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A convenient synthetic approach to 1,5-diiodonaphthalene derivatives

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Abstract

A convenient and efficient synthetic approach to the synthesis of 1,5-diiodonaphthalene derivatives is reported.

Keywords: naphthalenes; iodination.

Naphthalene-containing conjugated oligomers and polymers are a unique class of electrically active materials.[1–4] In particular, conjugated polymers incorporating the naphthalene units through the 1,5-positions have shown potential as electroluminescence materials.[4] To incorporate naphthalene units into a conjugated polymer backbone, 1,5-difunctionalized naphthalenes must be synthesized. While synthetic approaches to 1,5-dibromonaphthalene derivatives have been reported,[5] we have found that the dibromides are not ideal intermediates for further functional group conversions. For example, arylvinylation and ethynylation of 1,5-dibromo-4,8-dimethoxynaphthalene through the Heck reaction[6] and the Sonogashira reaction,[7] respectively, have not been successful. Thus, more reactive 1,5-diiodonaphthalene derivatives are desirable. However, to the best of our knowledge, there has not been any report on the iodination of naphthalene units at their 1,5-positions. In this communication, we report a convenient and efficient approach for the synthesis of 1,5-diiodonaphthalene derivatives. We also demonstrate that, with the diiodo functional groups, naphthalene rings can be easily further functionalized with divinyl or diethynyl groups, paving the way for the synthesis of a variety of naphthalene containing conjugated oligomers and polymers.

Direct iodination of phenyl rings has been well studied and a number of iodination systems have been reported.[8–14] Our initial attempts were to apply those systems in the direct iodination of 1,5-dimethoxynaphthalene. Unfortunately, none of those common iodination systems gave satisfactory results. The $I_2/HIO_3/H_2SO_4$,[8] $I_2/HgCl_2$,[9] and HgO/CH_2Cl_2 systems[10] gave small

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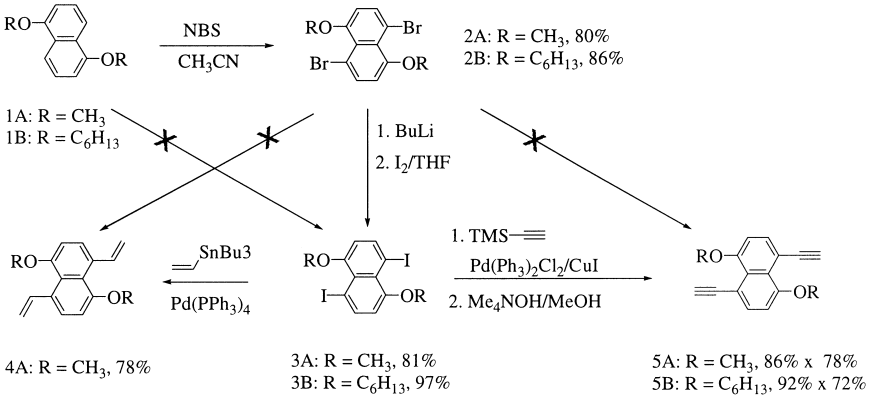
amounts of unknown side products. The $I_2/NaNO_3$/acetic acid system[11] resulted in a mono-substituted product in low yields. Direct iodination using other systems such as I_2/Bu_4N^{+-}-$SO_3OOSO_3^{-+}NBu_4$,[12] ICl,[13] and $(Me_3N^+CH_2Ph)(ICl_2)^-/CaCO_3$[14] also failed. Most reactions resulted in dark mixtures from which no product could be isolated in acceptable yields (< 20%) (Scheme 1).



Scheme 1.

We then turned to indirect iodination methods. It was found that 4,8-diiodo-1,5-dialkoxynaphthalenes, such as compounds **3A** and **3B**, could be prepared in excellent yields by lithiation of their corresponding dibromides, followed by treatment with iodine.[15] The reaction was carried out in THF at –78°C. The diiodides can be easily separated and purified through recrystallization.

The above procedure to 1,5-diiodonaphthalene derivatives is attractive because the dibromide analogs are easily accessible. Unlike iodination, direct bromination of 1,5-dialkoxynaphthalenes at the 4,8-positions was straightforward. Using *N*-bromosuccinimide (NBS) in acetonitrile, a mild and regiospecific bromination reagent first demonstrated by Carréno and co-workers,[5] and a modified procedure, 4,8-dibromo-1,5-dialkoxylnapthalenes, such as compounds **2A** and **2B**, can be synthesized in excellent yields. We have found that, instead of carrying out the bromination reaction at room temperature in an acetonitrile solution,[5] carrying out the reaction at 0°C and adding the solution of NBS in acetonitrile slowly to a suspension of 1,5-dialkoxynaphthalene in acetonitrile significantly reduces side reactions and greatly simplifies the purification process. The pure product can be isolated simply by filtration and washing with acetonitrile and methanol.

