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Destannylative Acylation of 1-(Tributylstannyl)-1-(Phenylsulfonyl)-cyclopropane and -ethene.

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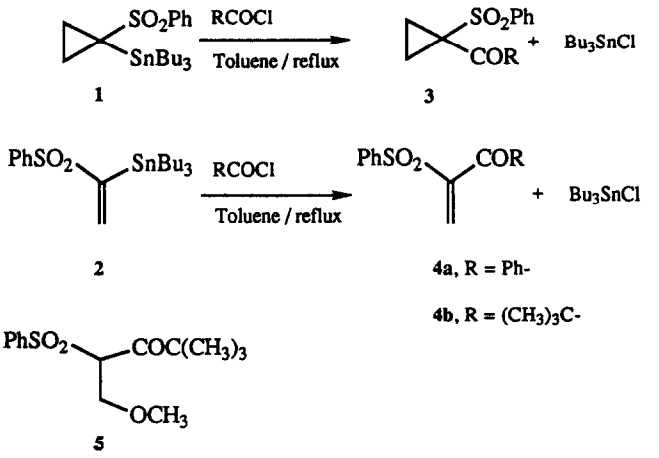
Abstract: The reaction of α-stannyl sulfones **1** and **2** with acyl chlorides in refluxing toluene, leading to 1-acyl-1-(phenylsulfonyl)cyclopropanes **3** and the labile 1-acyl-1-(phenylsulfonyl)ethenes **4**, is described.

The relative weakness of carbon-tin bonds allows organotin compounds to react with a variety of electrophiles. This provides useful methods for carbon-carbon formation. In particular, the cross-coupling reactions of organotin compounds with organic electrophiles catalyzed by transition metal catalysts such as palladium complexes as well as by Lewis acids[2] have received considerable attention in recent years. However, few reactions in the absence of catalysts have been reported. For examples, vinyltins give substitution products upon heating with α-haloesters,[3] and allyltins react smoothly under the same conditions with aldehydes, ketones[4] and immonium salts[5] to give the corresponding homoallyl alcohols and amines, respectively. Some α-stannyl -esters, -amides, -ketones and -nitriles can react with certain aldehydes and ketones.[6] Few α-heterosubstituted organotins, such as α--stannyl nitrosamines[7] and trihalomethyltributyltins[8] have also been demonstrated to react with acyl chlorides and aldehydes at ambient temperature. As a part of a programme involving the development of new carbon-carbon forming reactions and in connection with our continuing synthetic studies using α-stannyl substituted organosulfur compounds,[9] we are interested in examining the reaction of α-stannyl sulfones with acyl chlorides. It will be expected that the activated carbon-tin bonds in α-stannyl sulfones **1** and **2** can combine with acyl chloride to give the corresponding ketosulfones **3** and **4** without the addition of any catalyst.



RESULTS AND DISCUSSION

The starting α-stannyl sulfone **1** was prepared in 58% by treatment of 1-lithio-1-(phenylsulfonyl)cyclopropane[10] with tributyltin chloride, while the α-stannyl suffone **2** was achieved in 53% by the oxidation of the corresponding α-stannyl vinyl sulfide[11] with a mixture of 30% hydrogen peroxide-glacial acetic acid. Our investigation started with the α-stannyl sulfone **1**. Initially, the reaction of **1** with acetyl chloride in refluxing dichloromethane for 5 h gave no expected product **3a**, only **1** was recovered quantitatively. In contrast, treatment of **1** with acetyl chloride (2-2.2 equiv) in toluene at reflux for 5 h afforded **3a** in 70% yield after chromatography. The results for the reaction of **1** with other acyl chlorides are listed in Table 1. To test the generality of this coupling reaction, **1** was subjected to cinnamoyl chloride under the standard conditions. It was found that the reaction provided a complex mixture of prbducts. The less reactive ethyl- and methyl chloroformate did not combine with **1** to give the expected product of type **3**.

