

## Thione S-Imides. The Reaction with Carbon-Hetero Atom Double Bond

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9-Fluorenothione *S*-*p*-toluenesulfonimide reacted as a 1,3-dipole with imines, oximes, and thiones to form (3+2)cycloadducts, while with symmetrical azines and aldehydes, unsymmetrical azines, *N*-(*p*-tolylsulfonfyl) imines and fluorenone were obtained as a result of the decomposition of the cycloadducts.

Thione *S*-imides,<sup>1)</sup> new thiocumulenes, have recently been synthesized by several workers.<sup>2)</sup> However, there have been few reports on the cycloaddition reactions of the imides.<sup>3)</sup>

Previously,<sup>4)</sup> we reported the 1,3-dipolar, Diels-Alder-type cycloaddition, and ene reactions of 9-fluorenothione *S*-*p*-toluenesulfonimides (**1**) with compounds containing C=C bond(s). We have now attempted the reaction of **1** with compounds containing C=X bond(s) (X=NR, O, S) *i.e.*, imines (**2**), oximes (**6**), azines (**8**), aldehydes (**11**), and thiones (**14**).

## Results and Discussion

The treatment of **1** with aldimines (**2**) in 1,2-dichloroethane at room temperature gave (3+2)cycloadducts, spiro[fluorene-9,5'-[1,2,4]thiadiazolidine] derivatives (**3**), regiospecifically. The results are shown in Tables 1 and 2. The adducts showed no characteristic  $\nu$ S=N absorption band in the IR spectra, and their mass-spectral fragmentation patterns exhibited *N*-(fluorenylidene)-*p*-toluenesulfonamide (FI=NTs<sup>+</sup>), *N*-(fluorenyl-

idene)arylamine (FI=NC<sub>6</sub>H<sub>4</sub>R<sup>2+</sup>), and aldimine (R<sup>1</sup>C<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>R<sup>2+</sup>) ion peaks. Among these adducts, **3i** was a particularly unstable compound; it decomposed to form **5** in a solution. These observations are consistent with the proposed structure, **3**, rather than with the regioisomeric structure, **4**.

The reactions of **1** with *N*-alkylalkanamines or *N*-alkylarylmethanimines (*N*-cyclohexyl-2-butanamine, *N*-cyclohexyl-1-(2-methyl)propanamine, *N*-(2-butyl)-2-butanamine, *N*-cyclohexylphenylmethanimine, and *N*-(2-propyl)phenylmethanimine) resulted in complicated decomposition reactions, fluorenone and tar being formed. Reactions with ketimines such as *N*-phenyldiphenylmethanimine did not proceed under the same reaction conditions, whereas prolonged treatment at room temperature or by refluxing the 1,2-dichloroethane solution caused only decomposition reactions.

The reaction of **1** with oximes (**6**) proceeded rapidly to give (3+2)cycloadducts **7** (Tables 3 and 4). The IR spectra of **7** showed a distinct band at 3220—3320 cm<sup>-1</sup> due to the hydroxyl group, but no  $\nu$ S=N band. The mass-spectral fragmentation pattern resembled that of **3**.

TABLE 1. 3',4'-DIARYL-2'-*p*-TOLUENESULFONYLSPIRO[FLUORENE-9,5'-[1,2,4]THIA DIAZOLIDINES] (**3**)

Compd	R <sup>1</sup>	R <sup>2</sup>	X	Reaction time/h	Yield %	Mp °C (dec)
<b>3a</b>	H	H	H	2	90	128—130
<b>3b</b>	H	CH <sub>3</sub>	H	3	91	104—105
<b>3c</b>	H	Cl	H	4	80	117—119
<b>3d</b>	H	NO <sub>2</sub>	H	16	91	126—128
<b>3e</b>	H	OCH <sub>3</sub>	H	5	77	99—101
<b>3f</b>	OCH <sub>3</sub>	H	H	0.5	86	88—90
<b>3g</b>	Cl	H	H	1.5	90	95—97
<b>3h</b>	Cl	Cl	H	4	87	113—114
<b>3i</b>	H	H	NO <sub>2</sub>	2.5	53	119—120

