Reaction of *N*-Sulfinylamine with Phosphonium Ylide

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N-sulfinyl-*p*-toluenesulfonamide (**1a**) reacted with triphenylphosphonium fluorenylides **3a–f** on the S=O bond of the -N=S=O group to afford thione *S*-imide **4** and triphenylphosphine oxide (**6**), while *N*-sulfinyl-*p*-nitroaniline (**1b**) reacted with the ylide on the N=S bond of the -N=S=O group to give sulfine **5** and *p*-nitrophenyliminotriphenylphosphorane (**7**). Triphenylphosphonium phenylbenzoylmethylide (**3g**) reacted with **1a** on both the ylide moiety and the carbonyl group to give 4,5-diphenyl-2,3-di(*p*-toluenesulfonyl)-Δ^4-1,2,3-thiadiazoline (**14b**).

The reactivity of *N*-sulfinylamines **1**[1] resembles that of isocyanates **2** in many respects as expected from their resonance structures. Usually both of the compounds react as dipolarphile 1-A or 2-A with a variety of the other dipoles such

$$\underset{\textbf{1-A}}{\text{R-}\overset{-}{\text{N}}\text{-}\overset{+}{\text{S}}\text{=O}} \longleftrightarrow \underset{\textbf{1}}{\text{R-N=S=O}} \longleftrightarrow \underset{\textbf{1-B}}{\text{R-N=}\overset{+}{\text{S}}\text{-}\overset{-}{\text{O}}}$$

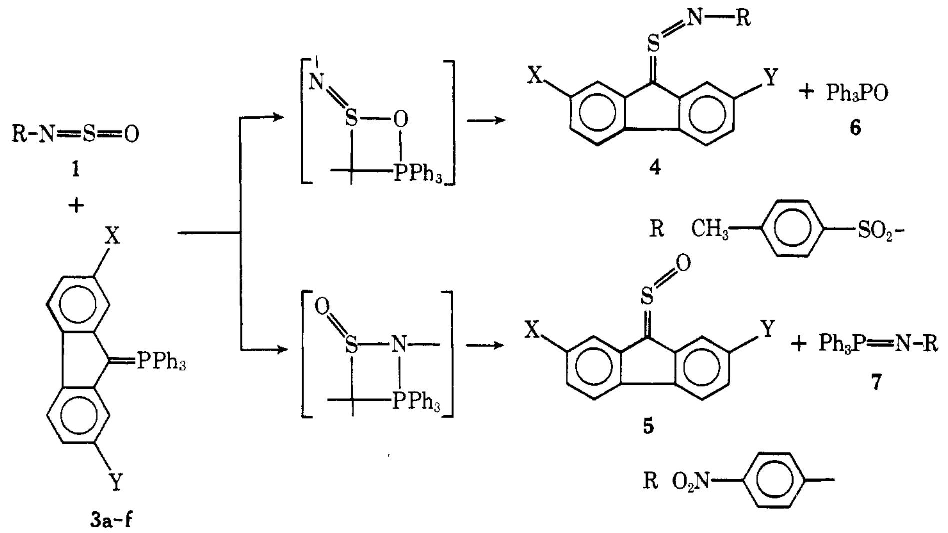
$$\underset{\textbf{2-A}}{\text{R-}\overset{-}{\text{N}}\text{-}\overset{+}{\text{C}}\text{=O}} \longleftrightarrow \underset{\textbf{2}}{\text{R-N=C=O}} \longleftrightarrow \underset{\textbf{2-B}}{\text{R-N=}\overset{+}{\text{C}}\text{-}\overset{-}{\text{O}}}$$

as >C=O, >C=S, >C=N–, >S=O, >P=O and >P=S.[2] In the case of the reaction with >P=N– or >P=C< (carrying no hydrogen on the ylide carbon), **2** undergoes Wittig-type reactions as 2-B to afford carbodiimide or ketenimine, respectively.[3] There are a few reports in the literature dealing with 1,2-cycloaddition/fragmentation reaction across the S=O bond in **1**. In the present paper, we wish to report the reaction of **1** with phosphonium ylides **3** which afforded thione *S*-imides **4** or sulfines **5**.