Table 1. Preparation of 1-Acyl-1-(phenylsulfonyl)cyclopropanes (**3**).

Acyl Chloride	Product 3	Yield (%)
CH_3COCl	**3a**, R = CH_3-	70
PhCOCl	**3b**, R = Ph-	78
$CH_3CH_2CH_2COCl$	**3c**, R = $CH_3CH_2CH_2$-	80
$(CH_3)_2CHCOCl$	**3d**, R = $(CH_3)_2CH$-	66
$CH_3(CH_2)_3COCl$	**3e**, R = $CH_3(CH_2)_3$-	87
$(CH_3)_3CCOCl$	**3f**, R = $(CH_3)_3C$-	89

Similarly, the reaction of the α-stannyl sulfone **2** with benzoyl chloride (1.2 equiv) in refluxing toluene for 45 minutes afforded, after workup with aqueous potassium fluoride in ether in order to remove tributyltin chloride, the crude product **4a**, which was solidified upon cooling to -78 °C and then allowing to warm to room temperature. Recrystallisation of this solid product from an ether-hexane mixture gave **4a**[12] in 70%. We observed that **4a** slowly decomposed upon standing. Attempts to purify the crude product **4a** by preparative thin-layer and flash column chromatography (silica gel) were unsuccessful due to its gradual polymerisation. Furthermore, treatment of the α-stannyl sulfone **2** with pivaloyl chloride (1.1 equiv) under the same conditions provided the labile product **4b**. The ^{1}H-NMR spectrum of the crude product **4b** shows peaks at δ 1.3 (s, *tert*-Bu), 6.0 and 6.53 (each s, olefinic protons), 7.35-7.95 (m, $PhSO_2$). Again, purification of **4b** by chromatography (silica gel, PLC and flash column) led to polymerisation, giving a mixture of products. Fortunately, on treatment of the crude product **4b** with methanol at room temperature (overnight), compound **5** could be isolated in good yield (86%). It should be mentioned that the reaction of the α-stannyl sulfone **2** with both benzoyl chloride and pivaloyl chloride leading to the acylated products **4a** and **4b** proceeded very rapidly and cleanly as revealed by thin-layer chromatography monitoring of the reaction mixtures. Efforts were also made to react the α-stannyl sulfone **2** with other acyl chlorides, such as acetyl chloride, isobutyryl chloride and *n*-valeroyl chloride. However, all reactions furnished unsatisfactory results. We reasoned that the expected products of type **4** were produced , but they polymerised during workup.[12]

CONCLUSION

Our results showed that the α-stannyl sulfones **1** and **2** underwent the destannylative acylation reaction on treatment with acyl chlorides in refluxing toluene to yield the α-acylated sulfones **3** and the unstable α-acylated sulfones **4**. The products of type **3** are expected to be useful in organic synthesis, since they are activated cyclopropanes, which are normally capable of undergoing many transformations.[13] In addition , the α,β-unsaturated ketosulfones **4** may be useful as reactive Michael acceptors and dienophiles.[12] The reactions of compounds of type **4**, which are generated in *situ*, with suitable nucleophiles and dienes are now in progress.

EXPERIMENTAL PART

General Methods. The IR spectra were determined on a Jasco A-302 spectrophotometer. The ^{1}H-NMR spectra were recorded at 60 MHz with a Varian EM-360L spectrometer. Mass spectra were obtained on an INCOS 50 Mass spectrophotometer at 70 eV. Melting points were determined by a Buechi 510 Meltting Point Apparatus and are uncorrected.

Preparation of 1-(Phenylsulfonyl)-1-(tributylstannyl)cyclopropane (1).

