July, 1993] © *1993 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***66****, 2121—2123(1993)* 2121

# Desulfonylative Iodination of Naphthalenesulfonyl Chlorides with Zinc Iodide or Potassium Iodide Catalyzed by Dichlorobis(benzonitrile)palladium(II) in the Presence of Lithium Chloride and Titanium(IV) Isopropoxide

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(Received February 12, 1993)

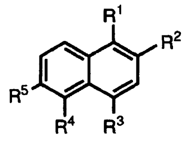
**Synopsis.** Iodination of naphthalenesulfonyl chlorides accompanied by desulfonylation efficiently proceeded on treatment with either zinc iodide or potassium iodide using a catalyst system of $[\mathrm{PdCl_2(PhCN)_2}]/\mathrm{LiCl}/\mathrm{Ti(OPr}^i)_4$.

Iodoarenes are the most reactive aromatic halides and have been widely used for synthesis of various aromatic fine compounds, especially by means of transitionmetal catalysis.[1] Consequently, various methods for the preparation of iodoarenes have been explored and the recent advances have also been reviewed.[2]

We have recently reported palladium-catalyzed desulfonylative carbonylation,[3] vinylation,[4] and homocoupling reactions[5] of arenesulfonyl chlorides to give aromatic esters, arylethenes, and biaryls, respectively, with good catalyst efficiency. Since both 1- and 2-naphthalenesulfonic acids are well-known to be prepared by sulfonation reactions, whilst either halogenation or nitration predominantly gives the 1-substituted compounds,[6] the palladium-catalyzed reactions using arenesulfonyl chlorides seem to be particularly advantageous for the synthesis of the naphthalene derivatives, compared with those using other aryl compounds, e.g. halides[1] and diazonium salts.[7]

During the course of the study, we observed that iodination of arenesulfonyl chlorides efficiently proceeded accompanied by desulfonylation on treatment with zinc iodide or potassium iodide by using a catalyst system of $[\mathrm{PdCl_2(PhCN)_2}]/\mathrm{LiCl}/\mathrm{Ti(OPr}^i)_4$ (Eq. 1).

$$\underset{\mathbf{1}}{\mathrm{ArSO_2Cl}} + \underset{\mathrm{M{=}Zn,\ K}}{\mathrm{MI}_n} \xrightarrow[\text{bis(2-methoxyethyl) ether, under } \mathrm{N_2}]{[\mathrm{PdCl_2(PhCN)_2}]\ /\ \mathrm{LiCl}\ /\ \mathrm{Ti(OPr}^i)_4} \underset{\mathbf{2}}{\mathrm{ArI}} \qquad (1)$$



| | |
|---|---|
| **1a**: $R^1=SO_2Cl$, $R^2=R^3=R^4=R^5=H$ | **2a**: $R^1=I$, $R^2=R^3=R^4=R^5=H$ |
| **1b**: $R^2=SO_2Cl$, $R^1=R^3=R^4=R^5=H$ | **2b**: $R^2=I$, $R^1=R^3=R^4=R^5=H$ |
| **1c**: $R^1=SO_2Cl$, $R^3=Cl$, $R^2=R^4=R^5=H$ | **2c**: $R^1=I$, $R^3=Cl$, $R^2=R^4=R^5=H$ |
| **1d**: $R^2=SO_2Cl$, $R^5=CH_3$, $R^1=R^3=R^4=H$ | **2d**: $R^2=I$, $R^5=CH_3$, $R^1=R^3=R^4=H$ |
| **1e**: $R^1=R^4=SO_2Cl$, $R^2=R^3=R^5=H$ | **2e**: $R^1=R^4=I$, $R^2=R^3=R^5=H$ |
| **1f**: $R^2=R^5=SO_2Cl$, $R^1=R^3=R^4=H$ | **2f**: $R^2=R^5=I$, $R^1=R^3=R^4=H$ |

While it is known that desulfonylation of arenesulfonyl fluorides, chlorides, and bromides with platinum-group metal complexes gives the corresponding aryl halides,[8] such an iodination has not been so far reported.