TABLE 2a. IR AND NMR SPECTRAL DATA OF **3**

Compd	IR, cm <sup>-1</sup> $\nu$ SO <sub>2</sub>		CH <sub>3</sub> (Ts)	NMR, $\delta$ in CDCl <sub>3</sub> <sup>a)</sup> Ar-H	Others
<b>3a</b>	1320	1160	2.42(s, 3H)	6.3—8.1(m, 22H)	
<b>3b</b>	1310	1165	2.44(s, 3H)	7.0—8.0(m, 17H), 6.31, 6.72 (dd, 4H)	2.07(s, 3H, CH <sub>3</sub> -Ar)
<b>3c</b>	1305	1160	2.46(s, 3H)	7.0—8.0(m, 17H), 6.30, 6.80 (dd, 4H)	
<b>3d</b>	1310	1165	2.47(s, 3H)	7.0—8.0(m, 17H), 6.24 (d, 2H)	
<b>3e</b>	1290	1165	b)	b)	b)
<b>3f</b>	1310	1165	2.39(s, 3H)	6.2—8.0(m, 21H)	3.77 (s, 3H, CH <sub>3</sub> O)
<b>3g</b>	1310	1165	2.44(s, 3H)	6.3—8.0(m, 21H)	
<b>3h</b>	1315	1165	2.44(s, 3H)	7.0—8.0(m, 16H), 6.28, 6.80 (dd, 4H)	
<b>3i</b>	1315	1165	b)	b)	

a) s: singlet, d: doublet, m: multiplet. b) Clear spectral data could not be obtained because of their instability in solution.

TABLE 2b. ELEMENTAL ANALYSES OF **3**

Compd	Molecular formula (MW)	Calcd (%)			Found (%)		
		C	H	N	C	H	N
<b>3a</b>	C <sub>33</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> (546.7)	72.50	4.79	5.12	72.30	4.79	4.98
<b>3b</b>	C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> (560.7)	72.83	5.03	4.99	72.78	5.17	5.01
<b>3c</b>	C <sub>33</sub> H <sub>25</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Cl (581.1)	68.21	4.34	4.82	68.01	4.30	4.85
<b>3d</b>	C <sub>33</sub> H <sub>25</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> (591.7)	66.99	4.26	7.10	66.65	4.39	7.12
<b>3e</b>	C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (576.7)	70.81	4.89	4.86	70.70	4.81	4.88
<b>3f</b>	C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (576.7)	70.81	4.89	4.86	70.61	4.91	4.74
<b>3g</b>	C <sub>33</sub> H <sub>25</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Cl (581.1)	68.21	4.34	4.82	68.50	4.68	4.81
<b>3h</b>	C <sub>33</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub> (615.6)	64.39	3.93	4.55	64.10	4.18	4.60
<b>3i</b>	C <sub>33</sub> H <sub>25</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> (591.7)	66.99	4.26	7.10	c)	c)	c)

c) An analytically pure sample could not be obtained because of the instability of **3i**.

TABLE 3. 4'-HYDROXY-3',3'-DISUBSTITUTED 2'-*p*-TOLUENESULFONYLSPIRO[FLUORENE-9,5'-[1,2,4]THIA DIAZOLIDINES] (**7**)

Compd	R <sup>1</sup>	R <sup>2</sup>	X	Reaction time/min	Yield %	Mp/°C (dec)
<b>7a</b>	CH <sub>3</sub>	CH <sub>3</sub>	H	5	92	127—129
<b>7b</b>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	H	5	89	120—121
<b>7c</b>	—(CH <sub>2</sub> ) <sub>5</sub> —		H	5	92	125—126
<b>7d</b>	CH <sub>3</sub>	CH <sub>3</sub> CO	H	30	83	142—143
<b>7e</b>	H	C <sub>6</sub> H <sub>5</sub>	H	60	84	oil <sup>a)</sup>
<b>7f</b>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	15	88	116—117
<b>7g</b>	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	10	87	106—107
<b>7h</b>	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub>	H	10	93	107—108
<b>7i</b>	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	H	15	95	168—170
<b>7j</b>	CH <sub>3</sub>	CH <sub>3</sub>	NO <sub>2</sub>	5	89	161—162

a) Compound **7e** was purified by means of column chromatography on silica gel, with benzene as the eluent.

