by-products.

As shown above the high partition coefficient of the reactive species is the basic requirement of any PTC under two phase system.<sup>1)2g)</sup> By considering the fact that arenediazonium TFPB is practically insoluble in water,<sup>2d)</sup> the absence of the catalytic effect of the

amides (1) and the methanide (**TTM**) under dichloromethane/water system is attributed to the low lipophilicity of the diazonium amides (1) and the methanide (**TTM**). We have previously determined the partition coefficients ( $\alpha$ ) for *p*-methoxybenzenediazonium ion in dichloromethane/water system with several anionic catalysts such as 3,5-di-*t*-butyl-2-hydroxybenzenesulfonate (2), 3,7-di-*t*-butylnaphthalene-1-sulfonate (3), dodecyl sulfate (4), and **TFPB** (Table 3).<sup>2g)</sup>

Table 3 shows that without any organic anion only about 0.5% of the diazonium ions is partitioned in the dichloromethane phase, while, with catalysts, 2, 3, and 4, this  $\alpha$  value increased only by 2.2, 6.3, and 7.7%, respectively. On the other hand, with **TFPB**, 97.4% of the diazonium ion was partitioned in the dichloromethane phase. The striking influence of **TFPB** to increase  $\alpha$  can be explained by the characteristic structure of **TFPB**, in which a hydrophilic anionic center of the boron atom is symmetrically shielded, against hydration, by four bulky phenyl groups with strongly lipophilic trifluoromethyl groups. In this aspect, the structure of the **TFPB** anion is different from that of the organic sulfonate ions (2)–(4), the amides ions (1), and the methanide ions (**TTM**), whose anionic oxygen/nitrogen/carbon atoms are exposed to the surrounding media and provide a strongly hydrophilic center. The small, but obvious, increase in  $\alpha$  with the sulfonates (2)–(4) might be caused by an increased lipophilicity of the organic sulfonate anions, compared with that of tetrafluoroborate anion. The results in Tables 1, 2, and 3 indicate that the long  $C_8F_{17}$  group in  $NC_1C_8$  increases the hydrophobicity of the imide ions compared to the short  $CF_3$  group in  $NC_1C_1$  but the lipophilicity of the amide ions themselves is still too small for the effective anionic PTC catalysts for the azo coupling reaction under dichloromethane/water two-phase conditions.

#### Azo Coupling Reaction in Dichloromethane/Solid System

One way to avoid the problem of the anions with low partition coefficient in a liquid/liquid system is to change the phase system itself, *i. e.*, to use a solid/liquid system in which the liquid phase is an organic solvent. Some diazo coupling reactions in such an environment are already known and well investigated.<sup>2g)</sup>

Into a 20 ml dichloromethane solution of *N*-ethylcarbazole ( $0.25 \pm 0.01$  mmol,  $10^{-2}$  mol  $l^{-1}$ ) containing pyridine ( $0.25 \pm 0.02$  mmol) and one of the lithium amides (1) or sodium **TFPB** ( $0.05 \pm 0.01$  mmol, 20 mol % related to the coupler) as a catalyst, *p*-nitrobenzenediazonium fluoroborate ( $0.9 \pm 0.1$  mmol) was added, and the suspended reaction mixture was stirred vigorously at 25 °C. The time-courses of the formation of the azo compound were shown in Fig. 4 and the pseudo first-order rate constants ( $k_{obs}$ ) of the azo coupling reactions were shown in Table 4 with the yields of the azo compound formed in the reactions for 20 h.

