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Thione *S*-Imide. Reaction with Heterocumulenes

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9-Fluorenethione *S*-*p*-toluenesulfonimide reacted with diphenylketene to give two regioisomeric 1,3-dipolar cycloadducts. The thione *S*-imide and symmetrical dialkylcarbodiimides produced 3-tosylimino-1,2,4-thiadiazolidines. In the reaction with ketenimines, there occurred siteselective cycloaddition reactions on C=N *vs.* C=C bonds in the imines and further rearrangement of the 1,2,4-thiadiazolidine adducts.

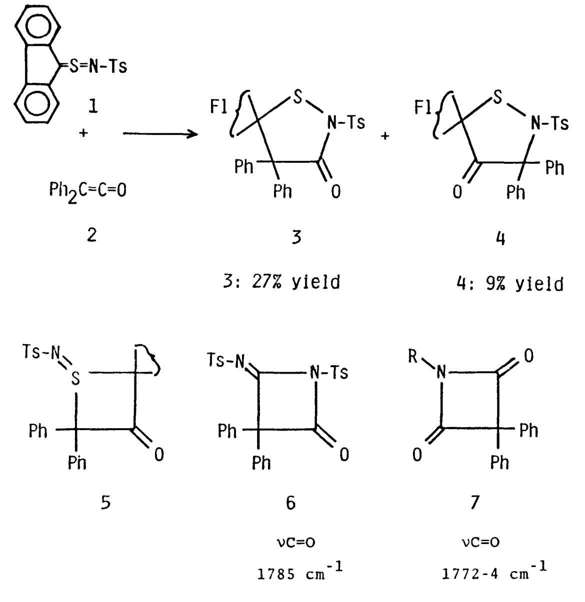
In the preceding papers, we reported that 9-fluorenethione *S*-*p*-toluenesulfonimides (**1**)[1] prepared by a Wittig-type reaction of phosphonium fluorenylides with *N*-sulfinyl-*p*-toluenesulfonamide underwent 1,3-dipolar and Diels-Alder type cycloaddition and ene reactions as a 4π or 2π component with the compounds containing C=C[2] or C=X[3] (X=NR, S, O) double bonds. The present report involves cycloaddition reactions of **1** with some heterocumulenes, *i.e.* diphenylketene, ketenimines, and carbodiimides.

When **1** was allowed to react with diphenylketene (**2**) in 1,2-dichloroethane at room temperature for a week, two regioisomeric (3+2)cycloadducts (**3**, **4**) were obtained. Their IR spectra showed νC=O absorptions at 1715 and 1718 cm^{-1} respectively, so four-membered structures such as **5** were excluded by a comparison with the νC=O values of the related compounds (**6**, **7**).[4] However, it was difficult to distinguish these adducts from each other strictly for the following reasons. (1) Assignment of the νC=O absorptions to Ph_2C–CO–N or Ph_2C–CO–Fl group was difficult. (2) Both adducts showed similar mass-spectral fragmentation patterns. (3) Both adducts were inert to hydrolysis and to 2,4-dinitrophenylhydrazine.

The reaction of **1** with symmetrical dialkylcarbodiimides (**8**) in 1,2-dichloroethane at room temperature afforded 1:1 cycloadducts (**9**). The IR spectra showed strong and broad absorptions at 1530—1560 cm^{-1} assigned to the νC=N–Ts but not to the νC=N–R (alkyl).[5] The mass-spectral fragmentation patterns which exhibited Fl=S$^{\cdot+}$, Ts–NCN–R$^{\cdot+}$, and Fl=NR$^{\cdot+}$ ion peaks also supported the 1,2,4-thiadiazolidine structure. Furthermore, in the NMR spectra of **9a**, the resonance for one CH_3CH_2N group appeared at a rather high field, probably due to the shielding effect exerted by the diamagnetic anisotropy of the adjacent fluorenylidene group (δ 0.56 (CH_3), δ 2.79 (CH_2)). The NMR signal of the other CH_3CH_2N group shifted to lower field (δ 1.42 (CH_3), δ 4.13 (CH_2)) than is found in the usual case. This may be attributed to the deshielding effect of the fluorenylidene ring because this ethyl group would be located near the plane of the fluorenylidene ring. The adduct **9** is considered to be the rearranged product of the hypothetical initial adduct **10**, but we cannot elucidate this at present.[6]