TABLE 4a. IR AND NMR SPECTRAL DATA OF **7**

Compd	IR, cm <sup>-1</sup>			NMR, δ in CDCl <sub>3</sub>			
	ν OH	ν SO <sub>2</sub>		OH	CH <sub>3</sub> (Ts)	Ar-H	Others
<b>7a</b>	3320	1320 1160		5.87(s, 1H)	2.35 (s, 3H)	7.0—7.9 (m, 12H)	1.93 (s, 6H, CH <sub>3</sub> )
<b>7b</b>	3310 3230	1320 1160		5.87(s, 1H)	2.37 (s, 3H)	7.0—7.9 (m, 12H)	1.90 (s, 3H, CH <sub>3</sub> ) 1.67 (t, 3H, CH <sub>3</sub> ) 2.30 (q, 2H, CH <sub>2</sub> )
<b>7c</b>	3220	1295 1165		5.82(s, 1H)	2.38 (s, 3H)	7.0—8.0 (m, 12H)	1.1—3.0 (m, 10H, (CH <sub>2</sub> ) <sub>5</sub> )
<b>7d</b>	3200 3300	1330 1165		6.07(s, 1H)	2.39 (s, 3H)	7.1—8.0 (m, 12H)	2.00 (s, 3H, CH <sub>3</sub> ) 2.43 (s, 3H, CH <sub>3</sub> CO)
<b>7e</b>	3250	1295 1170		6.57(s, 1H)	2.28 (s, 3H)	7.0—8.1 (m, 17H)	
<b>7f</b>	3220	1320 1165		5.80(s, 1H)	2.33 (s, 3H)	7.0—8.0 (m, 22H)	
<b>7g</b>	3220	1320 1165		5.79(s, 1H)	2.38 (s, 3H)	7.0—7.9 (m, 21H)	2.35 (s, 3H, CH <sub>3</sub> )
<b>7h</b>	3280	1295 1175		5.82(s, 1H)	2.30 (s, 3H)	7.0—8.0 (m, 26H)	
<b>7i</b>	3260	1305 1170		6.01(s, 1H)	2.33 (s, 3H)	7.0—8.0 (m, 21H)	
<b>7j</b>	3290	1320 1160		5.89(s, 1H)	2.36 (s, 3H)	7.0—7.9 (m, 9H) 8.12 (dd, 1H) 8.46 (d, 1H)	1.92 (s, 6H, CH <sub>3</sub> )

The treatment of **1** with azines (**8**) afforded unsymmetrical azines (**9**) and *N*-(*p*-tolylsulfonyl) imines (**10**) (Tables 5 and 6). In this case, one of the arylmethylene moiety of **8** was replaced by the fluorenylidene group. This *trans*-imidation reaction can be explained by assuming a path involving a 1,3-dipolar cycloaddition reaction,<sup>5)</sup> followed by ring fragmentation with an elimination of sulfur, as is shown in the scheme.

Aromatic aldehydes (**11**) reacted slowly with **1a** to afford *N*-(*p*-tolylsulfonyl)arylmethanimines (**12**) and

fluorenone (**13**) (Table 7). The formation of these products also suggests the presence of an intermediary cycloadducts, as is shown in the scheme. No reaction was observed between **1a** and ketones, such as 2-propanone, 2-butanone, and benzophenone under the same conditions. On the contrary, diaryl thioketones (**14**) reacted with **1a** to form (3+2)cycloadducts, 1,4,2-dithiazolidines (**15**) (Tables 8 and 9). The mass-spectral fragmentations which involve R<sub>2</sub>C=NTs<sup>+</sup>, Fl=S<sup>+</sup>, Fl=NTs<sup>+</sup>, and R<sub>2</sub>C=S<sup>+</sup> ion peaks are compatible

TABLE 4b. ELEMENTAL ANALYSES OF **7**

Compd	Molecular formula (MW)	Calcd (%)			Found (%)		
		C	H	N	C	H	N
<b>7a</b>	C <sub>23</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (438.6)	62.99	5.06	6.38	62.79	5.17	6.42
<b>7b</b>	C <sub>24</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (452.6)	63.69	5.34	6.19	63.60	5.44	6.17
<b>7c</b>	C <sub>26</sub> H <sub>26</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (478.6)	65.25	5.48	5.85	65.20	5.46	5.52
<b>7d</b>	C <sub>24</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub> (466.6)	61.78	4.75	6.00	62.34	4.77	5.97
<b>7e</b>	C <sub>27</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (486.6)	66.65	4.56	5.75	66.81	4.62	5.66
<b>7f</b>	C <sub>33</sub> H <sub>26</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (562.7)	70.43	4.66	4.98	70.21	5.01	4.72
<b>7g</b>	C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (576.7)	70.81	4.89	4.86	70.90	4.88	4.91
<b>7h</b>	C <sub>39</sub> H <sub>30</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> (638.8)	73.33	4.73	4.38	73.18	4.77	4.69
<b>7i</b>	C <sub>33</sub> H <sub>25</sub> N <sub>2</sub> O <sub>3</sub> S <sub>2</sub> Cl (597.1)	66.38	4.22	4.69	66.78	4.31	4.79
<b>7j</b>	C <sub>23</sub> H <sub>21</sub> N <sub>3</sub> O <sub>5</sub> S <sub>2</sub> (483.5)	57.13	4.38	8.69	57.38	4.26	8.81