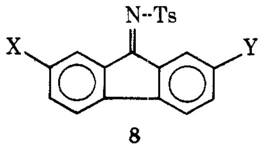
Stable ylides such as triphenylphosphonium fluorenylide or phenylbenzoylmethylide and relatively reactive *N*-sulfinylamines such as *N*-sulfinyl-*p*-toluenesulfonamide or *N*-sulfinyl-*p*-nitroaniline were used as starting materials. The fluorenylidene residue and electron-withdrawing *p*-toluenesulfonyl or *p*-nitrophenyl group should stabilize the expected products **4** or **5**.

Colored thione *S*-imides **4a–f**[4] and triphenylphosphine oxide (**6**) were readily obtained by treatment of *N*-sulfinyl-*p*-toluenesulfonamide (**1a**) with triphenylphosphonium fluorenylides **3a–f** at room temperature. Fluorene-*p*-toluenesulfonylimine (**8**), formed by the desulfurization of **4**, and the *p*-toluenesulfonyliminotriphenylphosphorane–triphen-

Scheme I



	X	Y		X	Y
3a, 4a, 5a	H	H	3d, 4d, 5d	PhCO	H
3b, 4b, 5b	NO_2	H	3e, 4e, 5e	CH_3O	H
3c, 4c, 5c	Br	Br	3f, 4f, 5f	$N(CH_3)_2$	H



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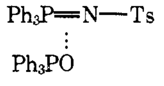

$$\begin{matrix}Ph_3P\text{=N—Ts}\\ \vdots\\ Ph_3PO\end{matrix}$$

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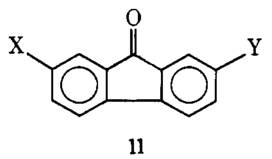
Ph_3PS

10



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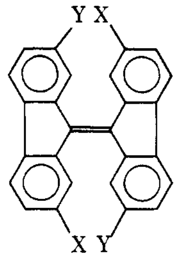

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Table I. Reaction of *N*-Sulfinyl-*p*-toluenesulfonamide (1a) with Triphenylphosphonium Fluorenylides 3a–f. Reaction Time and Product Distribution.

Phosphonium ylide	Reaction time, h	Products 4[a]			By-products yield, %				
		Yield	Color	Mp, °C	6	8	9	10	11
3a	4	83	Red	134–135	58	0	11	0	0
3b	5	42	Orange	160–170	0	24	25	0	0
3c	4.5	77	Brown	223–225	53	12	12	0	0
3d	4	0			0	53	28	20	Trace
3e	4	81	Brown	134–136	36	0	0	0	0
3f	4	42	Green	110–112	63	35	7	8	8

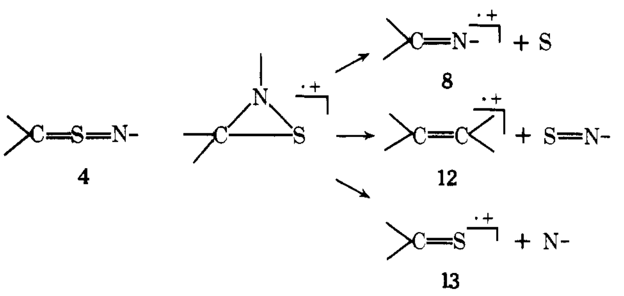
[a] Satisfactory analytical data (±0.3% for C, H, N, and S) were reported for **4a–c,e,f.**

Table II. Reaction of *N*-Sulfinyl-*p*-nitroaniline (1b) with Triphenylphosphonium Fluorenylides 3a–f. Reaction Condition and Product Distribution.