Table 4 and Fig. 4 indicated that the chain-length effect of perfluoroalkylsulfonyl group was not clear, although the PTC activity of bis((perfluoroalkyl)sulfonyl) amide ions (1) was obvious, as large as 1/3–1/4 of that of **TFPB**. The amide  $NC_1C_4$  was more effective than the amide  $NC_1C_1$ , while the amide with longer chain  $NC_1C_8$  was less effective than the amide

**Table 5.** Syntheses of  $NC_1C_4$  and  $NC_1C_8$ .

Entry	RfSO <sub>2</sub> F	Bath Temp./°C	Reaction Conditions	Yield/%
1	C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> F	100	in autoclave for 3.5 h	20
2	C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> F	100	in autoclave for 5 h	50
3	C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> F	130	reflux for 48 h	10
4	C <sub>4</sub> F <sub>9</sub> SO <sub>2</sub> F	110	in autoclave for 61.5 h	80
5	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> F	130	reflux for 26.5 h	50
6	C <sub>8</sub> F <sub>17</sub> SO <sub>2</sub> F	130	reflux for 90 h	83

$\text{NC}_1\text{C}_1$ . Iwamoto has studied the azo coupling reactions in liquid/solid systems under PTC conditions with **TFPB** and  $\text{BF}_4$  ions as anionic catalysts.<sup>13)</sup> In changing the counter anions from  $\text{BF}_4$  ions to **TFPB** ions, a significant increase in the efficiency of the catalyst was observed; the size of counter anion seemed to affect the electrophilic reactivity of the diazonium ions. The similar size effect was found also in the metal ion-catalyzed Diels-Alder reactions in Fig. 3.<sup>14)</sup> Since we did not measure the solubility and the reactivity of the individual diazonium amides (1) and methanide (**TTM**), we do not discuss further the details of the mechanism of this azo coupling reaction under PTC conditions.

In summary, we have prepared several bis((perfluoroalkyl)sulfonyl)amides (1) and tris((trifluoromethyl)sulfonyl)methanide (**TTM**), which are stable conjugate bases of nitrogen- and carbon-superacids:

- 1) The solubility of the benzyltrimethylammonium amides (1) in water decreases by increasing the chain length of perfluoroalkyl group ( $[\text{NC}_1\text{C}_1]/[\text{NC}_1\text{C}_4]/[\text{NC}_1\text{C}_8] = 80/12/1$ ) mainly due to the increased molecular weight and hydrophobicity, while there are no apparent changes in the partition coefficients ( $\alpha$ ) of these amides in dichloromethane/water system.
- 2) The amide (1) and the methanide (**TTM**) anions are lipophilic in nonpolar solvent such as dichloromethane and toluene and highly stable, compared to the common inorganic anions such as halides, fluoroborate, and perchlorate ions, and easily isolated from conc. sulfuric acid by sublimation.
- 3) These amides and methanide were not effective as anionic PTC catalysts in the azo coupling reaction in dichloromethane/water system, while the same coupling reaction was promoted effectively with catalytic amounts of the amides and methanide in dichloromethane/solid system.

## Experimental

Most of the starting reagents were commercially available and were appropriately purified as needed.  $\text{CF}_3\text{SO}_2\text{NH}_2$ , which was a starting material for the amides ( $\text{NC}_1\text{C}_4$ ) and ( $\text{NC}_1\text{C}_8$ ), and lithium bis((trifluoromethyl)sulfonyl)amide ( $\text{NC}_1\text{C}_1$ ) were available from the Ube Research Center of Central Glass Co., Ltd.<sup>9)</sup> Potassium tris((trifluoromethyl)sulfonyl)-methanide (**TTM**) was prepared by the known method<sup>10)</sup> and our method.<sup>11)</sup> All solvents were purified before used. The acids and their lithium salts were very hygroscopic and treated in a dry box. The following instruments were used in the determination of the structures and purities of all the compounds prepared: NMR spectra were measured with a JEOL JNM-FX-100 spectrometer at 99.6 and 93.65 MHz for  $^1\text{H}$  and  $^{19}\text{F}$  nuclides, respectively. IR spectra were recorded on a JASCO IR-700 infrared spectrophotometer. UV spectra were with a Hitachi U-3200 spectrophotometer. Melting points were on a Yanaco MP-S3 apparatus and uncorrected.

