Pergamon

Tetrahedron Letters, Vol. 38, No. 6, pp. 1005-1008, 1997

0040-4039/97 \$17.00 + 0.00

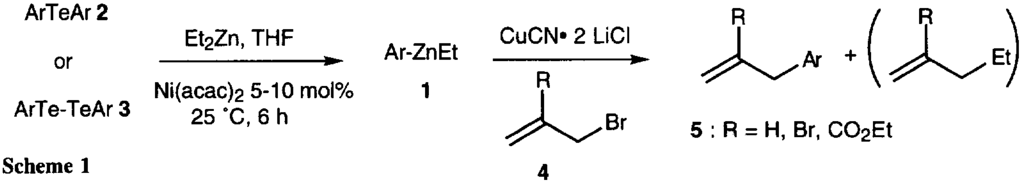
PII: S0040-4039(96)02482-3

Nickel Catalyzed Tellurium-Zinc Exchange Reactions. A New Preparation of Arylzinc Reagents

Thomas Stüdemann,[a] Vijay Gupta,[b] Lars Engman[b,*] and Paul Knochel[a,*]
[a]Fachbereich Chemie der Philipps-Universität Marburg, 35032 Marburg, Germany
[b]Uppsala University, Institute of Chemistry, Department of Organic Chemistry,
Box-531, 75121 Uppsala, Sweden

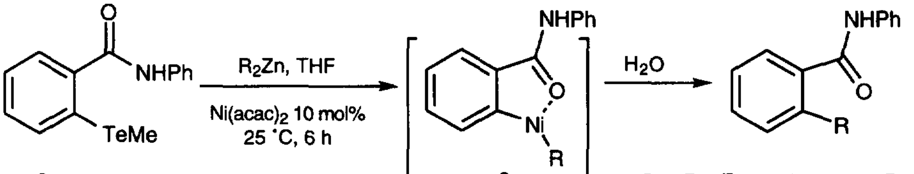
Summary: Diaryltellurides 2 and diarylditellurides 3 undergo a smooth tellurium-zinc exchange reaction in the presence of catalytic amounts of Ni(acac)$_2$ (5-10 mmol %) leading to arylzinc derivatives 1. The reaction can be extended to the preparation of alkylzinc compounds and allows a stereoselective cyclization to a 2,4-disubstituted tetrahydrofuran by a radical ring closure of an unsaturated telluride.

Organozincs (RZnX or R$_2$Zn) are useful organometallic intermediates, since they are compatible with a great variety of functional groups and react in the presence of the appropriate transition metal catalyst with a broad range of organic electrophiles.[1] Diorganozincs are especially useful reagents due to their higher reactivity and numerous applications in asymmetric synthesis.[2] Whereas several methods are available for preparing dialkylzincs[3] and dialkenylzincs,[4] no general method is available for preparing diarylzincs. Herein, we report a method allowing the preparation of mixed arylethylzincs **1** from diaryltellurides **2** or diarylditellurides **3** using a nickel[5,6] catalyzed tellurium-zinc exchange[7] mediated by Et$_2$Zn (Scheme 1). Diorganotellurides and diorganoditellurides are readily available and usually more stable than the corresponding aryl or heteroaryl iodides.



