JOC Article

Synthesis of Substituted Naphthalenes and Carbazoles by the Palladium-Catalyzed Annulation of Internal Alkynes

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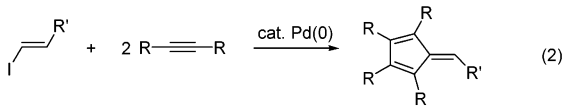
An efficient synthesis of highly substituted naphthalenes has been developed by the palladium-catalyzed annulation of a variety of internal alkynes, in which two new carbon−carbon bonds are formed in a single step under relatively mild reaction conditions. This method has also been used to synthesize carbazoles, although a higher reaction temperature is necessary. The process involves arylpalladation of the alkyne, followed by intramolecular Heck olefination and double-bond isomerization. This method accommodates a variety of functional groups and affords the anticipated highly substituted naphthalenes and carbazoles in good to excellent yields.

Introduction

Highly substituted naphthalenes are common structural units in numerous biologically significant natural products and pharmaceuticals,[1] and improved methods for their construction are highly desirable.[2−6] Among the most important synthetic routes to such compounds are annulation via Fischer carbenes (the Dötz reaction)[3] and the palladium-catalyzed cyclization of alkynes by arylsilyl triflates via in situ generation of highly reactive benzynes.[4] Another method of synthesis is based on the cyclopropane-shift reaction of diaryl(2-halogenocyclopropyl)methanols.[5] Very recently, substituted naphthalenes have been prepared using the gallium-catalyzed cyclization of carbonyl compounds or epoxides with alkynes.[6]

Annulation processes have proven quite valuable in organic synthesis because of the ease with which a variety of complicated hetero- and carbocycles can be rapidly constructed.[7] In our own laboratories, it has been demonstrated that palladium-catalyzed annulation[8] can be effectively employed for the synthesis of indoles,[9] isoindolo[2,1-*a*]indoles,[10] benzofurans,[11] benzopyrans,[12] isocoumarins,[11,12] α-pyrones,[12,13] indenones,[14] isoquinolines,[15] carbolines,[16] and polycyclic aromatic hydrocarbons[17] (eq 1). More recently, Takahashi et al. have reported that pentasubstituted fulvene derivatives can be prepared using the palladium-catalyzed annulation of disubstituted alkynes (eq 2).[18]



Due to our continuing interest in the palladium-catalyzed annulation of internal alkynes, we have inves-

* Corresponding author.

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(7) (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567. (c) Negishi, E.; Copéret, C.; Ma, S.; Liou, S.; Liu, F. *Chem. Rev.* **1996**, *96*, 365. (d) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635.

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SCHEME 1

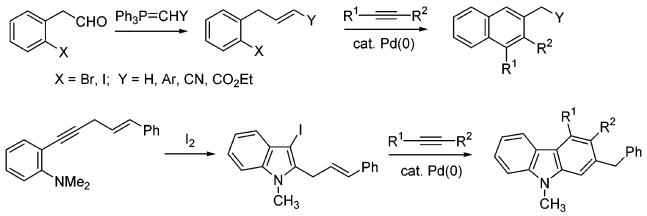
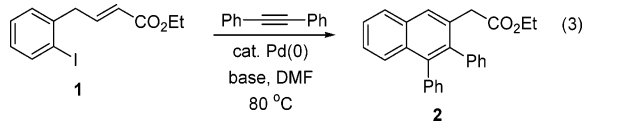


TABLE 1. Optimization of the Synthesis of Naphthalene 2 (eq 3)[a]



entry	alkyne (equiv)	catalyst	ligand	base	time (h)	% yield
1	2	10% $Pd(OAc)_2$		3 NaOAc	12	58
2	2	10% $Pd(OAc)_2$		3 Na_2CO_3	12	40
3	2	10% $Pd(OAc)_2$		3 $NaHCO_3$	8	49
4	2	10% $Pd(PPh_3)_4$		3 Na_2CO_3	24	trace
5	2	10% $Pd(OAc)_2$		3 Bu_3N	10	71
6	2	10% $Pd(OAc)_2$		3 Et_3N	12	76
7	2	10% $Pd(OAc)_2$		3 pyridine	24	trace
8	2	5% $Pd(OAc)_2$		3 Et_3N	10	80
9	1.2	5% $Pd(OAc)_2$		3 Et_3N	12	58
10	5	5% $Pd(OAc)_2$		3 Et_3N	12	81
11	2	5% $Pd(OAc)_2$		3 Et_3N	12	80[b]
12	2	5% $Pd(OAc)_2$		1.5 Et_3N	12	70
13	2	5% $Pd(OAc)_2$		2 Et_3N	12	79
14	2	5% $Pd(OAc)_2$	10% PPh_3	2 Et_3N	12	86
15	2	5% $Pd(OAc)_2$	10% PPh_3	1.5 Et_3N	12	78

