Stable Thallium(I) Derivatives of *N*-Alkyl-arylsulfonamides as Intermediates in the Preparation of *N*-Alkyl-*N*-triflyl-(or tresyl)-arylsulfonimides[1]

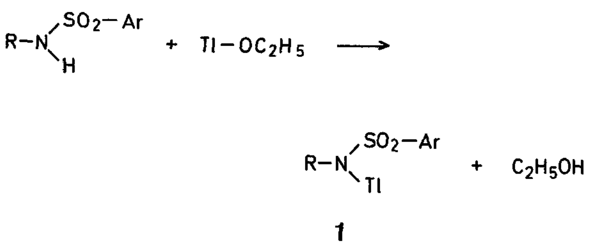
Hsi-Lung Pan and T. Lloyd Fletcher*

Pacific Northwest Research Foundation (The Fred Hutchinson Cancer Research Center), 1102 Columbia Street, Seattle, Washington 98104, U.S.A.

During the past few years, a number of thallium compounds have been found to be superior, or even unique, reagents in a wide variety of synthetic applications[2,3]. In this communication we report the preparation of stable, crystalline, thallium(I) derivatives of *N*-alkyl-arylsulfonamides, as intermediates in the preparation of the title sulfonimides. The latter were needed for a study of ease of scission of the R—N bond in compounds of type **2**.

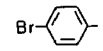
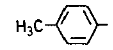
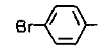
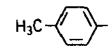
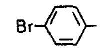
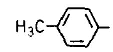
Initial attempts to prepare certain trifluoroalkanesulfonyl derivatives of *N*-alkyl-arylsulfonamides by the method using sodium hydride[4], either failed completely or resulted in the formation of mixtures which were difficult to purify. Use of the thallium(I) intermediates, however, afforded synthesis of readily purified imides in good yields.

The thallium(I) compounds, **1** (Table 1), were prepared by treating a benzene solution of the amide with thallium(I) ethoxide under a blanket of nitrogen at room temperature.



The products were purified by recrystallization from inert solvents and can be stored indefinitely without appreciable deterioration.

Table 1. *N*-Alkyl-*N*-thallium(I)-arylsulfonamides (**1**)[a]

1	R	Ar	M.p.	Yield (%)
a	H_3C		182.5–185°	100
b	H_3C		189–192°	96
c	C_2H_5		134–139°	95
d	C_2H_5		132–135°	98
e	n-C_6H_{13}		92–95°	93
f	n-C_6H_{13}		117–120°	84

[a] The I.R. (KBr) spectra of these compounds showed absence of the amide N—H absorption at the 3300 cm^{-1} region. Other prominent absorptions: ν_{max} = 1195–1170, 1140–1120, 1065–1058 cm^{-1}.

The usefulness of these thallium compounds is demonstrated by the preparation of *N*-alkyl-*N*-trifluoroalkanesulfonyl-arylsulfonimides (**2**) (Table 2). Conversion of **1** to **2** was effected with the use of 2,2,2-trifluoroethanesulfonyl chloride (tresyl chloride), or trifluoromethanesulfonic anhydride (triflic anhydride) in refluxing benzene. The conversion was complete in 1–3 hours.

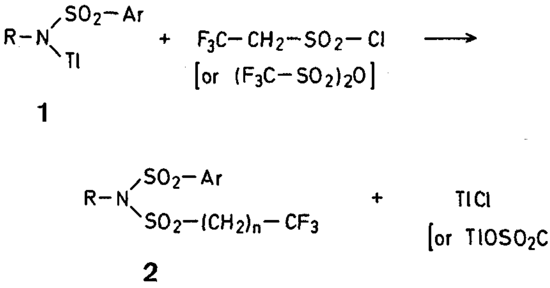
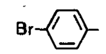
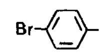
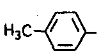
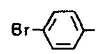


Table 2. *N*-Alkyl-*N*-trifluoroalkanesulfonyl-arylsulfonimides (**2**)[a]

2	R	Ar	n	m.p.	Yield (%)
a	H_3C		0	104.5–105°	80
b	H_3C		1	118.5–119.5°	62
c	H_3C		1	107–108°	76
d	C_2H_5		1	94–95°	44

[a] I.R. (KBr): ν_{max} = 1400–1380, 1225–1160, 1140–1125 cm^{-1}.

