

The Reaction of Fluorenethione S-Tosylimide with Grignard Reagents

Takao SAITO, Michio NAKANE, and Shinichi MOTOKI*

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162

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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 inde-

pendently, 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).

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.

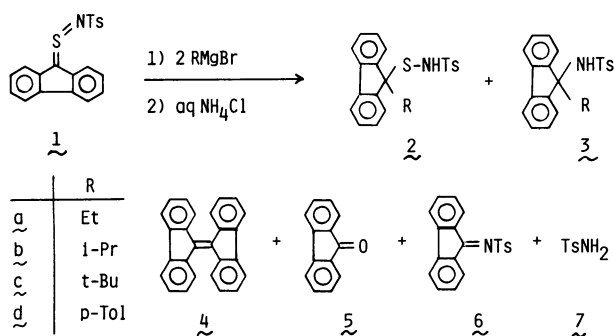
In the reactions in diethyl ether, the yields of the carbophilic adducts (**2**, **3**) are in the order of c(R=*t*-Bu) ≥ b(R=*i*-Pr) > a(R=Et), and the yields of the thiophilic adducts (**4**) are in the order of a(R=Et) > b(R=*i*-Pr) > c(R=*t*-Bu). This result is consistent with the view that the more 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 ionizing potential of 70 eV. ¹H- and ¹³C-NMR spectra were measured on a JEOL-FX 100 spectrometer in CDCl₃ 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 cm³) of a Grignard reagent (7.0 mmol) was added with stirring to a suspension of **1** (1.21 g, 3.32 mmol) in 48 cm³ 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

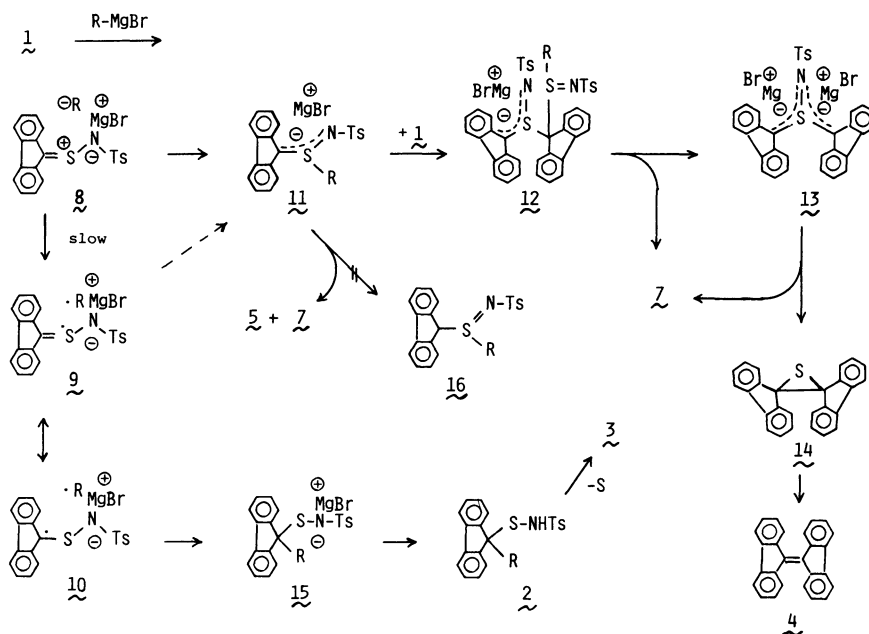


Scheme 1.

TABLE 1. REACTION OF FLUORENETHIONE S-TOSYLIMIDE (**1**) WITH GRIGNARD REAGENTS

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

a) Trace amount, checked by TLC.



Scheme 2.

ether (30 cm³) was added to *p*-tolylmagnesium bromide ethereal solution (37 cm³) 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 NH₄Cl and water, dried over Na₂SO₄, 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 (SO₂); MS *m/z* 395 (3%, M⁺), 193 (100, M⁺–SNHTs); ¹H-NMR (CDCl₃) δ 0.44 (t, *J*=8 Hz, 3H, CH₃), 2.34 (s, 3H, CH₃(Ts)), 2.60 (q, *J*=8 Hz, 2H, CH₂), 5.70 (s, 1H, NH), 7.13–7.70 (m, 12H, Ar–H); ¹³C-NMR (CDCl₃) δ 65.0 (9-C), 28.7 (CH₂), 21.5 (CH₃(Ts)), 8.8 (CH₃). Found: C, 66.88; H, 5.37; N, 3.33; S, 16.13%. Calcd for C₂₂H₂₁NS₂O₂: 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 (SO₂); MS *m/z* 409 (1, M⁺), 207 (100, M⁺–SNHTs); ¹H-NMR (CDCl₃) δ 0.94 (d, *J*=7 Hz, 6H, CH₃), 2.37 (s, 3H, CH₃(Ts)), 2.86 (sept, *J*=7 Hz, 1H, CH), 5.59 (s, 1H, NH), 7.12–7.68 (m, 12H, Ar–H); ¹³C-NMR (CDCl₃) δ 68.9 (9-C), 32.7 (CH), 21.5 (CH₃(Ts)), 8.8 (CH₃). Found: C, 67.51; H, 5.68; N, 3.26; S, 15.63%. Calcd for C₂₃H₂₃NS₂O₂: 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 (SO₂); MS *m/z* 423 (1, M⁺), 221 (100, M⁺–SNHTs); ¹H-NMR (CDCl₃) δ 0.98 (s, 9H, CH₃), 2.34 (s, 3H, CH₃(Ts)), 5.16 (s, 1H, NH), 6.90–7.62 (m, 12H, Ar–H); ¹³C-NMR (CDCl₃) δ 73.3 (9-C), 38.5 (C(CH₃)₃), 21.5 (CH₃(Ts)), 27.0 (CH₃). Found: C, 68.10; H, 5.94; N, 3.20; S, 15.06%. Calcd for C₂₄H₂₅NS₂O₂: C, 68.50; H, 5.95; N, 3.31; S, 15.14%.

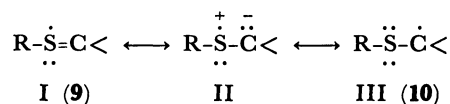
2d: Mp 131–135 °C; IR (Nujol) 3325 cm^{–1} (NH), 1170, 1100 (SO₂); MS *m/z* 365 (1, M⁺–Tol), 287 (21, M⁺–NHTs), 196 (81, M⁺–Ts), 91 (100, Tol⁺); ¹H-NMR (CDCl₃) δ 2.25 (s, 3H, CH₃(Tol)), 2.30 (s, 3H, CH₃(Ts)), 5.88 (s, 1H, NH), 6.84–7.48 (m, 16H, Ar–H). Found: C, 70.89; H, 5.10; N, 3.08; S, 14.00%. Calcd for C₂₇H₂₃NS₂O₂: 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 (SO₂); MS *m/z* 425 (27, M⁺), 270 (37, M⁺–Ts), 255 (100, M⁺–NHTs), 91 (23, Tol⁺); ¹H-NMR (CDCl₃) δ 2.16 (s, 3H, CH₃), 2.22 (s, 3H, CH₃(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 C₂₇H₂₃NSO₂: C, 76.21; H, 5.45; N, 3.29; S, 7.53%.

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