### Synthesis of the Bis((perfluoroalkyl)sulfonyl)amines:

The results in the synthesis of the bis((perfluoroalkyl)sulfonyl)amines ( $\text{NC}_1\text{C}_4$ ) and ( $\text{NC}_1\text{C}_8$ ) in the reactions of Eqs. 3 and 4 of Scheme 1 are shown in Table 5.

Table 5 shows that the reflux conditions were not suitable for the reaction of Eq. 3. The condition of heating for at least 20 h in autoclave was necessary. Under the reflux conditions the reactants were insoluble. The reaction mixtures were first separated in three phases and it became one phase when the reactions finished. The reactions could be monitored by the  $^{19}\text{F}$  NMR spectra of the reaction mixtures. As commercially available  $\text{C}_8\text{F}_{17}\text{SO}_2\text{F}$  contains small amount of isomers, it was impossible to get 100% pure  $n\text{-C}_8\text{F}_{17}\text{SO}_2\text{NHSO}_2\text{CF}_3$  in our experiments.

### Synthesis of $\text{C}_4\text{F}_9\text{SO}_2\text{NHTf}$ :

(1):  $\text{CF}_3\text{SO}_2\text{NH}_2$  7.45 g (50 mmol) was dissolved in 10 ml of dry methanol. A methanol solution of sodium methoxide prepared from 1.17 g (50 mmol) of sodium metal and 15 ml of methanol was added to the  $\text{CF}_3\text{SO}_2\text{NH}_2$  solution. After 30 min methanol was removed by evaporation. The resulting solid was washed with benzene, yielding 8.36 g (0.049 mol, 98%) of  $\text{TfNHNa}$ . mp: 238-241 °C.

(2):  $\text{TfNHNa}$  5.47 g (32 mmol) was transferred to a 50-ml. two-necked flask fitted with a condenser and a drying tube. After addition of 25 g of  $(\text{Me}_3\text{Si})_2\text{NH}$  (HMDS) and 5 ml dioxane to prevent polymerization of HMDS, the mixture was refluxed at 140 °C for 20 h. During the reaction ammonia was evolved. After HMDS/dioxane solvent was distilled under vacuum and the remaining salt was dried under 0.3 mmHg at 100 °C for 3 h in the same flask, 7.95 g (33 mmol) of white solid was obtained. The product  $\text{NaN}(\text{Tf})\text{SiMe}_3$  was directly used for the next reaction.

(3): The above product, 10.747 g (35.6 mmol) of  $\text{C}_4\text{F}_9\text{SO}_2\text{F}$ , and 40 ml of dioxane were placed in a 200-ml. stainless-steel bomb, and this bomb was heated to 110 °C for 61.5 h. The solvent was removed by evaporation and 13.80 g of yellow solid of  $\text{NaN}(\text{Tf})\text{SO}_2\text{C}_4\text{F}_9$  (95% crude yield) remained. The  $^{19}\text{F}$ NMR spectrum of the product showed that the reaction was carried out completely.

(4):  $\text{NaN}(\text{Tf})\text{SO}_2\text{C}_4\text{F}_9$  13.8 g and 14 g of concentrated sulfuric acid were put into a sublimator and sublimed twice at 85 °C under 1 mmHg. A very hygroscopic and white crystalline solid 11.0 g (26 mmol, 80% yield) was obtained. mp: 53-55°C.

$\text{CF}_3^a\text{SO}_2\text{NHSO}_2\text{CF}_2^d\text{CF}_2^b\text{CF}_3^c$

$^1\text{H}$ NMR ( $\text{CD}_3\text{CN}/\text{TMS}$ ):  $\delta$ ; 11.33 (s, NH).  $^{19}\text{F}$ NMR ( $\text{CD}_3\text{CN}/\text{C}_6\text{F}_6$ ):  $\delta$ ; 38.20 (m, 2F, b), 43.04 (m, 2F, c), 52.39 (t, 2F, d,  $^2J=15$  Hz), 83.00 (t, 3F, a,  $^2J=9.8$  Hz), 85.61 (s, 3F, a'). IR spectrum ( $\text{CCl}_4$  solution,  $\text{cm}^{-1}$ ): 3200(vw), 1550(s), 1343(m), 1203(s), 1143(m), 1073(w), 1008(m), 978(w), 920(w), 795(s), 766(s).