To a cooled (0 °C) solution of (phenylsulfonyl)cyclopropane in THF (50 ml) was added dropwise BuLi (1.4 M in hexane, 19.3 ml, 27 mmol). After stirring for an hour, the resulting mixture was cooled down to -78 °C and tributyltin chloride (7.3 ml, 27 mmol) was slowly added. The reaction mixture was slowly warmed up to room temperature by stirring overnight (14 h) and then worked up by diluting with water followed by extracting with ethyl acetate (3x75 ml). The combined organic layers were washed successively with water, brine and dried over anhydrous $MgSO_4$. Filtration followed by evaporation gave the crude product (12.3 g),

which was purified by flash column chromatography (silica gel, 5-20% ethyl acetate in hexane) to afforded a colorless liquid of **1** (6.7 g, 58%) and the recovered starting (phenylsulfonyl)cyclopropane (0.9 g, 20%). IR(neat):ν_{max} 3075, 2950, 1590, 1460, 1450, 1420, 1380, 1220, 1150, 1130, 1080, 1025, 1000, 960, 910, 880, 790, 730, 690 cm^{-1}; NMR(CCl_4): δ 0.4-2.0 (m, 31H, *-SnBu3* and *methylene protons*), 7.25-8.0 (m, 5H, *-SO_2Ph*); MS: m/e(%) relative intensity 471(M^++1,1), 415(100), 414(74), 411(38), 407(1), 301(8), 299(5), 261(3), 197(18), 196(6), 195(13), 177(2), 121(2). Anal. Calcd for $C_{21}H_{36}O_2SSn$: C, 53.52; H, 7.70. Found: C, 53.94, H,7.94.

Preparation of 1-(Alkanoyl)-1-(phenylsulfonyl)cyclopropane (3).

1-(Acetyl)-1-(phenylsulfonyl)cyclopropane (3a).
General procedure: 1-(Tributylstannyl)-1-(phenylsulfonyl)cyclopropane (**1**) (4.6 g, 9.8 mmol) was stirred in dry toluene (15 ml) under an argon atmosphere. Acetyl chloride (1.5 ml, 21.1 mmol) was then added. The solution was refluxed under argon for 5 h, then quenched with a saturated aqueous KF solution (15 ml) and stirred at room temperature overnight (16 h). The precipitates of Bu_3SnF were filtered and washed several times with ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2x25 ml). The organic layers were combined and washed with a saturated aqueous $NaHCO_3$ solution, water, brine and dried over anhydrous $MgSO_4$. Filtration followed by evaporation gave a yellow liquid of the crude product (2.4 g), which was purified by preparative thin-layer chromatography (PLC) (silica gel, 5% ethyl acetate in hexane) to afford a white solid of **3a** (1.5 g, 70%). The solid product was recrystallized from ether/hexane to give colorless crystals of **3a** (mp 64-66 °C). IR($CHCl_3$):ν_{max} 3050, 1700, 1590, 1485, 1450, 1420, 1365, 1310, 1230, 1210, 1150, 1130, 1110, 1080, 1050, 990, 935, 910, 820, 800, 720, 690, 640, 605, 580 cm^{-1}; NMR(CCl_4): δ 1.3-2.0 (m, 4H, *methylene protons*), 2.3 (s, 3H -$COCH_3$), 7.4-8.1 (m, 5H, *-SO_2Ph*); MS: m/e(%) relative intensity 225(M^++1,1), 209(2), 160(11), 159(22), 145(21), 125(11), 117(15), 116(28), 105(16), 78(28), 77(57), 51(33), 43(100). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.98, H, 5.36.

1-Benzoyl-1-(phenylsulfonyl)cyclopropane (3b): A mixture of **1** (1.4 g, 3.0 mmol) and benzoyl chloride (0.7 ml. 6.0 mmol) in dry toluene (15 ml) was refluxed under argon for 5 h. After stirring with a saturated aqueous KF solution and workup as usual, the reaction gave a yellow liquid of the crude product (1.5 g), which was purified by PLC (silica gel, 5% ethyl acetate in hexane) to give a white solid of **3b** (0.7 g, 78%): mp 174-176 °C (ether-hexane). IR($CHCl_3$): ν_{max} 3025, 1675, 1600, 1580, 1450, 1420, 1320, 1220, 1180, 1150, 1090, 1050, 990, 960, 930, 890, 690 cm^{-1}; NMR(CCl_4): δ 1.2-2.05 (m, 4H, *methylene protons*), 7.2-7.8 and 7.8-8.2 (each m, 10H, *-$COPh$* and *-SO_2Ph*); MS: m/e(%) relative intensity 286(M^+, 2), 194(43), 181(20), 178(72), 153(21), 152(34), 105(100), 77(67), 41(34). Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11, H, 4.93. Found: C, 67.05; H, 4.93.

