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Dilithium aryl cyanocuprates from butyl aryl tellurides

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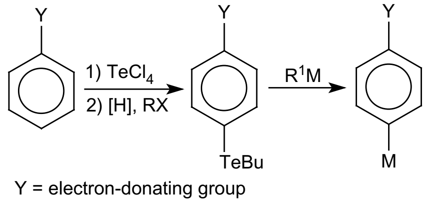
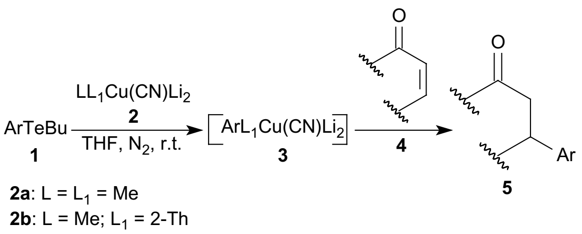
Abstract—Butyl aryl tellurides reacted with dilithium dimethyl cyanocuprate and with dilithium methyl(2-thienyl)cyanocuprate to give the corresponding dilithium aryl cyanocuprates, which were captured with enones leading to 4-aryl ketones in good yields.

The preparation of aryl organometallics continues to attract the attention of the synthetic organic chemists.[1,2] The direct deprotonation is a well established method, specially for the preparation of organometallics with a *ortho*-stabilizing group, through the DOM methodology.[1,3] The preparation of aryl organometallics with other substitution patterns in the aromatic core (*meta* and *para*), is still made by a metal (specially lithium) halogen exchange.[1] In the course of the last decade we[4] and others[5] have shown that the sp_2-Te bond, mainly in vinylic tellurides, are prone to tellurium–metal exchange, giving the organometallic species in a short reaction time and in high yield. Similar reactions involving aromatic tellurides were much less studied. Diphenyl telluride was transformed into phenyllithium by reaction with *n*-butyllithium,[5b] telluroferrocenes were transformed into lithioferrocenes in a similar way,[6] butyl 2-pyridyl telluride was transmetallated with zincates to give butyl 2-pyridylzincates,[7] diaryltellurides and diarylditellurides were transmetallated with diethylzinc leading to ethylarylzinc, which on reaction with copper cyanide gave arylcopper intermediates.[8] On the other hand, the direct telluration of aromatic activated hydrocarbons is a long known reaction. In most cases, the *para*-substituted isomer is the only product formed.[9] The application of the tellurium–metal exchange methodology to the aromatic tellurides prepared in this way[10] would be an advantageous alternative to access *para*-substituted organometallics (Scheme 1). In order to test the viability to prepare directly aryl cyanocuprates from aryl tellurides[8] we reacted some butyl aryl tellurides with easily prepared higher order dilithium cyanocuprates. Initially we treated butyl phenyl telluride (**1a**) with dilithium dimethyl cyanocuprate (**2a**) (Scheme 2).



Scheme 1.

Telluride **1a** was added to a solution of **2a** in THF at room temperature and the reaction was monitored by TLC. After 5 min telluride **1a** was completely consumed. Then cyclohexenone (**4a**) was added and after 40 min the reaction was complete, leading to the 1,4-addition product **5a** in 84% isolated yield. The reaction with butyl(*p*-phenoxyphenyl)telluride (**1b**) also occurred in 5 min at room temperature. Capture of **3b** with cyclohexenone gave **5b** in 77% yield. Similar results were



Scheme 2.

Keywords: Dilithium arylcyanocuprates; Butylaryltellurides.

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obtained when butyl(*p*-methoxyphenyl)telluride (**1c**) was used to generate the cyanocuprate (Table 1, entry 3). In this case, the tellurium–copper exchange reaction was slower, requiring 10 min to consume **1c** completely. The reaction worked satisfactorily also with methyl vinyl ketone (Table 1, entry 4).[11] The dilithium *p*-phenoxyphenyl cyanocuprate showed to be unstable. By keeping it at room temperature for 40 min and then adding cyclohexenone, only a mixture of diphenyl ether, *p*-methylphenyl ether and bis-(*p*-phenoxy)biphenyl was isolated. In this way, it is recommended to add the enone immediately after the consumption of the starting telluride **1b**.

Preliminary experiments using hindered enones with dilithium dimethyl cyanocuprate showed that, besides the addition of the aryl cyanocuprate to the enone, a methyl transfer also occurred. In view of these results we performed the reaction with *R*-(+)-pulegone (**4c**), using the cuprate derived from butyl(*p*-methoxyphenyl)telluride (**1c**) and dilithium methyl(2-thienyl)cyanocuprate (**2b**) (Table 1, entry 5). Addition of the enone **4c** (1 mmol) to the dilithium aryl cyanocuprate **3c** (1 mmol), followed by $BF_3{\cdot}Et_2O$ (1 mmol) at −78 °C and then stirring for 40 min at the same temperature, gave the 1,4-addition product in 82% yield as a 2:1 diastereomeric mixture (Table 1, entry 5, compounds **5e** and **5f**). The same procedure was used in the reaction with mesityl oxide leading to the 1,4-addition product **5g** in 84% yield (Table 1, entry 6).