#### Synthesis of $\text{C}_8\text{F}_{17}\text{SO}_2\text{NHTf}$ :

(1):  $\text{C}_8\text{F}_{17}\text{SO}_2\text{F}$  14.22g (28 mmol) and 20 ml of dioxane were added into a flask contained 4.65 g of  $\text{TfN}(\text{Na})\text{SiMe}_3$ , and the reaction mixture was heated under reflux. When the solution became clear (one phase) after 90 h, the reaction was stopped. Evaporating the solvent gave 12.30 g of a yellow solid.

(2): Concentrated sulfuric acid 12 g and the solid obtained above were mixed and sublimation twice at 120 °C under 0.8 mmHg gave 10.96 g (17.4 mol, 83% yield) of  $\text{C}_8\text{F}_{17}\text{SO}_2\text{NHTf}$ . mp: 85-87 °C.

$\text{CF}_3^a\text{SO}_2\text{NHSO}_2\text{CF}_2^d(\text{CF}_2)_8\text{CF}_2^b\text{CF}_3^c$

$^1\text{H}$ NMR ( $\text{CD}_3\text{CN}/\text{TMS}$ ):  $\delta$ ; 10.16 (s, NH).  $^{19}\text{F}$ NMR ( $\text{CD}_3\text{CN}/\text{C}_6\text{F}_6$ ):  $\delta$ ; 37.97 (m, 2F, b), 42.1~43.8 (m, 10F, c), 50.86 (t, 2F, d), 82.98 (t, 3F, a,  $^2J=9.8$  Hz), 84.36 (s, 3F, a'), 91.94~92.02 (m, small, assigned as isomer peaks).<sup>15)</sup> IR spectrum ( $\text{CCl}_4$  solution,  $\text{cm}^{-1}$ ): 3200(vw), 1550(s), 1342(w), 1251(m), 1213(m), 1067(w), 1005(m), 979(m), 793(s).

#### Synthesis of Lithium Bis((perfluoroalkyl)sulfonyl)amides:

The  $\text{HNTfSO}_2\text{Rf}$  ( $\text{Rf}=\text{C}_4\text{F}_9$ ,  $\text{C}_8\text{F}_{17}$ ) was dissolved in 10 ml water, and a stoichiometric amount of lithium carbonate was gradually added into the aqueous solution of  $\text{HNTfSO}_2\text{Rf}$  with stirring. The reaction completed in 1 h at room temperature. After remaining lithium carbonate was filtered, evaporation gave a white powder of the lithium salt which was dried under ca.  $10^{-3}$  mmHg at 50-100 °C for 15 h. The yields were almost quantitatively. The lithium salts were very hygroscopic. The number of hydrated water molecules was determined by  $^1\text{H}$  NMR spectra of the lithium salts with  $\text{CHCl}_3$  as an external standard.

$\text{LiNTfSO}_2\text{C}_4\text{F}_9 \cdot <0.2 \text{H}_2\text{O}$ : mp; 248-250 °C.  $^1\text{H}$ NMR ( $\text{CD}_3\text{CN}/\text{TMS}$ ):  $\delta$ ; 2.99 (s,  $\text{H}_2\text{O}$ ).  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}/\text{C}_6\text{F}_6$ ):  $\delta$ ; 37.86 (m, 2F), 43.00 (m, 2F), 50.67 (t, 2F), 82.85 (t, 3F), 84.67 (s, 3F). IR spectrum (Nujol): 1635 (m), 1353 (s), 1291 (m), 1208 (s), 1144 (m), 1074 (m), 1029 (w), 1010

(w), 732 (m).

