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The Reaction of Fluorenethione *S*-Tosylimide with Grignard Reagents

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Synopsis. Fluorenethione *S*-tosylimide reacted with Grignard reagents to afford both the thiophilic and carbophilic products depending on the solvent used.

Thione *S*-imides have three potential reactive sites (carbon, sulfur, nitrogen atoms) on the cumulated system, and hence reactions with nucleophiles, *e.g.* Grignard reagents include interesting possible modes of the site selectivity, *viz.* carbophilic, thiophilic, and azophilic reactions.

Only one example has been reported first by Senning *et al.*[1)] on the reaction of thione *S*-imide (*S,S'*-diphenyl trithiocarbonate *S,S*-dioxide *S''*-*t*-butylimide) with organometallic reagents (phenyllithium) giving carbophilic adduct.[2)]

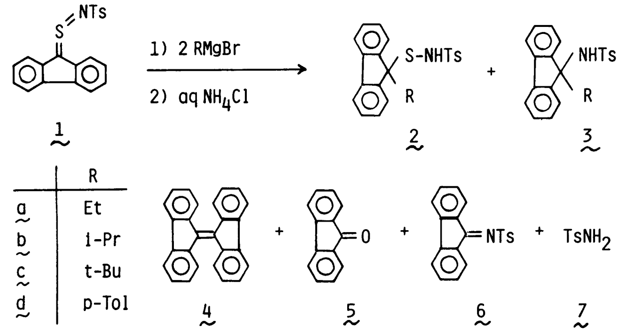
In this paper we will describe the reaction of fluorenethione *S*-tosylimide (**1**) with some Grignard reagents.

Results

The reactions were carried out by adding a twofold excess of a Grignard reagent to thione *S*-imide (**1**) at low temperature in diethyl ether or THF (method A), or *vice versa* (method B).[3)]

The reactions in diethyl ether (0.06 mol/l of **1**) afforded products **2**—**7** (Scheme 1, Table 1). It is unambiguous that sulfenamide **2** was produced by the attack of the nucleophile R of the Grignard reagent to the 9-carbon of the fluorenylidene ring in **1**. *N*-Substituted tosylamide (**3**) would be formed by the sulfur extrusion from **2**, which was observed independently, and/or by the reaction of **6** with a Grignard reagent.

In contrast, the reactions in THF gave 9,9'-bifluorenylidene (**4**) as a major product, and the formation of **2** and **3** was not detected (Table 1).



Scheme 1.

Table 1. Reaction of fluorenethione *S*-tosylimide (**1**) with Grignard reagents

R	Solvent (Method)	Reaction time/h	Yield/% Carbophilic adducts **2**	Yield/% Carbophilic adducts **3**	Yield/% Thiophilic adduct **4**	Yield/% By-products **5**	Yield/% By-products **6**	Yield/% By-products **7**
a	E (A)	2.5	17	a)	29	12	2	48
b	E (A)	3.5	23	a)	18	28	15	32
c	E (A)	2.5	24	a)	2	18	10	62
d	E (B)	1.0	6	16	2	54	0	35
a	THF (A)	1.0	0	0	99	a)	a)	99
d	THF (B)	1.0	0	0	87	6	5	64

a) Trace amount, checked by TLC.

Discussion

Probable mechanisms of the reaction are shown in Scheme 2 on the basis of polar and single electron transfer (SET) mechanisms in general Grignard reactions.[4)] The negatively charged nitrogen of **1** coordinates the positive magnesium of the reagent (**8**), followed by the slow SET giving **9** and **10**.[5)] The intermediary **8** (**9**) and **10** are key species giving thiophilic and carbophilic adducts, respectively. The carbophilic attack of R˙ to the 9-carbon of the fluorenylidene ring in **10** gives **2** *via* **15**. The new Grignard reagent (**11**) formed by the thiophilic attack of R in **8** (**9**) further reacts with another molecule of **1** on the sulfur atom to afford **4** *via* **12**—**14**.

Similar reaction mechanisms have been reported in the reaction of fluorenethione *S*-oxide (sulfine) with organolithium reagents,[6)] where no carbophilic reaction product was obtained.[7)] On the contrary, sulfilimine **16** which corresponds to sulfoxide formed by the thiophilic reaction of the sulfine was not detected. The sulfilimine **16** or **11** might produce **5** and **7** by hydrolysis.