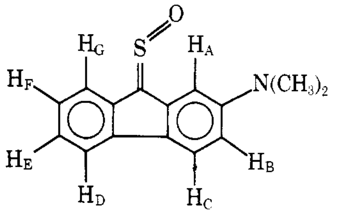
Phosphonium ylide	Reaction condition[a]	Time, h	Products 5[a]			By-products yield, %					Recovered materials	
			Yield	Color	Mp, °C	7	6	10	11	12	1b	3
3a	A	8	61	Orange	105–107	81	0	0	0	0	15	0
3b	B[b]	17.5	0			0	34	8	5	34	96	45
3c	A	15	11	Red	<360	14	0	0	0	0	55	59
3d	B[b]	17.5	0			41	0	5	0	81	20	0
3e	A	12	20	Orange		90	0	0	0	61	0	0
3f	A	8	56	Blue Blue	88–89 (cis) 118–120 (trans)	85	0	8	0	0	9	1

[a] A, in benzene, reflux. B, in toluene, reflux. [b] Most quantities of the starting materials were recovered after refluxing in benzene for 20 h. [c] Satisfactory analytical data were reported for **5a, c, e** and **f** (cis and trans).

ylphosphine oxide complex (**9**)[2d] were obtained as by-products. The results are shown in Table I. The IR spectra of 4 showed characteristic strong absorption bands due to ν (>C=S=N–) at the region of 960–990 cm^{-1} and ν (SO$_2$) at 1150–1160 and 1080–1085 cm^{-1}. These data are similar to those reported by Oae for some thione *S*-imides.[4a,b] The mass spectra of 4 were similar to those of the imine **8**,[5] except for the peaks of bis(fluorenylidene) (**12**) ion, thione (**13**) ion, and the small molecular ion (Table III, see Supplementary Material). These data suggest that rearrangement and fragmentation of 4 on electron impact proceed via transient thiaziridine ring.[6]

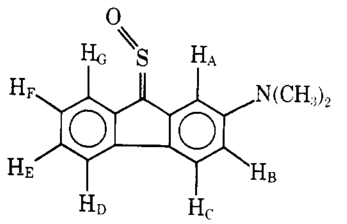


Treatment of *N*-sulfinyl-*p*-nitroaniline (**1b**) with **3a–f** at room temperature resulted in recovery of the starting materials. However, refluxing of the benzene or toluene solution of the reactants gave sulfines **5a–f** and *p*-nitrophenyliminotriphenylphosphorane (**7**). Yields of **5** were low except for **5a** and a considerable amount of bis(fluorenylidene) (**12**), presumably formed by the decomposition of **5**, and recovered starting materials were obtained. These results are shown in Table II. We obtained relatively simple IR spectra of **5**, in which the absorption bands due to the >C=S=O group were observed at 1110–1140 and 1015–1020 cm^{-1} (Table IV, see Supplementary Material). Sulfines **5c**, **5e**, and **5f** exhibited characteristic mass spectra resembling those of **5a** which had already been reported by Zwanenburg et al.[7] The sulfine **5f** was separated into its cis and trans isomers by means of column chromatography and recrystallization.[8] Distinct differences in these isomers were observed in their melting points, NMR, and IR spectra. In the NMR spectrum, the bent >C=S=O group deshielded the protons at H$_A$ in *cis*-**5f** (δ 8.07) or at H$_G$ in *trans*-**5f** (δ 8.49) to shift their signals to lower field than those of the remaining aromatic protons (δ 6.6–7.6).



cis-**5f**

6 H$_{N-CH_3}$, 2.98, s, J_{AB} = 2.5 Hz
1 H$_A$, 8.07, d, J_{BC} = 8.8 Hz
1 H$_B$, 6.66, dd
5 H$_{C-G}$, 6.8–7.6, m



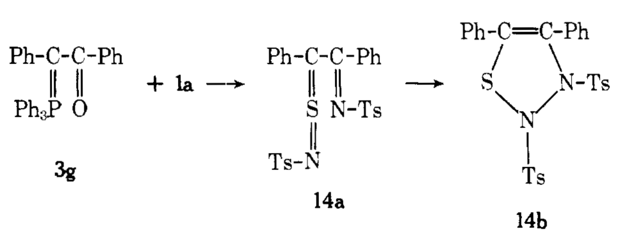
trans-**5f**

6 H$_{N-CH_3}$, 2.93, s, J_{AB} = 2.5 Hz
1 H$_A$, 6.83, d, J_{BC} = 9.0 Hz
1 H$_B$, 6.59, dd, J_{FG} = 7.6 Hz
1 H$_G$, 8.49, d
4 H$_{C-F}$, 7.0–7.5, m