Scheme 1

After transmetalation with CuCN·2LiCl,[8] the arylcopper intermediates were allylated with an allylic bromide **4** furnishing the expected products **5** in good to excellent yields (Table 1). Organotellurium compounds are readily available from simple organic precursors[9] and they have recently found increasing use in organic synthesis.[10] Several recent applications rely on tellurium-metal (Li, Cu, Al) exchange reactions.[11] However, the treatment of a diaryltelluride **2** with Et$_2$Zn does not lead to any reaction, whereas a very slow exchange reaction is observed with a diarylditelluride **3**. In the presence of catalytic amounts of Ni(acac)$_2$ (5-10 mol %), we have now observed a fast exchange reaction which is complete within 6-8 h at rt and transfers *both* aryl groups from tellurium to zinc. The resulting mixed arylethylzinc **1** can be readily trapped by an electrophile (Table 1). In this reaction, diarylditellurides (Ar$_2$Te$_2$ (**3**)) give cleaner reactions and higher yields than diaryltellurides (Ar$_2$Te (**2**)); see entry 1 of Table 1. This is synthetically interesting since diarylditellurides are often precursors of diaryltellurides.[9] Various substituents can be attached to the aromatics ring (bromide or dimethylamino group entries 6-8) and heteroaryltellurium derivatives give excellent results (entries 9-10). Remarkably, the cross-coupling reaction between aryltellurides and Et$_2$Zn leading to ethylated aromatics is not observed in most cases. This coupling reaction is well known between aryl iodides and organozinc reagents in the presence of nickel or palladium catalysts.[12] In the case of *bis*(*p*-bromophenyl)telluride, we have observed the formation of 4-bromo-1-ethylbenzene as side-product (15 % yield; see entry 7 of Table 1). By using the corresponding *diarylditelluride*, this side-reaction was not observed at all. This reduced tendency to undergo cross-coupling reaction may be explained by the presence of the excess of telluride anions which complex the nickel center making it prone to undergo oxidative addition but hampering the reductive elimination step. If an electron withdrawing group like an ester coordinates to the nickel center,[13] then the reductive coupling can become the major reaction pathway. Thus, the reaction of the arylmethyltelluride **6** with Et_2Zn produces only the ethylated cross-coupling product **7a** (84 % yield) via intermediate nickel(II) complex **8**. With dipentylzinc both tellurium-zinc exchange (leading to **7c** in 23 % yield) and cross-coupling (affording **7b** in 54 % yield) are observed (Scheme 2).



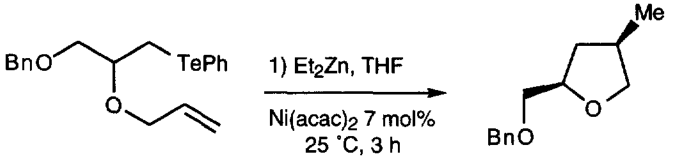
6 **8**

7a : R = Et; 84 % + **7c** : R = H; 0%

7b : R = Pent; 54 % + **7c** : R = H; 23%.

Scheme 2

This nickel-catalyzed tellurium-zinc exchange reaction can be extended to the preparation of alkylzinc derivatives. Thus, the treatment of PhTeOct with excess Et_2Zn furnishes both an octylzinc and a phenylzinc derivative in equal amounts as shown by quenching experiments with electrophiles. Oct_2Te also undergoes exchange but the reaction is significantly slower (55 h at rt compared to 6 h for Ph_2Te or OctTePh). After a copper catalyzed allylation with ethyl (α-bromomethyl)acrylate, the expected product, ethyl 2-nonylacrylate is obtained in 55 % yield. In contrast, Oct_2Te_2 undergoes the tellurium-zinc exchange reaction more rapidly. A complete conversion is obtained after 18 h at rt. Allylation leads to ethyl 2-nonylacrylate in 64 % yield. The nickel catalyzed exchange process can be accompanied by cyclization. Thus, the reaction of tellurium derivative **9** with Et_2Zn furnishes the cyclized product **10** in 56 % yield as a 95:5 mixture of *cis* and *trans* diastereomers (rt, 3 h; Scheme 3). Since trapping experiments with D_2O did not lead to any deuterium incorporation (indicating the absence of an organometallic intermediate), the reaction probably proceeds via radical intermediate. Interestingly, group transfer cyclization of a similar compound was recently found to afford a configurationally inverted tetrahydrofuran derivative (*cis*:*trans* = 1:10).[14]



