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Synthesis of *o*-Arylenedizinc Compounds from 1-Iodo-2-trifluoromethylsulfonyloxybenzenes and Zinc Powder and Their Synthetic Application

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Abstract

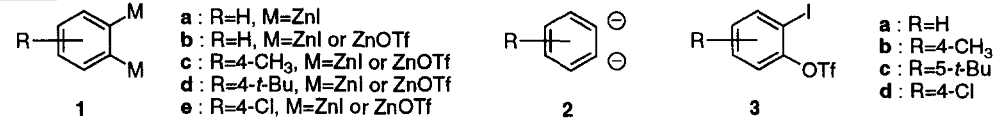
1-Iodo-2-trifluoromethylsulfonyloxybenzenes readily reacted with Zn powder to yield *o*-arylenedizinc compounds, efficient synthetic equivalents of *o*-arylene dianions in Pd(0)-catalyzed cross-coupling reactions, wherein the novel insertion of Zn powder into the C-O bond of aryl triflates took place. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Aryl halides; Palladium and compounds; Phenols; Zinc and compounds

o-Phenylenedimetals **1** (R=H) possess formal negative charges on the adjacent carbons of the benzene ring, posing as useful building blocks of the *o*-phenylene segment **2** (R=H) when synthesizing 1,2-disubstituted benzenes. However, their synthetic application has been scarcely evaluated, presumably due to the lack of reactive, readily available, and/or easily handling ones [1,2]. In the course of our study on the synthesis and synthetic application of arylzinc compounds [3,4], we had found that the *o*-phenylenedizinc compound **1a** is readily produced by the reaction of Zn powder with *o*-diiodobenzene and just fulfills the above requirements as the synthetic reagent affording **2** (R=H) [1]. Thereupon, we were interested in synthesizing similar compounds from the derivatives of *o*-iodophenols in place of *o*-diiodobenzene in view of the flexibility in obtaining the starting materials (vide infra). In this paper, we wish to report the first synthesis of *o*-arylenedizinc compounds from 1-iodo-2-trifluoromethylsulfonyloxybenzenes **3** via the novel insertion of Zn powder into the C-O bond.

Initially, the reactivity of Zn powder to a variety of esters like *o*-iodophenyl triflate, methylsulfonate, 4-tolylsulfonate, or acetate was examined in 1,1,3,3-tetramethylurea (TMU) at 90 °C. The oxidative addition of Zn powder into the C-I bond readily took place with every ester, but only with triflate did the reaction also cleanly take place at the C-O bond to give **1b** in

Scheme 1



1

a : R=H, M=ZnI
b : R=H, M=ZnI or ZnOTf
c : R=4-CH_3, M=ZnI or ZnOTf
d : R=4-*t*-Bu, M=ZnI or ZnOTf
e : R=4-Cl, M=ZnI or ZnOTf

2

3

a : R=H
b : R=4-CH_3
c : R=5-*t*-Bu
d : R=4-Cl

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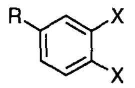
Table 1. Synthesis of **1** from **3**[a]

Entry	Conditions	Product	(Yield / %)
1	1. **3a**, TMU, **4** in TMU, RT, 0.5 h 2. 60 °C, 3 h	**1b**	(84)
2	**3b**, N,N'-Dimethylpropyleneurea (DMPU), 90 °C, 24 h	**1c**	(75)
3	**3c**, TMU, 90 °C, 24 h	**1d**	(52)
4	1. **3d**, TMU, **4** in TMU, RT, 0.5 h 2. 90 °C, 5 h	**1e**	(67)

[a] Molar ratio: **3** / Zn / Me_3SiCl / **4** = 1 / 4 / 0.04 / 0.05 (if used). One ml of solvent was used for 0.8 mmole of aryl triflate.