[a] All reactions were run under the following reaction conditions, unless otherwise specified: 0.25 mmol of aryl halide **1** and the indicated amount of diphenylacetylene were stirred in 3 mL of DMF at 80 °C in the presence of the specified amount of the indicated base, $Pd(OAc)_2$, and PPh_3. [b] One equivalent of *n*-Bu_4NCl was added.

tigated the reaction of internal alkynes and *o*-(2-alkenyl)-aryl halides derived from aldehydes and ylides and have communicated that excellent yields of highly substituted naphthalenes can be synthesized by employing this method.[19] Herein, we wish to report the full details of this new naphthalene synthesis and its extension to the formation of substituted carbazoles (Scheme 1).

Results and Discussion

Our initial studies focused on achieving optimal reaction conditions for the palladium-catalyzed annulation employing ethyl (*E*)-4-(2-iodophenyl)-2-butenoate (**1**). The reaction of aryl halide **1** and diphenylacetylene was chosen as the model system for optimization of this process (eq 3), and the results are summarized in Table 1.

Using 10 mol % of $Pd(OAc)_2$ and 3 equiv of NaOAc afforded the desired naphthalene product **2** in a 58% yield (entry 1, Table 1). Carbonate bases, such as Na_2CO_3 and $NaHCO_3$, gave naphthalene **2** in 40% and 49% yields, respectively (entries 2 and 3). However, the use of $Pd(PPh_3)_4$ as a catalyst and Na_2CO_3 as a base gave only a trace of the desired product (entry 4). Our previous work has shown that carbonate bases usually work better for palladium-catalyzed annulation chemistry than organic bases.[9−17] However, it turned out that organic bases work better than carbonate salts in this annulation chemistry. For example, when the organic bases *n*-Bu_3N and Et_3N were employed, the reaction of halide **1** gave 71% and 76% yields of naphthalene **2**, respectively, in the presence of 10 mol % of $Pd(OAc)_2$ (entries 5 and 6). This is probably because the ester group can be hydrolyzed in the presence of the carbonate bases and the resulting yield of naphthalene suffers. The use of pyridine afforded only a trace of the desired product (entry 7). Further optimization work showed that 5 mol % of $Pd(OAc)_2$ and 2 equiv of diphenylacetylene are necessary to achieve decent yields of naphthalene **2** (entries 8−10). In entry 11, the addition of 1 equiv of *n*-Bu_4NCl gave an 80% yield, which is the same yield as the reaction without *n*-Bu_4NCl (entry 8). We have also explored the effects on the yield of other variables, such as the ligand and the amount of the base (entries 12−15). The optimal reaction conditions thus far developed employ 0.25 mmol of aryl halide **1**, 2 equiv of diphenylacetylene, 5 mol % of $Pd(OAc)_2$, 10 mol % of PPh_3, and 2 equiv of Et_3N as a base in 3 mL of DMF stirred at 80 °C. This afforded an 86% yield of naphthalene **2** (entry 14).

Using our optimal reaction conditions, the scope of the annulation process has been explored using a variety of substrates carefully selected in order to establish the generality of the process and its applicability to commonly encountered synthetic problems (Table 2). While the reaction of aryl halide **1** and diphenylacetylene afforded naphthalene **2** in 86% yield (entry 1), only a 61% yield of naphthalene **3** was obtained from the reaction of aryl halide **1** and di(*p*-methoxyphenyl)acetylene (entry 2). The decrease in the yield of the reaction indicates that electron-rich diarylacetylenes disfavor the annulation chemistry. However, when an electron-deficient diarylacetylene, such as di(*p*-ethoxycarbonylphenyl)acetylene, was allowed to react with aryl halide **1**, an 83% yield of naphthalene **4** was obtained (entry 3), comparable to the yield obtained from the reaction of aryl halide **1** and diphenylacetylene (entry 1). When 4-octyne, a dialkylacetylene, was allowed to react with aryl halide **1**, a 60% yield of naphthalene **5** was obtained (entry 4).

To test the regioselectivity of this annulation process, 1-phenylpropyne was allowed to react with aryl halide **1** and a 53:47 mixture of two regioisomers **6** and **7** was obtained in a 75% overall yield (entry 5). According to our previous work,[9−17] the bulkiness of the substituents on the acetylene plays a major role in determining the regioselectivity of alkyne insertion. The aryl moiety of the arylpalladium intermediate adds preferentially to the less hindered end of the carbon−carbon triple bond. In this naphthalene synthesis, the regioselectivity appears to be significantly lower than we have normally observed in the annulation of unsymmetrical alkynes. Similarly, the reaction of aryl halide **1** and ethyl phenylpropiolate afforded a 76:24 mixture of two regioisomers **8** and **9** (entry 6). In this case, the major product **8** results from aryl addition to the 3-position of the phenylpropiolate. Electronic effects appear to play a major role here. As in