Reactions with diarylcarbodiimides did not proceed under the same reaction conditions, while **1** and unsymmetrical carbodiimides (**11**) afforded guanidines (**12**) and fluorenone (**13**) as unexpected products.

In the reaction of **1** with ketenimines (**14**), 1,3-thiazolidine (**15**) and 1,2,4-thiadiazolidine (**16**) deriv-



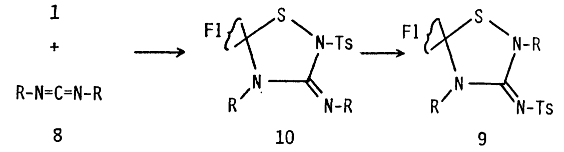
3: 27% yield 4: 9% yield

6: νC=O 1785 cm^{-1}

7: νC=O 1772-4 cm^{-1}

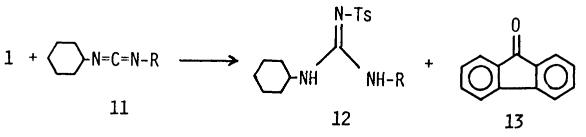
Fl: fluorenylidene group, Ts: p-toluenesulfonyl group

Scheme 1.



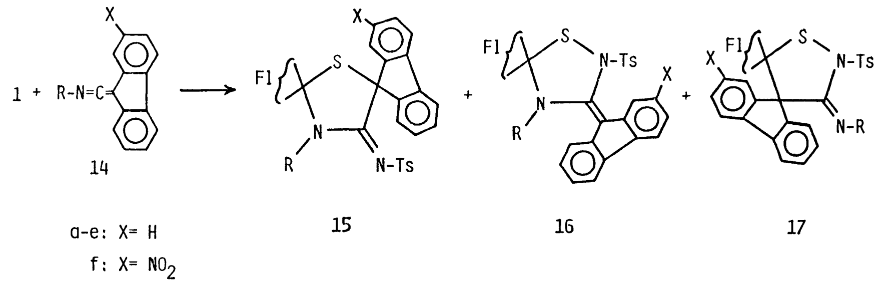
a: R = C_2H_5 9a: 21% yield
b: R = i-C_3H_7 9b: 19% yield
c: R = n-C_4H_9 9c: 14% yield
d: R = c-C_6H_{11} 9d: 43% yield

Scheme 2.



a: R= CH_3 12a: 37% yield
b: R= C_2H_5 12b: 29% yield
c: R= p-ClC_6H_4 12c: 27% yield

Scheme 3.



Scheme 4.

Table 1. Reaction of thione *S*-imide (**1**) with ketenimines (**14**)

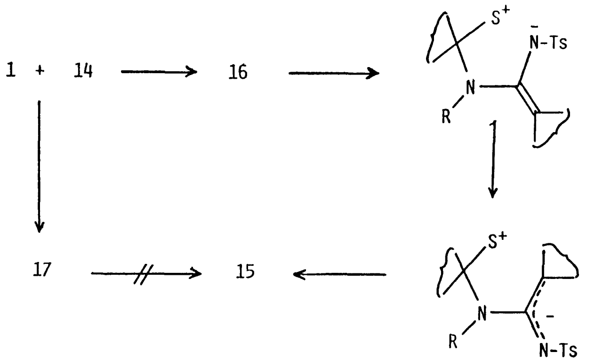
	R	X	Yield (%)		
			15	**16**	**17**
a	C_6H_5	H	87	8	0
b	p-$CH_3C_6H_4$	H	0	55	16
c	p-ClC_6H_4	H	67	17	0
d	1-Naphthyl	H	93	3	0
e	c-C_6H_{11}	H	75	0	0
f	C_6H_5	NO_2	17	20	0

