Tin for Organic Synthesis, 7[1]

New Regioselective Syntheses of Diaryl Sulfones, Arenesulfonamides, and Arenesulfonic Acid Sodium Salts

Wilhelm P. Neumann* and Christian Wicenec

Department of Chemistry, University of Dortmund,
Otto-Hahn-Straße 6, W-4600 Dortmund 50, F.R.G.

Received September 10, 1992

Key Words: Aromatic substitution, electrophilic / Sulfones, synthesis of / Sulfonamides, synthesis of / Sulfonic acids, sodium salts, synthesis of / Stannanes, trialkylaryl-, application of

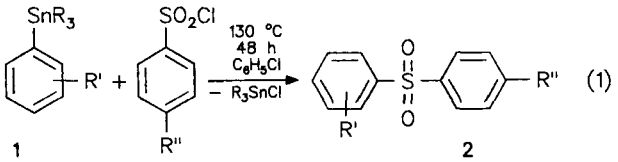
The reaction of (trialkylstannyl)arenes **1** with corresponding reagents containing a chlorosulfonyl group leads, by exclusive *ipso* substitution, to important diaryl sulfones **2a–i**, *N*-alkylarenesulfonamides **8a–f**, and sodium arenesulfonates **13a–c** in high yields under mild conditions. The specific leaving ability of the stannyl group allows, moreover, the preparation of arylsulfonyl isomers which are not accessible under the influence of the conventional directing forces of substituents. With *N,N*-dialkylamidosulfonyl chloride/$AlCl_3$ complexes no destannylation takes place, but the first intramolecular sulfonyltin complex **11** is formed. This result is used to discuss details of the mechanism involved.

Aryl sulfones, sulfonamides, and sulfonates are of high technical and pharmacological interest[2a,b]. Sulfones may be used in organic synthesis[2b]. A number of methods for the preparation of diaryl sulfones[3a–c], arylsulfonamides[3d–e], and sodium arenesulfonates[3f,g] have been published. Nevertheless, there are some drawbacks inherent in these methods. These include: i) frequent application of drastic conditions[3a–c], like Lewis-acid catalysts and high temperatures, which may destroy sensitive compounds; ii) in most cases only formation of *para*-substituted products[3c,h]; iii) several reaction steps required for the preparation of sulfonamides to build up the functionality[3d].

To eliminate the aforementioned disadvantages some attempts have been undertaken to use organometallic substrates like organomagnesium[4a], organosilicon[4b–f], and organotin compounds[4d], which unfortunately often still need $AlCl_3$ as a catalyst or highly toxic reagents like sulfonyl fluorides[4a]. Animated by the early use of tetraphenyltin in the diaryl sulfone synthesis[5,6], we are now able to present new routes to diaryl sulfones, *N*-alkylarylsulfonamides, and sodium arenesulfonates using the excellent leaving group ability of the trialkylstannyl group in electrophilic aromatic substitutions. *ipso* Substitutions of a trialkyltin group have already led to the highly regioselective formation of aromatic aldehydes, benzylamines, ketones, carboxamides, thio compounds, isocyanato sulfones, and diaryldiazenes[1,7]. By reducing the reaction temperatures and working without a catalyst we have succeeded in obtaining nearly quantitative yields in isomer patterns which have previously not been obtained by conventional electrophilic aromatic substitution reactions. Thus, the latter type of reaction as well as the use of stannylarenes in organic syntheses have been extended.

Diaryl Sulfones

Trialkylarylstannanes **1**, **3**, and **5** react with arenesulfonyl chlorides within 48 h at 131 °C. The resulting diaryl sulfones **2**, **4**, and **6** are formed in good to excellent yields (the figures given correspond to isolated, pure compounds). By using tributyltin or, because of their clear-cut ^{1}H-NMR analyses, trimethyltin derivatives, we arrive at exclusive *ipso* substitution of the trialkyltin group, eq. (1).



(1)

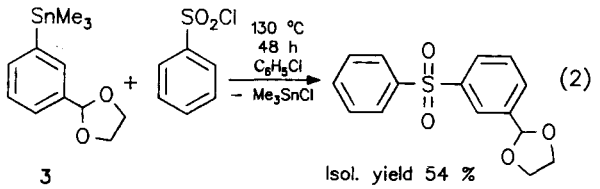
	1		2	Isol. yield
	R, R'	R''	R', R''	(%)
a	Me, 2-Me	H	2-Me, H	95
b	Me, 3-Me	H	3-Me, H	62
c	Bu, 4-Me	H	4-Me, H	73
d	Me, 2-OMe	H	2-OMe, H	<1
e	Me, 3-OMe	H	3-OMe, H	53
f	Me, 4-OMe	H	4-OMe, H	58
g	Me, 4-Cl	H	4-Cl, H	42
h	Bu, 3-OMe	Me	3-OMe, Me	52
i	Bu, 3-Me	Cl	3-Me, Cl	66

The known directing forces of the methyl, chloro, and even the methoxy group can be completely overcompensated, so that direct electrophilic arylsulfonations in the 3-position with respect to such groups are possible. Only the strongly electron-donating methoxy group in the 2-position of **1d** suppresses the reaction by steric hindrance. In com-

  0009–2940/93/0303–0763 $ 10.00+.25/0

parison to the early experiments[5,6] the temperatures can be lowered from 200 to 131 °C, and the use of aggressive Lewis-acid catalysts like $AlCl_3$ can be avoided. Different arenesulfonyl chlorides exhibit an individual reactivity, obviously depending on the I effect of the substituent R″, eq. (1). While weak −I effects on the sulfonyl group, like that of the phenyl or *p*-chlorophenyl group, strenghten its electrophilicity and increase its reactivity toward the trialkylarylstannanes, +I effects like that of a tolyl group decrease its reactivity drastically. Thus, 4-toluenesulfonyl chloride reacts only with activated (electron-rich) stannanes, like 3-(tributylstannyl)anisole (**1h**), but not with tolylstannanes (**1a–c**), to form diaryl sulfones by *ipso* substitution. Obviously, any kind of arenesulfonyl chloride bearing electron-withdrawing substituents at the aromatic ring may be used for the mentioned arylsulfodestannylation.

