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A facile synthesis of 2-arylindenes by Pd-catalyzed direct arylation of indene with aryl iodides

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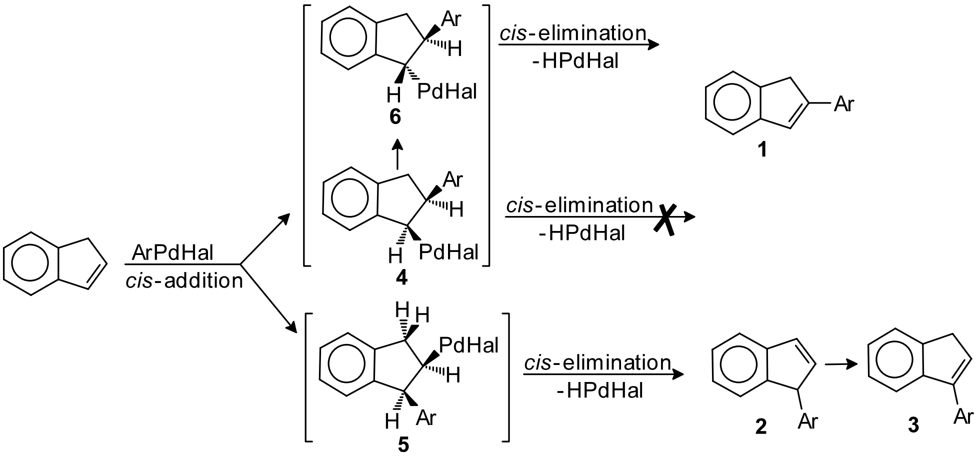
Abstract—A series of 2-arylindenes were prepared by the reaction of aryl iodides with indene in the presence of a catalytic amount of $Pd(OAc)_2$. © 2002 Elsevier Science Ltd. All rights reserved.

Zirconocenes derived from 2-arylindenes **1** demonstrate an excellent catalytic performance in the polymerization of α-olefins.[1,2] It is known that the nature of substituents in the aryl fragment strongly affects the catalytic properties of such zirconocenes.[1] Unfortunately, no general and simple procedures for the synthesis of 2-arylindenes **1** have been developed as yet. These compounds are usually obtained by dehydration of arylindanols which can be synthesized either by the reaction of indan-2-one with arylmagnesium halides,[3] or by the reaction of a dimagnesium derivative of *o*-xylene with ethyl benzoate.[4] Both approaches have some drawbacks such as moderate yields, relatively expensive reagents, the impossibility of introducing substituents incompatible with organomagnesium compounds, etc. In this work, we describe a new synthetic approach to 2-arylindenes. We found that these compounds could be readily obtained by direct arylation of indenes catalyzed by palladium salts.

Previously,[5–7] it has been shown that several 2-arylindenes could be obtained in low to moderate yields by a *stoichiometric* reaction between indene and the corresponding arylpalladium derivative. It would be



Scheme 1.

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expected that the corresponding catalytic process known as the Heck reaction would not proceed in this case. This reaction is known to proceed as a successive *cis*-addition of PhPdHal and *cis*-elimination of HPdHal (see reviews on the Heck reaction,[8] for Density Functional Theory study of the Heck reaction see Ref. 9) (Scheme 1). Since *cis*-elimination of HPdHal from intermediate **4** formed by *cis*-addition of PhPdHal to the multiple bond of indene is impossible, the catalytic cycle cannot proceed. Of course, 1- and 3-arylindenes can also be formed via intermediate **5**, however, this reaction is complicated by steric hindrance encountered upon attack of the aryl group at C-1 of indene. In this case it would be expected that [1,3]-proton migration in the 1-arylindene would result in the formation of the thermally more stable 3-arylindene.

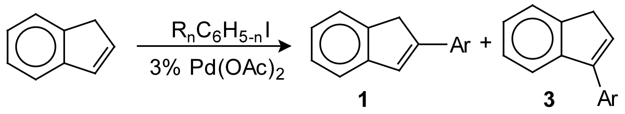
We found that no reaction between indene and iodobenzene proceeded under typical Heck reaction conditions. Assuming that the intermediate **4** may undergo a thermal isomerization to give the *trans*-product **6**, we undertook a study of the reaction between indene and iodobenzene in the presence of palladium acetate with more extensive heating than is usually required for the Heck-reaction. It was found that the reaction in refluxing triethylamine did proceed and that 80% of indene was consumed during 6 h. After refluxing for 10 h, the indene conversion exceeded 90% and a mixture of 2- and 3-phenylindenes in a ~4/1 ratio was formed.

2-Phenylindene **1a** is a crystalline substance and can be isolated by recrystallization in 63% yield. It should be noted that it is impossible to isolate all the 2-phenylindene by recrystallization since this compound forms inseparable mixtures with oily 3-phenylindene **3a**. The reaction accelerates substantially if DMF is used as the solvent (in this case, a stoichiometric amount of triethylamine was added to absorb the liberated HI). At 100°C, conversion of indene is at least 90% after 4 h. Presumably, the acceleration of the process is due to the higher polarity of DMF compared to that of triethylamine. It is important to note that the **1a**/**3a** ratio in this case remains almost the same as for the reaction in triethylamine alone.