Table 2. ^{13}C NMR spectral data of **15** and **16**

	C(2)	C(3)	C(4)	C(5)	CH_3(Ts)
15a	71.8 s	—	162.9 s	69.0 s	21.3 q
15b	70.9 s	—	163.7 s	67.6 s	21.7 q
15f	72.1 s	—	163.2 s	68.4 s	21.2 q
16a	—	142.2 s	—	68.3 s	21.5 q
16b	—	150.6 s	—	67.1 s	21.8 q

s: Singlet, q: quartet in SFORD measurement.

atives were obtained (Table 1). The IR spectra of **15** and **16** displayed strong νC=N-Ts absorption at 1560—1565 cm^{-1} and νC=C at 1670—1685 cm^{-1}, respectively. The ^{13}C NMR spectra of **15a**, **b**, **f** (indicating the presence of two quarternary carbon atoms and one ring-carbon atom attached to the tosylimino group) and **16a**,**b** (indicating the presence of one quarternary carbon atom and one olefinic ring-carbon atom bonded with nitrogens) also supported the proposed structures (Table 2). In the reaction of **1** and **14b**, a third adduct (**17b**) which exhibits νC=N-Tol-*p* absorption at 1595 cm^{-1} was obtained. This is the 1,3-cycloadduct of **1** onto the C=C bond in **14**. The adducts **16a**,**b** were found to rearrange gradually into **15a**,**b** on standing in dichloromethane or deuteriochloroform; this conversion was confirmed by monitoring the NMR spectra and by isolating **15a**,**b**. The reaction is rationally explained by assuming the sulfur-nitrogen bond cleavage in **16** and a subsequent recombination of sulfur-carbon bond, as considered in the formation of **9**.[7] On the other hand, **17b**, a direct 1,3-cycloadduct, did not rearrange into **15b** (and *vice versa*) at room temperature. The sum of the yields of **15** and **16** which result from the cycloaddition of **1** onto the C=N bond in **14** is much larger than that of **17**, as shown in Table 1. Therefore the cycloaddition of **1** onto the C=N bond predominates with kinetic preference over that onto the C=C bond.



Scheme 5.

Experimental

All the melting points are uncorrected. The IR spectra were determined on a Hitachi Model 260-10 spectrometer. The ^1H NMR and ^{13}C NMR spectra were measured on JEOL JNM-PMX 60 and/or JNM-FX 100 spectrometers in δ values from Me_4Si as an internal standard in deuteriochloroform. The mass spectra were recorded on a Hitachi double-focusing mass spectrometer RMU-7M operating at an ionizing potential of 70 eV. The elemental analyses were performed using a Shimadzu universal organic micro analyzer UM-3B and a rapid-nitrogen analyzer NA-1.

Starting Materials. Diphenylketene (**2**)[8] and carbodiimides (**8**, **11**)[9] were prepared by the methods in the literature. New ketenimines (**14**) were synthesized from the corresponding isocyanates and triphenylphosphonium fluorenylides by the modified method reported by Frøyen.[10]

A mixture of phenyl isocyanate (1.19 g, 0.01 mol) and triphenylphosphonium fluorenylide (4.26 g, 0.01 mol) was refluxed in 50 ml of dry benzene for 2 h until the IR absorption of νN=C=O at 2200 cm^{-1} disappeared; the ketenimine formation was recognized from the strong maximum νC=C=N absorption at 2025 cm^{-1}. After the evaporation of the benzene solvent, the residue was extracted with 60 m of hot ligroine and the yellow-orange extract was passed through a short Florisil column. From the colored fraction, the ketenimine **14a** was obtained quantitatively as yellow plates (recrystallized from hexane); mp 85.0—85.5 °C; MS (70 eV) *m/e* 267 (100, M^+), 190 (58), 164 (66). Found: C, 89.94; H, 4.73%. Calcd for $C_{20}H_{13}N$: C, 89.86; H, 4.90%. The other ketenimines **14b**—**f** were similarly prepared, as is shown in Table 3.