9

10 cis : trans = 95 : 5; 56 %

Scheme 3

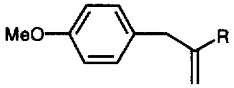
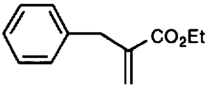
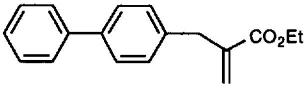
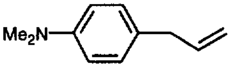
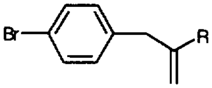
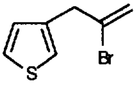
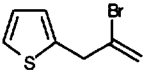
In summary, we have shown that nickel catalysis allows to convert diaryltellurides **2** and diarylditellurides **3** to arylzinc derivatives. This methodology is especially useful, when the corresponding organic iodides, the usual precursors for the preparation of zinc organometallics are difficult to prepare or not available. Further extensions of this reaction are currently underway in our laboratories.[15-17]

Acknowledgment: This work was supported by the Fonds der Chemischen Industrie, the Swedish Natural Science Research Council and the Deutsche Forschungsgemeinschaft (SFB 260). We thank the BASF AG, Witco GmbH, Schering AG, Bayer AG, Sipsy SA, Chemetall GmbH and Chiroscience for the generous support and the gift of chemicals.

References and Notes

1. (a) Knochel, P.; Singer, R. *Chem. Rev.* **1993**, *93*, 2117. (b) Knochel, P. *Synlett* **1995**, 393.
2. (a) Ostwald, R.; Chavant, P.-Y.; Stadtmüller, H.; Knochel, P. *J. Org. Chem.* **1994**, *59*, 4143. (b) Eisenberg, C.; Knochel, P. *J. Org. Chem.* **1994**, *59*, 3760. (c) Vettel, S.; Knochel, P. *Tetrahedron Lett.*

Table 1. Allylated products of type **5** obtained from Ar_2Te **2** and Ar_2Te_2 **3** by a Te-Zn exchange reaction with Et_2Zn followed by a reaction with an allylic bromide **4** in the presence of CuCN•2LiCl.

entry	Ar	allylic bromide **4** (R)	product of type **5**	yield (%)[a]
1	*p*-MeO-C_6H_4	CO_2Et	 **5a** : R = CO_2Et	66 (86)
2	*p*-MeO-C_6H_4	H	**5b** : R = H	63
3	*p*-MeO-C_6H_4	Br	**5c** : R = Br	70
4	C_6H_5	CO_2Et	 **5d**	(92)
5	*p*-C_6H_5-C_6H_4	CO_2Et	 **5e**	(78)
6	*p*-Me_2N-C_6H_4	H	 **5f**	60
7	*p*-Br-C_6H_4	H	 **5g** : R = H	72[b]
8	*p*-Br-C_6H_4	Br	**5h** : R = Br	(88)
9	3-thienyl	Br	 **5i**	(72)
10	2-thienyl	Br	 **5j**	(77)

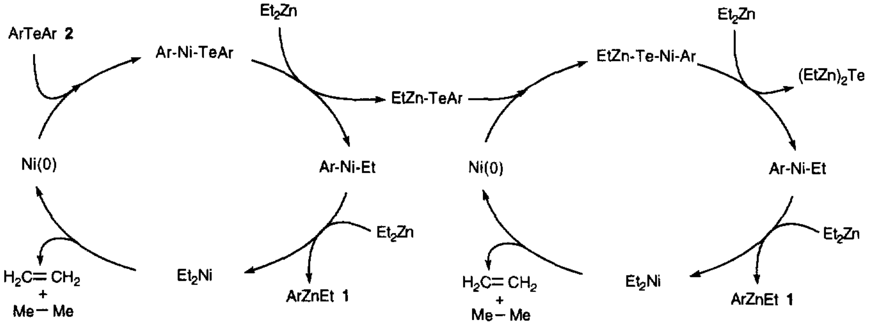
[a] Isolated yields of analytically pure products. The yields indicated in parenthesis refer to reactions performed with the diarylditellurides **3**, whereas the yields indicated without parenthesis were obtained from the diaryltellurides **2**. [b] Besides **5f**, the cross-coupling product 4-bromo-1-ethylbenzene was isolated in 15 % yield.