Our procedure allows now, working under non-acidic conditions, the arylsulfonation of acid-sensitive molecules like the benzaldehyde acetal **3**, eq. (2), or the benzene-1,2-diol acetal **5**, eq. (3). These compounds are arylsulfonated with benzenesulfonyl chloride to the new diaryl sulfones **4** and **6** regiospecifically in good yield, the acetal functions remaining unchanged.

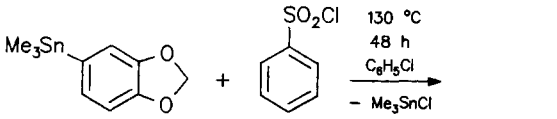


(2)

3

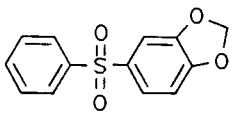
Isol. yield 54 %

4



5

(3)

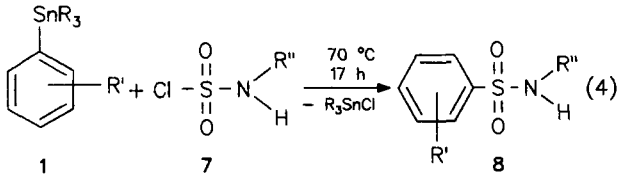


Isol. yield 58 %

6

N-Alkylarenesulfonamides

Sulfonamides are mostly built up from sulfonyl chlorides and amines[3d]. In contrast, the direct functionalization of aromatics by sulfamoyl chlorides is very seldom, and in general these are coupled to Lewis-acid catalysts[3c,4a–c]. *N*-Monoalkylamidosulfonyl chlorides have never been used. But when the N-alkylamidosulfonyl chlorides **7a, b** are mixed with one of the (trialkylstannyl)benzenes **1b, e, g, j–l**, an exothermic reaction leads, without any catalyst, to the corresponding *N*-alkylarenesulfonamides by strict *ipso* substitution of the trialkyltin group, eq. (4). Again, the conventional directing forces of the substituents, e.g. a 3-Me (**1b**) or even a 3-OMe group in **1e**, are overrun.



(4)

1 7 8

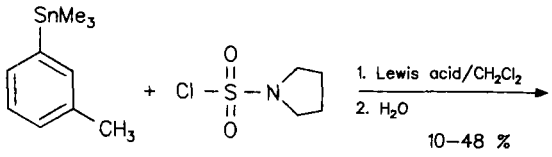
1	R, R'
j	Me, 4–Me
b	Me, 3–Me
e	Me, 3–OMe
g	Me, 4–Cl
k	Bu, 4–Cl
l	Me, 3–CF_3

7	R"
a	Me
b	Et

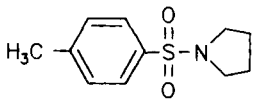
8	R', R"	Isol. yield (%)
a	4–Me, Me	84
b	4–Me, Et	87
c	3–Me, Et	54
d	3–OMe, Et	85
e	4–Cl, Me	83 [49]
f	3–CF_3, Et	0

Under mild conditions, exclusively **8c** and **8d** are formed. The less toxic tributylstannanes (e.g. **1k**) should be preferentially used in laboratory synthesis. The lower yield of sulfonamide **8e** depends on a modified workup, which has to be improved in the future. Slightly deactivating substituents like a chlorine atom have no significant influence on the reaction rate and the yield of **8**, but the strongly deactivating trifluoromethyl group prevents any reaction, and the starting compounds can be recovered completely.

As in the case of arenesulfonyl destannylations, I effects on the electrophilic center are important. While sulfamoyl chloride itself is very reactive, the *N*-monoalkyl derivatives **7** are weakened in their reactivity apparently by the +I effect of the alkyl group. *N,N*-dialkylsulfamoyl chlorides (e.g. **9**), consequently, are unreactive even toward activated trialkylarylstannanes, e.g. **1b**. When a Lewis-acid catalyst is used, a reaction takes place, but surprisingly the *ipso* substitution can no longer be achieved, eq. (5).



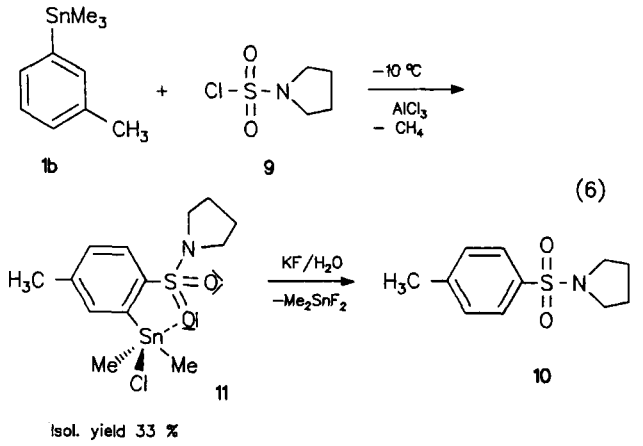
1b 9



(5)

10

cine Substitution yielding the *p*-substituted product **10** occurs. Obviously, this reaction proceeds by a different mechanism. The directing force of the methyl group then dominates. The yield depends on the strength of the Lewis acids. The use of $TiCl_4$, a strong acid, yields 48% of **10**, while the use of $ZnCl_2$, a weak acid, affords **10** in only 10% yield. A surprising reaction takes place by using one of the strongest Lewis acids, $AlCl_3$. When **1b** reacts with a complex of **9** and $AlCl_3$, not only *cine* substitution is observed, but also an intramolecular complex **11** can be isolated in 33% yield.