Reaction of Thione S-Imide (1) with Diphenylketene (2). A mixture of **1** (2.46 g, 6.7 mmol) and **2** (1.30 g, 6.7 mmol)

Table 3. Ketenimines (**14**)

Compound	Reaction time	Yield %	Mp (°C) [Bp(°C/mm)]	IR νC=C=N	Appearance
14a	2 h	98	85.0—85.5	2025	yellow plates
14b	2 h	93	—	2010	yellow oil
14c	2 h	82	84.5—85.5	2010	yellow crystals
14d	5 h	57	165—166	2030	yellow needles
14e	3 d	90	[180/0.05]	2040	yellow oil
14f	1 d	20	89—90	2010	orange needles

was stirred in dry 1,2-dichloroethane (70 ml) for a week at room temperature. After the evaporation of the solvent, the residue was chromatographed on silica gel, using benzene as the eluent, to give **3** (the latter fraction) and **4** (the former fraction) together with small amounts of fluorenone (**13**) and *N*-fluorenylidene-*p*-toluenesulfonamide.[11]

3: Colorless crystals (benzene–chloroform); mp 264—265 °C; IR (KBr) 1715 cm^{-1} (C=O), 1250 cm^{-1}; MS (70 eV) *m/e* 559 (17, M^+), 206 (100, M^+ —Ts —Fl=S), 196 (16, Fl=S^+), 194 (10, Ph_2CCO^+); NMR ($CDCl_3$) δ 2.42 (s, 3H, CH_3(Ts)), 6.8—7.7 (m, 22H, arom). Found: C, 73.01; H, 4.55; N, 2.54; S, 11.42%. Calcd for $C_{34}H_{25}NO_3S_2$: C, 72.96; H, 4.50; N, 2.50; S, 11.46%.

4: Colorless crystals (benzene–chloroform); mp 249—250 °C; IR (KBr) 1718, 1724 (shoulder) (C=O), 960 cm^{-1}; MS (70 eV) *m/e* 559 (10, M^+), 206 (46, M^+ —Ts —Fl=S), 196 (100, Fl=S^+), 194 (62, Ph_2CCO^+); NMR ($CDCl_3$) δ 2.42 (s, 3H, CH_3(Ts)), 6.7—7.8 (m, 22H, arom). Found: C, 72.99 H, 4.56; N, 2.56; S, 11.48%. Calcd for $C_{34}H_{25}NO_3S_2$: C, 72.96; H, 4.50; N, 2.50; S, 11.46%.

Reaction of Thione S-Imide (1) with Symmetrical Carbodiimides (8). A Typical Procedure: A mixture of **1** (1.83 g, 5 mmol) and dicyclohexylcarbodiimide (**8d**) (1.03 g, 5 mmol) was stirred in dry 1,2-dichloroethane (30 ml) for 2 h at room temperature. The solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel, using benzene as the eluent, to give **9d** in a 43% yield as colorless crystals recrystallized from chloroform–ethanol. The reactions of **1** with **8a**—**c** were similarly carried out (reaction times: **a**, **b**, and **d**, 2 h; **c**, 4 h).