1994, *35*, 5849. (d) Knochel, P.; Vettel, S.; Eisenberg, C. *Applied. Organomet. Chem.* **1995**, *9*, 175.

3. (a) Rozema, M. J.; AchyuthaRao, S.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 1956. (b) Langer, F.; Devasagayaraj, A.; Chavant, P.-Y.; Knochel, P. *Synlett* **1994**, 410.
4. (a) Oppolzer, W.; Radinov, R. N. *Tetrahedron Lett.* **1991**, *32*, 5777. (b) Oppolzer, W.; Radinov, R. N. *Helv. Chim. Acta* **1992**, *75*, 170. (c) Oppolzer, W.; Radinov, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1593.
5. (a) Stadtmüller, H.; Lentz, R.; Dörner, W.; Stüdemann, T.; Tucker, C. E.; Knochel, P. *J. Am. Chem Soc.* **1993**, *115*, 7027. (b) Stadtmüller, H.; Tucker, C. E.; Vaupel, A.; Knochel, P. *Tetrahedron Lett.* **1993**, *34*, 7911. (c) Klement, I.; Chau, K.; Cahiez, G.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 1177. (d) Vaupel, A.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 8349. (e) Vaupel, A.; Knochel, P. *Tetrahedron Lett.* **1995**, *36*, 231. (f) Stadtmüller, H.; Knochel, P. *Synlett* **1995**, 463. (g) Stadtmüller, H.; Vaupel, A.; Tucker, C. E.; Stüdemann, T.; Knochel, P. *Chem. Eur. J.* **1996**, *2*, 108. (h) Riguet, E.; Klement, I.; Reddy, K. C.; Cahiez, G.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 5865.
6. For transition metal promoted carbodetelluration reactions of organotellurium compounds see: (a) Bergman, J. *Tetrahedron* **1972**, *28*, 3323. (b) Bergman, J.; Engman, L. *J. Organomet. Chem.* **1979**, *175*, 233. (c) Bergman, J.; Engman, L. *Tetrahedron* **1980**, *36*, 1275. (d) Uemura, S.; Fukuzawa, S.-I.;

Patil, S. R. *J. Organomet. Chem.* **1983**, *243*, 9. (e) Wenkert, E.; Leftin, M. H.; Michelotti, E. L. *J. Chem. Soc., Chem. Commun.* **1984**, 617. (f) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* **1987**, *52*, 4859. (g) Barton, D. H. R.; Ozbalik, N.; Ramesh, M. *Tetrahedron Lett.* **1988**, *29*, 3533. (h) Nishibayashi, Y.; Cho, C. S.; Uemura, S. *J. Organomet. Chem.* **1996**, *507*, 197.