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TABLE 2. Synthesis of Substituted Naphthalenes and Carbazoles by the Palladium-Catalyzed Annulation of Internal Alkynes[a]

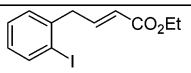
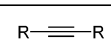
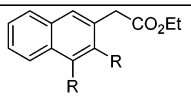
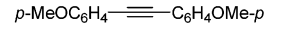
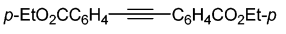
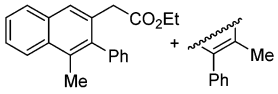
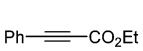
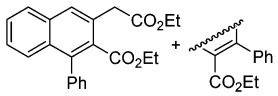
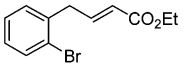
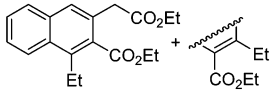
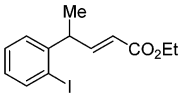
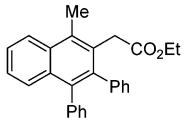
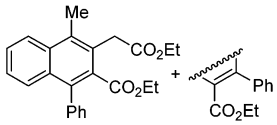
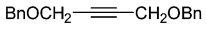
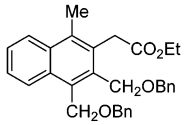
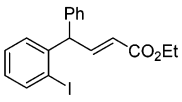
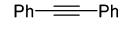
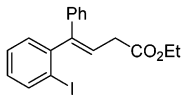
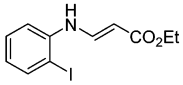
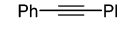
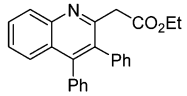
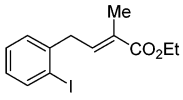
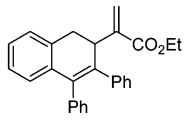
entry	haloalkene		alkyne	time (h)	product(s)	% isolated yield	
		**1**					
1				12		**2**	86
2				24		**3**	61
3				30		**4**	83
4				48		**5**	60
5				24		**6** + **7**	75[b] (53 : 47)
6				12		**8** + **9**	88[b] (76 : 24)
7		**10**		40		**2**	75
8				72		**5**	46
9				72		**11** + **12**	52[b] (60 : 40)
10		**13**		26		**14**	72
11				5		**15** + **16**	86[b] (67 : 33)
12				12		**17**	56
13		**18**		8		**19**	48
14		**20**		24		**21**	0
15		**22**		12		**23**	73

Table 2 (Continued)

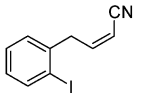
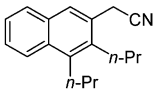
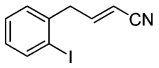
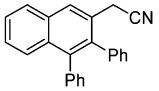
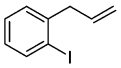
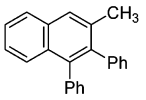
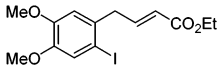
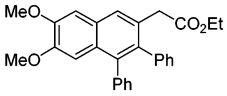
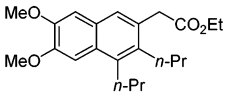
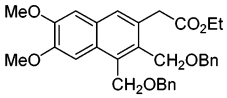
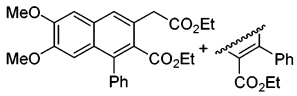
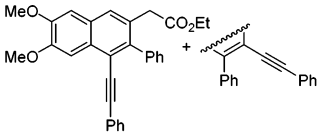
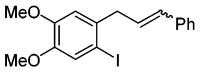
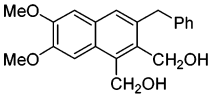
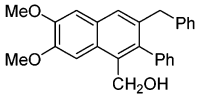
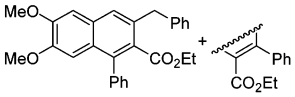
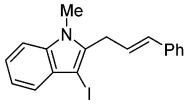
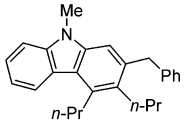
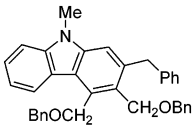
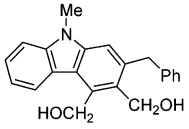
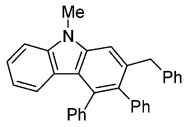
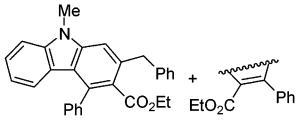
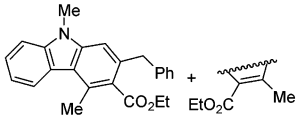
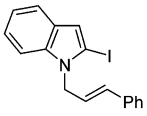
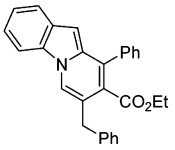
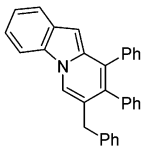
entry	haloalkene		alkyne	time (h)	product(s)		% isolated yield
16		**24**	*n*-Pr—≡—*n*-Pr	7		**25**	74
17		**27**	*n*-Pr—≡—*n*-Pr	7		**25**	72
18		**24**	Ph—≡—Ph	16		**26**	45
19		**27**	Ph—≡—Ph	12		**26**	43
20		**28**	Ph—≡—Ph	16		**29**	32
21		**30**	Ph—≡—Ph	24		**31**	71
22			*n*-Pr—≡—*n*-Pr	16		**32**	73
23			$BnOCH_2$—≡—CH_2OBn	7		**33**	60
24			Ph—≡—CO_2Et	12		**34** + **35**	73 + 8
25			Ph—≡—≡—Ph	18		**36** + **37**	66[b] (83 : 17)
26		**38**[c]	$HOCH_2$—≡—CH_2OH	16		**39**	73
27			$HOCH_2$—≡—Ph	8		**40**	31
28			Ph—≡—CO_2Et	8		**41** + **42**	76 + 8
29		**43**	*n*-Pr—≡—*n*-Pr	24		**44**	33[d]
30			$BnOCH_2$—≡—CH_2OBn	4		**45**	56[e]

