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Isoquinolinium Salts from *o*-Halobenzaldehydes, Amines, and Alkynes Catalyzed by Nickel Complexes: Synthesis and Applications

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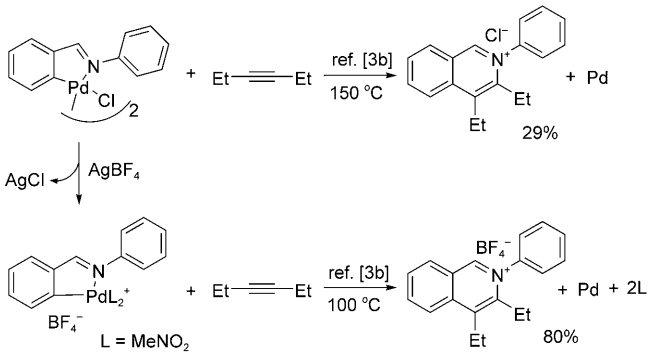
Despite the wide presence[1a] and application[1,2] of isoquinolinium salts in natural product and drug formulations, there is no general synthetic method available for these derivatives. Traditional synthesis of isoquinolinium salts from isoquinolines and alkyl halide derivatives is limited by the number of substituted isoquinolines that are readily available. Moreover, it is not feasible for *N*-aryl substituted salts. Previously, Heck and co-workers observed the formation of isoquinolinium salts from the reaction of cyclopalladated benzaldimines and alkynes,[3a,b] but they did not succeed in making the reaction catalytic. It is necessary to convert the *N*-phenylbenzaldimine cyclopalladated chloro dimer to the corresponding cyclopalladated tetrafluoroborate for efficient formation of the isoquinolinium derivative (Scheme 1).[3] The use of stoichiometric amounts of the palladium complex for the reaction greatly limits its application. Later, Larock and co-workers reported the synthesis of isoquinoline derivatives from *N*-*tert*-butyl *o*-halobenzaldimines and alkynes catalyzed by palladium systems.[4] We also observed a similar but much more rapid reaction catalyzed by nickel complexes.[3c] In these reactions, isoquinolinium salts were proposed as the intermediates although they were not observed.

Recently, the formation of dihydroisoquinolines through the catalytic electrophilic activation of the alkyne group in *o*-alknylbenzaldimines were described.[5] In all of these reactions, isoquinolinium salts were proposed as the intermediates but were not isolated, probably owing to the high reactivity of these salts. Herein, we report an efficient regioselective nickel-catalyzed annulation of *o*-halobenzaldimines with various alkynes to give isoquinolinium salts. For the first time a general method for the synthesis of *N*-aryl isoquinolinium salts, a difficult task by using classical methods, was achieved. The easy isolation of these salts is important because they can be transformed into various useful organic species.[2,6] We demonstrate an interesting application of the salts in the synthesis of isoquinolinones,[2] which are key intermediates in the total synthesis of diverse isoquinoline alkaloids.[6] The construction of isoquinolinone structures through previous methods requires multistep synthesis. Recent disclosure of the therapeutic utility of *N*-aryl isoquinolinium salts and *N*-aryl isoquinolinones in the treatment of infections,[1b] diseases by cytokines,[2b,c] and ADP–platelet aggregation[2a] by pharmaceutical companies further shows the importance of the present research.



Scheme 1. Stoichiometric synthesis of isoquinolinium derivatives from cyclopalladated benzaldimine and alkynes.

When we employed [$NiBr_2$(dppe)]/zinc powder for the treatment of *N*-tolyl *o*-iodobenzaldimine (**1a**) with diphenyl acetylene (**2a**), our original reaction conditions for the synthesis of isoquinolines,[3c] no expected isoquinolinium salt **3a** was observed (see below). Fortunately, by using [$Ni(cod)_2$] alone without Zn, the expected salt **3a** was obtained in 93% yield. When [$Ni(cod)_2$] was used with 2 equiv of PPh_3 or P-(*o*-Tol)$_3$, the corresponding isoquinolinium derivative **3a** was obtained in 87 and 99% yield, respectively (the yields were determined by the NMR spectroscopic integration method, see the Supporting Information). Also, the present reaction can be carried out by using Ni^0 species generated in situ from air-stable Ni^{II} complexes and Et_3B or *n*BuLi.

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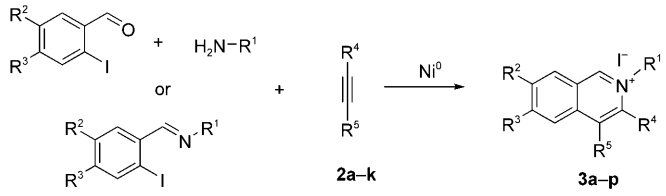
These experiments show that most Ni^0 complexes, under suitable conditions, are effective catalysts. Attempts to use palladium complexes including $[Pd(PPh_3)_4]$, $[Pd(dba)_2]$, and $[Pd(OAc)_2]$ as catalysts under various reaction conditions failed to produce the isoquinolinium salt **3a**. The results are in accordance with those previously reported.[3b] The reaction could also be carried out by using *o*-iodobenzaldehyde and *p*-toluidine in a 1:1 molar ratio to generate imine **1a** in situ. As shown in Table 1, entry 1, both reaction conditions gave nearly the same yield of **3a**. Note that the reaction also proceeded smoothly, even at room temperature, to give **3a** in approximately the same yield in 12 h. Similarly, the reaction of *o*-iodobenzaldehyde and *p*-toluidine with 3-hexyne (**2b**) gave **3b** in 91% yield (Table 1, entry 2).