$\text{LiNTfSO}_2\text{C}_8\text{F}_{17} \cdot <0.3 \text{ H}_2\text{O}$  : mp :  $>260 \text{ }^\circ\text{C}$  with color change.

$^1\text{HNMR}(\text{CD}_3\text{CN}/\text{TMS})$ :  $\delta$ ; 2.83 (s,  $\text{H}_2\text{O}$ ).

$^{19}\text{FNMR}(\text{CD}_3\text{CN}/\text{C}_6\text{F}_6)$ :  $\delta$ ; 37.90 (m, 2F), 41-44 (m, 10F), 50.73 (t, 2F), 82.93 (t, 3F), 84.53 (s, 3F), 92.00 (m, assigned as isomers).<sup>15)</sup>

IR spectrum (Nujol): 1638 (m), 1353 (s), 1328 (s), 1205 (s), 1147 (s), 1096 (s), 1171 (m), 986 (w), 949 (w), 735 (m).

#### Synthesis of Lithium TTM:

Potassium **TTM** 0.5531 g (1.23 mmol) and lithium chloride 4.29 g (101.2 mmol) were dissolved in 50 ml of water and treated with ultrasonication for 1 h. The water was removed by rotary evaporation until a white solid remained. This solid was extracted with ether for three times and after filtration ether was evaporated. The

purity of the remaining solid was checked by the atomic absorption and flame spectrophotometer (lithium ion: 670.8 nm; potassium ion: 766.5 nm). It showed a small amount of the potassium **TTM** still remained. Thus the exchange reaction was tried again with lithium nitrate of high quality (purity  $>99.99 \%$ ) and 0.510 g (1.17 mmol, 95 % yield) of very hygroscopic white powder of pure lithium **TTM** was obtained. The  $^1\text{HNMR}$  spectrum of **LiTTM** with chloroform as an external standard showed that the lithium salt was coordinated with one water molecule, *i. e.*,  $\text{LiTTM} \cdot \text{H}_2\text{O}$ , and ever after drying overnight at  $100 \text{ }^\circ\text{C}$  under  $3 \times 10^{-5}$  mmHg the concentration ratio of  $\text{H}_2\text{O}$  to **LiTTM** was more than 0.7. mp  $277 - 280 \text{ }^\circ\text{C}$ .

$^1\text{HNMR}(\text{CDCl}_3 + \text{CD}_3\text{CN}/\text{TMS})$ :  $\delta$ ; 2.78 (s,  $\text{H}_2\text{O}$ ).  $^{19}\text{FNMR}(\text{CDCl}_3 + \text{CD}_3\text{CN}/\text{C}_6\text{F}_6)$ :  $\delta$ ; 85.40 (s,  $\text{CF}_3$ ). Elemental analysis; Calcd for  $\text{C}_4\text{H}_2\text{O}_7\text{F}_9\text{S}_3\text{Li}(\text{LiTTM} \cdot \text{H}_2\text{O})$ : C, 11.10; H, 0.46 %. Found: C, 11.48; H, 0.67 %.

#### Syntheses of the Benzyltrimethylammonium Salts of Bis((perfluoroalkyl)sulfonyl)-amides:

Stoichiometric amounts of the lithium bis((perfluoroalkyl)sulfonyl)amide and benzyltrimethylammonium chloride were dissolved in 20 ml of methanol in 50-ml. flask, and sonicated for 30 min. After methanol was removed by evaporation the remaining mixture was dissolved in dichloromethane-water mixture. After the organic layer was separated, water layer was extracted three times with dichloromethane. The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , and the evaporation of the solvent gave the product, which was purified by recrystallization or, in the case of the liquid, was dried overnight under ca. 0.001 mmHg at  $80 \text{ }^\circ\text{C}$ .