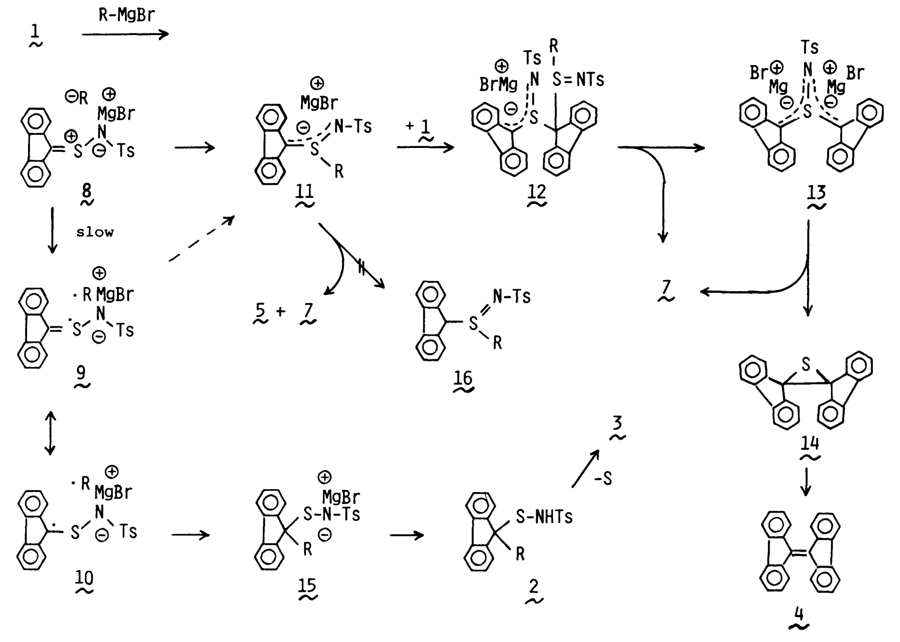
In the reactions in diethyl ether, the yields of the carbophilic adducts (**2**, **3**) are in the order of **c**(R=*t*-Bu) ≥**b**(R=*i*-Pr)>**a**(R=Et), and the yields of the thiophilic adducts (**4**) are in the order of **a**(R=Et)>**b**(R=*i*-Pr)> **c**(R=*t*-Bu). This result is consistent with the view that the more radical property of tertiary alkyl (*t*-Bu) stabilized preferentially attacks the carbon atom in **10** whereas the less radical property of primary alkyl (Et) instantly forms the thiophilic adduct **11**.[8)] On the other hand, the reaction in THF implies that the solvent effect (higher solubility for **1**: concentration dependence, polarity) of THF makes the route to thiophilic adduct **4** favorable.

Experimental

All the melting points are uncorrected. IR spectra were measured on a Hitachi Model 260-10 spectrometer. Mass spectra were recorded on a Hitachi double-focusing mass spectrometer RMU-7M operating at an ioninzing potential of 70 eV. ^{1}H- and ^{13}C-NMR spectra were measured on a JEOL-FX 100 spectrometer in $CDCl_3$ using TMS as an internal standard.

Fluorenethione *S*-tosylimide (**1**) was prepared by the method reported previously.[9)]

Reaction of 1 with Grignard Reagents. General Procedure: 1) A diethyl ether solution (7 cm^3) of a Grignard reagent (7.0 mmol) was added with stirring to a suspension of **1** (1.21 g, 3.32 mmol) in 48 cm^3 of diethyl ether at −15 °C (0 °C in THF) under nitrogen atmosphere (method A). 2) A suspension of **1** (1.47 g, 4.02 mmol) in



Scheme 2.

ether (30 cm^3) was added to *p*-tolylmagnesium bromide ethereal solution (37 cm^3) under the same conditions as described for method A (method B). After being stirred for 1—3.5 h at −15 °C (0 °C in THF), the reaction mixture was rinsed with aq NH$_4$Cl and water, dried over Na$_2$SO$_4$, and concentrated *in vacuo*. The residue was column-chromatographed on silica gel (Wako C-200) using hexane, benzene, dichloromethane, and methanol as eluents to give the products **2**—**7**. The products **4**—**7** were identified by comparison of the spectral data with those of authentic samples.

2a: Mp 150—151 °C; IR (Nujol) 3320 cm^{-1} (NH), 1160, 1100 (SO$_2$); MS *m/z* 395 (3%, M$^+$), 193 (100, M$^+$−SNHTs); ^{1}H-NMR (CDCl$_3$) δ 0.44 (t, *J*=8 Hz, 3H, CH$_3$), 2.34 (s, 3H, CH$_3$(Ts)), 2.60 (q, *J*=8 Hz, 2H, CH$_2$), 5.70 (s, 1H, NH), 7.13—7.70 (m, 12H, Ar-H); ^{13}C-NMR (CDCl$_3$) δ 65.0 (9-C), 28.7 (CH$_2$), 21.5 (CH$_3$(Ts)), 8.8 (CH$_3$). Found: C, 66.88; H, 5.37; N, 3.33; S, 16.13%. Calcd for C$_{22}$H$_{21}$NS$_2$O$_2$: C, 66.81; H, 5.35; N, 3.53; S, 16.22%.