This deshielding effect of the >C=S=O group on the neighboring protons has been found in related sulfines.[9]

The remarkable regiospecific selectivity found in these Wittig-type reactions of **1a** and **1b** seems to be interesting; however, we can not elucidate the detailed mechanism of the reaction in the present study.

On the other hand, refluxing of the benzene solution of **1a** and **3g** for about 20 h afforded colorless solid and unidentified blue paste together with a little amount of **10**. Elementary analyses, molecular weight measurement, and mass and IR spectra proved that the formula of the former product was represented as $Ph_2Ts_2C_2N_2S$ (**14**). This indicated that the ylide **3g** reacted with two molecules of **1a** on both the ylide moiety and the carbonyl group. Furthermore, the product showed the conspicuous peaks of $C_6H_5CS^{+}\cdot$ and $C_6H_5CSN^{+}\cdot$ in the mass spectrum but no characteristic absorption band due to ν (>S=N–) and/or ν (>C=N–) on the IR spectrum. On the basis of these data, the product was identified as thiadiazoline **14b** which was presumably provided by intramolecular cycloaddition of initially formed **14a**.



Experimental Section

Melting points are uncorrected. IR spectra were determined on Hitachi Model EPI-G2 spectrometer and NMR spectra were measured on either a JEOL JNM-4H-100 spectrometer or JEOL JNM-PMX60 spectrometer in δ values (parts per million) from Me_4Si as an internal standard. Mass spectra were recorded on Hitachi double-focusing mass spectrometer RMU-7M operating at an ionizing potential of 70 eV. Elementary analyses were performed using Shimadzu Universal Organic Micro Analyzer UM-3B and Shimadzu Rapid-Nitrogen Analyzer NA-1.

Starting Materials. New phosphonium ylides **3d** and **3e** were prepared in the following way.

Triphenylphosphonium 2-Benzoylfluorenylide (3d). Bromination of 2-benzoylfluorene by bromine in refluxing glacial acetic acid gave 9-bromo-2-benzoylfluorene as a yellowish solid (recrystallized from ethanol) in 57% yield: mp 110.5–113.5 °C; IR (nujol) 1655 (C=O) and 660 cm^{-1} (C–Br). Refluxing of the benzene solution in an equimolar amount of 9-bromo-2-benzoylfluorene and triphenylphosphine for 5 h yielded 2-benzoylfluorene-9-triphenylphosphonium bromide in 44% yield as a white solid. Deprotonation of the phosphonium bromide with alcoholic ammonia gave **3d** as orange needles (benzene–*n*-hexane) in 95% yield: mp 247–249 °C (dec); IR (nujol) 1640 (C=O), 1600, 1440, 1300, 1100 and 1000 cm^{-1}. Anal. Calcd for $C_{38}H_{27}OP$: C, 86.02; H, 5.13. Found: C, 85.90; H, 5.31.

Triphenylphosphonium 2-Methoxyfluorenylide (3e). 9-Bromo-2-methoxyfluorene was allowed to react with triphenylphosphine in nitromethane on a steam bath to give 2-methoxyfluorene-9-triphenylphosphonium bromide (colorless plates, mp 260–261 °C, quantitative yield), which was then converted into **3e** (91% yield): mp 251.5–253.5 °C; IR (nujol) 1615, 1590, 1455, 1440, 1300, 1165 and 1110 cm^{-1}. Anal. Calcd for $C_{32}H_{25}OP$: C, 84.19; H, 5.52. Found: C, 84.17; H, 5.56. The other starting materials were prepared according to the methods given in the literatures.