TABLE 5. REACTION OF THIONE S-IMIDE (**1a**) WITH AZINES (**8**)

	R <sup>1</sup>	R <sup>2</sup>	Yield/%		Mp/°C	
			<b>9</b>	<b>10</b>	<b>9</b>	<b>10</b>
<b>a</b>	Ph	H	47	76	87—88	108—109
<b>b</b>	<i>p</i> -CH <sub>3</sub> Ph	H	46	59	132—133	114—116
<b>c</b>	<i>p</i> -CH <sub>3</sub> OPh	H	61	a)	115—116	*
<b>d</b>	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NPh	H	36	a)	155—157	*
<b>e</b>	Ph	CH <sub>3</sub>	12	a)	127—129	*

a) *p*-Toluenesulfonamide and the corresponding carbonyl compounds were obtained instead of **10**.

TABLE 6a. NMR AND MASS SPECTRAL DATA OF **9**

Compd	NMR, $\delta$ in CDCl <sub>3</sub>			MS, rel. intens.		
	Ar-H	R <sup>2</sup>	Others	M <sup>+</sup>	M <sup>+</sup> - R <sup>1</sup>	M <sup>+</sup> - N <sub>2</sub>
<b>9a</b>	7.0—8.0 (m, 1H) 8.0—8.7 (m, 12H)	8.53 (s, 1H)		100	82	49
<b>9b</b>	7.1—8.0 (m, 11H) 8.3—8.6 (m, 1H)	8.54 (s, 1H)	2.42 (s, 3H, <i>p</i> -CH <sub>3</sub> )	100	74	38
<b>9c</b>	6.8—8.0 (m, 11H) 8.4—8.6 (m, 1H)	8.50 (s, 1H)	3.83 (s, 3H, <i>p</i> -CH <sub>3</sub> O)	100	50	14
<b>9d</b>	7.0—8.5 (m, 10H) 6.75 (d, 2H)	8.53 (s, 1H)	3.05 (s, 6H, <i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> N)	100	29	26
<b>9e</b>	7.1—7.7 (m, 9H) 7.8—8.2 (m, 4H)	2.42 (s, 3H)		100	44	2

TABLE 6b. ELEMENTAL ANALYSES OF **9**

Compd	Molecular formula (MW)	Calcd (%)			Found (%)		
		C	H	N	C	H	N
<b>9a</b>	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> (282.3)	85.04	5.00	9.92	84.91	5.01	9.71
<b>9b</b>	C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> (296.4)	85.11	5.44	9.45	84.76	5.47	9.31
<b>9c</b>	C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O (312.4)	80.75	5.16	8.97	81.13	5.39	9.00
<b>9d</b>	C <sub>22</sub> H <sub>19</sub> N <sub>3</sub> (325.4)	81.21	5.89	12.91	80.94	6.07	13.05
<b>9e</b>	C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> (296.4)	85.11	5.44	9.45	84.98	5.71	9.56

TABLE 7. REACTION OF THIONE S-IMIDE (**1a**) WITH AROMATIC ALDEHYDES (**11**)

	Ar	Reaction time/d	Yield/%	
			<b>12</b>	<b>13</b>
<b>a</b>	Ph	6	23	98
<b>b</b>	<i>p</i> -CH <sub>3</sub> Ph	6	24	65
<b>c</b>	<i>p</i> -CH <sub>3</sub> OPh	7	a)	95
<b>d</b>	<i>p</i> -ClPh	12	a)	67

a) *p*-Toluenesulfonamide and the corresponding aldehydes were obtained instead of **12**.

with the proposed structure.