In conclusion, the tellurium–copper exchange is a straight forward way to prepare dilithium arylcyanocuprates, constituting an advantageous method to access *para*-substituted organometallics.

Acknowledgements

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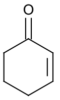
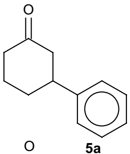
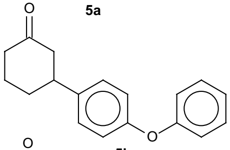
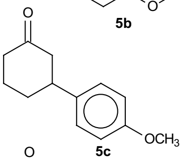
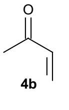
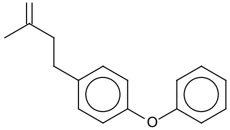
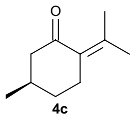
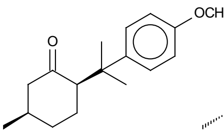
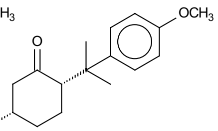
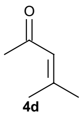
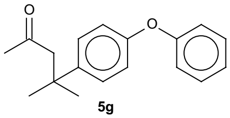
Table 1. Transmetallation/1,4 addition

Entry	Ar	L	L_1	Enone	Product	Yield (%)[d,e]
1	Ph, **1a**[a]	Me	Me	 **4a**	 **5a**	84
2	*p*-$C_6H_5OC_6H_4$, **1b**[b]	Me	Me	**4a**	 **5b**	77
3	*p*-$CH_3OC_6H_4$, **1c**[c]	Me	Me	**4a**	 **5c**	86
4	**1b**	Me	Me	 **4b**	 **5d**	74
5	**1c**	Me	2-Th	 **4c**	 **5e**  **5f**	82[f]
6	**1b**	Me	2-Th	 **4d**	 **5g**	84

[a] Transmetallation time: 5 min.

[b] Transmetallation time: 5 min.

[c] Transmetallation time: 10 min.

[d] Isolated yield.

[e] All products presented analytical data in accordance with the proposed structures.

[f] The diastereomeric ratio was determined by ^1H NMR. Compound **5e** presented coupling constants consistent with a *cis* arrangement between the two substituents, being the minor constituent of the mixture and the isomer **5f** presented coupling constants compatible with a *trans* arrangement constituting the major constituent of the mixture.

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10. Organotellurium trihalides are transformed into arylalkyl tellurides by reduction with sodium borohydride followed by alkylation: Chieffi, A.; Menezes, P. H.; Comasseto, J. V. *Organometallics* **1997**, *16*, 809.
11. Typical procedure for the transmetallation/1,4-addition reaction: To a two necked round bottomed flask under nitrogen was added CuCN (0.089 g, 1 mmol) in THF (5 mL). To the suspension cooled to 78 °C was added MeLi (2 mL, from a 1 M solution in THF/cumene, 2 mmol). The mixture was warmed to room temperature and then butyl(*p*-methoxyphenyl)telluride (**1c**, 0.29 g, 1 mmol) was added, monitoring by TLC. After 10 min **1c** was completely consumed. The reaction mixture was then cooled again to −78 °C and cyclohexenone (**4a**, 0.10 g, 1 mmol) was added. After 40 min stirring the mixture was diluted with ethyl acetate (15 mL) and washed with a mixture of ammonium chloride and ammonium hydroxide (3:1) (4 × 20 mL). The organic phase was dried with magnesium sulfate and the solvent was evaporated. The residue was purified by column chromatography in silica gel eluting with hexane/ethyl acetate (9:1). 3-(4-Methoxyphenyl)-cyclohexanone (CAS number 107203-08-7); yield: 0,17 g (86%). ^{1}H NMR ($CDCl_3$, 300 MHz) (ppm): 7.2–7.1 (m, 2H); 6.9–7.1 (m, 2H); 6.9–6.8 (m, 2H); 3.79 (s, 3H); 3.0–2.9 (m, 1H); 2.6–2.3 (m, 4H); 2.2–2.03 (m, 2H); 1.9–1.7 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 210.9; 158.2; 136.5; 127.4; 114.0; 55.2; 49.1; 43.9; 41.1; 32.9; 25.4. LRMS *m/e* (rel int.): 204 (47) (M^+); 161 (20); 147 (100); 134 (26); 91 (26); 42 (37). IR (film) (cm^{-1}): 2998, 2936, 2865, 2836, 1712, 1611, 1513, 1464, 1447, 1422, 1303, 1289, 1256, 1225, 1180, 1034, 829, 810, 545, 511.