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Iridium-Catalyzed Reaction of Aroyl Chlorides with Internal Alkynes to Produce Substituted Naphthalenes and Anthracenes

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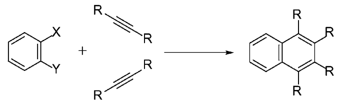
Selective synthesis of substituted polycyclic aromatic hydrocarbons has become increasingly important, because they have been finding increasing application as π-conjugated functional materials.[1,2] Among modern potential strategies to prepare condensed aromatics is the metal-promoted or -catalyzed homologation, such as benzene to naphthalene and the latter to anthracene, of a given aromatic substrate with two alkyne molecules (Scheme 1).[3−6] Using dialkylacetylenes may produce the corresponding homologated aromatics having substantial solubilities. Recently, Takahashi et al. have described an effective copper-promoted method for the coupling of 1,2-dihalobenzenes and 1,2,4,5-tetrahalobenzenes with zirconacyclopentadienes prepared using dialkylacetylenes to produce polyalkylated naphthalenes and anthracenes.[3a,b] The palladium-catalyzed 1:2 coupling of aryl halides with alkynes is a method for Scheme 1 using more readily available monofunctionalized aromatic substrates. In this case, acetylenedicarboxylates[6a] and diphenylacetylene[6b] can be employed to afford the corresponding naphthalenes with moderate yields, but use of dialkylacetylenes gives nonfused 1:3 coupling products as the major ones.[6b]

Meanwhile, we previously demonstrated that benzoyl chlorides react with dialkylacetylenes in the presence of a rhodium catalyst to give 2,3-disubstituted indenones as the predominant products along with small amounts of 1,2,3,4-tetrasubstituted naphthalenes (Scheme 2).[7] We now report our new findings that the naphthalenes can be produced exclusively by the reaction using iridium in place of rhodium. This is the first efficient example of transition-metal-catalyzed aromatic homologation using aliphatic alkynes and appears to provide a simple, straightforward method for preparing polyalkyl-substituted condensed aromatics.

When benzoyl chloride (**1a**) (1 mmol) was treated with 4-octyne (**2a**) (3 mmol) in the presence of $[IrCl(cod)]_2$ (0.01 mmol) and PPh_3 (0.04 mmol) in refluxing *o*-xylene for 18 h, 1,2,3,4-tetrapropylnaphthalene (**3a**) was formed in 71% yield (entry 1 in Table 1). In contrast to the indenone synthesis using rhodium,[7] addition of Na_2CO_3 as base retarded the reaction (entry 2).[8] Use of a bulky ligand, $P(t\text{-Bu})_3$, was found to afford an almost quantitative yield of **3a** (entry 3).[9] It was somewhat surprising that the reaction also proceeded efficiently in the absence of any phosphine ligand (entry 5). However, this phosphine-free protocol was not always effective as described below.

Table 2 summarizes the results for the reactions of various 4- or 2-substituted benzoyl chlorides **1a**−**h** with dialkylacetylenes **2a**−**c** and diphenylacetylene **2d** using $[IrCl(cod)]_2$ in the presence or absence of $P(t\text{-Bu})_3$. In each reaction, the corresponding naphthalene could be obtained, while the yields were affected by existence of the ligand and identity of the substituents. It is worth noting that the relatively labile C-halogen bonds were tolerable under the conditions. The reaction of 2-thenoyl chloride (**7**) in place of **1** with **2a** also proceeded smoothly to give benzothiophene **8** (Scheme 3). Treatment of **1a** with 1-octyne, however, gave a complex mixture.

