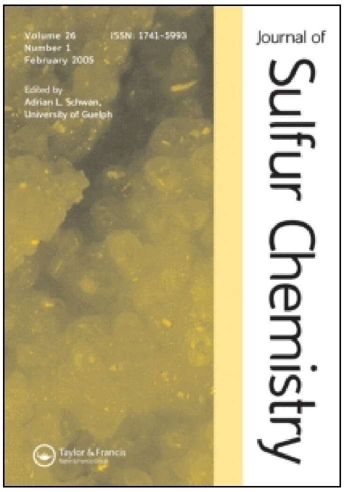

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José Luis García Ruano[a]; Sara Duce[a]; José Alemán[a]; Jesús López-Cantarero[a]; Modesto J. Remuiñán[a]; M. Belén Cid[a]
[a] Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid Cantoblanco, Madrid, Spain

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The role of the sulfinyl group in the copper catalyzed benzyl reactions from 2-*p*-tolylsulfinylbenzylstannanes

José Luis García Ruano*, Sara Duce, José Alemán, Jesús López-Cantarero, Modesto J. Remuiñán and M. Belén Cid*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid Cantoblanco, 28049 Madrid, Spain

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

2-*p*−Tolylsulfinyl benzyltributyltin undergoes smooth coupling conditions with allyl and alkynyl derivatives in the presence of Cu(I) salts. It demonstrates that the sluggish benzyl transfer in Stille coupling reactions mediated by copper can be significantly improved by the presence of a sulfinyl group at the *ortho* position.

Keywords: Stille reaction; palladium; copper; sulfoxides

1. Introduction

Stille coupling reactions have evolved into a powerful tool for the construction of carbon–carbon bonds (*1*, *2*). In most cases, the reactive organometallic intermediates (usually Pd (*1*) and more recently Cu (*2*)) exhibit a σ bond between an sp^2-hybridized carbon atom and the transition metal (*3*). As the transmetallation rate of benzyl stannanes in the palladium-catalyzed reactions is rather low (*4*), their coupling reactions are limited to few electrophiles (mainly acyl chlorides) (*5–7*) and they need harsh conditions such as the use of microwave (*6*) or solvents like HMPA (*7*). The C−Sn bond elongation produced by the coordination of different groups to the metal has been used to accelerate the transfer of alkyl groups from tin (*8*, *9*). The coupling of secondary alkyl groups attached to the metal has been also possible in compounds bearing coordinating groups close to the reaction center (*10*). Sulfoxides have demonstrated to be efficient as coordinating agents of the tin atoms, affording penta- or even hexa-coordinate structures (*5*, *11*) and consequently, DMSO has been proposed as the solvent of choice in problematical couplings (*12*). There are also several papers evidencing that sulfoxides can determine the outcome of reactions catalyzed by Pd (*13*, *14*), and another proves that sulfoxides form strong complexes with Pd(II) (*15*). However, to our knowledge, this ability of the sulfinyl group for increasing the reactivity

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*Corresponding authors. Emails: joseluis.garcia.ruano@uam.es; belen.cid@uam.es

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of organotin reagents in coupling reactions has never been explored when the sulfinyl group is supported by organotin, thus providing an intramolecular activation.

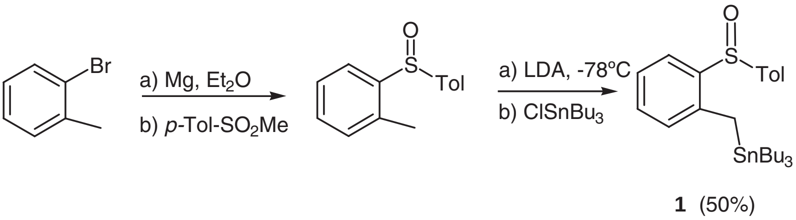
In the frame of an ongoing program on the study of the use of the sulfinyl group as a remote inductor in benzylic systems (*16*), we have investigated the role of the sulfinyl group on the reactivity of the tin derivative **1** in the presence of acyl chlorides (*17*). However, this role could not be established because the expected *ortho*-sulfinylbenzyl ketones were not obtained but the oxygenated thioethers at benzylic position, resulting in a novel asymmetric vinylogous tin-Pummerer rearrangement (*17*) due to the attack of acyl chloride on the sulfinyl oxygen in the first step of the process. We then decided to study Stille-type reactions, with Pd and Cu as catalysts, starting from compound **1** as benzyl-transfer agent. In this paper, we describe the coupling reactions of this compound with allyl, vinyl, phenyl and alkynyl bromides (used as prototypes of X−C(sp^3), X−C(sp^2) and X−C(sp) bonds), and the experiences that allowed us to demonstrate the positive influence of the sulfinyl group as the intramolecular promoter of the benzyl transfer.