Table 2 (Continued)

entry	haloalkene	alkyne	time (h)	product(s)	% isolated yield
31		$HOCH_2$—≡—CH_2OH	12		**46** 41[e]
32		Ph—≡—Ph	24		**47** Trace[e,f]
33		Ph—≡—CO_2Et	16		**48** + **49** 91[b,d] (60 : 40)
34		Me—≡—CO_2Et	72		**50** + **51** 78[b,d] (82 : 18)
35	 **52**	Ph—≡—CO_2Et	7		**53** 42
36		Ph—≡—Ph	12		**54** 0

[a] All reactions were run under the following conditions, unless otherwise specified: 0.25 mmol of the aryl halide, 0.5 mmol of the alkyne, 0.5 mmol of Et_3N, 5 mol % of $Pd(OAc)_2$ and 10 mol % of PPh_3 were stirred in 3 mL of DMF at 80 °C under an Ar atmosphere. [b] The products are inseparable. [c] Compound **34** was prepared and utilized as a 55:45 mixture of *E*/*Z* isomers. [d] The reaction was run at 100 °C. [e] The reaction was run at 120 °C. [f] 65% of the starting materials was recovered.

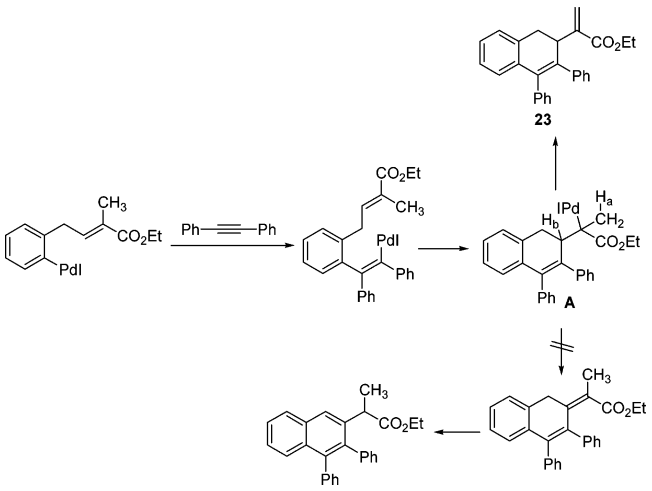
most Heck reactions, the aryl group of the initial Pd intermediate is more likely to add to the end of the carbon−carbon multiple bond furthest from the electron-withdrawing ester moiety, which results in naphthalene **8** as the major product.

The reactions of aryl halide **1** and 2-butyne-1,4-diol or 3-phenyl-2-propyn-1-ol failed to afford any recognizable product. It appears that the problem may be transesterification of the ester group by the acetylenic alcohols, which is further supported by the results described later. No recognizable naphthalene products could be obtained when bulky symmetrical or unsymmetrical alkynes, like di-*tert*-butylacetylene, phenyl(trimethylsilyl)acetylene, and 4,4-dimethyl-2-pentyne, were allowed to react with aryl halide **1**. Presumably, the problem here is the difficulty in adding the hindered vinylic palladium intermediate across the relatively hindered internal alkene to place three bulky substituents in contiguous positions on the resulting carbocyclic ring.