Thione *S*-Imide 4: Reaction of *N*-Sulfinyl-*p*-toluenesulfonamide (1a) with Triphenylphosphonium Fluorenylides 3a–f. A solution of 1.09 g (5 mmol) of **1a** in 30 mL of dry benzene was slowly added dropwise to a solution of 2.13 g (5 mmol) of **3a** in 70 mL of dry benzene at room temperature with stirring under nitrogen atmosphere. The yellow solution turned dark red immediately, and then the deep red-colored precipitate was separated. After 4 h, ca. 10 mL of *n*-hexane was added in order to complete the precipitation. The colored precipitates were collected by filtration and recrystallized quickly from methyl ethyl ketone. Glittering deep red crystals of **5a** were obtained in 1.51 g (82.7 %), mp 134–135 °C (dec). The filtrate was condensed under reduced pressure and a suitable amount of *n*-hexane was added to precipitate **9**, which was crystallized from chloroform–*n*-hexane, mp 136–138 °C (lit.[2d] mp 123–140 °C); IR (nujol) 1600, 1440, 1335, 1155 and 1120 cm^{-1}; MS *m/e* (rel intensity) 278 (54) [$(C_6H_5)_3PO^{+}$ (M^{+})], 277 (100) (M^{+} − 1), and 155 (22) [$CH_3C_6H_4SO_2^{+}$(Ts^{+})]. Triphenylphosphine oxide (**6**) was obtained from the filtrate by evaporation of the solvent. Recrystallization from benzene–*n*-hexane gave colorless leaflets, mp 155 °C.

The reaction of **1a** with the other phosphonium ylides **3b–f** was carried out similarly. Usually, **4** was first separated as precipitates by addition of *n*-hexane to the reaction mixture. The filtrate was evaporated and the residue was treated by either column chromatography (silica gel, benzene eluent followed by methanol) or fractional recrystallization with suitable solvents to separate the by-products. Thione *S*-imides **4b–f** could not be recrystallized owing to their thermal instability; however, these were found to be analytically pure.

2-Nitrofluorene-*p*-toluenesulfonylimine (8b): Yellow crystals (benzene–*n*-hexane); mp 218 °C; IR (nujol) 1620 (C=N), 1520 (NO_2), 1340 (NO_2), 1160 and 1085 (SO_2) cm^{-1}; MS *m/e* 378 (14) (M^{+}), 314 (8) ($M^{+} - SO_2$), 224 (4) (M^{+} − Ts + 1), 177 (14) ($M^{+} - Ts - NO_2$), 155 (56) (Ts^{+}) and 91 (100) ($CH_3C_6H_4^{+}$). Anal. Calcd for $C_{20}H_{14}N_2O_4S$: C, 63.48; H, 3.73. Found: C, 63.72; H, 3.67.

2,7-Dibromofluorene-*p*-toluenesulfonylimine (8c): Orange-red needles (benzene); mp 238–239 °C; IR (nujol) 1620 (C=N), 1150 and 1085 (SO_2) cm^{-1}; MS *m/e* (middle peak; ^{79}Br 50.52%, ^{81}Br 49.48%) 491 (4) (M^{+}), 427 (7) ($M^{+} - SO_2$), 346, 348 (2) ($M^{+} - SO_2 - Br$), 255, 257 (13) (M^{+} − Ts − Br), 155 (78) (Ts^{+}) and 91 (100) ($CH_3C_6H_4^{+}$). Anal. Calcd for $C_{20}H_{13}NO_2SBr_2$: C, 48.90; H, 2.67; N, 2.85. Found: C, 49.11; H, 2.55; N, 2.97.

2-Benzoylfluorene-*p*-toluenesulfonylimine (8d): Orange needles (benzene–*n*-hexane); mp 112–115 °C; IR (nujol) 1660 (C=O), 1620 (C=N), 1150 and 1085 (SO_2) cm^{-1}; MS *m/e* 437 (5) (M^{+}), 373 (5) ($M^{+} - SO_2$), 296 (2) ($M^{+} - SO_2 - C_6H_5$), 178 (4) ($M^{+} - Ts - C_6H_5CO$), 155 (3) (Ts^{+}), 105 (7) ($C_6H_5CO^{+}$) and 91 (8) ($CH_3C_6H_4^{+}$). Anal. Calcd for $C_{27}H_{19}NO_3S$: C, 74.13; H, 4.38; N, 3.20. Found: C, 73.94; H, 4.35; N, 3.18.