As has been described above, it has been found that **1** underwent 1,3-dipolar cycloaddition reactions with the dipolarophiles containing carbon-hetero atom double bond(s), such as **2**, **6**, **8**, **11**, and **14**, to afford the adducts as isolable products or unstable intermediates regiospecifically. However, the adducts, **3**, **7**, and **15**, are not quite stable and are gradually decomposed on long standing in a solid state or in a solution. When **3** or **7** adducts were dissolved in warm 1,2-dichloroethane, the solution turned orange-red immediately,<sup>6)</sup> while the

**Decomposition of 3i.** A solution of **3i** in 1,2-dichloroethane was allowed to stand overnight at room temperature. The solvent was then evaporated *in vacuo*, and the residue was subjected to column chromatography on silica gel, using

benzene as the eluent. *N*-(2-nitrofluorenylidene)aniline (**5**) was obtained as orange crystals in an 81% yield (recrystallized from benzene-hexane); mp 146–147 °C (lit.<sup>7</sup> mp 141 °C), IR (KBr) 1655 (C=N), 1520 and 1340 cm<sup>-1</sup> (NO<sub>2</sub>); NMR (CDCl<sub>3</sub>) δ 6.6–8.0 (m, 10H), 8.28 (dt, 1H, *J*=2.0, 8.0 Hz), 8.72 (d, 1H, *J*=2.0 Hz); MS (70 eV) *m/e* 300 (100, M<sup>+</sup>), 254 (43, M<sup>+</sup> - NO<sub>2</sub>). Found: C, 76.01; H, 4.11; N, 9.51%. Calcd for C<sub>19</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>: C, 75.99; H, 4.03; N, 9.33%.

**Reaction of Thione S-Imides (1) with Oximes (6).** A mixture of **1a** (1.00 g, 2.74 mmol) and acetone oxime (**6a**) (0.25 g, 3.42 mmol) was stirred in dry 1,2-dichloroethane (20 cm<sup>3</sup>) at room temperature for 5 min. A work-up similar to that described for the preparation of **3** gave **7a** as colorless crystals in a 92% yield; mp 127–129 °C (dec); MS (70 eV) *m/e* 333 (14), 236 (19), 196 (10), 180 (50), 155 (34), 91 (85), 73 (10), 56 (100).

**Reaction of Thione S-Imide (1a) with Azines (8).** A mixture of **1a** (0.5 g, 1.37 mmol) and benzaldehyde azine (**8a**) (0.30 g, 1.44 mmol) was stirred in dry 1,2-dichloroethane at room temperature for 4 d. The solvent was then evaporated *in vacuo*, and the residue was column-chromatographed on silica gel, using benzene as the eluent, to give **9a** as orange needles (recrystallized from benzene-hexane) in a 47% yield; mp 87–88 °C. Subsequent elution with the same solvent gave **10a** as colorless crystals in a 76% yield; mp 108–109 °C (lit.<sup>8</sup> mp 107 °C) (recrystallized from benzene-hexane).<sup>9</sup>

**Reaction of Thione S-Imide (1a) with Aromatic Aldehydes (11).** A mixture of **1a** (0.50 g, 1.37 mmol) and excess benzaldehyde (**11a**) was stirred in 1,2-dichloroethane at room temperature for 6 d. After the evaporation of the solvent, the residue was column-chromatographed on silica gel, using benzene as the eluent (followed by chloroform), to give **12a** (mp 105–106 °C (lit.<sup>9</sup> mp 107 °C))<sup>9</sup> in a 23% yield and fluorenone (**13**) (mp 83–84 °C (lit.<sup>10</sup> mp 83.0–83.5 °C); IR 1720 cm<sup>-1</sup> (C=O)) in a 98% yield (accompanied by the excess aldehyde). The yields of **13** and the recovered excess aldehyde were estimated by GLC.

**Reaction of Thione S-Imide (1a) with Thiones (14).** Into a suspension of **1a** (0.73 g, 2.0 mmol) in 1,2-dichloroethane (10 cm<sup>3</sup>), a solution of 4,4-dimethoxythiobenzophenone (**14c**) (0.62 g, 2.4 mmol) in 1,2-dichloroethane (10 cm<sup>3</sup>) was stirred, drop by drop, at room temperature. A colorless solid precipitated in a few min. After stirring for 30 min, the solid was collected and washed with ether-hexane to give **15c** in an 88%

yield; mp 140–142 °C (dec); NMR (CDCl<sub>3</sub>) δ 6.67–7.67 (m, 20H, arom), 3.85 (s, 6H, OCH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>(Ts)), MS *m/e* 395 (11, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>C=NTs<sup>+</sup>), 333 (20, Fl=NTs<sup>+</sup>) 269 (12, Fl=N-Tol-*p*<sup>+</sup>), 258 (25, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CS<sup>+</sup>), 240 (62, (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CN<sup>+</sup>), 196 (100, Fl=S<sup>+</sup>). In the other cases, the reaction mixture was concentrated *in vacuo*, since no precipitation occurred. The residue was triturated in ether-hexane to afford the product.<sup>11</sup>

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