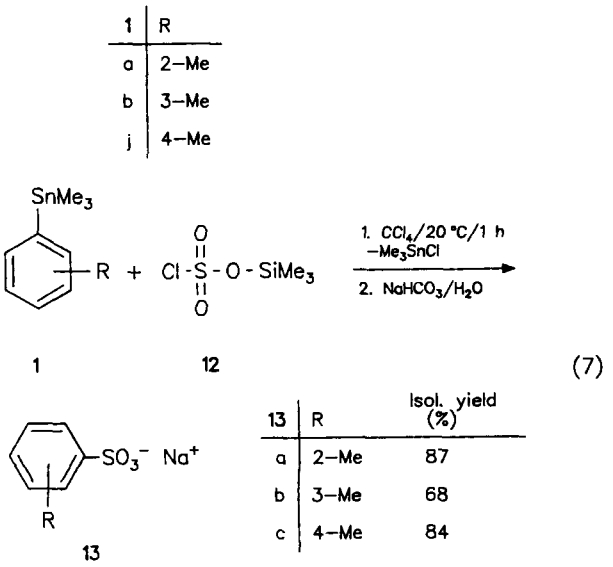
This complex resembles other intramolecular tin complexes, formed in attempted aromatic substitutions, as reported recently[8]: 1. $AlCl_3$ acts in a still unknown manner here, not only catalyzing the substitution; 2. coordinating forces must be responsible for the demethylation at the tin being now preferred to the aromatic destannylation.

It seems that a *cine* substitution occurs first, forming a 1-stannyl-2-(sulfonylamino)toluene which is then demethylated to yield a chlorodimethylstannyl group strongly coordinated by an oxygen atom of the sulfonylamino group. An X-ray crystal analysis of **11**[9] shows a very small Sn–O distance of 2.529(6) Å which proves the strong coordination. The intramolecular Sn–OSO complex can be decomposed by stirring with an aqueous KF solution to yield the same product **10** which has been obtained by other Lewis-acid catalysts, eq. (5).

Sulfonation

Another use of trialkylstannanes **1a**, **b**, **h** has become obvious, when we applied trimethylsilyl chlorosulfonate (**12**), eq. (7). In the first step it forms *ipso*-specifically the trimethylsilyl arenesulfonates, which are easily hydrolyzed by $NaHCO_3/H_2O$ to the corresponding sodium arenesulfonates. The conditions applied are very mild (room temperature, no catalyst), the reaction times short (1 h) (e.g., toluene itself needs 12 h at 80 °C to be sulfonated in the *p*-position[3h]). The regioselectivity is complete, even 3-stannylated toluene is exclusively converted into sodium 3-toluenesulfonate. These exothermic sulfodestannylations take place much easier than desilylations[4e,f] with **12** with respect to both shorter reaction times and lower temperatures.

We are grateful to the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft* for their support.



Experimental

Melting points: Büchi SMP 20. – IR: Shimadzu 3289. – NMR: Varian EM 360 (60 MHz, ^1H) and Bruker AM 300 (300 MHz, 75.47 MHz ^{13}C, 111.92 MHz ^{119}Sn). – MS: Finnigan Mat 8230, 70 eV. – Elemental analyses: Carlo Erba 1106.

Diaryl Sulfones **2a–i**, **4**, **6**. – *General Procedure I:* To a solution of 5 ml of an arenesulfonyl chloride in 5 ml of anhydrous chlorobenzene under argon 5 mmol of a trialkylarylstannane **1a–i**, **4**, **5**[10] is added, and the mixture is heated to reflux (131 °C) for 48 h. After the solvent has been removed in vacuo (0.01 Torr/25 °C) the residue is subjected to short-path distillation to separate the trialkyltin chloride (0.01 Torr/180 °C). The remaining crude product is recrystallized from *n*-hexane (50 ml) or ethanol (10 ml).

2-Methylphenyl Phenyl Sulfone (**2a**): From 1 ml (5.5 mmol) of **1a** and 0.70 ml (5.5 mmol) of benzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 1.21 g (95%) of **2a** is obtained according to the general procedure I, m.p. 78 °C (from *n*-hexane) (ref.[11] 81 °C). – ^1H NMR ($CDCl_3$): δ = 2.47 (s, 3H, CH_3), 7.0–8.23 (m, 9H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 20.09 (CH_3), 126.36, 127.49, 128.91, 129.27, 132.57, 133.52 (CH), 137.83, 138.68, 141.14 (Cq). – IR (KBr): $\tilde{\nu}$ = 1305 cm^{-1}, 1152.

3-Methylphenyl Phenyl Sulfone (**2b**): From 1 ml (5.5 mmol) of **1b** and 0.70 ml (5.5 mmol) of benzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 0.79 g (62%) of **2b** is obtained according to the general procedure I, m.p. 116 °C (from *n*-hexane) (ref.[12] 119–120.5 °C). – ^1H NMR ($CDCl_3$): δ = 2.37 (s, 3H, CH_3), 7.05–8.13 (m, 9H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.19 (CH_3), 124.67, 127.43, 127.76, 129.00, 129.10, 132.96, 133.87 (CH), 139.41, 141.30, 141.62 (Cq). – IR (KBr): $\tilde{\nu}$ = 1303 cm^{-1}, 1151.