**PhCH<sub>2</sub>NMe<sub>3</sub>NTf<sub>2</sub>**: mp:  $67 - 68.5 \text{ }^\circ\text{C}$ .  $^1\text{HNMR}(\text{CD}_3\text{CN}/\text{TMS})$ :  $\delta$ ; 3.00 (s, 3H,  $\text{CH}_3$ ), 4.38 (s, 2H,  $\text{CH}_2$ ), 7.53 (m, 5H, Ph).  $^{19}\text{FNMR}(\text{CD}_3\text{CN}/\text{C}_6\text{F}_6)$ :  $\delta$ ; 84.34 (s,  $\text{CF}_3$ ).

IR spectrum (KBr): 3050 (w), 2340 (w), 1465 (s), 1340 (s), 1180 (s, B), 1040 (s), 890 (m), 790 (m), 735 (w).

**PhCH<sub>2</sub>NMe<sub>3</sub>NTfSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub>**: colorless liquid.  $^1\text{H NMR}(\text{CD}_3\text{CN}/\text{TMS})$ :  $\delta$ ; 3.00 (s, 3H,  $\text{CH}_3$ ), 4.39 (s, 2H,  $\text{CH}_2$ ), 7.53 (m, 5H, Ph).

$^{19}\text{FNMR}(\text{CD}_3\text{CN}/\text{C}_6\text{F}_6)$ :  $\delta$ ; 37.88 (m, 2F), 42-86 (m, 2F), 50.97 (t, 2F), 82.90 (t, 3F), 84.34 (s,

**Table 6.** Absorbance of  $\text{PhCH}_2\text{NMe}_3\text{Cl}$  in  $\text{H}_2\text{O}$  at  $25 \text{ }^\circ\text{C}$

$[\text{C}] \times 10^4 / \text{mol l}^{-1}$	$\lambda_{\text{max}} / \text{nm}$	Abs.
99.8	268	3.010
	262	4.074
	257	3.333
49.9	268	1.483
	262	1.961
	257	1.645
9.98	268	0.318
	262	0.414
	257	0.342
4.99	268	0.163
	262	0.210
	257	0.174
0.998	268	0.033
	262	0.042
	257	0.035

3F).

IR spectrum (liquid film): 3030(w), 2300(w), 1480(s), 1460(s), 1330(s), 1180(s, B), 1060(s), 870(m), 770(m), 722(w).

**PhCH<sub>2</sub>NMe<sub>3</sub>NTfSO<sub>2</sub>C<sub>8</sub>F<sub>17</sub>**: mp: 60.5–63 °C. <sup>1</sup>H NMR(CD<sub>3</sub>CN/TMS): δ; 3.00(s, 3H, CH<sub>3</sub>), 4.38(s, 2H, CH<sub>2</sub>), 7.53(m, 5H, Ph).

<sup>19</sup>F NMR(CD<sub>3</sub>CN/C<sub>6</sub>F<sub>6</sub>): δ; 37.93(m, 2F), 42–44(m, 10F), 50.75(t, 2F), 82.96(t), 84.28(s, 3F), 92.00(m, assigned as isomer).<sup>15)</sup>

IR spectrum (liquid film): 3020(w), 2350(w), 1480(s), 1460(s), 1320(s); 1240–1120(B); 1060(s); 980(w), 890(m), 780(w).

### **The Solubility of Benzyltrimethylammonium Bis((perfluoroalkyl)sulfonyl)amides in Water and the Partition Coefficient in Dichloromethane/Water System**

Benzyltrimethylammonium chloride was used as a standard to determine the molar extinction coefficient ( $\epsilon$ ) of benzyltrimethylammonium ion in water at 25.0 °C:  $\lambda_{\max} = 268$  nm ( $\epsilon = 300$  l mol<sup>-1</sup> cm<sup>-1</sup>); 262 nm ( $\epsilon = 400$ ); 257 nm ( $\epsilon = 330$ ). The correlation line of the absorbance of benzyltrimethylammonium ion with the concentration of the cation in water was obtained as shown in Table 6. In the determination of the solubility of the ammonium salts, a flask containing an excess amount of the ammonium salt in a given volume of water was heated at 100 °C for 1 h, then put into a thermostat to cool gradually down to 25 °C. After 24 h the UV spectra of the saturated water solution were measured at 25 °C. The results were shown in Table 1.