1-(Butanoyl)-1-(phenylsulfonyl)cyclopropane (3c): A mixture of **1** (1.4 g, 3.0 mmol) and *n*-butyryl chloride (0.6 ml, 6.1 mmol) in dry toluene (15 ml) was refluxed under argon for 5 h. After stirring with a saturated aqueous KF solution and workup as usual, the reaction gave a yellow liquid of the crude product (1.4 g), which was purified by PLC (silica gel, 5% ethyl acetate in hexane) to give a white solid of **3c** 9(0.6, 80%): mp 66-67 °C (ether-hexane). IR($CHCl_3$): ν_{max} 3050, 2975, 2950, 2900, 1700, 1590, 1480, 1470, 1450, 1370, 1310, 1290, 1230, 1210, 1150, 1120, 1090, 1060, 950, 930, 720, 690 cm^{-1}; NMR(CCl_4): δ 0.8 (t, J = 7 Hz, 3H, -CH_2CH_3), 1.15-2.1 (m, 6H -$COCH_2CH_2CH_3$ and *cyclopropyl protons*), 1.65 (t, J = 7 Hz, 2H, -$COCH_2CH_2CH_3$), 7.3-8.1 (m, 5H, *SO_2Ph*); MS: m/e(%) relative intensity 253(M^++1, 2), 209(36), 188(37), 187(11), 145(49), 141(11), 125(16), 117(21), 105(63), 95(17), 78(24), 77(100), 71(65), 51(41), 43(82). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found : C, 62.01; H, 6.32.

1-(2-Methylpropanoyl)-1-(phenylsulfonyl)cyclopropane (3d): A mixture of **1** (1.5 g, 3.1 mmol) and isobutyryl chloride (0.7 ml, 6.8 mmol) in dry toluene (15 ml) was refluxed under argon for 4 h. After stirring with a saturated aqueous KF solution and workup as usual, the reaction gave a yellow liquid of the crude product (1.0 g), which was purified by PLC (silica gel, 3% ethyl acetate in hexane) to give a pure pale yellow liquid of **3d** (0.5 g, 66%). IR(neat): ν_{max} 3100, 3075, 2975, 2950, 2875, 1700, 1590, 1470, 1420, 1390, 1360, 1310, 1240, 1150, 1090, 1050, 1030, 950, 915, 860, 760, 750, 730, 690 cm^{-1}; NMR(CCl_4) : δ 0.96 (d, J = 7 Hz, 6H, -$CH(CH_3)_2$], 1.4-2.1 (m, 4H, *cyclopropyl protons*), 3.23 [sept, J = 7 Hz, 1H, -$COCH(CH_3)_2$], 7.25-8.1 (m, 5H, *-SO_2Ph*); MS: m/e(%) relative intensity 252(M^+, 6), 209(100), 188(10), 145(19), 141(16), 125(19),

117(17), 110(21), 105(83), 78(91), 71(91), 71(11), 51(30), 125(19), 117(21), 105(83), 78(24), 77(91), 71(11), 51(30). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 61.37, H, 6.42.