4-Methylphenyl Phenyl Sulfone (**2c**): From 1 ml (3.3 mmol) of **1c** and 0.42 ml (3.3 mmol) of benzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 0.56 (73%) of **2c** is obtained according to the general procedure I, m.p. 124 °C (from *n*-hexane) (ref.[13] 126 °C). – ^1H NMR ($CDCl_3$): δ = 2.43 (s, 3H, Me), 7.07–8.03 (m, 9H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.44 (CH_3), 127.35, 127.85, 129.09, 129.79, 132.87 (CH), 138.58, 141.91, 144.04 (Cq). – IR (KBr): $\tilde{\nu}$ = 1309 cm^{-1}, 1156.

2-Methoxyphenyl Phenyl Sulfone (**2d**): From 1 ml (4.8 mmol) of **1d** and 0.61 ml (4.8 mmol) of benzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene surprisingly only traces of **2d** can be obtained (GLC). Most of the parent compounds remains unchanged.

3-Methoxyphenyl Phenyl Sulfone (**2e**): From 1 ml (5.2 mmol) of **1e** and 0.66 ml enesulfonyl chloride in 5 ml of anhydrous chlorobenzene 0.68 g (53%) of **2e** is obtained according to the general procedure I, m.p. 83 °C (from *n*-hexane) (ref.[14] 90.5 °C). – ^1H NMR ($CDCl_3$): δ = 3.77 (s, 3H, OCH_3), 7.85–8.05 (m, 9H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 55.40 (OCH_3), 112.10, 119.49, 127.20, 129.01, 130.17, 132.97 (CH), 141.21, 142.39, 159.73 (Cq). – IR (KBr): $\tilde{\nu}$ = 1305 cm^{-1}, 1245, 1151, 1025.

4-Methoxyphenyl Phenyl Sulfone (**2f**): From 1 ml (5.2 mmol) of **1f** and 0.66 ml (5.2 mmol) of benzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 0.74 (58%) of **2f** is obtained according to the general procedure I, m.p. 81°C (from *n*-hexane) (ref.[14] 90°C). – ^{1}H NMR ($CDCl_3$): δ = 3.90 (s, 3H, OCH_3), 6.87–8.13 (m, 9H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 55.56 (OCH_3), 114.42, 127.14, 129.08, 129.74, 132.73 (CH), 138.04, 142.28, 163.27 (Cq). – IR (KBr): $\tilde{\nu}$ = 1300 cm^{-1}, 1265, 1150, 1019.

4-Chlorophenyl Phenyl Sulfone (**2g**): From 1 ml (4.7 mmol) of **1g** and 0.60 ml (4.7 mmol) of benzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 0.51 g (42%) of **2g** is obtained according to the general procedure I, m.p. 91°C (from *n*-hexane) (ref.[3b] 93°C). – ^{1}H NMR ($CDCl_3$): δ = 7.18–8.03 (m, 9H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 127.43, 128.93, 129.25, 129.42, 133.29 (CH), 139.64, 140.97, 141.31 (Cq). – IR (KBr): $\tilde{\nu}$ = 1311 cm^{-1}, 1154.

3-Methoxyphenyl 4-Methylphenyl Sulfone (**2h**): From 2 ml (6.6 mmol) of **1h** and 1.26 g (6.6 mmol) of 4-toluenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 0.90 g (52%) of **2h** is obtained according to the general procedure I, m.p. 73°C (from ethanol). – ^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.83–7.93 (m, 8H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.40 (CH), 55.52 (OCH_3), 112.09, 119.06, 159.82 (Cq). – IR (KBr): $\tilde{\nu}$ = 1315 cm^{-1}, 1151, 1044. – MS, *m/z* (%): 262 [M^+] (100), 155 [$CH_3C_6H_5SO_2^+$] (45), 139 [$CH_3OC_6H_4S^+$] (58), 77 [$C_6H_5^+$] (14).

$C_{14}H_{14}O_3S$ (262.3) Calcd. C 64.10 H 5.38
Found C 64.1 H 5.4

4-Chlorophenyl 3-Methylphenyl Sulfone (**2i**): From 2 ml (6.3 mmol) of **1i** and 1.33 g (6.3 mmol) of 4-chlorobenzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 1.10 g (66%) of **2i** is obtained according to the general procedure I, m.p. 96°C (from ethanol). – ^{1}H NMR ($CDCl_3$): δ = 2.46 (s, 3H, CH_3), 7.20–8.10 (m, 8H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.25 (CH_3), 124.70, 127.80, 128.98, 129.15, 129.45, 134.13 (CH), 129.64, 139.61, 140.54, 141.29 (Cq). – IR (KBr): $\tilde{\nu}$ = 1320 cm^{-1}, 1152. – MS, *m/z* (%): 266 [M^+] (50), 159 [$ClC_6H_4SO^+$] (72), 139 [$CH_3C_6H_4SO^+$] (100), 111 [$ClC_6H_4^+$] (21), 91 [$CH_3C_6H_4^+$] (39).