Scheme 1



Scheme 2

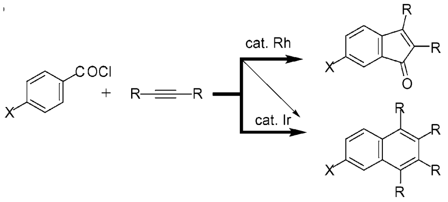
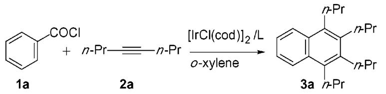


Table 1. Iridium-Catalyzed Reaction of Benzoyl Chloride (**1a**) with 4-Octyne (**2a**)[a]



entry	L	time (h)	% yield of **3a**[b]
1	PPh_3	18	71
2[c]	PPh_3	24	46
3	$P(t\text{-Bu})_3$	15	98
4[d]	$P(t\text{-Bu})_3$	25	87
5		19	99 (93)

[a] Reaction conditions: **1a** (1 mmol), **2a** (3 mmol), $[IrCl(cod)]_2$ (0.01 mmol), L (0.04 mmol), in refluxing *o*-xylene. [b] GLC yield based on amount of **1a** used. Value in parentheses indicates isolated yield. [c] Na_2CO_3 (2 mmol) was added. [d] $CaCO_3$ (2 mmol) was added.

A plausible mechanism for the reaction of aroyl chloride **1** with alkyne **2** is illustrated in Scheme 4, in which neutral ligands are omitted. Oxidative addition of **1** to chloroiridium(I) species generates aroyliridium(III) **A**, which undergoes decarbonylation to give aryliridium(III) **B**.[10] Insertion of **2** then gives vinyliridium **C**. The subsequent *ortho*-iridation affords five-membered iridacycle **D**. Further insertion of **2** and reductive elimination affords products **3**−**6**, regenerating chloroiridium(I). It should be noted that in the corresponding rhodium catalysis,[7] CO coordinated to the metal participates in the reaction to give indenones. In contrast, in the present reaction, the second alkyne insertion should be faster than that of CO. This represents a remarkable difference of catalytic nature between the metals.

To confirm the reaction sequence, an aryliridium(III) complex, $4\text{-}t\text{-BuC}_6H_4\text{-IrCl}_2(CO)(PPh_3)_2$ (t-Bu-**B**), was prepared by the reaction of **1c** with Vaska's complex according to the literature method.[10] t-Bu-**B** (0.02 mmol) could efficiently catalyze the reaction of **1c** (1 mmol) with **2a** (3 mmol) for 20 h to afford **3c** in 92% yield. t-Bu-**B** was also treated with 1 equiv of **2a** in $CDCl_3$ in a sealed

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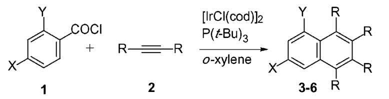
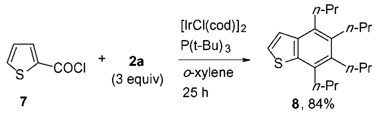
Table 2. Preparation of Naphthalenes by the Reaction of Aroyl Chlorides with Internal Alkynes[a]



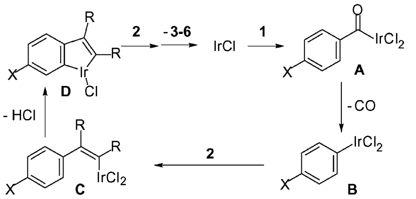
entry	chloride **1**, X, Y	alkyne **2**, R	time (h)	product, % yield[b]
1	**1b**, Me, H	**2a**, *n*-Pr	25	**3b**, 91 (97)
2[c]	**1b**, Me, H	**2a**, *n*-Pr	25	**3b**, (68)
3	**1c**, *t*-Bu, H	**2a**, *n*-Pr	16	**3c**, 96
4	**1d**, OMe, H	**2a**, *n*-Pr	25	**3d**, 50
5[d]	**1e**, H, OMe	**2a**, *n*-Pr	25	**3e**, 35
6	**1f**, Cl, H	**2a**, *n*-Pr	25	**3f**, 67 (70)
7[c]	**1f**, Cl, H	**2a**, *n*-Pr	25	**3f**, (56)
8	**1g**, Br, H	**2a**, *n*-Pr	18	**3g**, 69
9	**1h**, I, H	**2a**, *n*-Pr	16	**3h**, 63
10	**1a**, H, H	**2b**, *n*-Bu	16	**4**, 79
11	**1a**, H, H	**2c**, *i*-pentyl	16	**5**, 80
12	**1a**, H, H	**2d**, Ph	25	**6**, 70