2. Results and discussion

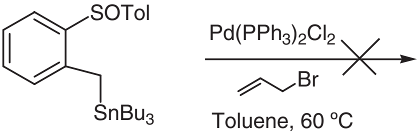
Racemic sulfinylstannane (±)-**1** was easily prepared by the stannylation of 2-*p*-tolylsulfinyl toluene with LDA and $ClSnBu_3$ (Scheme 1), following the procedure described for the synthesis of (*S*)-**1** (*17*). The starting sulfoxide was obtained by reaction of the Grignard derivative of 2-bromotoluene with (±)-methyl *p*-tolylsulfinate.

We first studied the coupling reaction of stannane **1** with allyl bromide. Surprisingly, under standard conditions, using $PdCl_2(PPh_3)_2$ as catalyst in toluene, the expected cross-coupled product **2** (Scheme 2) was not detected in the reaction mixture. Also, negative results were obtained by using coordinating solvents such as DMF or DMSO, or bromo-bis (triphenylphosphine) (*N*-succinimide) palladium as catalyst, despite it being reported as highly efficient for the coupling of allylic and benzylic substrates (*18*). The use of additives like *p*-benzoquinone, which favor the reductive elimination step (*19*), and stannanes supporting more bulky phosphines at the tin atom, which make more difficult the transmetalation step,[1] was unsuccessful too.

Subsequently, we studied the reaction of **1** with allylbromide in the presence of different Cu(I) salts. The best results were obtained from tributyl tin derivatives (Table 1).[2] Toluene (Entries 5–7) provides better yields than THF (Entries 1 and 2), whereas more coordinating solvents like DMF



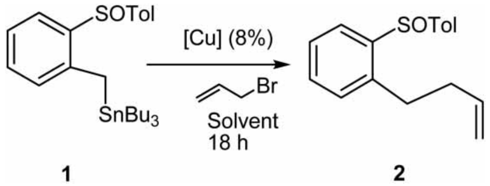
Scheme 1.



1 **2**

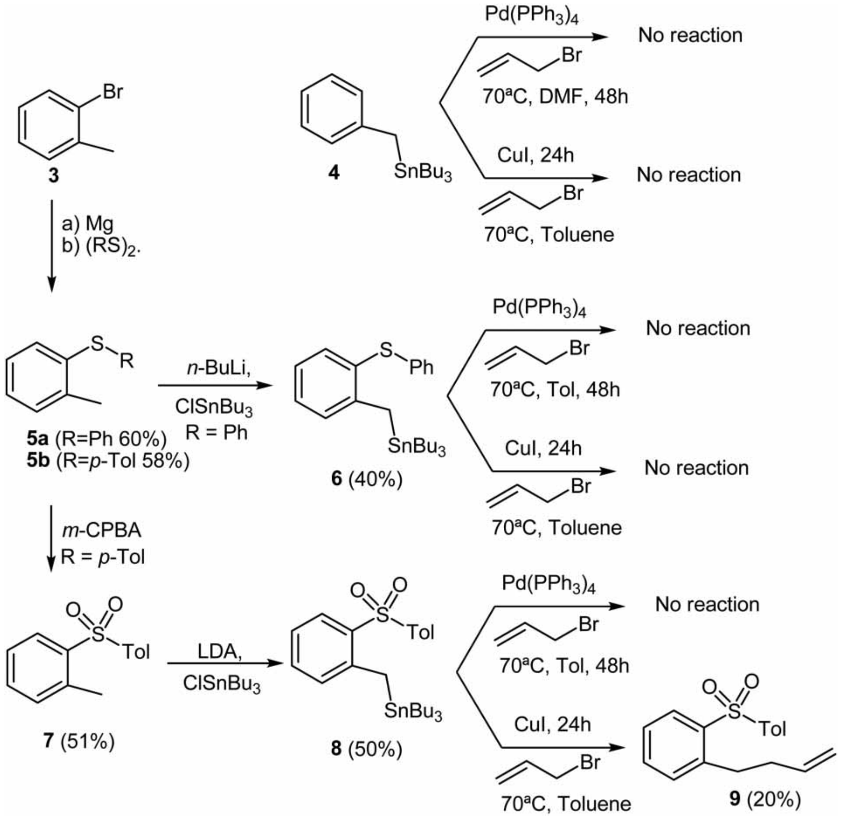
Scheme 2.