2-[3-(Trimethylstannyl)phenyl]-1,3-dioxolane (**3**): To the Grignard reagent prepared from 33.0 ml (0.22 mol) of 2-(3-bromophenyl)-1,3-dioxolane and 5.3 g (0.22 mol) of magnesium turnings in 300 ml of anhydrous THF a solution of 43.0 g (0.22 mol) of trimethyltin chloride in 50 ml of anhydrous THF is added at 20°C within 30 min. After heating of the reaction mixture at reflux for 8 h the solution is hydrolyzed with 300 ml of water. Twofold extraction of the aqueous phase with 100 ml each of diethyl ether, drying of the combined organic phases with Na_2SO_4 and fractional distillation yields 34.1 g (51%) of colorless **3**, b.p. 105–107°C/0.01 Torr. – ^{1}H NMR ($CDCl_3$): δ = 0.35 [s, 9H, $Sn(CH_3)_3$, $^2J_{SnH}$ = 55 Hz], 4.07 (m, 4H, CH_2), 5.78 (s, 1H, CHO_2), 7.47 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = –9.61 [$(CH_3)_3Sn$, $^1J_{SnC}$ = 343.3 Hz], 65.09 (CH_2), 103.75, 126.17 (CH), 127.74 (CH, $^2J_{SnC}$ = 45.5 Hz), 133.44 (CH, $^2J_{SnC}$ = 37.9 Hz), 136.73 (CH), 136.95 (Cq), 142.19 (Cq, $^1J_{SnC}$ = 488.6 Hz). – ^{119}Sn NMR ($CDCl_3$): δ = –27.44.

$C_{12}H_{18}O_2Sn$ (313.0) Calcd. C 46.05 H 5.80
Found C 45.9 H 5.6

2-[3-(Phenylsulfonyl)phenyl]-1,3-dioxolane (**4**): From 2 ml (7.7 mmol) of **3** and 0.98 ml (7.7 mmol) of benzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 1.20 g (54%) of **4** is obtained according to the general procedure I, m.p. 48°C (from *n*-hexane). – ^{1}H NMR ($CDCl_3$): δ = 4.12 (s, 4H, CH_2), 5.85 (s, 1H, CH), 7.22–8.23 (m, 9H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 65.29 (CH_2), 102.34, 125.61, 127.62, 128.17, 129.05, 129.17, 131.23, 133.12 (CH), 139.80, 141.28, 141.66 (Cq). – IR (KBr): = 1304 cm^{-1}, 1152, 1100. – MS, *m/z* (%): 289 [M^+] (53), 245 [$M^+ - C_2H_4O$] (37), 148 [$M^+ - SO_2Ph$] (67), 141 [$PhSO_2^+$] (6), 125 [$PhSO^+$] (25), 109 [PhS^+] (6), 77 [Ph^+] (32), 73 [$(CH_2)_2O_2CH^+$] (100).

$C_{15}H_{14}O_4S$ (290.3) Calcd. C 62.05 H 4.86
Found C 61.7 H 4.8

5-(Phenylsulfonyl)-1,3-benzodioxole (**6**): From 1 ml (5.3 mmol) of **5** and 0.68 ml (5.3 mmol) of benzenesulfonyl chloride in 5 ml of anhydrous chlorobenzene 0.80 g (58%) of **6** is obtained according to the general procedure I, m.p. 113°C (from *n*-hexane). – ^{1}H NMR ($CDCl_3$): δ = 6.07 (s, 2H, CH_2), 6.87–8.10 (m, 8H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 102.29 (CH_2), 107.58, 108.36, 123.40, 127.14, 129.08, 132.84 (CH), 134.63, 141.85, 148.20, 151.73 (Cq). – IR (KBr): $\tilde{\nu}$ = 2910 cm^{-1}, 1305, 1245, 1146, 1085. – MS, *m/z* (%): 262 [M^+] (69), 137 [$(C_6H_3O)O_2CH_2^+$] (100), 121 [$M^+ - PhSO_2$] (14), 107 [$C_6H_3O_2^+$] (24), 77 [$C_6H_5^+$] (21).

$C_{13}H_{10}O_4S$ (262.3) Calcd. C 59.53 H 3.84
Found C 59.1 H 3.8

N-Alkylarenesulfonamides **8a–f**. – *General Procedure II:* To 11 mmol of a trialkylstannane **1b**, **1e**, **1g**, **1j–l** 11 mmol of a *N*-alkylamidosulfonyl chloride **7** is added under argon, and the mixture is stirred at room temp. for 30 min. During this time a strong exothermic reaction may occur. To complete the reaction stirring at 70°C for 17 h is necessary. The mixture is subjected to short-path distillation, and the raw product is recrystallized from *n*-hexane (20 ml).

N-Methyl-4-toluenesulfonamide (**8a**): From 2 ml (10.2 mmol) of **1j** and 0.82 ml (10.2 mmol) of **7a** 1.70 g (84%) of **8a** is obtained after 17 h at 70°C, m.p. 74°C (from *n*-hexane) (ref.[15] 76°C). Trimethyltin chloride can be recovered from the reaction mixture up to 65% (1.40 g). – ^{1}H NMR ($CDCl_3$): δ = 2.47 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 5.07 (s, 1H, NH), 7.10–7.97 (AA'BB', 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.31, 29.06 (CH_3), 127.04, 129.52 (CH), 135.54, 143.24 (Cq). – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1}, 1599, 1364, 1158, 663. – MS, *m/z* (%): 185 [M^+] (54), 155 [$M^+ - NHCH_3$] (32), 121 [$M^+ - SO_2$] (13), 108 [$CH_3C_6H_4OH^+$] (39), 91 [$CH_3C_6H_4^+$] (100), 77 [$CH_3N{=}S{=}O^+$] (9).