### **The Partition Coefficient of Benzyltrimethylammonium Bis((perfluoroalkyl)sulfonyl)amides in Dichloromethane/Water**

The  $\epsilon$  values of benzyltrimethylammonium ion in dichloromethane at 25 °C was determined with benzyltrimethylammonium amide (NC<sub>1</sub>C<sub>1</sub>). By using the standard correlations of the concentration of the ammonium in water and in dichloromethane, the partition coefficients of the ammonium amides were obtained as shown in Table 2.

Saturated aqueous solution (5 ml) of the ammonium amides, which was prepared as mentioned above, and dichloromethane (5 ml) were put into a test tube with a sealed cap. After 10 min sonication the tube was kept in a thermostat at 25 °C for 24 h so that the equilibrium between the two phases could be achieved and then, given volumes of both the aqueous and organic layers were taken to measure the UV spectra at 25 °C. The results were shown in Table 2.

### **The Diazo Coupling Reactions of *p*-Nitrobenzenediazonium Ions with *N*-Ethylcarbazole in Dichloromethane/Water and Dichloromethane Solution with PTC Catalysts.**

Similarly to the previous investigations of the same coupling reaction using TFPB as catalyst,<sup>13)</sup> the reaction mixture was stirred vigorously by mechanical stirring with more than 1000 r.p.m. at 25 °C in a water bath whose temperature was regulated by an EYELA CTP-200 temperature controller.

### **The Diazo Coupling Reactions with TFPB in Dichloromethane/Water.**

When a dichloromethane solution of  $(2.0 \pm 0.1) \times 10^{-4}$  mol l<sup>-1</sup> *N*-ethylcarbazole and  $(6.5 \pm 0.3) \times 10^{-5}$  mol l<sup>-1</sup> sodium TFPB was vigorously stirred at 25 °C with an aqueous solution containing  $(2.0 \pm 0.05) \times 10^{-3}$  mol l<sup>-1</sup> of *p*-nitrobenzenediazonium fluoroborate, which was buffered with  $(2.0 \pm 0.2) \times 10^{-2}$  mol l<sup>-1</sup> of NaHPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>, then after 20 min 70 % yield (referred to the carbazole concentration) of *N*-ethyl-3-(*p*-nitrophenylazo)carbazole was formed (the coupling reaction still proceeded) and the pseudo-first order rate constant ( $k_{\text{obs}}$ ) was  $(8.0 \pm 0.5) \times 10^{-4}$  s<sup>-1</sup>.

### **The Diazo Coupling Reactions in Dichloromethane/Solid System with PTC Catalysts.**

For kinetic measurements a 0.5 ml portion of the dichloromethane layer was taken out after various intervals and diluted to ten-fold volume by the same solvent and analyzed

photometrically. An absorption maximum of the azo product ( $\epsilon = 28000$  at  $\lambda_{\max} = 430$  nm) was used to investigate the product's concentration. The details of the kinetic measurements were shown in Iwamoto's dissertation.<sup>13)</sup>

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- 14) In this case metal bis((perfluoroalkyl)sulfonyl)amides are highly soluble in dichloromethane compared to the corresponding metal trifluoromethanesulfonates ( $\text{OSO}_2\text{CF}_3$ ) and fluoroborates ( $\text{BF}_4$ ), then the counter metal ions showed the extremely high Lewis acidity to promote Diels-Alder reaction in catalytic way. However the increase in the molecular weight of the amide ions with longer perfluoroalkylsulfonyl group such as  $\text{NC}_1\text{C}_8$  decreased the solubility in dichloromethane which resulted in reducing their catalytic activity.<sup>6)</sup>

15) Commercial  $C_8F_{17}SO_2F$  contains small amounts of several isomers with branched  $C_8F_{17}$  chain.