Table 1. Reaction of **1** with allyl bromide and Cu(I) salts.

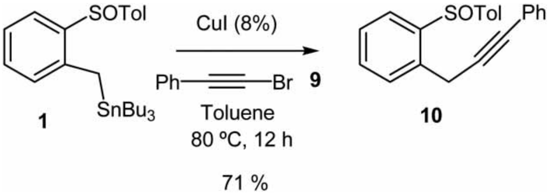


Entry	Copper salt	Solvent	Yield (%)
1	CuTc	THF	40
2	CuI	THF	55
3	CuI	DMF	Complex mixture
4	CuI	MeCN	Complex mixture
5	CuI	Toluene	75
6	CuCl	Toluene	50
7	CuCN	Toluene	80

or CH_3CN afforded complex mixtures (Entries 3 and 4). CuI (Entries 2–5) and CuCN (Entry 7) were more efficient catalysts than CuCl (Entry 6) and CuTc (Entry 1). The different behavior of compound **1** under Pd and Cu catalysis is not surprising taking into account that each one interacts with a different coordinating center at the sulfinyl group. Thus, palladium prefers the association to the lone electron pair, whereas the sulfinyl oxygen is a better ligand for Cu (*20*, *21*).



Scheme 3.



Scheme 4.

In order to evaluate the role of the sulfinyl group in Stille coupling reactions catalyzed by Pd and Cu, the behavior of benzylstannane **4**, as well as that of thioether **6** and sulfone **8**, lacking the sulfinyl group, was studied under different conditions (Scheme 3). Compounds **6** and **8** were prepared as outlined in Scheme 3, by simple stannylation of the corresponding sulphur derivatives **5** and **7**, which in turn were easily obtained from 2-bromotoluene.

Reactions of compounds **4** and **6** under conditions similar to that used with the sulfinyl derivative **1** in Scheme 1 and Table 1 do not work (Scheme 3). Starting from sulfone **8**, the reaction catalyzed by palladium was unsuccessful, but in the presence of CuI, the coupling product **9** could be isolated in 20% yield after 24 h (Scheme 3). These results suggest that the larger coordinative ability of the sulfinyl oxygen at **1** assists the tin–copper transmetallation, thus making the coupling of the benzyl group with the allyl residue easier.

The transfer of the benzyl group to an alkynyl residue also took place by the reaction of compound **1** with 1-bromo-2-phenyl acetylene under copper catalysis. The best result for this sp^3–sp coupling affording compound **10** was obtained with CuI (8%) in toluene at 80 °C (Scheme 4).

Finally, we have studied the reactions of compound **1** with alkenyl and aryl halides in order to get the sp^3–sp^2 coupling. However, unsuccessful results were obtained under conditions used. The reaction of **1** with 3-iodoacrilate gave only traces of the coupled product, whereas aromatic iodo derivatives containing groups with different electronic properties (iodobenzene, iodoanisole and 2-iodopyridine) afforded unaltered starting material.

3. Conclusion

In summary, we have checked that the sulfinyl group is able to act as an intramolecular activator of the benzyl transfer in Stille reactions of benzyl stannanes with allyl and alkynyl bromides catalyzed by copper. The reaction conditions used in these cases did not work with aryl and alkenyl bromides.

4. Experimental

4.1. *General procedures*

All moisture-sensitive reactions were performed in flame-dried glassware equipped with rubber septa under positive pressure of argon. Silica gel 60 (230–400 mesh ASTM) was used for flash column chromatography. NMR spectra were determined in $CDCl_3$ solutions, unless otherwise indicated, at 300 and 75 MHz for ^{1}H- and ^{13}C-NMR, respectively; chemical shifts (δ) are reported in ppm and J values are given in Hz. RT denotes the room temperature. All starting materials were purchased from Aldrich. Compounds **1** (*16a*), **2** (*16b*) and **7** (*16g*) were previously described in the literature.