9a: Mp 122—124 °C; IR (KBr) 1560 (C=N), 1280, and 1145 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.56 (t, *J*=7.2 Hz, 3H, CH_3), 1.42 (t, *J*=7.0 Hz, 3H, CH_3), 2.36 (s, 3H, CH_3 (Ts)), 2.79 (q, *J*=7.2 Hz, 2H, CH_2), 4.13 (q, *J*=7.0 Hz, 2H, CH_2), 7.1—8.1 (m, 12H, arom); MS (70 eV) *m/e* 463 (13, M^+), 308 (40, M^+ —Ts), 280 (2, M^+ —Ts —Et +1), 224 (9, $TsNCNEt^+$), 207 (21, Fl=NEt^+), 196 (35, Fl=S^+), 155 (27, Ts^+), 122 (100, M^+ —Ts —Fl=S), 91 (64, Tol^+). Found: C, 64.81; H, 5.45; N, 8.94; S, 13.90%. Calcd for $C_{25}H_{25}N_3O_2S_2$: C, 64.77; H, 5.44; N, 9.06; S, 13.83%.

9b: Mp 208—209 °C; IR (KBr) 1540 (C=N), 1280 and 1145 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.8 (d, *J*=6.8 Hz, 6H, CH_3), 1.42 (d, *J*=6.4 Hz, 6H, CH_3), 2.37 (s, 3H, CH_3 (Ts)), 2.90 (sep, *J*=6.8 Hz, 1H, CH), 5.33 (sep, *J*=6.4 Hz, 1H, CH), 7.1—8.0 (m, 12H, arom); MS (70 eV) *m/e* 491 (15, M^+), 449 (13), 336 (57, M^+ —Ts), 294 (29), 238 (35, Ts-NCNPr-i^+), 220 (46), 196 (47, Fl=S^+), 155 (48, Ts^+), 140 (79, M^+ —Ts—Fl=S), 91 (100, Tol^+). Found: C, 65.83; H, 5.90; N, 8.50; S, 13.20%. Calcd for $C_{27}H_{29}N_3O_2S_2$: C, 65.96; H, 5.95; N, 8.55; S, 13.02%.

9c: Mp 113—114 °C; IR (KBr) 1550 (C=N), 1290 and 1145 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.2—2.1 (m, 14H, $CH_2CH_2CH_3$), 2.36 (s, 3H, CH_3 (Ts)), 2.67 (t, *J*=7.5 Hz, 2H, CH_2), 4.06 (t, *J*=7.3 Hz, 2H, CH_2), 7.1—8.1 (m, 12H, arom); MS (70 eV) *m/e* 519 (4, M^+), 463 (8), 364 (65, M^+ —Ts), 308 (12), 235 (18, Fl=NBu-n^+), 196 (35, Fl=S^+), 168 (17, M^+ —Ts —Fl=S), 155 (54, Ts^+), 91 (100, Tol^+). Found: C, 67.21; H, 6.31; N, 8.14; S, 12.36%. Calcd for $C_{29}H_{33}N_3O_2S_2$: C, 67.03; H, 6.40; N, 8.08; S, 12.33%.

9d: Mp 195—196 °C; IR (KBr) 1530 (C=N), 1280 and 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.2—2.5 (m, 20H, $(CH_2)_5$), 2.37 (s, 3H, CH_3 (Ts)), 2.75 (broad s, 1H, CH), 4.78 (broad s, 1H, CH), 7.0—8.0 (m, 12H, arom); MS (70 eV) *m/e* 571 (4, M^+), 489 (38), 416 (47, M^+ —Ts), 334 (37), 260 (22), 220 (48, M^+ —Ts —Fl=S), 196 (31, Fl=S^+), 155 (52, Ts^+), 91 (100, Tol^+). Found: C, 69.74; H, 6.65; N, 7.60; S, 11.22%. Calcd for $C_{33}H_{37}N_3O_2S_2$: C, 69.32; H, 6.52; N, 7.35; S, 11.21%.