2b: Mp 138—139 °C; IR (Nujol) 3210 cm^{-1} (NH), 1165, 1100 (SO$_2$); MS *m/z* 409 (1, M$^+$), 207 (100, M$^+$−SNHTs); ^{1}H-NMR (CDCl$_3$) δ 0.94 (d, *J*=7 Hz, 6H, CH$_3$), 2.37 (s, 3H, CH$_3$(Ts)), 2.86 (sept, *J*=7 Hz, 1H, CH), 5.59 (s, 1H, NH), 7.12—7.68 (m, 12H, Ar-H); ^{13}C-NMR (CDCl$_3$) δ 68.9 (9-C), 32.7 (CH), 21.5 (CH$_3$(Ts)), 8.8 (CH$_3$). Found: C, 67.51; H, 5.68; N, 3.26; S, 15.63%. Calcd for C$_{23}$H$_{23}$NS$_2$O$_2$: C, 67.45; H, 5.66; N, 3.42; S, 15.66%.

2c: Mp 161—163 °C; IR (Nujol) 3250 cm^{-1} (NH), 1165, 1100 (SO$_2$); MS *m/z* 423 (1, M$^+$), 221 (100, M$^+$−SNHTs); ^{1}H-NMR (CDCl$_3$) δ 0.98 (s, 9H, CH$_3$), 2.34 (s, 3H, CH$_3$(Ts)), 5.16 (s, 1H, NH), 6.90—7.62 (m, 12H, Ar-H); ^{13}C-NMR (CDCl$_3$) δ 73.3 (9-C), 38.5 ($\underline{\mathrm{C}}$(CH$_3$)$_3$), 21.5 (CH$_3$(Ts)), 27.0 (CH$_3$). Found: C, 68.10; H, 5.94; N, 3.20; S, 15.06%. Calcd for C$_{24}$H$_{25}$NS$_2$O$_2$: C, 68.50; H, 5.95; N, 3.31; S, 15.14%.

2d: Mp 131—135 °C; IR (Nujol) 3325 cm^{-1} (NH), 1170, 1100 (SO$_2$); MS *m/z* 365 (1, M$^+$−Tol), 287 (21, M$^+$−NHTs), 196 (81, Fl=S$^+$), 91 (100, Tol$^+$); ^{1}H-NMR (CDCl$_3$) δ 2.25 (s, 3H, CH$_3$(Tol)), 2.30 (s, 3H, CH$_3$(Ts)), 5.88 (s, 1H, NH), 6.84—7.48 (m, 16H, Ar-H). Found: C, 70.89; H, 5.10; N, 3.08; S, 14.00%. Calcd for C$_{27}$H$_{23}$NS$_2$O$_2$: C, 70.87; H, 5.07; N, 3.06; S, 14.01%.

3d: Mp 182.5—184 °C; IR (Nujol) 3250 cm^{-1} (NH), 1165, 1100 (SO$_2$); MS *m/z* 425 (27, M$^+$), 270 (37, M$^+$−Ts), 255 (100, M$^+$−NHTs), 91 (23, Tol$^+$); ^{1}H-NMR (CDCl$_3$) δ 2.16 (s, 3H, CH$_3$), 2.22 (s, 3H, CH$_3$(Ts)), 6.33 (s, 1H, NH), 6.72—7.44 (m, 16H, Ar-H). Found: C, 76.11; H, 5.44; N, 3.30; S, 7.55%. Calcd for C$_{27}$H$_{23}$NSO$_2$: C, 76.21; H, 5.45; N, 3.29; S, 7.53%.

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$$\underset{\mathrm{I}\ (\mathbf{9})}{\mathrm{R\text{-}}\overset{\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}\mathrm{=C<}} \longleftrightarrow \underset{\mathrm{II}}{\mathrm{R\text{-}}\overset{+}{\underset{\cdot\cdot}{\mathrm{S}}}\mathrm{\text{-}}\overset{-}{\ddot{\mathrm{C}}}\mathrm{<}} \longleftrightarrow \underset{\mathrm{III}\ (\mathbf{10})}{\mathrm{R\text{-}}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}\mathrm{\text{-}}\dot{\mathrm{C}}\mathrm{<}}$$

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