1-(Pentanoyl)-1-(phenylsulfonyl)cyclopropane (3e): A mixture of **1** (1.5 g, 3.1 mmol) and *n*-valeroyl chloride (0.7 ml, 6.8 mmol) in dry toluene (15 ml) was refluxed under argon for 6 h. After stirring with a saturated aqueous KF solution and workup as usual, the reaction gave a yellow liquid of the crude product (1.0 g), which was purified by PLC (silica gel, 5% ethyl acetate in hexane) to give a pale yellow liquid of **3e** (0.7 g, 87%). IR(neat): ν_{max} 3075, 2975, 2950, 2875, 1700, 1585, 1450, 1380, 1290, 1150, 1120, 1085, 1060, 1020, 950, 760, 730, 690 cm^{-1}; NMR(CCl_4): δ 0.6-2.1 (m, 11H, *methyl* and *methylene protons*), 2.6 (br.t, J = 7 Hz, 2H,- CH_2CH_2CO), 7.25-8.2(m, 5H, -SO_2Ph); MS: m/e(%) relative intensity 267(M^++1,1), 266(M^+,1) 224(34), 209(69), 202(64), 160(27), 145(67), 142(27), 125(34), 117(30), 116(43), 105(77), 95(35), 85(66), 77(100), 69(36), 57(75), 41(38). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13, H, 6.81. Found: C, 62.60; H, 7.01.

1-(2,2-Dimethylpropanoyl)-1-(phenylsulfonyl)cyclopropane (3f): A mixture of **1** (1.4 g, 3.0 mmol) and pivaloyl chloride (0.8 ml, 6.1 mmol) in dry toluene (15 ml) was refluxed under argon for 6 h. After stirring with a saturated aqueous KF solution and workup as usual, the reaction gave a yellow liquid of the crude product (1.1 g), which was purified by PLC (silica gel, 5% ethyl acetate in hexane) to give a pale yellow liquid of **3f** (0.7 g, 89%). IR (neat): ν_{max} 3075, 2975, 2925, 2875, 1690, 1590, 1485, 1450, 1420, 1400, 1370, 1320, 1310, 1290, 1240, 1210, 1200, 1180, 1140, 1090, 1050, 1020, 1000, 950, 930, 920, 900, 830, 760, 750, 730, 690, 590, 560 cm^{-1}; NMR(CCl_4) : δ 1.25 [s, 9H, -$C(CH_3)_3$], 1.45-1.8 (m, 4H, *cyclopropyl protons*), 7.25-7.85 (m, 5H, -SO_2Ph); MS: m/e(%) relative intensity 266(M^+, 1), 251(3), 212(13), 211(100), 209(40), 182(13), 143(14), 142(24), 125(66), 110(17), 105(26), 77(42), 69(14), 57(77). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81. Found: C, 63.09; H, 7.04.

Preparation of 1-(Tributylstannyl)-1-(phenylsulfonyl)ethene (2).

1-(Tributylstannyl)-1-(phenylthio)ethene[11] (8.5 g, 20.0 mmol) was dissolved in glacial acetic acid (10 ml) and 30% hydrogen peroxide (12 ml) was added at 0 °C by dropping 2 ml every half an hour. After complete addition, it was slowly warmed up to room temperature by stirring overnight (14 h). The resulting mixture was diluted with water (50 ml) and dichloromethane (100 ml) and then adjusted to neutral with 10% sodium hydroxide. The CH_2Cl_2 layer was separated and the aqueous layer was extracted with dichloromethane (3x50 ml). The combined organic layers were washed with water, brine and dried over anhydrous $MgSO_4$. The crude product (8.4 g) was purified by flash column chromatography (silica gel, 5-10% ethyl acetate in hexane) to afford a pure colorless liquid of **2** (4.9 g, 53%). IR(neat): ν_{max} 3050, 2975, 2925, 2875, 2850, 1590, 1485, 1470, 1450, 1420, 1380, 1340, 1300, 1180, 1145, 1110, 1080, 1030, 1000, 965, 880, 780, 755, 730, 695 cm^{-1}; NMR(CCl_4): δ 0.5-2.0 (m, 27H, -$SnBu_3$), 5.8 and 6.13 (each br.s, 2H, *olefinic protons*), 7.35- 7.95 (m, 5H -SO_2Ph); MS: m/e (%) relative intensity 457(M^++1, 1), 405(16), 403(18), 402(19), 401(100), 400(46), 399(90), 398(41), 397(65), 261(26), 259(21), 257(13), 2011(13), 199(29), 198(10), 197(63), 196(22),195(47), 194(14), 193(23), 177(11), 121(16), 120(12), 119(14), 77(11), 57(13). Anal. Calcd for $C_{20}H_{34}O_2SSn$: C, 52.54; H, 7.49. Found: C, 52.48; H, 7.53.