Reaction of Thione S-Imide (1) with Unsymmetrical Carbodiimides (11). The reaction was carried out in the manner used for **8** (reaction time; **a** and **b**: 30 min, **c**: 15 h). The resultant reaction mixture was subjected to chromatography on silica gel, using chloroform as the eluent, to give **12** and **13**.[11]

12a: Colorless crystals (chloroform-hexane); mp 163—165 °C; IR (KBr) 3370, 3345 (N–H), 1590 (C=N), 1260 and 1145 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.9—2.1 (m, 10H, $(CH_2)_5$), 2.39 (s, 3H, CH_3 (Ts)), 2.80 (d, *J*=4.8 Hz, 3H, CH_3), 3.50 (broad s, 1H, CH), 5.3—6.6 (broad m, 2H, NH), 7.21 (d, *J*=7.8 Hz, 2H, arom), 7.76 (d, *J*=7.8 Hz, 2H, arom); MS (70 eV) *m/e* 309 (3, M^+), 162 (7), 154 (58), 98 (84), 91 (62), 28 (100). Found: C, 58.03; H, 7.45%. Calcd for $C_{15}H_{23}N_3O_2S$: C, 58.23; H, 7.49%.

12b: Colorless crystals (chloroform-hexane); mp 106—107 °C; IR (KBr) 3340 (N–H), 1580 (C=N), 1260 and 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.8—2.1 (m, 11H, $(CH_2)_5CH$), 1.10 (t, *J*=7.0 Hz, 3H, CH_3), 2.38 (s, 3H, CH_3 (Ts)), 2.9—3.9 (m, 3H, CH_2, NH), 6.2 (broad, 1H, NH), 7.20 (d, 2H, *J*=8.0 Hz, arom), 7.73 (d, 2H, *J*=8.0 Hz, arom); MS (70 eV) *m/e* 323 (2, M^+), 225 (3), 168 (70), 155 (18), 98 (96), 91 (47), 44 (100). Found: C, 59.55; H, 7.81%. Calcd for $C_{16}H_{25}N_3O_2S$: C, 59.42; H, 7.79%.

12c: Colorless crystals (chloroform–hexane); mp 165—166 °C; IR (KBr) 3350 (N–H), 1625 (C=N), 1250 and 1140 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 0.7—2.2 (m, 10H, $(CH_2)_5$), 2.41 (s, 3H, CH_3 (Ts)), 3.8 (broad, 1H, CH), 5.0 (broad, 1H, NH), 7.0—7.5 (m, 6H, arom), 7.79 (d, 2H, *J*=8.2 Hz, arom), 8.66 (broad, 1H, NH); MS (70 eV) *m/e* 405 (2, M^+), 322 (2), 250 (10), 155 (13), 127 (100), 98 (24), 91 (31). Found: C, 59.22; H, 6.01%. Calcd for $C_{20}H_{24}N_3O_2SCl$: C, 59.18; H, 5.96%.

Reaction of Thione S-Imide (1) with Ketenimines (14). A Typical Procedure: To a partial suspension of **1** (0.92 g, 2.5 mmol) in 30 ml of 1,2-dichloroethane, a solution of **14a** (0.67 g, 2.5 mmol) in 10 ml of 1,2-dichloroethane was added dropwise at room temperature. The red suspension of **1** gradually disappeared within 2—4 h, but the mixture remained colored. The reaction mixture was stirred overnight at room temperature to complete the reaction. The evaporation of the solvent gave the oily residue, which was subjected to column chromatography on silica gel with benzene as the eluent, followed by dichloromethane. The evaporation of the benzene elution gave **16** together with a trace amount of **14** and fluorenone (**13**). From the second dichloromethane elution, **15** (**17b**) was obtained. The crude **15**, **16**, and **17b** were recrystallized from the appropriate solvents as indicated below. In the case of **c** and **d**, the mixed elution solvent was used instead of the first benzene elution because of the low solubility of **15c**, **d** and **16c**, **d** into benzene (CH_2Cl_2/benzene; **c**: *ca.* 1, **d**: *ca.* 2).