The diiodonaphthalene derivatives are important intermediates for further functional group conversions. For example, the two iodo groups can be converted into two vinyl groups (compound **4A**) through the Heck coupling reaction in excellent yields.† The diethylnyl analogs (compounds **5A** and **5B**) can also be synthesized in good yields by the Sonogashira reaction.‡ These

† Compound **4A**: white solid, mp 147–148°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.91 (s, 6H, OCH_3), 5.09 (dd, 2H, J = 11.0 Hz, 2.5 Hz), 5.28 (dd, 2H, J = 17.1 Hz, 2.5 Hz), 6.84 (d, 2H, J = 8.60 Hz), 7.35 (d, 2H, J = 8.60 Hz), 7.73 (dd, 2H, J = 11.0 Hz, 17.1 Hz).

‡ Compound **5A**: light yellow solid, mp > 300°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.29 (s, 2H), 3.96 (s, 6H), 6.83 (d, 2H, J = 8.50 Hz), 7.70 (d, 2H, J = 8.50 Hz). Compound **5B**: 72%, light yellow solid, mp 144°C (decomposed). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.91 (t, 6H, J = 7.30 Hz), 1.34–1.27 (m, 8H), 1.60–1.52 (m, 4H), 2.01–1.89 (m, 4H), 3.21 (S, 2H), 4.12 (t, 4H, J = 7.30 Hz), 6.80 (d, 2H, J = 8.50 Hz), 7.67 (d, 2H, J = 8.50 Hz).

compounds are important monomers for the synthesis of naphthalene-containing conjugated oligomers and polymers.[16]

In summary, we report a convenient and efficient synthetic approach to 1,5-diiodonaphthalene derivatives, which are important intermediates for the synthesis of other 1,5-difunctionalized naphthalenes.

General procedure for the synthesis of 4,8-dibromo-1,5-dialkoxynaphthalene: to a suspension of 1,5-dialkoxynaphthalene in acetonitrile (3 ml/1 mmol) cooled in an ice bath was added dropwise a solution of *N*-bromosuccinimide (2.2 equiv.) in acetonitrile (1.5 ml/1 mmol). The resulting mixture was stirred at room temperature under nitrogen for 2.5 h. The solid was collected by filtration, washed with acetonitrile (50 ml×2) and then with methanol (20 ml) to give the title compounds as white solids.

Compound **2A**: 80%, mp 185–187°C, literature 187–189°C,[17] 191–193°C,[18] 191–192°C.[19] ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.92 (s, 6H), 6.74 (d, 2H, $J=8.50$ Hz), 7.70 (t, 2H, $J=8.50$ Hz).

Compound **2B**: 86%, mp 127–128°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.91 (t, 6H, $J=7.30$ Hz), 1.38–1.33 (m, 8H), 1.59–1.46 (m, 4H), 2.00–1.87 (m, 4H), 4.04 (t, 4H, $J=7.30$ Hz), 6.70 (d, 2H, $J=8.50$ Hz), 7.67 (d, 2H, $J=8.50$ Hz).

General procedure for the synthesis of 4,8-diiodo-1,5-dialkoxynaphthalene: a solution of butyllithium in hexane (2.5 equiv.) was added dropwise to a suspension of 4,8-dibromo-1,5-dimethoxynaphthalene (1 equiv.) in THF (5 ml/1 mmol) at –78°C. The resulting golden–yellowish solution was stirred at –78°C for 30 min. A solution of iodine (5 equiv.) in anhydrous THF (0.4 ml/1 mmol) was then added dropwise to the above solution. The resulting mixture was warmed to room temperature and stirred at room temperature for 2 h before it was poured into a saturated sodium bisulfite solution. The precipitate was collected by filtration, washed with water and then acetone, and recrystallized from hexane–ethyl acetate to give the title compounds as white solids.

Compound **3A**: 81%, melted/turned black at 226°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.90 (s, 6H), 6.58 (*d*, 2H, $J=8.50$ Hz), 8.12 (*t*, 2H, $J=8.50$ Hz).

Compound **3B**: 97%, mp 131–132°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.91 (t, 6H, $J=7.30$ Hz), 1.37–1.34 (m, 8H), 1.58–1.50 (m, 4H), 2.04–1.95 (m, 4H), 4.08 (t, 4H, $J=7.30$ Hz), 6.53 (d, 2H, $J=8.60$ Hz), 8.10 (d, 2H, $J=8.60$ Hz).

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