2-*N,N*-Dimethylaminofluorene-*p*-toluenesulfonylimine (8f): Deep-blue leaflets (benzene–*n*-hexane); mp 147–148 °C; IR (nujol) 1615 (C=N), 1155 and 1085 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 2.43 (s, 3 H, CH_3), 2.96 (s, 6 H, N–CH_3), 6.62 (m, 1 H, arom), 7.0–7.4 (m, 8 H, arom), and 7.97 (d, $J = 8$ Hz, 2 H, arom); MS *m/e* 376 (66) (M^{+}) 221 (100) (M^{+} − Ts), 206 (14) ($M^{+} - Ts - 2CH_3$) and 178 (21) [$M^{+} - Ts - N(CH_3)_2$].

Sulfine (5): Reaction of *N*-Sulfinyl-*p*-nitroaniline (1b) with Triphenylphosphonium Fluorenylides 3a–f. A solution of 1.84 g (10 mmol) of **1b** and 4.26 g (10 mmol) of **3a** in 100 mL of dry benzene was refluxed for 8 h under nitrogen atmosphere. After ca. 50 mL of *n*-hexane was added to the hot solution, the mixture was cooled overnight. The yellow precipitate that separated was collected by filtration and recrystallized from benzene–*n*-hexane (or ethanol) to give **7** as yellow plates, mp 161–164 °C (lit.[10] mp 156–158 °C). The IR spectrum was identical with that reported by L. Horner et al.[10] The filtrate was condensed and *n*-hexane was then added to remove the additional portion of **7**. This operation was carefully repeated until **7** did not separate as a precipitate any longer. Finally, the filtrate was evaporated and the residue was recrystallized from *n*-hexane–benzene to give **5a** as orange plates, mp 105–107 °C (lit.[11] mp 111.0–111.8 °C).

The reaction of **1b** with the other phosphonium ylides **3b–f** was carried out similarly. Usually, recovered starting materials or **7** was first separated as precipitates by addition of *n*-hexane to the reaction mixture. The filtrate was evaporated and the residue was column chromatographed on silica gel with suitable eluent (**5c**, benzene; **5e**, carbon tetrachloride; **5f**, benzene–*n*-hexane). In the reaction of **1b** with **3b** or **3c**, bis(fluorenylidene) (**12b** or **12c**) was precipitated preceding to the separation of the other products, and the filtrate was treated similarly. Bis(2-methoxyfluorenylidene) (**12e**) was formed after evaporation of the filtrate, presumably by the decomposition of **5e** during the operation.

Bis(2-nitrofluorenylidene) (12b):[12] Red needles; mp >310 °C; IR (nujol) 1520 and 1340 (NO_2) cm^{-1}.

Bis(2-benzoylfluorenylidene) (12d): Red plates; mp 280–282 °C; IR (nujol) 1650 (C=O) cm^{-1}; MS *m/e* 536 (51) (M^{+}), 459 (3) ($M^{+} - C_6H_5$), 431 (4) ($M^{+} - C_6H_5CO$), 105 (100) ($C_6H_5CO^{+}$), and 77 (25) ($C_6H_5^{+}$).

Bis(2-methoxyfluorenylidene) (12e): Red plates (*n*-hexane); mp 90–94 °C; IR (nujol) 1610, 1580, 1400, 1270, and 1040 cm^{-1}; MS *m/e* 388 (100) (M^{+}), 373 (11) ($M^{+} - CH_3$), 357 (50) ($M^{+} - OCH_3$), and 342 (20) ($M^{+} - CH_3 - OCH_3$).