A synthetically interesting question is whether aryl bromides can also undergo this palladium-catalyzed annulation chemistry. To answer this question, compound **10** was prepared and employed in reactions with various alkynes. Generally, compared to the results from aryl iodide **1**, the annulation reactions of aryl bromide **10** with alkynes result in a longer reaction time and lower yields, although the reactions proceed smoothly (entries 7 and 8). The observed lower reactivity of the aryl bromide **10** is consistent with our other annulation chemistry.[9−17] Notice that the reaction of compound **10** and ethyl 2-pentynoate gave a 60:40 mixture of regioisomers **11** and **12** (entry 9).

To vary the linkage between the alkene and the iodoarene unit, substrates **13**, **18**, and **20** have been prepared and employed in this annulation chemistry. The reaction of aryl iodide **13** and diphenylacetylene afforded a 72% yield of the expected product (entry10), a little lower than the yield from the reaction of aryl halide **1** and diphenylacetylene (entry 1). When ethyl phenylpropiolate was allowed to react with compound **13**, a 67:33 mixture of regioisomers **15** and **16** was obtained in an 86% overall yield (entry 11). Comparing the results from entries 6 and 11, it is clear that the introduction of a methyl group into the starting material decreases the regioselectivity of the annulation chemistry. When aryl halide **13** was allowed to react with 2-butyne-1,4-diol, none of desired product was obtained. However, the use of a benzyl-protected 2-butyne-1,4-diol resulted in a 56% yield (entry 12). While compound **13** underwent the annulation chemistry very well and gave good to excellent yields, the annulation reaction of aryl halides **18** and **20** gave none of the desired products (entries 13 and 14). It

SCHEME 2



is not too surprising that aryl halide **18** was isomerized to the more stable trisubstituted alkene **19** which was isolated in a 48% yield after 8 h. Note that compound **19**, which is a possible starting material for this annulation chemistry, is relatively unstable under the reaction conditions employed. If the reaction of compound **18** was allowed to proceed for 28 h, compound **19** disappeared and no other significant product was observed. The readily prepared aryl halide **20** may also be undergoing double-bond isomerization because no recognizable products could be isolated from its reaction with diphenylacetylene.

It is interesting that the reaction of aryl halide **22** and diphenylacetylene afforded compound **23** in a 73% yield (entry 15). A mechanism for the formation of product **23** is shown in Scheme 2. From the intermediate **A** that is formed, there are two possible pathways for palladium β-hydride elimination to occur. Intermediate **A** can eliminate H_b on the ring and eventually generate the naphthalene product after isomerization. The other pathway involves elimination of H_a from the methyl group which would afford compound **23** bearing a disubstituted terminal alkene. The result indicates that the elimination of H_a is much faster than that of H_b. This may be because the methyl group has three hydrogens increasing the chances of elimination. Alternatively, when the vinylic palladium iodide adds cis to the alkene, H_b is not syn to the alkylpalladium iodide generated. To undergo β-hydride elimination, rotation of the C−C bond is necessary before H_b and PdI are aligned cis to each other for elimination. Thus, the elimination of H_a may be achieved before this rotation can actually occur.

To examine whether the geometry of the carbon−carbon double bond affects the annulation process, nitriles **24** and **27**, which are *E*/*Z* isomers, were prepared and allowed to react with 4-octyne and diphenylacetylene (entries 16−19). When 4-octyne was employed, both reactions reached completion in 7 h and afforded very similar yields (entries 16 and 17). The reactions of nitriles **24** and **27** with diphenylacetylene also resulted in very similar yields (entries 18 and 19), although they gave lower yields than the reactions of 4-octyne. Notice that the reactions of diphenylacetylene also required a longer reaction time. This is probably because 4-octyne, which is an electron-rich alkyne, is more reactive than diphenylacetylene. These results (entries 16−19) indicate that the geometry of the carbon−carbon double bond has little effect on this annulation process.

Since aryl halides bearing electron-deficient olefins work very well in this annulation chemistry, it was important to determine if the introduction of an electron-withdrawing group on the alkene is really necessary to achieve success. To answer this question, compound **28** was prepared and allowed to react with diphenylacetylene. Only a 32% yield of naphthalene **29** was isolated (entry 20). It appears that the presence of an electron-withdrawing group, which presumably makes the olefin a better acceptor for the Heck reaction, facilitates this chemistry. In this comparison, however, we cannot rule out the possibility that the terminal alkene in aryl iodide **28** may be undergoing intermolecular Heck processes resulting in a lower yield.

The reactions of aryl halide **30**, bearing two methoxy groups on the aromatic ring, with symmetrical alkynes such as diphenylacetylene, 4-octyne, and 1,4-di(benzyloxy)-2-butyne afforded the corresponding naphthalenes **31**−**33** in 71%, 73%, and 60% yields, respectively (entries 21−23). When aryl halide **30** was allowed to react with ethyl phenylpropiolate, two regioisomers **34** (73%) and **35** (8% yield) were isolated (entry 24). Comparing this result with that from the reaction of aryl halide **1** and ethyl phenylpropiolate (entry 6), it appears that the introduction of electron-donating substituents, like methoxy groups, onto the arene moiety increases the regioselectivity in this annulation process. The use of a diyne afforded an 83:17 mixture of alkynes **36** and **37** in a 66% overall yield (entry 25).