[a] Reaction conditions: **1** (1 mmol), **2** (3 mmol), $[IrCl(cod)]_2$ (0.01 mmol), $P(t\text{-}Bu)_3$ (0.04 mmol), in refluxing *o*-xylene. [b] Isolated yield based on amount of **1** used. Value in parentheses indicates GLC yield. [c] Without ligand. [d] $CaCO_3$ (2 mmol) was added.

Scheme 3



Scheme 4

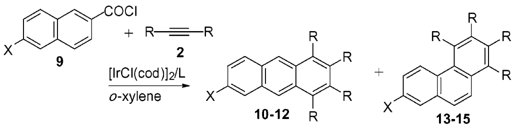


tube at 150 °C. ^1H and ^{31}P NMR of the solution indicated that about one-half the amount of *t*-Bu-**B** was consumed to give **3c** (ca. 0.5 equiv).[11] This suggests that the second alkyne insertion is relatively faster than the first one. In an alternative sequence, **B** may undergo successive insertion of two molecules of **2** and the subsequent *ortho*-iridation to form directly a seven-membered iridacycle. Participation of this route cannot be excluded. Anyway, the efficacy of cyclization seems to be due to the smooth *ortho*-iridation and the lack of β-elimination to produce arylallenes.[4c]

We also attempted to control the direction of homologation using 2-naphthoyl chlorides **9** (Table 3). The reaction of 2-naphthoyl chloride (**9a**) with **2a** proceeded without any phosphine ligand to give anthracene **10** and phenanthrene **13** in a ratio of 74:26, the total yield being 70%. Addition of $P(t\text{-}Bu)_3$ only little affected the reaction. Fortunately, it was found that use of PPh_3 (0.06 mmol) improved both the yield and the selectivity of **10** up to 83 and 96%, respectively. Anthracene **10** could be purified easily due to its good solubility. The catalyst system was also applicable to the reactions of **9a** with **2c** and 6-methoxy-2-naphthoyl chloride (**9b**) with **2a** to produce tetraalkylanthracenes **11** and **12** with high yields and selectivities.

In summary, we have developed a new, useful method for aromatic homologation with two aliphatic alkyne molecules using an iridium catalyst, giving condensed aromatics with substantial solubilities. The reaction proceeds efficiently without causing β-elimination[4c] and excessive insertion of alkyne.[6b] The tolerance of C-halogen bonds under the iridium catalysis[12] enables various catalytic derivatizations of the products.[13]

Table 3. Reaction of 2-Naphthoyl Chlorides with Internal Alkynes[a]



entry	chloride **9**, X	alkyne **2**, R	L	total yield[b] (%)	product ratio[c]
1	**9a**, H	**2a**, *n*-Pr		70	**10**:**13** = 74:26
2	**9a**, H	**2a**, *n*-Pr	$P(t\text{-}Bu)_3$	73	**10**:**13** = 70:30
3	**9a**, H	**2a**, *n*-Pr	PPh_3	67	**10**:**13** = 90:10
4[d]	**9a**, H	**2a**, *n*-Pr	PPh_3	83	**10**:**13** = 96:4
5[d]	**9a**, H	**2c**, *i*-pentyl	PPh_3	93	**11**:**14** = 98:2
6[d]	**9b**, OMe	**2a**, *n*-Pr	PPh_3	80	**12**:**15** = 97:3

[a] Reaction conditions: **9** (1 mmol), **2** (3 mmol), $[IrCl(cod)]_2$ (0.01 mmol), L (0.04 mmol), in refluxing *o*-xylene. [b] Isolated yield based on amount of **9** used. [c] Determined by GLC or ^1H NMR. [d] PPh_3 (0.06 mmol) was used.

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Supporting Information Available: Standard experimental procedure and characterization data for new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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