Structures and purity of the compounds in Tables 1 and 2 were confirmed with I.R., T.L.C., and microanalysis.

General Procedure for the Preparation of 1:

The *N*-alkyl-arylsulfonamide[5] (0.01 mol) dissolved in dry benzene (50–80 ml), was stirred in an atmosphere of dry nitrogen while an equimolar amount of thallium(I) ethoxide was added in one portion. Immediate precipitation of the product usually took place. The reaction mixture was continuously stirred for one hour and the product was rapidly filtered and immediately dried under reduced pressure to minimize contact with atmospheric moisture. One or two recrystallizations from benzene or benzene/petroleum ether (b.p. 30–60°) gave the analytically pure sample.

Table 3. Elemental Analyses for Compounds **1** and **2**.

Compound	Empirical Formula	Analysis			
1a	$C_7H_7BrNO_2STl$	calc.	C 18.54	H 1.56	N 3.01
	(453.48)	found	18.73	1.70	3.19
1b	$C_8H_{10}NO_2STl$	calc.	C 24.73	H 2.59	N 3.60
	(388.61)	found	24.54	2.58	3.50
1c	$C_8H_9BrNO_2STl$	calc.	C 20.55	H 1.94	N 3.00
	(467.51)	found	20.59	1.99	2.90
1d	$C_9H_{12}NO_2STl$	calc.	C 26.85	H 3.00	S 7.96
	(402.64)	found	27.10	3.23	7.55
1e	$C_{12}H_{17}BrNO_2STl$[a]	calc.	C 27.53	H 3.27	N 2.68
	(523.62)	found	27.49	3.36	2.74
1f	$C_{13}H_{20}NO_2STl$	calc.	C 34.04	H 4.39	S 6.99
	(458.74)	found	34.15	4.29	6.50
2a	$C_8H_7F_3BrNO_4S_2$[b]	calc.	C 25.67	H 1.85	N 3.67
	(382.18)	found	25.34	1.93	3.53
2b	$C_9H_9F_3BrNO_4S_2$	calc.	C 27.28	H 2.29	S 16.19
	(396.21)	found	27.43	2.35	16.09
2c	$C_{10}H_{12}F_3NO_4S_2$	calc.	C 36.25	H 3.65	S 19.35
	(331.34)	found	36.14	3.76	19.73
2d	$C_{10}H_{11}F_3BrNO_4S_2$	calc.	C 29.28	H 2.70	S 15.63
	(410.24)	found	29.38	2.70	15.71

[a] Br: calc. 15.26 found 15.00
[b] S: calc. 16.78 found 16.85

General Procedure for the Preparation of 2:

Compound **1a**, **1b**, or **1c** (0.005 mol) was suspended in dry benzene (50–100 ml) and stirred under dry nitrogen while triflic anhydride (or tresyl chloride) (1–1.5 equivalents) was added in one portion. The reaction mixture was continuously stirred for several hours and then refluxed for 1–3 hours and cooled. The solid thallium salt was removed by filtration. The benzene filtrate was evaporated to give the product. One or two recrystallizations from benzene/petroleum ether (b.p. 30–60°) gave the analytically pure sample.

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[2] E. C. Taylor, A. McKillop, *Accounts Chem. Res.* **3**, 338 (1970).

[3] A. McKillop, E. C. Taylor, *Chem. Brit.* **9**, 4 (1973), and references therein.

[4] R. S. Glass, *Chem. Commun.* **1971**, 1546.

[5] All of the amides are known compounds and were prepared from arylsulfonyl chlorides and alkylamines. Melting points agree with the literature.