Scheme 2 Cross-Coupling Products of **1** with X^+



5 : R, X ; Yield / %
a : H, C_6H_5 ; 92
b : H, 4-$C_2H_5O_2CC_6H_4$; 93
c : H, C_6H_5CO ; 72
d : H, 4-NCC_6H_4CO ; 89
e : CH_3, 4-$C_2H_5O_2CC_6H_4$; 71
f : CH_3, 4-NCC_6H_4CO ; 76
g : Cl, 4-ClC_6H_4CO ; 75

Molar ratio: **1** / ArI or ArCOCl / $Pd(PPh_3)_4$ = 1 / 2.2 / 0.04, 40 °C, 6 h.

a yield of 58% after stirring for 6h.[1] Here, it is noteworthy that 1) the unprecedented reaction of Zn powder with aryl triflates [5,6] is possible only if an iodine is situated at the *o*-position; neither the C-O bond in *o*-phenylene ditriflate, *o*-cyanophenyl triflate, phenyl triflate, nor *p*-iodophenyl triflate reacted with Zn powder under the examined conditions, although the last triflate afforded an arylzinc compound (*p*-trifluoromethylsulfonyloxyphenylzinc iodide) in a yield of 83% [7]. 2) The addition of a dehydrating agent improved the yield of **1b**, which may be concerned with the reduced reactivity of aryl triflates themselves; in the presence of molecular sieves 4A (120 mg per 1 mmole of aryl triflate), **1b** was obtained in a yield of 77% after 8h stirring at 80 °C. Since organozinc compounds are very sensitive to water, their addition (for example, the addition of a TMU solution of *o*-chlorophenylzinc iodide **4**, prepared separately) also afforded the preferred result as shown in Table 1 (entry 1). This methodology of vicinal dizincation was then applied to substituted ones, resulting in the production of the corresponding *o*-arylenedizinc compounds in good yields (entries 2~4).[1] The TMU or DMPU solution of **1**, thus obtained, was stable at ambient temperature under nitrogen for months and played the role of the stock solution of the synthetic equivalents of *o*-arylene dianions **2** in Pd(0)-catalyzed cross-coupling with aryl iodides or acyl chlorides as electrophiles (scheme 2).[2] Since *o*-arylenedizinc compounds are readily obtained from 1-iodo-2-trifluoromethylsulfonyloxybenzenes, which in turn are available from phenols by conventional *o*-iodination followed by triflation procedures [8,9], a new, general, efficient, and facile synthetic route from phenols to 1,2-disubstituted benzenes has been established.

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[1] Yields of arylzincs were determined by the iodolysis of reaction aliquots followed by GLC analysis of formed aryl iodides.

[2] **5b**: Mp 98-99 °C; IR ($CDCl_3$) 1707 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.37 (t, 6H), 4.35 (q, 4H), 7.1-7.9 (m, 12H). Found; C, 76.66; H, 5.76%. Cacld for $C_{24}H_{22}O_4$; C, 77.0; H, 5.9%. **5d**: Mp 177-178 °C, Lit. [1] 175-177 °C. **5e**: Mp 106-108 °C; IR ($CDCl_3$) 1708 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.37 (t, 3H), 2.44 (s, 3H), 4.35 (q, 4H), 7.1-7.9 (m, 11H). Found; C, 77.32; H, 6.41%. Calcd for $C_{25}H_{24}O_4$; C, 77.3; H, 6.2%. **5f**: Mp 138-139 °C; IR ($CDCl_3$) 1662, 2228 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=2.50 (s, 3H), 7.3-7.9 (m, 11H). Found; C, 78.67; H, 4.28; N, 7.91%. Calcd for $C_{23}H_{14}N_2O_2$; C, 78.8; H, 4.0; N, 8.0%. **5g**: Mp 113-115 °C; IR ($CDCl_3$) 1670 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=7.3-7.7 (m, 11H). Found; C, 61.41; H, 3.02%. Calcd for $C_{20}H_{11}Cl_3O_2$; C, 61.7; H, 2.9%.