When a mixture of 1-naphthalenesulfonyl chloride (**1a**) (2 mmol), $[\mathrm{PdCl_2(PhCN)_2}]$ (0.02 mmol), LiCl (0.4 mmol), and $\mathrm{Ti(OPr}^i)_4$ (1 mmol) in bis(2-methoxyethyl) ether (5 cm³) was heated at 150 °C for 1 h, 1-iodonaphthalene (**2a**) was produced in a yield of 86% (by GLC analysis) (Run 1 in Table 1). 2-Iodonaphthalene was not detected in the reaction mixture, while the homocoupling reaction of **1a** with $[\mathrm{PdCl_2(PhCN)_2}]$ in the presence of $\mathrm{Ti(OPr}^i)_4$ gave 1,1′-binaphthyl along with the 1,2′-isomer, as previously reported.[5] No chloronaphthalenes were also formed. In the absence of LiCl and/or $\mathrm{Ti(OPr}^i)_4$, the yield of **2a** was considerably reduced (Runs 4 and 5), suggesting that these additives synergistically promote the iodination. Although the iodide **2a** was formed without the palladium catalyst,

Table 1. Desulfonylative Iodination of Naphthalenesulfonyl Chlorides **1**[a)]

| Run | **1** (mmol) | Iodide (mmol) | Temp °C | Yield of **2**[b)] % |
|---|---|---|---|---|
| 1 | **1a**(2) | $\mathrm{ZnI_2}$(2) | 150 | (86) |
| 2 | **1a**(2) | $\mathrm{ZnI_2}$(1) | 150 | (83) |
| 3 | **1a**(5) | $\mathrm{ZnI_2}$(5) | 162 | 72 |
| 4[c)] | **1a**(2) | $\mathrm{ZnI_2}$(2) | 150 | (54) |
| 5[d)] | **1a**(2) | $\mathrm{ZnI_2}$(2) | 150 | (32) |
| 6[c,d)] | **1a**(2) | $\mathrm{ZnI_2}$(2) | 150 | (26) |
| 7[e)] | **1a**(2) | $\mathrm{ZnI_2}$(2) | 150 | (14) |
| 8 | **1a**(2) | KI(4) | 150 | (63) |
| 9 | **1a**(2) | KI(2) | 162 | (82) |
| 10 | **1b**(1) | $\mathrm{ZnI_2}$(0.5) | 150 | (41) |
| 11 | **1b**(1) | $\mathrm{ZnI_2}$(0.5) | 162 | (54) |
| 12 | **1b**(1) | KI(1) | 150 | (56) |
| 13 | **1b**(1) | KI(1) | 162 | (70) |
| 14 | **1b**(5) | KI(5) | 162 | 57 |
| 15 | **1b**(1) | NaI(1) | 150 | (19) |
| 16 | **1b**(1) | LiI(1) | 150 | (44) |
| 17 | **1c**(3) | $\mathrm{ZnI_2}$(3) | 162 | 53 |
| 18 | **1d**(3) | $\mathrm{ZnI_2}$(3) | 162 | 60 |
| 19 | **1d**(3) | KI(3) | 162 | (45) |
| 20 | **1e**(1) | $\mathrm{ZnI_2}$(2) | 162 | 70 |
| 21 | **1f**(1) | $\mathrm{ZnI_2}$(1) | 162 | 32 |

a) The reaction of **1** was carried out using $[\mathrm{PdCl_2(PhCN)_2}]$ (1 mol%), LiCl (0.2 equiv), $\mathrm{Ti(OPr}^i)_4$ (0.5 equiv), and metal iodide in bis(2-methoxyethyl) ether under nitrogen for 1 h. b) Isolated yields. Values in parentheses were determined by GLC analysis. c) Without $\mathrm{Ti(OPr}^i)_4$. d) Without LiCl. e) Without $[\mathrm{PdCl_2(PhCN)_2}]$.

the yield was very low (Run 7). Potassium iodide could also be used in place of $ZnI_2$; it was less effective at 150 °C, but a satisfactory result was obtained by refluxing the solvent (Run 9).

The results for the reactions of other naphthalenesulfonyl (**1b**—**d**) and naphthalenedisulfonyl chlorides (**1e**, **f**) are also recorded in Table 1. The corresponding monoiodides (**2b**—**d**) and diiodides (**2e**, **f**) were obtained in modest to good yields.

The present reaction may involve oxidative addition of arenesulfonyl chloride to Pd(0) species generated in situ followed by loss of $SO_2$ to afford arylpalladium intermediate, as for the catalytic desulfonylation of arenesulfonyl chlorides to chloroarenes.[8)] A possible role of lithium chloride added is the ligation of the chloride ion to the Pd(0) species to stabilize it.[9)] Such a stabilization of low ligated zerovalent palladium species has also been considered to occur in the oxidative addition of iodobenzene. Although the substrates themselves may provide chloride ion, the observed results do not indicate that they can act as an effective chloride source. On the other hand, one of the possible functions of $Ti(OPr^i)_4$ may be acceleration of the reduction of $[PdCl_2(PhCN)_2]$ to the Pd(0) species.[10)]

An advantageous point of the present method as a route to iodonaphthalenes appears to be that it can be avoided to use highly toxic naphthylamines, as well as the ready availability of the starting materials.