The phenyl-substituted aryl iodide **38** has been found to react well with 2-butyne-1,4-diol to produce naphthalene **39** in a 73% yield (entry 26). This result confirms our suspicion that the earlier problem with alkynols had more to do with transesterification of the ester group than any inherent problems with the alcohol functionality. Surprisely, only one regioisomer **40** was isolated, when 3-phenyl-2-propyn-1-ol was allowed to react with aryl halide **38** (entry 27), although the yield of 31% was not very good. The reaction of aryl iodide **38** and ethyl phenylpropiolate afforded two regioisomers **41** (76%) and **42** (8%) with a yield and ratio of the two regioisomers similar to those from the reaction of **30** and ethyl phenylpropiolate (entry 24).

Carbazoles have attracted much attention due to their biological activity[20] and their potential as functional materials,[21] and the synthesis of carbazoles has been extensively studied.[22] Our palladium-catalyzed annulation chemistry provides an alternative, very efficient method to synthesize substituted carbazoles. Iodoindole **43** was first prepared using iodocyclization chemistry currently under investigation in our group.[23] This compound was allowed to react with a variety of alkynes,

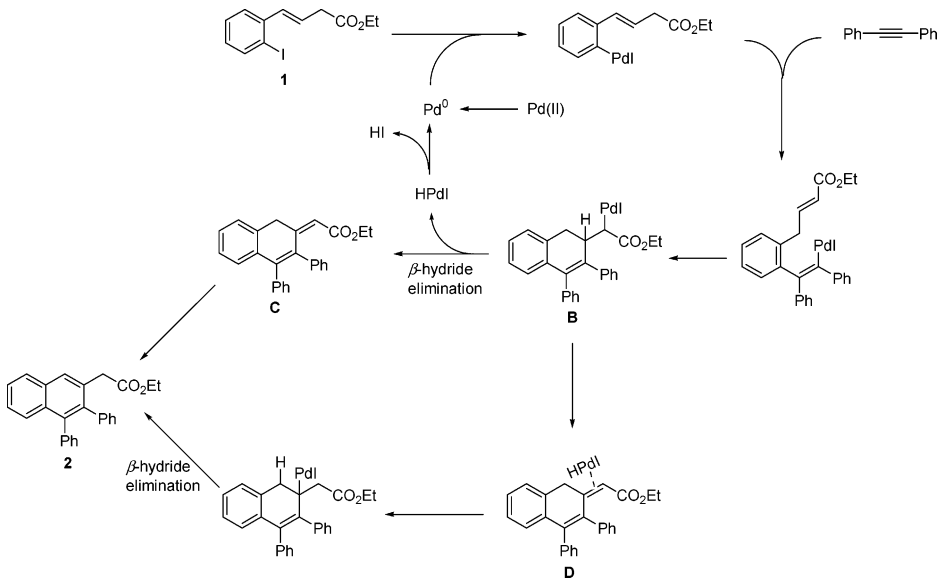
(20) For recent reviews, see: (a) Knoelker, H.-J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303. (b) Kirsch, G. H. *Curr. Org. Chem.* **2001**, *5*, 507. (c) Knoelker, H.-J. *Chem. Soc. Rev.* **1999**, *28*, 151. (d) Knoelker, H.-J. *Synlett* **1992**, 371.

(21) For a recent review, see: Zhang, Y.; Wada, T.; Sasabe, H. *J. Mater. Chem.* **1998**, *8*, 809.

(22) For recent reviews, see: (a) Pindur, U.; Lemster, T. *Rec. Devel. Org. Bioorg. Chem.* **1997**, *1*, 33. (b) Kawasaki, T.; Sakamoto, M. *J. Ind. Chem. Soc.* **1994**, *71*, 443.

(23) Yue, D.; Larock, R. C. Work in process.