Reaction of *N*-Sulfinyl-*p*-toluenesulfonamide (1a) with

Triphenylphosphonium Phenylbenzoylmethylide (3g). A solution of 0.730 g (3.36 mmol) of **1a** and 1.52 g (3.33 mmol) of **3g** in 60 mL of dry benzene was refluxed for 20 h. The yellow solution turned blue gradually. After evaporation of the solvent in vacuo, the blue pasty residue was column chromatographed on silica gel with benzene–ethyl acetate (5:1) as eluent to give **14b** (25%), **10** (6%) and two unidentified blue pastes.

4,5-Diphenyl-2,3-di(*p*-toluenesulfonyl)-Δ^4-1,2,3-thiadiazoline (14b): Colorless fluffy needles (benzene), mp 183.5–183.7 °C; IR (nujol) 1600, 1590, 1555 (C=C), 1450, 1360, 1340, 1160 (SO_2), 1085 (SO_2), and 1060 cm^{-1}; MS *m/e* 379 (3) ($M^+ - Ts - N$), 258 (9) ($TsNCPh^+$), 238 (15) ($M^+ - 2\ Ts$), 224 (9) ($M^+ - 2\ Ts - N$), 155 (64) (Ts^+), 135 (23) ($PhCSN^+$), 121 (85) ($PhCS^+$), 103 (13) ($PhCN^+$), and 91 (100) ($CH_3C_6H_4^+$). Anal. Calcd for $C_{28}H_{24}N_2O_4S_3$ (548.7): C, 61.29; H, 4.41; N, 5.11; S, 17.53. Found: C, 61.38; H, 4.17; N, 5.12; S, 17.31. Mol wt 554 (VPO method in chloroform, cholesterol as calibration standard).

Supplementary Material Available. Tables III and IV containing mass spectral data for 4 and 5 will appear following this article in the microfilm edition of this journal. Ordering information is given on any current masthead page.

Registry No.—**1a**, 4104-47-6; **1b**, 13165-67-8; **3a**, 4756-25-6; **3b**, 7151-67-9; **3c**, 24764-32-7; **3d**, 63609-86-9; **3e**, 7293-75-6; **3f**, 63609-87-0; **3g**, 30416-76-3; **4a**, 63609-88-1; **4b**, 63609-89-2; **4c**, 63609-90-5; **4e**, 63609-91-6; **4f**, 63609-92-7; **5a**, 4440-32-8; **5c**, 63609-93-8; **5e**, 63609-94-9; *cis*-**5f**, 63609-95-0; *trans*-**5f**, 63609-96-1; **6**, 791-28-6; **8b**, 63609-97-2; **8c**, 63609-98-3; **8d**, 63609-99-4; **8f**, 63610-00-4; **9**, 63610-01-5; **12b**, 6967-03-9; **12d**, 63610-02-6; **12e**, 18374-46-4; **14b**, 63610-03-7; 2-benzoylfluorine, 15860-31-8; 9-bromo-2-benzoylfluorene, 63610-04-8; triphenylphosphine, 603-35-0; 2-benzoylfluorine-9-triphenylphosphonium bromide, 63626-33-5; 9-bromo-2-methoxyfluorene, 63610-05-9; 2-methoxyfluorene-9-triphenylphosphonium bromide, 7293-61-0.

References and Notes

(1) (a) G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6** (2), 149 (1967). (b) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *ibid.*, **1** (2) 89 (1962).

(2) (a) Henri Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York and London, 1967. (b) A. W. Johnson, "Ylid Chemistry" Academic Press, New York and London, 1966. (c) A. Senning, *Acta Chem. Scand.*, **18**, 1958 (1964). (d) A. Senning, *ibid.*, **19**, 1755 (1965).

(3) Reference 2b, page 226.