4.2. *Compounds 6 and 8*

4.2.1. *Tributyl[2-(phenylthio)benzyl]stannane (**6**)*

A solution of *o*-tolylmagnesium bromide, prepared from 2-bromotoluene (3 ml, 25 mmol) and Mg (0.68 g, 28 mmol) in THF, was added over a solution of diphenyl disulfide (4.3 g, 20 mmol) in THF under Ar atmosphere at 0 °C. The mixture was stirred overnight at room temperature and when the reaction was finished (followed by TLC), a saturated solution of NH_4Cl was added at 0 °C. The organic layer was separated and the aqueous was extracted with EtOAc (2×40 ml) and subsequently washed with a 40% solution of KOH (2×25 ml). The combined organic layers were dried over Na_2SO_4 and the solvent eliminated under vacuum to yield 2.44 g of **5a,** which was used in the next step without further purification. A solution of *n*-BuLi (7.6 mmol, 2.5 M in hexane) was added to a solution of thioether **5a** (1.26 g, 6.3 mmol) in THF (10 ml) under Ar atmosphere at −78 °C. After 1 h of stirring, *n*-Bu_3SnCl (12.6 mmol) was added at RT. When the reaction was completed (15 min), the mixture was hydrolyzed with saturated NH_4Cl, extracted (3×10 ml Et_2O), washed (2×10 ml NaCl sat.), dried over $MgSO_4$ and the solvent evaporated. The residue was purified by flash chromatography (*n*-hexane) to afford **6** in 40% overall yield as a colorless oil. ^{1}H-NMR (300 MHz) δ 7.29–7.08 (m, 8H), 6.95 (td, 1H, $J = 7$ and 1.6 Hz), 2.39 (bs, 2H, $J_{Sn-H} = 28.1$ Hz), 1.46–1.18 (m, 12H), 0.87–0.79 (m, 15H). ^{13}C-NMR δ (75 MHz) 146.4 (CH), 136.6 (C), 133.3 (CH), 130.0 (C), 129.1 (2CH), 129.0 (2CH), 128.3 (CH), 128.0 (C), 126.0 (CH), 124.0 (CH), 29.0 ($3CH_2$), ($J_{Sn-C} = 9.9$ Hz), 27.3 ($J_{Sn-C} = 27.5$ Hz) (CH_2), 18.2 ($3CH_3$), 13.7 ($3CH_2$), 10.7 ($3CH_2$).

4.2.2. *Tributyl[2-(p-tolylsulfonyl)benzyl]stannane (**8**)*

Compound **8** was obtained following the route outlined in Scheme 2 by stannylation of sulfone **7,** which in turn was obtained from **5b**. Thioether **5b** was prepared following the procedure described above for **5a** using *p*-tolyl disulfide instead of diphenyl disulfide and used without prior purification. A solution of *m*-CPBA in CH_2Cl_2 (50 ml) prepared from 4.0 g of commercial *m*-CPBA (70%) previously dried over $MgSO_4$ was added to a solution of **5b** (1.7 g, 7.8 mmol) in CH_2Cl_2 (10 ml) at 0 °C. The reaction was stirred at this temperature for 2 h and quenched with $NaHSO_3$. The organic layer was separated, washed with saturated $NaHCO_3$ and dried over Na_2SO_4. The solvent was removed under vacuum and purified by flash chromatography (hexane/EtOAc = 15:1) to yield **7** in 51% overall yield as a colorless oil. A solution of sulfone **7** (2.8 mmol) in THF (2 ml) was added to a solution of LDA (3.4 mmol) freshly prepared in THF (5 ml) at −78 °C. After stirring for 1 h, *n*-Bu_3SnCl (5.6 mmol) was added at the same temperature. When the reaction was completed (15 min), the mixture was hydrolyzed with saturated NH_4Cl, extracted (3×10 ml Et_2O), washed (2×10 ml NaCl sat.), dried ($MgSO_4$) and the solvent evaporated. The residue was purified by flash chromatography (*n*−hexane) to afford **8** in 50% yield as a colorless oil.^{1}H-NMR (300 MHz) δ 8.06 (dd, 1H, $J = 8$ and 1.2 Hz), 7.71 (d, 2H, $J = 8.3$ Hz), 7.34 (td, 1H, $J = 7.6$ and 1.4 Hz), 7.27 (d, 2H, $J = 7.8$ Hz), 7.13 (td, 1H, $J = 8.2$ and 1.1 Hz), 7.02 (dd, 1H, $J = 7.01$ (dd, 1H, $J = 1.0$ and 7.6 Hz), 2.41 (bs, 2H, $J_{Sn-H} = 28.0$ Hz), 2.40 (s, 3H), 1.44–1.19 (m, 12H), 0.88–0.82 (m, 15). ^{13}C-NMR δ (75 MHz) 145.9 (C), 143.5 (C), 139.0 (C), 134.8 (C), 133.2 (CH), 130.1 (CH), 129.6 (CH), 129.5 (2CH), 127.4 (2CH), 123.01 (CH), 28.9 ($3CH_2$), 27.3 (CH_2), 21.5 (CH_3), 19.0 ($3CH_3$), 13.7 ($3CH_2$), 10.6 ($3CH_2$).