15a: Yellow crystals (recrystallized from benzene-ether); mp 232—233.5 °C; IR (KBr) 1560 (C=N), 1320, 1150, and 1095 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.28 (s, 3H, CH_3 (Ts)), 6.8—7.8 (m, 25H, arom); MS (70 eV) *m/e* 632 (3, M^+), 477 (6, M^+ −Ts), 436 (12, M^+ −Fl=S), 281 (27, M^+ −Ts −Fl=S), 139 (100). Found: C, 76.17; H, 4.40; N, 4.53%. Calcd for $C_{40}H_{28}N_2O_2S_2$: C, 75.94; H, 4.46; N, 4.43%.

15b: Yellow crystals (benzene-ether); mp 267—269 °C; IR (KBr) 1560 (C=N), 1320, 1155, and 1100 cm^{-1} (SO_2); MS (70 eV) *m/e* 646 (4, M^+), 491 (3, M^+ −Ts), 450 (30, M^+ −Fl=S), 295 (78, M^+ −Ts −Fl=S), 255 (100), 139 (60). Found: C, 76.21; H, 4.72; N, 4.39%. Calcd for $C_{41}H_{30}N_2O_2S_2$: C, 76.13; H, 4.68; N, 4.33%.

15c: Yellow prisms (dichloromethane–benzene); mp 240—242 °C; IR (KBr) 1565 (C=N), 1315, 1150, and 1090 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.27 (s, 3H, CH_3 (Ts)), 6.9—8.1 (m, 24H, arom); MS (70 eV) *m/e* 666 (4, M^+), 511 (7, M^+ −Ts), 470 (15, M^+ −Fl=S), 315 (31, M^+ −Ts −Fl=S), 139 (100). Found: C, 72.19; H, 4.12; N, 4.08%. Calcd for $C_{40}H_{27}N_2O_2S_2Cl$: C, 72.00; H, 4.08; N, 4.08%.

15d: Yellow crystals (benzene); mp 218—220 °C; IR (KBr) 1560 (C=N), 1315, 1150, and 1090 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.18 (s, 3H, CH_3 (Ts)), 6.7—8.3 (m, 27H, arom); MS (70 eV) *m/e* 682 (45, M^+), 527 (16, M^+ −Ts), 486 (29, M^+ −Fl=S), 331 (100, M^+ −Ts −Fl=S), 196 (94, Fl=S^+), 139 (19). Found: N, 3.92%. Calcd for $C_{44}H_{30}N_2O_2S_2$: N, 4.10%.

15e: Colorless crystals (benzene–hexane); mp 270—271 °C; IR (KBr) 1560 (C=N), 1300, 1155, and 1095 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.24 (s, 3H, CH_3 (Ts)), 1.1—2.4 (m, 11H, $(CH_2)_5CH$), 6.8—7.5 (m, 20H, arom); MS (70 eV) *m/e* 638 (20, M^+), 483 (6, M^+ −Ts), 442 (6, M^+ −Fl=S), 196 (28, Fl=S^+), 139 (100). Found: N, 4.33%. Calcd for $C_{40}H_{34}N_2O_2S_2$: N, 4.38%.

15f: Pale yellow needles (dichloromethane–benzene); mp 221—222 °C; IR (KBr) 1560 (C=N), 1525, 1340 (NO_2), 1310, 1155, and 1095 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.27 (s, 3H, CH_3 (Ts)), 6.7—8.3 (m, 24H, arom); MS (70 eV) *m/e* 682 (45, M^+), 527 (16, M^+ −Ts), 486 (29, M^+ −Fl=S), 331 (100, M^+ −Ts −Fl=S), 196 (94, Fl=S^+), 139 (19). Found: N, 6.23%. Calcd for $C_{40}H_{27}N_3O_4S_2$: N, 6.20%.