N-Ethyl-4-toluenesulfonamide (**8b**): From 2 ml (10.2 mmol) of **1j** and 0.98 ml (10.2 mmol) of **7b** 1.90 g (87%) of **8b** is obtained after 17 h at 70°C, m.p. 61°C (from *n*-hexane) (ref.[15] 64°C). Trimethyltin chloride can be recovered from the reaction mixture up to 70% (1.50 g). – ^{1}H NMR ($CDCl_3$): δ = 1.17 (t, 3H, CH_3), 2.46 (s, 3H, CH_3), 3.07 (dq, 2H, CH_2), 5.30 (s, 1H, NH), 7.13–8.03 (AA'BB', 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.77, 21.30 (CH_3), 38.04 (CH_2), 126.92, 129.47 (CH), 136.87, 143.07 (Cq). – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1}, 1599, 1322, 1160, 667. – MS; *m/z* (%): 199 [M^+] (38), 184 [$M^+ - CH_3$] (68), 155 [$M^+ - C_2HNH$] (100), 108 [$C_2H_5NHSO_2^+$] (21), 91 [$CH_3C_6H_3^+$] (90).

N-Ethyl-3-toluenesulfonamide (**8c**): From 2 ml (11.0 mmol) of **1b** and 1.05 ml (11.0 mmol) of **7b** 1.20 g (55%) of **8c** is obtained after 17 h at 70°C, m.p. 46°C (from *n*-hexane). Trimethyltin chloride can be recovered from the reaction mixture up to 64% (1.40 g). – ^{1}H NMR ($CDCl_3$): δ = 1.07 (t, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.03 (m, 2H, CH_2), 5.20 (s, 1H, NH), 7.20–7.90 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.79, 21.13 (CH_3), 38.07 (CH_2), 123.98, 127.20, 128.73, 133.14 (CH), 139.07, 139.58 (Cq). – IR (KBr): $\tilde{\nu}$ = 3290 cm^{-1}, 1602, 1327, 1157.

N-Ethyl-3-methoxybenzenesulfonamide (**8d**): From 2.00 ml (10.4 mmol) of **1e** and 0.99 ml (10.4 mmol) of **7b** 1.90 g (85%) of **8d** is obtained as an oily product. Trimethyltin chloride can be recovered from the reaction mixture up to 73% (1.50 g). – ^{1}H NMR ($CDCl_3$):

δ = 1.17 (t, 3H, CH_3), 3.03 (dq, 2H, CH_2), 3.87 (s, 3H, OCH_3), 5.20 (t, 1H, NH), 6.73–7.67 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 14.03, 55.52 (CH_3), 38.17 (CH_2), 111.63, 118.81, 119.04, 129.97 (CH), 140.98, 159.81 (Cq). – (KBr): $\tilde{\nu}$ = 3290 cm^{-1}, 1601, 1320, 1159, 1041, 689. – MS, *m/z* (%): 215 [M^+] (24), 200 [$M^+ - CH_3$] (10), 171 [$M^+ - C_2H_5NH$] (47), 107 [$CH_3OC_6H_4^+$] (74), 64 [SO_2^+] (14), 44 [$C_2H_5NH^+$] (100).

$C_9H_{13}NO_3S$ (215.3) Calcd. C 50.22 H 6.09 N 6.54
Found C 49.9 H 6.1 N 6.5

4-Chloro-N-methylbenzenesulfonamide (**8e**): From 2 ml (9.4 mmol) of **1g** or 2.00 ml (6.5 mmol) of **1k** and 0.77 ml (9.4 mmol) or 0.53 ml (6.5 mmol) of **7a**, 1.70 g (83%) or 0.70 g (49%) of **8e** is obtained after 17 h at 70°C (from *n*-hexane). Trimethyltin chloride can be recovered from the reaction mixture up to 64% (1.20 g). The lower yield obtained by use of the tributyltin derivative can be attributed to the modified workup by using a KF solution for the separation of the tin compounds as fluorides. This procedure is unfortunately accompanied by losses of the product. – ^{1}H NMR ($CDCl_3$): δ = 2.70 (d, 3H, CH_3), 5.10 (m, 1H, NH), 7.30–8.07 (AA'BB', 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 29.13 (CH_3), 128.57, 129.30 (CH), 137.13, 139.05 (Cq). – IR (KBr): $\tilde{\nu}$ = 3310 cm^{-1}, 1588, 1322, 1159.

N-Ethyl-3-(trifluoromethyl)benzenesulfonamide (**8f**): No reaction occurs when 2 ml (10.4 mmol) of **1l** and 1.00 ml (10.4 mmol) of **7b** are mixed and the mixture is heated at 70°C for 25 h. The starting compounds can be recovered completely.

Reaction of **1b** *with* **9** *in the Presence of Lewis Acids:* When 2 ml (11.0 mmol) of **1b** reacts with complexes formed by mixing different types of Lewis acids (11.0 mmol) with 1.40 g (11.0 mmol) of **9** an exothermic reaction occurs. After 30 min the dark brown mixture is hydrolyzed with 20 ml of ice/water and extracted twice with 20 ml each of CH_2Cl_2. Tin compounds are separated by stirring the combined organic layers with 5 ml of a saturated KF solution, filtering off the tin fluorides and drying with $CaCl_2$. After removal of the solvent the raw product is recrystallized from *n*-hexane. No *ipso* substitution can be achieved but exclusively 4-toluenesulfono pyrrolidide (**10**) is isolated. The different yields depend on the strength of the Lewis acid. – $TiCl_4$/1.20 g (48%) of **10**, $SnCl_4$/1.00 g (40%) of **10**, $ZnCl_2$/0.25 g (10%) of **10**, m.p. 121°C (from *n*-hexane) (ref.[16] 121.5–123°C). – ^{1}H NMR ($CDCl_3$): δ = 1.87 (m, 4H, CH_2), 2.50 (s, 3H, CH_3), 3.30 (m, 4H, CH_2), 7.23–7.93 (AA'BB', 4H, aromatic H). – IR (KBr): $\tilde{\nu}$ = 1335 cm^{-1}, 1163.