To investigate the regioselectivity of the catalytic reaction, unsymmetrical alkynes were tested. Both 1-phenylpropyne (**2c**) and ethyl 3-phenylpropiolate (**2d**) reacted highly regioselectively with *o*-iodobenzaldehyde and *p*-toluidine to give isoquinolinium salts **3c** and **3d** in yields of 84 and 87%, respectively. In both products, the phenyl substituent is adjacent to the nitrogen atom, despite the great difference in the electronic properties of alkynes **2c** and **2d**, which have an electron-donating Me and an electron-withdrawing CO_2Et group, respectively. In addition, only one regioisomeric product was observed in each case. Apart from the NMR spectroscopic analysis, the structure of **3d** was further confirmed by single-crystal X-ray diffraction. When imines **1b**, which have two electron-rich methoxy groups on the aromatic ring, and **1c** and **1d**,

Table 1. Multicomponent synthesis of polysubstituted isoquinolinium and pyridinium salts.[a]



2a: $R^4 = R^5 =$ Ph; **2b**: $R^4 = R^5 =$ Et; **2c**: $R^4 =$ Ph, $R^5 =$ Me; **2d**: $R^4 =$ Ph, $R^5 = CO_2Et$; **2e**: $R^4 = R^5 = CH_2OMe$; **2f**: $R^4 =$ Ph, $R^5 =$ H; **2g**: $R^4 = 4\text{-}FC_6H_4$, $R^5 =$ H; **2h**: $R^4 =$ 3-thiofuryl, $R^5 =$ H; **2i**: $R^4 =$ 1-cyclohexenyl, $R^5 =$ H; **2j**: $R^4 =$ hexyl, $R^5 =$ H; **2k**: $R^4 = R^5 =$ H

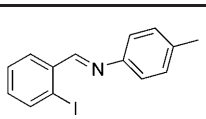
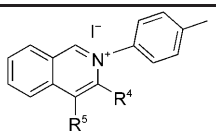
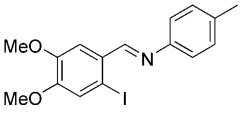
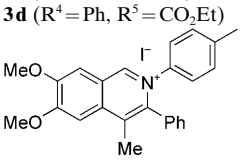
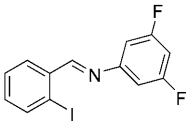
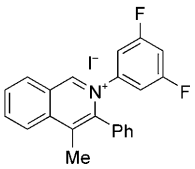
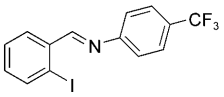
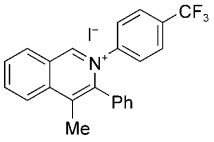
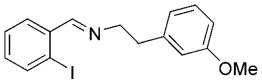
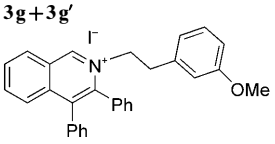
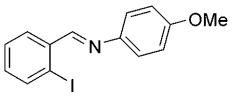
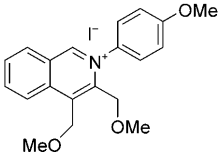
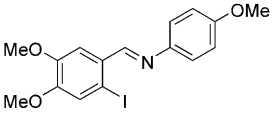
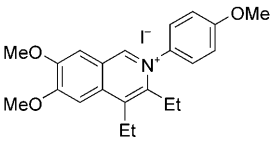
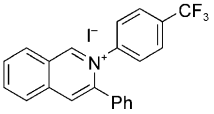
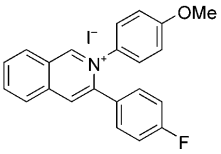
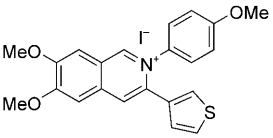
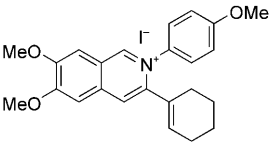
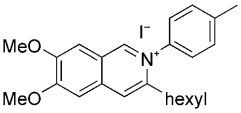
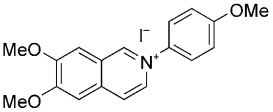
Entry	Imine[b]	2	Product	Yield [%][c,d]
				