4.3. *General procedure for the coupling reactions catalyzed Pd (PPh_3)$_4$*

To a sealed tube equipped with a magnetic stirring bar, the corresponding stannanyl derivative (0.18 mmol), catalyst (0.036 mmol for $Pd(PPh_3)_4$) and toluene (1 ml) were sequentially added.

Then, the electrophile (0.36 mmol) was added, and the tube closed and heated at 80 °C. The reaction is followed by TLC (see Scheme 3 for reaction times). When the reaction was finished, the mixture was filtered through a short pad of celite and washed with CH_2Cl_2. The solvent was removed under vacuum and the product was purified by flash chromatography using the eluent indicated in each case.

4.4. *General procedure for the coupling reactions catalyzed by Cu(I)*

To a sealed tube equipped with a magnetic stir, the corresponding stannanyl derivative (0.18 mmol), catalyst (0.015 mmol for CuI) and toluene (1 ml) were sequentially added. Then, the electrophile (0.36 mmol) shown in each case was added, and the tube was closed and heated at 80 °C. The reaction is followed by TLC, and when the reaction was finished, the mixture was filtered through a short pad of celite and washed with CH_2Cl_2. The solvent was removed under vacuum and the product was purified by flash chromatography using the eluent indicated in each case.

4.4.1. *2-[(But-3-enyl)phenyl](p-tolyl)sulfoxide (**2**)*

Eluent: hexane/EtOAc (10:1); yield: 75%; ^{1}H-NMR (300 MHz): δ 7.94 (d, $J = 9.3$ Hz, 1H), 7.46 (d, $J = 8.3$ Hz, 2H), 7.42–7.35 (m, 2H), 7.24–7.16 (m, 3H), 5.86–5.70 (m, 1H), 5.02–4.92 (m, 2H), 2.93–2.80 (m, 1H), 2.77–2.64 (m, 1H), 2.34 (s, 3H), 2.32–2.12 (m, 2H). ^{13}C-NMR (75 MHz): 142.9, 141.8, 141.6, 139.6, 136.9, 130.9, 129.9, 129.6, 127.3, 125.9, 124.8, 115.5, 34.5, 31.1, 21.3. EM (FAB) m/z: 271 ($M + 1$, 100), 253 (17), 154 (40), 137 (279), 136 (29), 107 (12). IR (NaCl): 2924, 1640, 1595, 1493, 1471 cm^{-1}. EMAR [$M + 1$]: calculated $C_{17}H_{19}OS$: 271.1156. Found: 271.1145. Anal. calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71; S, 11.86. Found: C, 74.98; H, 6.76; S, 11.69.

4.4.2. *[2-(3-Phenylprop-2-ynyl)phenyl](p-tolyl)sulfoxide (**10**)*

Eluent: hexane/EtOAc = 7:1; yield: 71%; ^{1}H-NMR (300 MHz): δ 7.60–7.10 (m, 13H), 3.89 (AB system, $J = 13.5$ Hz, 2H), 2.35 (s, 3H).

Acknowledgements

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Notes

1. The reaction with other stannyl derivatives did not afford the cross-coupled product.
2. The more reactive trimethyl tin derivatives gave lower yields.

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