2-(Chlorodimethylstannyl)-4-methylbenzenesulfono Pyrrolidide (**11**): To a solution of 1.40 ml (11.0 mmol) of **9** in 10 mol of anhydrous *n*-hexane 1.50 g (11.0 mmol) of anhydrous $AlCl_3$ is added under argon, and the separating oily Lewis acid base complex is filtered through glass wool. This complex is added slowly to 2 ml (11.0 mmol) of **1b** at –10°C, and the mixture is stirred at room temp. for 3 h. Subsequently, it is hydrolyzed with 20 ml of ice/water, the organic layer separated and washed twice with cold water; then 10 ml of methanol is added. The separating white perticipate is collected by suction filtration and washed with small amounts of cold methanol. Recrystallization from CH_2Cl_2 yields 0.80 g (33%) of **11** (clear crystalline plates with a length of up to 20 mm), m.p. 146°C. – ^{1}H NMR ($CDCl_3$): δ = 0.88 [s, 6H, $(CH_3)_2Sn$, $^2J_{SnH}$ = 52 Hz], 1.90 (m, 4H, CH_2), 2.51 (s, 3H, CH_3), 3.31 (m, 4H, CH_2), 6.78–8.77 (m, 3H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 1.84 (CH_3, $^1J_{SnC}$ = 521.3 Hz), 21.43 (CH_3), 25.29, 47.97 (CH_2), 126.06 (CH, $^2J_{SnC}$ = 40.7 Hz), 131.07 (CH, $^3J_{SnC}$ = 11.5 Hz), 137.32 (CH, $^2J_{SnC}$ = 33.1 Hz), 138.39 (Cq, $^3J_{SnC}$ = 40.7 Hz), 142.90 (Cq, $^1J_{SnC}$ = 607.8 Hz), 143.57 (Cq, $^2J_{SnC}$ = 48.3 Hz). – IR (KI): $\tilde{\nu}$ = 1313 cm^{-1}, 1133, 661, 296. – MS, *m/z* (%): 394 [$M^+ - 15$] (100), 374 [M^+ – Cl] (20), 155 [$SnCl^+$] (19), 120 [Sn^+] (4), 91 [$CH_3C_6H_4^+$] (12), 70 [$C_4H_8N^+$] (25). – The X-ray structural analyses of **11**[9] shows a strong intramolecular coordination of the tin atom by one of the oxygen atoms of the sulfonyl group.

Reaction of **11** *with a Saturated Aqueous KF Solution:* 0.30 g (0.7 mmol) of **11** is dissolved in 5 ml of CH_2Cl_2, and the solution is stirred for 2 h with 5 ml of a saturated aqueous KF solution at room temp. The organic layer is separated, filtered, and dried with $CaCl_2$. After removal of the CH_2Cl_2 the residue is dissolved in $CDCl_3$ and examinated by ^{1}H-NMR spectroscopy. Exclusively **10** can be detected (analytical data see above). So it is proved that complex **11** can be destroyed by using KF solution.

Sodium Toluenesulfonate Hydrates **13a–c**. – *General Procedure III:* To a solution of 5.5 mmol of trimethylsilyl chlorosulfonate (**12**) in 20 ml of anhydrous CCl_4 5.5 mmol of a trimethyltolylstannane **1a**, **1b**, **1h** is slowly added under argon at room temp. After 1 h the exothermic reaction is complete, and the mixture is hydrolyzed with 30 ml of a saturated aqueous $NaHCO_3$ solution and stirred for 20 min. The phases are separated and the aqueous one is washed three times with 10 ml of each ether. The water is removed and the residue is digested with 70 ml of boiling ethanol and filtered off. The ethanol is evaporated and the white residue is washed twice with 20 ml each of *n*-hexane and dried in vacuo.

Sodium 2-Toluenesulfonate Hydrate (**13a**): From 1.00 ml (5.5 mmol) of **1a** and 0.86 ml (5.5 mmol) of **12** in 20 ml of anhydrous CCl_4 1.00 g (87%) of **13a** is obtained after 1 h, m.p. >360°C. – ^{1}H NMR (D_2O): δ = 2.60 (s, 3H, CH_3), 6.93–7.97 (m, 4H, aromatic H). – ^{13}C NMR (D_2O): δ = 21.95 (CH_3), 128.25, 129.07, 133.91, 134.40 (CH), 138.54, 143.00 (Cq). – IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1}, 1194, 1030.

Sodium 3-Toluenesulfonate Hydrate (**13b**): From 1.00 ml (5.5 mmol) of **1b** and 0.86 ml (5.5 mmol) of **12** in 20 ml of anhydrous CCl_4 0.8 g (68%) of **13b** is obtained after 1 h, m.p. >360°C. – ^{1}H NMR (D_2O): δ = 2.40 (s, 3H, CH_3), 7.17–7.87 (m, 4h, aromatic H). – ^{13}C NMR (D_2O): δ = 22.84 (CH_3), 124.69, 128.03, 131.18, 134.46 (CH), 141.76, 144.65 (Cq). – IR (KBr): $\tilde{\nu}$ = 3445 cm^{-1}, 1187, 1055.