16a: Colorless plates (benzene–hexane); mp 173—175 °C; IR (KBr) 1670 (C=C), 1365, 1150, and 1085 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.60 (s, 3H, CH_3 (Ts)), 6.5—7.9 (m, 25H, arom); MS (70 eV) *m/e* 632 (4, M^+), 477 (9, M^+ −Ts), 436 (13, M^+ −Fl=S), 281 (31, M^+ −Ts −Fl=S), 267 (19, FlCNPh$^+$), 196 (9, Fl=S^+), 139 (100). Found: C, 76.02; H, 4.51; N, 4.32%. Calcd for $C_{40}H_{28}N_2O_2S_2$: C, 75.94; H, 4.46; N, 4.43%.

16b: Colorless plates (benzene–hexane); mp 206—207 °C; IR (KBr) 1670 (C=C), 1370, 1150, and 1095 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 1.88 (s, 3H, CH_3), 2.58 (s, 3H, CH_3 (Ts)), 5.8—8.3 (m, 24H, arom); MS (70 eV) *m/e* 646 (11, M^+), 491 (6, M^+ −Ts), 450 (22, M^+ −Fl=S), 295 (56, M^+ −Ts −Fl=S), 281 (25, FlCN-Tol-*p*$^+$), 196 (26, Fl=S^+), 139 (100). Found: C, 76.18; H, 4.70; N, 4.35%. Calcd for $C_{41}H_{30}N_2O_2S_2$: C, 76.13; H, 4.68; N, 4.33%.

16c: Colorless plates (dichloromethane–benzene); mp 193—196 °C; IR (KBr) 1670 (C=C), 1365, 1150, and 1090 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.27 (s, 3H, CH_3 (Ts)), 6.07—8.5 (m, 24H, arom); MS (70 eV) *m/e* 666 (13, M^+), 511 (13, M^+ −Ts), 470 (17, M^+ −Fl=S), 315 (56, M^+ −Ts −Fl=S), 301 (25, FlCNPh-Cl-*p*$^+$), 196 (34, Fl=S^+), 139 (100). Found: N, 4.18%. Calcd for $C_{40}H_{27}N_2S_2Cl$: N, 4.20%.

16d: Colorless crystals (dichloromethane–hexane); mp 170—172 °C; IR (KBr) 1670 (C=C), 1365, 1165, and 1090 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.18 (s, 3H, CH_3 (Ts)), 6.2—8.4 (m, 27H, arom); MS (70 eV) *m/e* 682 (46, M^+), 527 (20, M^+ −Ts), 486 (16, M^+ −Fl=S), 331 (100, M^+ −Ts −Fl=S), 317 (32, FlCN-Naph$^+$), 139 (15). Found: N, 3.95%. Calcd for $C_{40}H_{27}N_3O_4S_2$: N, 6.20%.

17b: Yellow crystals (dichloromethane–ether); mp 174—175 °C; IR (KBr) 1595 (C=N), 1290, 1165, and 1090 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 2.05 (s, 3H, CH_3), 2.52 (s, 3H, CH_3 (Ts)), 6.4—8.1 (m, 24H, arom); MS (70 eV) *m/e* 646 (1, M^+), 450 (17, M^+ −Fl=S), 295 (42, M^+ −Ts −Fl=S), 256 (100), 196 (53, Fl=S^+). Found: C, 76.29; H, 4.71%. Calcd for $C_{41}H_{30}N_2O_2S_2$: C, 76.13; H, 4.68%.

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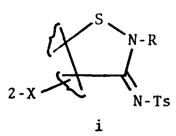
6) This type of rearrangement for 1,2,4-thiadiazolidine ring system was reported; Refs. 5b and 5d.

7) On the basis of the spectral data, we could not completely exclude the possibility of the 1,2-thiazolidine structure **i** for **15**.



i

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11) *N*-fluorenylidene-*p*-toluenesulfonamide and fluorenone (**13**) were identified by a comparison of the IR spectra with those of authentic samples.