We also studied the reactions of several substituted aryl iodides with indene. The results of our experiments are presented in Table 1. It was found that all the reactions proceeded smoothly with the reaction mixtures containing only isomeric 2- and 3-arylindenes as well as residual amounts of unreacted starting materials. The ratios of 2- and 3-arylindene isomers were determined by ^{1}H NMR analysis. The ^{1}H NMR spectra were analyzed taking into account that for 3-arylindenes, **3**, the signals for the protons at C-2 were observed in the region δ 5.5–6.5 with the vicinal coupling constant lying in the range 1.5–3.5 Hz. For 2-arylindenes, **1**, the signals of the vinyl proton at C-3 appeared in the region δ 7.0–8.0 and the corresponding coupling constant with the methylene protons was less than 1.5 Hz. All the 2-arylindenes obtained in this work were solids, their yields were determined after recrystallization.

To sum up, it is more appropriate to use DMF rather than triethylamine as the solvent since (i) the reaction in DMF proceeds at a higher rate than in triethylamine and (ii) sometimes a somewhat higher ratio of 2- and 3-arylindene isomers is observed in DMF. It was found that the nature of the substituent in the aryl iodide appreciably affects not only the rate of the reaction, but also the ratio of 2- and 3-isomers. As a rule, aryl iodides with acceptor substituents react faster than those with donor substituents and give a larger proportion of 2-arylindene.

Table 1. Reaction of indene with substituted aryl iodides in Et_3N (reflux, 10 h) or in DMF (100°C, 4 h)[10]



Run	R_n	Product	Solvent	Conversion (%)[a]	**1**/**3**[b]	Yield of **1** (%)[c]
1	H	**1a**[3a]	NEt_3	>90	80/20	63
2	–	–	DMF	>90	82/18	65
3	3,5-$(CF_3)_2$	**1b**[1b]	NEt_3	41	94/6	32
4	–	–	DMF	49	95/5	37
5	4-COMe	**1c**[3a]	NEt_3	>90	92/8	78
6	4-COOEt	**1d**[c,11]	NEt_3	>90	85/15	59
7	4-Me	**1e**[3a]	NEt_3	61	78/22	41
8	4-Br	**1f**[3a]	NEt_3	48	81/19	35
9	4-OMe	**1g**[3a]	NEt_3	40	76/24	29
10	4-Cl	**1h**[3a]	NEt_3	33	73/27	21
11	4-NHC(O)Me	**1j**[c,11]	NEt_3	30	74/36	13
12	–	–	DMF	41	86/14	34

[a] Determined by ^{1}H NMR.

[b] Isolated yield.

[c] This work, analytical data for **1d** and **1j** are given in Ref. 11.

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10. **Typical procedure for the arylation of indene**. In triethylamine: 20 ml of triethylamine, 2.2 g (20 mmol) of indene, 0.134 g (0.6 mmol) of $Pd(OAc)_2$ and 20 mmol of aryl iodide were stirred under reflux for 10 h after which triethylamine was removed under reduced pressure. The residue was treated with a mixture of dichloromethane (50 ml) and water (50 ml). The organic layer was separated, washed twice with water (100 ml), filtered and dried over Na_2SO_4. Dichloromethane was removed and the residue was recrystallized from 20 ml of ethanol or another appropriate solvent. In DMF: 20 ml of DMF, 3 ml of triethylamine, 2.2 g (20 mmol) of indene, 0.134 g (0.6 mmol) of $Pd(OAc)_2$ and 20 mmol of aryl iodide were stirred under reflux for 4 h. The reaction mixture was poured into a mixture of dichloromethane (50 ml) and water (150 ml). The organic layer was separated, washed twice with water (200 ml), filtered and dried over Na_2SO_4. Dichloromethane was removed and the residue was recrystallized from ethanol (20 ml) or another appropriate solvent.
11. Analytical data for **1d** and **1j**:
    Ethyl 4-(1*H*-2-indenyl)benzoate, **1d**: ^{1}H NMR ($CDCl_3$, 25°C) δ: 8.08 (d, $J=8.0$ Hz, 2H), 7.70 (d, $J=8.0$ Hz, 2H) (AA′BB′); 7.52 (d, $J=7.2$ Hz, 1H), 7.46 (d, $J=7.2$ Hz, 1H), 7.33 (t, $J=7.2$ Hz, 1H), 7.26 (t, $J=7.2$ Hz, 1H) (six-membered ring of indene); 7.37 (br.s, 1H, vinyl proton); 4.42 (q, $J=8.5$ Hz, 2H), 1.45 (t, $J=8.5$ Hz, 3H) (ethyl); 3.81 (br.s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 25°C) δ: 166.2, 145.0, 144.8, 143.2, 140.0, 129.8, 129.0, 128.8, 126.6, 125.3, 125.2, 123.6, 121.3, 60.7, 38.8, 14.2. Anal. calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.63; H, 6.15. *N*1-[4-(1*H*-2-indenyl)phenyl]acetamide, **1j**: ^{1}H NMR (DMSO-d_6, 25°C) δ: 9.95 (br.s., 1H, NH); 7.64 (br.s, 4H) (AA′BB′); 7.46 (d, $J=7.4$ Hz, 1H), 7.38 (d, $J=7.8$ Hz, 1H), 7.24 (dd, $J=7.4$ Hz, 7.8 Hz, 1H), 7.15 (dd, $J=7.4$ Hz, 7.8 Hz, 1H) (six-membered ring of indene); 7.27 (br.s, 1H, vinyl proton); 3.79 (br.s, 2H, CH_2); 2.08 (s, 3H) (acetamide group). ^{13}C NMR (DMSO-d_6, 25°C) δ: 168.1, 146.0, 145.1, 142.6, 138.7, 130.2, 126.3, 125.9, 124.8, 124.2, 123.4, 120.4, 119.0, 38.4, 23.8. Anal. calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.80; H, 6.11; N, 5.55.