Sodium 4-Toluenesulfonate Hydrate (**13c**): From 1.00 ml (5.1 mmol) of **1j** and 0.80 ml (5.1 mmol) of **12** in 20 ml of anhydrous CCl_4 0.9 g (85%) of **13c** is obtained after 1 h, m.p. >360°C. – ^{1}H NMR (D_2O): δ = 2.33 (s, 3H, CH_3), 7.10–7.87 (AA'BB', 4H, aromatic H). – ^{13}C NMR (D_2O): δ = 22.88 (CH_3), 127.69, 131.75 (CH), 141.84, 144.73 (Cq). – IR (KBr): $\tilde{\nu}$= 3385 cm^{-1}, 1188, 1049.

---

[1] For the 6th communication, see W. P. Neumann, *J. Organomet. Chem.* **1992**, *437*, 23–39.

[2] [2a] W. Jeblick, W. Bunge in *Ullmanns Encyklopädie der technischen Chemie*, 4th ed., VCH, Weinheim, **1982**, vol. 22, p. 323. – [2b] *Römpps Chemie Lexikon* (Ed.: O.-A. Neumüller), Franckh, Stuttgart, **1987**, vol. 5, p. 4051. – [2c] F. Vögtle, L. Rossa, *Angew. Chem.* **1979**, *91*, 534–549; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 226.

[3] [3a] A. Schöberl, A. Wagner, *Methoden Org. Chem. (Houben-Weyl)*, **1955**, vol. IX, p. 223. – [3b] H. Beckurts, R. Otto, *Ber. Dtsch. Chem. Ges.* **1878**, *11*, 2066–2070. – [3c] G. Holt, B. Pagdin, *J. Chem. Soc.* **1960**, 2508–2511. – [3d] F. Muth, *Methoden Org. Chem. (Houben-Weyl)*, **1955**, vol. IX, p. 599. – [3e] T. Gajda, A. Zwiekzak, *Synthesis* **1981**, 1005–1008. – [3f] D. Klamann, G. Hofbauer, *Liebigs Ann. Chem.* **1953**, *581*, 182–197. – [3g] B. Unterhalt, *Methoden Org. Chem. (Houben-Weyl)*, **1985**, vol. E11/2, p. 992. – [3h] R. Graf, *Chem. Ber.* **1959**, *92*, 509–513. – [3i] G. A. Olah, *Friedel-Crafts and Related Reactions*, vol. 1–4, Interscience, New York, **1963–1965**. – [3j] M. Schmidt, H. Schmidbaur, *Chem. Ber.* **1962**, *95*, 47–53. – [3k] K. Hoffmann, G. Simchen, *Liebigs Ann. Chem.* **1982**, 282–297.

[4] [4a] L. L. Frye, E. L. Sullivan, K. P. Cusack, J. M. Funaro, *J. Org. Chem.* **1992**, *57*, 697–701. – [4b] P. Babin, J. Dunogués, G. Felix, P. Lapouyade, R. Calas, *J. Chem. Res. (S)* **1982**, 16–17. – [4c] B. Bennetau, M. Krempp, J. Dunoguès, *Tetrahedron* **1990**, *46*, 8131–8142. – [4d] S. N. Bhattacharya, C. Eaborn, D. R. M. Walton, *J. Chem. Soc. (C)* **1969**, 1367–1369. – [4e] P. Bourgeois, R. Calas, E. Jousseaume, J. Gerval, *J. Organomet. Chem.* **1975**, *84*, 165–175. – [4f] R. J. P. Corriu, B. J. L. Henner, N. Duffaut, M. Grignon-Dubois, *Bull. Soc. Chim. Fr.* **1977**, *P2/Nu, 11–12*, 1249–1250.

[5] R. W. Bost, P. Borgstrom, *J. Am. Chem. Soc.* **1929**, *51*, 1922–1925.

[6] R. W. Bost, H. R. Baker, *J. Am. Chem. Soc.* **1933**, *55*, 1112–1113.

[7] W. P. Neumann, Proceedings of the 7th Internat. Confer. on the Organomet. and Coordin. Chem. of Ge, Sn, Pb, July 20–25th, **1992**, Riga, Latvia, in press.

[8] W. P. Neumann, C. Wicenec, *J. Organomet. Chem.* **1991**, *420*, 171–177.

[9] H. Preut, C. Wicenec, W. P. Neumann, *Acta Crystallogr., Sect. C*, **1992**, *48*, 366–368.

[10] All stannanes were prepared according to published procedures. For a compilation of various procedures, see U. Kobs, W. P. Neumann, *Chem. Ber.* **1990**, *123*, 2191–2194.

[11] S. N. Bhattacharya, C. Eaborn, K. Dey, D. R. M. Walton, *US Clearinghouse Sci. Tech. Inform.* AD 673274, Springfield **1969**.

[12] W. E. Truce, M. F. Amos, *J. Am. Chem. Soc.* **1951**, *73*, 3013–3017.

[13] C. A. Buehler, J. E. Masters, *J. Org. Chem.* **1939**, *4*, 262–265.

[14] M. E. Heppenstall, S. Smiles, *J. Chem. Soc.* **1938**, 899–905.

[15] F. M. Jaeger, *Proc. Acad. Sci. Amsterdam* **1920**, *23*, 347–362.

[16] D. Klamann, H. Bertsch, *Chem. Ber.* **1956**, *89*, 2007–2012.

[353/92]