## Experimental

$^1H$ NMR spectra were obtained with a JEOL JNM-GSX-400 spectrometer (400 MHz) for $CDCl_3$ solutions. GC-MS spectra were obtained with a JEOL JMS-DX-303 spectrometer or with a Shimadzu GCMS-QP2000A spectrometer. GLC analysis was carried out on a Shimadzu GC-8APF gas chromatograph equipped with a Silicone OV-17 glass column ($\phi$2.6 mm×1.5 m) or with a CBP-1 capillary column ($\phi$0.5 mm×25 m).

Dichlorobis(benzonitrile)palladium and the sulfonyl chlorides **1c**—**f** were prepared by the methods reported previously.[3,4)] other starting materials were commercially available. Bis(2-methoxyethyl) ether was distilled in the presence of calcium hydride before use.

**General Procedure for Iodination of Naphthalenesulfonyl Chlorides 1.** A mixture of **1** (2 mmol), zinc iodide (2 mmol, 638 mg), dichlorobis(benzonitrile)palladium (0.02 mmol, 7.7 mg), lithium chloride (0.4 mmol, 17.0 mg), and titanium(IV) isopropoxide (1 mmol, 284 mg) in bis(2-methoxyethyl) ether (5 $cm^3$) was stirred at 150 °C under nitrogen (1 atm) for 1 h. The resulting mixture was poured into dilute hydrochloric acid and extracted with diethyl ether. The organic layer was dried over sodium sulfate and evaporated. Iodides **2** were isolated by column chromatography on silica gel using dichloromethane-hexane as eluent.

**1-Iodonaphthalene (2a):** Colorless oil; $^1H$ NMR $\delta$= 7.18 (1H, t, $J$=8.3 Hz), 7.49—7.59 (2H, m), 7.75—7.78 (1H, m), 7.83 (1H, d, $J$=8.3 Hz), and 8.08 (2H, dd, $J$=1.0 and 8.3 Hz); MS $m/z$ 254 ($M^+$).

**2-Iodonaphthalene (2b):** Mp 51.0—52.0 °C (lit,[11)] 53.0—54.0 °C); $^1H$ NMR $\delta$=7.46—7.51 (2H, m), 7.57 (1H, d, $J$=8.8 Hz), 7.70—7.73 (2H, m), 7.77—7.81 (1H, m), and 8.24 (1H, d, $J$=1.0 Hz); MS $m/z$ 254 ($M^+$).

**1-Chloro-4-iodonaphthalene (2c):** Mp 50.0—51.0 °C (lit,[12)] 52.5—53.8 °C); $^1H$ NMR $\delta$=7.30 (1H, d, $J$=7.8 Hz), 7.60—7.66 (2H, m), 7.99 (1H, d, $J$=7.8 Hz), 8.09—8.14 (1H, m), and 8.21—8.26 (1H, m); MS $m/z$ 288, 290 ($M^+$).

**2-Iodo-6-methylnaphthalene (2d):** Mp 147—148 °C (lit,[13)] 146—147 °C); $^1H$ NMR $\delta$=2.49 (3H, s), 7.32 (1H, dd, $J$=1.5 and 8.3 Hz), 7.48 (1H, d, $J$=8.3 Hz), 7.55 (1H, s), 7.61 (1H, d, $J$=8.3 Hz), 7.66 (1H, dd, $J$=1.5 and 8.3 Hz), and 8.17 (1H, s); MS $m/z$ 268 ($M^+$).

**1,5-Diiodonaphthalene (2e):** Mp 151—152 °C (lit,[14)] 147 °C); $^1H$ NMR $\delta$=7.26 (2H, t, $J$=7.8 Hz), 8.13 (2H, d, $J$=7.8 Hz), and 8.14 (2H, d, $J$=7.8 Hz); MS $m/z$ 380 ($M^+$).

**2,6-Diiodonaphthalene (2f):** Mp 199—201 °C (lit,[15)] 203—204 °C); $^1H$ NMR $\delta$=7.45 (2H, d, $J$=8.8 Hz), 7.72 (2H, dd, $J$=1.3, 8.8 Hz), and 8.18 (2H, s); MS $m/z$ 380 ($M^+$).

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 04453100 from the Ministry Education, Science and Culture.

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10) Palladium black was precipitated on treatment of $[PdCl_2(PhCN)_2]$ (0.02 mmol) with $Ti(OPr^i)_4$ (1.0 mmol) in bis(2-methoxyethyl) ether (5 $cm^3$) at 60 °C for 5 min. Without $Ti(OPr^i)_4$, no precipitation occurred at the same temperature, but it was formed by refluxing the solvent for 5 min. These results suggest that both $Ti(OPr^i)_4$ and the solvent can reduce the divalent palladium complex to palladium(0) species, the former being relatively more effective. In the presence of LiCl, the Pd(0) species may be stabilized by LiCl as described and react with **1** without the formation of the metallic palladium.

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