7. For a tellurium-zinc exchange reaction allowing the preparation of alkenylzinc derivatives, see: Terao, J.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1996**, *37*, 4741.
8. Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390.
9. (a) Engman, L. *Acc. Chem. Res.* **1985**, *18*, 274. (b) Engman, L. *Organometallics* **1986**, *5*, 427. (c) Petragnani, N. in *Comprehensive Organometallic Chemistry II*, Eds. A. McKillop, Pergamon, **1995**, *Volume 11*, p. 571-602. (d) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1.
10. (a) Barros, S. M.; Comasseto, J. V.; Berriel, J. *Tetrahedron Lett.* **1989**, *30*, 7353. (b) Hiiro, T.; Atarashi, Y.; Kambe, N.; Fujiwara, S.; Ogawa, A.; Ryn, I.; Sonoda, N. *Organometallics* **1990**, *9*, 1355. (b) Comasseto, J. V.; Berriel, J. N. *Synth. Commun.* **1990**, *20*, 1681. (c) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414. (d) Nakahira, H.; Ryu, I. Han, L. Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1991**, *32*, 229. (e) Kanda, T.; Kato, S.; Sugino, T.; Kambe, N.; Sonoda, N. *J. Organomet. Chem.* **1994**, *473*, 71. (f) Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1994**, *35*, 4063. (g) Strohmann, C. *Angew. Chem.* **1996**, *108*, 600. (h) Terao, J.; Kambe, N.; Sonoda, N. *Synlett* **1996**, 779. (i) Tucci, F. C.; Chieffi, A.; Comasseto, J. V.; Marino, J. P. *J. Org. Chem.* **1996**, *61*, 4975.
11. Te-Li exchange: (a) Hiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem.* **1987**, *99*, 1221. (b) Engman, L.; Stern, D. *Organometallics* **1993**, *12*, 1445. (c) Kanda, T.; Kato, S.; Sugino, T.; Kambe, N.; Sonoda, N. *J. Organomet. Chem.* **1994**, *473*, 71. (d) Strohmann, C. *Angew. Chem.* **1996**, *108*, 600. Te-Cu exchange: (e) Tucci, F. C.; Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 5721. (f) Ogawa, A.; Tsuboi, Y.; Obayashi, R.; Yokoyama, K.; Ryu, I.; Sonoda, N. *J. Org.Chem.* **1994**, *59*, 1600. (g) Chieffi, A.; Comasseto, J. V. *Tetrahedron Lett.* **1994**, *35*, 4063. (h) Chieffi, A.; Comasseto, J. V. *Synlett* **1995**, 671. (i) Tucci, F. C.; Chieffi, A.; Comasseto, Y. V.; Marino, J. P. *J. Org. Chem.* **1996**, *61*, 4975. Te-Al exchange: (j) Terao, J.; Kambe, N.; Sonoda, N. *Synlett* **1996**, 779.
12. (a) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (b) Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc.; Chem. Commun.* **1972**, 144. (c) Tamo, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.
13. Devasagayaraj, A.; Stüdemann, T.; Knochel, P. *Angew. Chem.* **1995**, *107*. 2952.
14. Engman, L.; Gupta, V. *J. Chem. Soc. Chem. Commun.* **1995**, 2515.
15. **Typical procedure.** Preparation of 1-bromo-4-(2-bromo-2-propenyl)benzene (**5g**). A three-necked 50mL-flask equipped with an argon inlet, a rubber septum and an internal thermometer was charged with *bis*(*p*-bromophenyl)ditelluride[16] (1.7 g, 3.0 mmol, 1 equiv) and Ni(acac)$_2$ (77 mg, 0.3 mmol, 10 mol %). The reaction mixture was cooled to -40 °C and THF (6 mL) was added. It was further cooled to -78 °C and Et$_2$Zn (1.5 mL, 15 mmol, 5 equiv) was slowly added via syringe. The reaction was allowed to warm to rt and was stirred for 6 h. Meanwhile a mixture of copper cyanide (2.68 g, 23 mmol) and lithium chloride (2.54 g, 60 mmol) was dried under vacuum (130 °C, 2 h) and dissolved in THF (10 mL). This solution was added to this reaction mixture at -60 °C, followed by 2,3-dibromopropene (6.0 g, 30 mmol, 10 equiv). The reaction mixture was warmed up to rt and worked up as usual. The crude oil obtained after evaporation of the solvents was purified by flash chromatography (hexanes) affording **5g** (1.45 g, 5.2 mmol, 88 % yield) as a colorless oil.
16. Engman, L.; Persson, J. *J. Organomet. Chem.* **1990**, *388*, 71.
17. Tentative reaction mechanism.



(*Received in Germany* 31 *October* 1996; *revised* 28 *November* 1996; *accepted* 13 *December* 1996)