(4) Thione *S*-imides have recently been isolated by two different methods; one is the addition of nitrene to a thiocarbonyl compound and the other is a base-promoted 1,3-dehydrohalogenation of substituted sulfenamide. (a) S. Tamagaki and S. Oae, *Tetrahedron Lett.*, 1159 (1972). (b) S. Tamagaki, K. Sakaki, and S. Oae, *Bull. Chem. Soc. Jpn.*, **47** (12), 3084 (1974). (c) S. Holm, J. A. Boerma, N. H. Nilsson, and A. Senning, *Chem. Ber.*, **109**, 1069 (1976). (d) E. M. Burgess and H. R. Penton, Jr, *J. Org. Chem.*, **39** (19), 2885 (1974); *J. Am. Chem. Soc.*, **95** (1), 279 (1973).

(5) The IR and mass spectra of **8a** were identical with the data reported by A. Schönberg et al., *Chem. Ber.*, **102**, 2557 (1969).

(6) A similar change of the thione *S*-imides has been observed in the thermal decomposition of *S*-arylsulfonylimino-1,2-benzodithiol-3-thione; S. Tamagaki, K. Sakaki, and S. Oae, *Bull. Chem. Soc. Jpn.*, **46** (8), 2608 (1973).

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Reactions of Imidazoles with Isocyanates at Elevated Temperature

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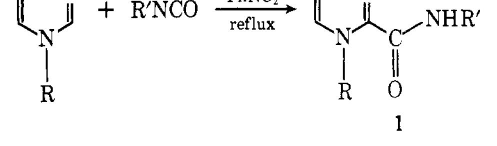
Imidazole and 1-methylimidazole react with isocyanates in boiling nitrobenzene or phenyl ether to form N-substituted imidazole-2-carboxamides in good yield. When 2-methylimidazole is used, the 4(5)-carboxanilide is obtained in low yield, but no corresponding product is isolated from the reaction involving 1,2-dimethylimidazole. Treatment of *N*-phenylimidazole-2-carboxamide with phenyl isocyanate and triethylamine results in formation of *N*-phenylimidazole-1,2-dicarboximide and *N,N'*-diphenylurea.

Imidazole is known to react with isocyanates under mild conditions to form N-substituted imidazole-1-carboxamides, which partially dissociate into their precursors upon melting, or in solution.[1] Under more drastic conditions, as in boiling nitrobenzene, 4,5-diarylimidazoles and their 1-alkyl derivatives were found to react with aryl isocyanates at the only available heterocyclic ring carbon atom to yield N-substituted imidazole-2-carboxamides.[2] Since the latter reactions are among very few known cases of imidazoles undergoing direct acylation at a ring carbon atom,[3] it was of interest to investigate analogous reactions of unsubstituted imidazole, where any one of three ring carbon atoms is in principle capable of reaction.

It has now been found that refluxing of a solution of equimolar amounts of imidazole and phenyl isocyanate in a high boiling solvent, such as nitrobenzene, *m*-nitrotoluene, or phenyl ether, yields *N*-phenylimidazole-2-carboxamide (**1a**) as the main product. There is considerable tar formation, but except for very small amounts of *N*-phenylimidazole-1-carboxamide (**2a**), *N,N'*-diphenylurea, and triphenyl isocyanurate, no other product has been detected. Structure **1a** is supported by spectral (IR, NMR) as well as microanalytical data. Appearance of the carbonyl stretching band at 1650 cm^{-1} in the infrared spectrum indicates attachment of the side chain to a ring carbon, rather than nitrogen atom.[2] On the other hand, spectra (IR, NMR) and depressed mixture melting point clearly establish the difference between this compound and the known, isomeric *N*-phenylimidazole-4(5)-carboxamide (**3**).[4]



1

a, R = H, R' = Ph
b, R = H, R' = 4-MeC_6H_4
c, R = H, R' = 3-ClC_6H_4
d, R = H, R' = 1-naphthyl
e, R = H, R' = *n*-Bu
f, R = Me, R' = Ph
g, R = Me, R' = 4-MeC_6H_4
h, R = Me, R' = 3-ClC_6H_4
i, R = Me, R' = 1-naphthyl
j, R = Me, R' = *n*-Bu

In a similar manner, reaction of imidazole with *p*-tolyl, *m*-chlorophenyl, and 1-naphthyl isocyanate in boiling nitro-