SCHEME 3



including symmetrical and unsymmetrical alkynes. While the reactions of 4-octyne, 2-butyne-1,4-diol, and 1,4-di-(benzyloxy)-2-butyne gave moderate yields ranging from 33% to 56%, the use of diphenylacetylene gave only a trace of the desired product (entries 29−32). The failure of the reaction of diphenylacetylene is probably a result of the fact that this alkyne appears to be less reactive than most other alkynes. Notice that for the carbazole synthesis, a higher reaction temperature is also required. There was no reaction at 80 °C when iodoindole **43** was employed. This may indicate that 5,6-fused ring systems are more difficult to form than 6,6-fused ring systems when employing this annulation chemistry. More reactive alkynes, such as ethyl phenylpropiolate and ethyl 2-butynoate, have also been allowed to react with iodoindole **43**, and better yields have been obtained (entries 33 and 34). The use of ethyl phenylpropiolate gave a 60:40 mixture of regioisomers **48** and **49** in a 91% overall yield, which indicates that the electronic effects appear to be more important than steric effects in this system (entry 33). Ethyl 2-butynoate, a less bulky alkyne, was allowed to react with iodoindole **43** and a 82:18 mixture of isomers **50** and **51** was isolated in a 78% overall yield (entry 34). The results from entries 33 and 34 indicate that both electronic and steric effects play a role in the regioselectivity of the alkyne insertion and the electronic effect apparently outweighs the steric effect.

When compound **52** was allowed to react with two alkynes, the reaction of the more reactive ethyl phenylpropiolate gave a 42% yield of compound **53** as a single isomer, while use of the less reactive diphenylacetylene results in none of the desired product (entries 35 and 36).

A mechanism for the reaction of aryl halide **1** and diphenylacetylene is proposed in Scheme 3. First, Pd(0) oxidatively inserts into the carbon−iodide bond of the aryl iodide to generate an arylpalladium species. Addition of the arylpalladium species to the carbon−carbon triple bond, followed by an intramolecular cis addition to the carbon−carbon double bond, generates an alkylpalladium species **B**. Intermediate **B** can undergo β-hydride elimination forming intermediate **C**, which subsequently isomerizes to naphthalene **2**. Alternatively, the intermediate **B** may undergo reversible palladium hydride elimination to an alkene complex **D**, which undergoes readdition of the palladium hydride to the double bond with the opposite regiochemistry. Further palladium hydride elimination would produce the observed aromatic product.

Conclusions

An efficient synthesis of highly substituted naphthalenes and carbazoles has been developed in which two new carbon−carbon bonds are formed in a single step under relatively mild reaction conditions. Both electronic and steric effects play a role in the regioselectivity of this process and the electronic effect predominates over the steric effect with certain ester-containing alkynes. The introduction of an electron-rich group onto the aryl halide increases the regioselectivity of this annulation process. When this method was employed to synthesize carbazoles, a higher reaction temperature was necessary due to the lower reactivity of the iodoindoles. This method accommodates a variety of functional groups and generally affords the anticipated highly substituted naphthalenes and carbazoles in good to excellent yields.

Experimental Section

Preparation of the *o*-(2-Alkenyl)aryl Halides. 2-(2-Iodophenyl)propanal. To a suspension of (methoxymethyl)-triphenylphosphonium chloride (2.87 g, 8.4 mmol) in dry THF (15 mL) was added KO-*t*-Bu (0.90 g, 8.0 mmol) portionwise under an Ar atmosphere at 25 °C. The resulting red suspension was stirred for 30 min at 25 °C, and a solution of 2-iodoacetophenone (0.98 g, 4.0 mmol) in dry THF (5 mL) was added dropwise. After the reaction mixture was stirred at 25 °C for 1 h, the THF was removed under reduced pressure and hexane (30 mL) was added to the residue. The resulting suspension was stirred for 20 min, and the Ph_3PO was removed by filtration. The filtrate was collected, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (20:1 hexane/EtOAc) on silica gel to afford 1.10 g of 2-(2-iodophenyl)-1-methoxypropene (E/Z = 90:10) in a 100% yield as a yellow oil. To a solution of 2-(2-iodophenyl)-1-methoxypropene (E/Z = 90:10) (0.55 g, 2.0 mmol) in CH_2Cl_2

(10 mL) was added 1.2 mL of hydroiodic acid (47%), and the mixture was stirred under an Ar atmosphere at 25 °C for 40 min. The reaction was then diluted with 30 mL of CH_2Cl_2, and the excess acid was carefully neutralized by 30 mL of satd aq $NaHCO_3$, during which time many bubbles were generated. The organic layer was collected, washed with 20 mL of brine, dried over Na_2SO_4, and filtered, and the solvent (CH_2Cl_2) was removed under reduced pressure. The residue was purified by flash chromatography (20:1 hexane/EtOAc) on silica gel to afford 0.36 g of 2-(2-iodophenyl)propanal in a 69% yield as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.40 (d, J = 6.8 Hz, 3H), 4.08 (q, J = 6.8 Hz, 1H), 6.99−7.03 (m, 1H), 7.06 (dd, J = 1.6, 8.0 Hz, 1H), 7.35−7.39 (m, 1H), 7.93 (dd, J = 1.2, 8.0 Hz, 1H), 9.73 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.7, 56.9, 102.3, 128.6, 129.2, 129.5, 140.3, 141.4, 200.5.