Reaction of 2 with Pivaloyl chloride.

Compound **2** (1.4 g, 3.0 mmol)was dissolved in dry toluene (15 ml) under an argon atmosphere, and pivaloyl chloride (0.4 mL, 3.3 mmol) was then added. The mixture was refluxed under argon for 35 min, then quenched with a saturated aqueous KF solution (15 mL) and stirred at room temperature for 2 h. The precipitates of Bu_3SnF were filtered and washed several times with ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2x25 ml). The organic layers were combined and washed with a saturated aqueous $NaHCO_3$ solution, water, brine and dried over anhydrous $MgSO_4$. Filtration followed by evaporation gave a yellow liquid of the crude product of **4b** (1.0 g). The NMR spectrum of the crude product in CCl_4 showed the main peaks as follows : δ 1.3 [s, 9H, -$C(CH_3)_3$], 6.0 and 6.53 (each br.s, 2H, *olefinic protons*), and 7.35-7.95 (m, 5H, -SO_2Ph). The minor peaks are two broad singlets at δ 5.8 and 6.4 ppm as well as a broad multiplet at δ 0.8-1.8 ppm due to the starting material **2**.

The crude product of **4b** (0.9 g) obtained was dissolved in absolute methanol (10 ml) and stirred at room temperature overnight. After evaporation off methanol, the crude product (1.0 g) was purified by PLC (silica gel, 20% ethyl acetate hexane) to give a pale yellow liquid of 4,4-dimethyl-1-methoxy-2-(phenylsulfonyl)-3-pentanone (**5**) (0.7 g, 86%). IR(neat): ν_{max} 3075, 2975, 2925, 2900, 2875, 1710, 1585, 1480, 1450, 1370, 1310, 1210, 1190, 1150, 1110, 1090, 1050, 1020, 980, 840, 760, 720, 690 cm^{-1}; NMR(CCl_4): δ 1.2 [s, 9H,

-C(CH_3)$_3$], 3.16(s, 3H, -OCH_3), 3.3-3.9 (m, 2H, -CH_2OCH_3), 4.75 (dd, J = 5,10 Hz, 1H, -$CHCH_2OCH_3$) 7.3-7.95(m, 5H, -SO_2Ph); MS: m/e(%)- relative intensity 284(M^+, 1), 200(22), 197(11), 169(24), 168(27), 143(14), 126(12), 125(73), 87(14), 78(10), 77(38), 70(15), 57(100), 51(13).

1-Phenyl-2-(phenylsulfonyl)-2-propen-1-one (4a).[12]

A mixture of **2** (1.0 g, 2.1 mmol) and benzoyl chloride (0.3 ml, 2.6 mmol) in dry toluene (10 ml) was refluxed under an argon atmosphere for 45 min. After stirring with a saturated aqueous KF solution and workup as usual, the reaction gave a yellow liquid the crude product, which was crystallized by cooling to -78 °C to give a pale yellow solid of **4a** (0.4 g, 70%; mp 97-100 °C); IR(nujol): ν_{max} 1660, 1590, 1320, 1210, 1280, 1150, 1130, 1080, 1000, 970, 940, 780, 760, 745, 725, 705, 690, 660 cm^{-1}; NMR($CDCl_3$): δ 6.25 and 7.05 (each br.s, 2H, *olefinic protons*), 7.2-8.15 (m, 10H, CO*Ph* and SO_2Ph); MS: m/e(%) relative intensity 272(M^+, 2), 208(19), 196(17), 106(13), 105(100), 78(11) 77(58), 69(12).

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