Ethyl (*E*)-4-(2-Iodophenyl)-2-pentenoate (13). To a suspension of (carbethoxymethylene)triphenylphosphorane (0.69 g, 1.95 mmol) in 5 mL of CH_2Cl_2 was added dropwise a solution of 2-(2-iodophenyl)propanal (0.34 g, 1.3 mmol) in 5 mL of CH_2Cl_2 at 0 °C under an Ar atmosphere. The resulting mixture was stirred at 25 °C for 3 h, and the solvent (CH_2Cl_2) was evaporated under reduced pressure. The solid residue was dissolved in 20 mL of hexane, and the mixture was then stirred at 25 °C for 0.5 h. The Ph_3PO was filtered, and the solvent was removed under reduced pressure. The oily residue was purified by flash chromatography (20:1 hexane/EtOAc) to afford 0.41 g of the indicated compound as a colorless oil in a 95% yield: ^{1}H NMR ($CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 1.39 (d, J = 7.2 Hz, 3H), 3.97−4.04 (m, 1H), 4.19 (q, J = 7.2 Hz, 2H), 5.84 (dd, J = 2.0, 16.0 Hz, 1H), 6.90−6.95 (m, 1H), 9.08 (dd, J = 5.6, 16.0 Hz, 1H), 7.15 (dd, J = 1.6, 8.0 Hz, 1H), 7.30−7.34 (m, 1H), 7.85 (dd, J = 1.2, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.5, 19.7, 45.9, 60.6, 101.3, 121.0, 127.9, 128.8, 129.0, 140.0, 145.8, 151.3, 166.9; IR (neat, cm^{-1}) 3058, 2976, 2933, 2902, 1716, 1465; HRMS calcd for $C_{13}H_{15}IO_2$ 330.0117, found 330.0123.

Compounds **1**, **10**, **24**, **27**, **30**, and **38** were reported in our earlier communication.[19] The preparation and characterization of other *o*-(2-alkenyl)aryl halides is reported in the Supporting Information.

General Procedure for the Preparation of Naphthalenes and Carbazoles. To a mixture of the alkyne (0.50 mmol), $Pd(OAc)_2$ (2.8 mg, 0.025 mmol), PPh_3 (6.6 mg, 0.05 mmol), and Et_3N (55.0 mg, 0.5 mmol) in 2 mL of DMF was added dropwise a solution of the aryl halide (0.25 mmol) in 1 mL of DMF. The resulting mixture was then stirred under an Ar atmosphere at the indicated temperature (see Table 2). The reaction was monitored by TLC to establish completion. When the reaction was complete, the reaction mixture was allowed to cool to 25 °C, poured into brine (25 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were concentrated, and the residue was purified by column chromatography on silica gel to afford the corresponding naphthalene or carbazole.

Ethyl (1-Methyl-3,4-diphenyl-2-naphthyl)acetate (14). The reaction mixture was chromatographed using 30:1 hexane/EtOAc to afford 68 mg of the indicated compound as a white solid in a 72% yield: mp 80−82 °C; ^{1}H NMR ($CDCl_3$) δ 1.18 (t, J = 7.1 Hz, 3H), 2.72 (s, 1H), 3.69 (s, 2H), 4.08 (q, J = 7.1 Hz, 2H), 7.01−7.21 (m, 10H), 7.32−7.38 (m, 1H), 7.48−7.54 (m, 2H), 8.16 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.4, 15.8, 38.0, 60.8, 124.3, 125.8, 126.0, 126.4, 126.6, 127.6, 127.7, 127.7, 129.3, 130.5, 131.3, 132.1, 132.3, 133.0, 137.5, 139.9, 140.1, 141.0, 171.9; IR ($CHCl_3$, cm^{-1}) 3019, 1729, 1216, 1179; HRMS calcd for $C_{27}H_{24}O_2$ 380.1776, found 380.1781.

Compounds **2**−**9**, **25**, **31**, **34**, **35**, and **39** were reported in our previous communication.[19] The preparation and characterization of other naphthalenes and carbazoles is described in the Supporting Information.

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Supporting Information Available: Compounds **1**−**10**, **24**, **25**, **27**, **30**, **31**, **34**, **35**, **38**, and **39** were reported in our earlier communication.[19] Compounds **20**[24] and **28**[25] were prepared according to previous literature procedures. Preparation and characterization of the starting materials **13**, **18**, **22**, **43** and **52**; characterization data for compounds **11**, **12**, **14**−**19**, **22**, **23**, **26**, **29**, **32**, **33**, **36**, **37**, **40**−**42**, **44**−**46**, **48**−**51**, and **53**; copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **11**−**23**, **26**, **29**, **32**, **33**, **36**, **37**, **40**−**46**, and **48**−**53**. This material is available free of charge via the Internet at http://pubs.acs.org.

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