1[b]	(**1a**)	**2a**	**3a** ($R^4 = R^5 =$ Ph)	94 (92)[c]
2[b]	**1a** (**1a**)	**2b**	**3b** ($R^4 = R^5 =$ Et)	(91)[c]
3[b]	(**1a**)	**2c**	**3c** ($R^4 =$ Ph, $R^5 =$ Me)	(84)[c]
4[b]	(**1a**)	**2d**	**3d** ($R^4 =$ Ph, $R^5 = CO_2Et$)	(87)[c]
5		**2c**		86:2
	1b		**3e+3e′**	
6[b]		**2c**		(86:4)[c]
	(**1c**)		**3f+3f′**	
7[b]		**2c**		(89:2)[c]
	(**1d**)		**3g+3g′**	
8		**2a**		81
	1e		**3h**	
9		**2e**		94
	1f		**3i**	
10		**2b**		96
	1g		**3j**	

Table 1. (Continued)

Entry	Imine[b]	2	Product	Yield [%][c,d]
11[b]	(**1d**)	**2f**	 **3k**	(95)[c]
12[b]	(**1f**)	**2g**	 **3l**	(98)[c]
13	**1g**	**2h**	 **3m**	96
14	**1g**	**2i**	 **3n+3n′**	92:5
15	**1b**	**2j**	 **3o+3o′**	71:11
16	**1g**	**2k**	 **3p**	78

[a] Reaction conditions: *o*-iodobenzaldimine **1** (0.20 mmol), alkyne **2** (0.25 mmol), acetonitrile (3.0 mL), [Ni(cod)$_2$] (0.011 mmol), and P(*o*-Tol)$_3$ (0.023 mmol) at 80 °C for 1.5 h. [b] The *o*-iodobenzaldimines in parentheses were generated in situ from the corresponding aldehydes (0.20 mmol) and amines (0.20 mmol). [c] Isolated yields. Yields in parentheses are for three-component reactions with aldehydes, amines, and alkynes. [d] No chromatography was necessary for product isolation.

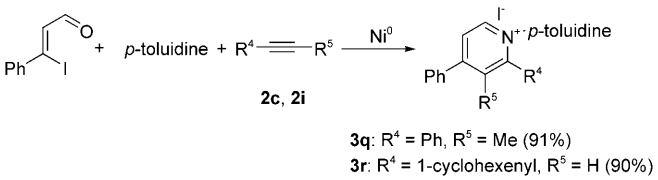
which have electron-withdrawing functionalities over the *N*-substituent, were employed for the reaction with alkyne **2c**, the salts **3e–g** were obtained in excellent yields, along with minor regioisomers **3e′–g′** in approximately 2–4% yield (Table 1, entries 5–7). Imines **1e–g** with different functionalities over the *N*-substituent also efficiently reacted with symmetric alkynes **2a**, **2e**, and **2b**, respectively, to give the expected salts **3h–j** in excellent yield (Table 1, entries 8–10).

The present catalytic reaction can be extended to terminal alkynes. Phenyl acetylene, 4-fluorophenyl acetylene, and 3-thiofuranyl acetylene reacted with **1d**, **1f**, and **1g**, respectively, to give the single regioisomeric products **3k–m** in excellent yield (the yields in parenthesis are for three-component reactions, see Table 1). On the other hand, cyclohexenylethyne and 1-octyne reacted with **1g** and **1b** to afford regioisomers **3n** and **3n′** in 92 and 5% yield and **3o** and **3o′** in 71 and 11% yield, respectively. Acetylene gas (**2k**) also reacted with **1g** to give isoquinolinium salt **3p** in 78% yield.

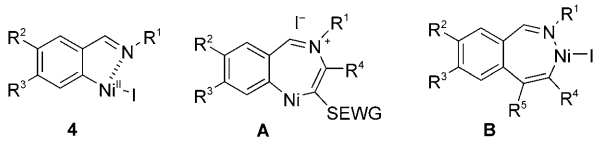
All of these salts are stable at room temperature for several months without decomposition.

The present reaction can also be applied to the synthesis of pyridinium salts. Thus, by treating (*Z*)-3-iodo-3-phenylacrylaldehyde and *p*-toluidine in 1:1 molar ratio with 1-phenylpropyne and 1-cyclohexenylethyne, the pyridinium salts **3q** and **3r** were obtained in yields of 91 and 90%, respectively (Scheme 2).

The reaction likely proceeds via an aza-nickelacycle **4**[7] intermediate obtained by a chelation-assisted oxidative insertion of Ni^0 to the aryl–iodine bond of 2-iodobezaldimine **1**. Then, regioselective alkyne insertion to either the C–Ni[8] or the N–Ni bond and reductive elimination of Ni^{II} leads to the formation of isoquinolinium salt **3** and Ni^0.[3c] There are two possible modes for the insertion reaction of alkynes with **4**. For the insertion of electron-deficient alkynes such as **2d**, the insertion is likely to be into the N–Ni bond through a Michael-type addition (intermediate **A**, SEWG = strong electron-withdrawing group), whereas for alkynes without a strong electron-withdrawing substituent, the insertion is into the C–Ni bond (**B**).[8] In both situations, the aryl substituent on the alkyne is generally next to the nitrogen atom of **3**. For aryl alkynes without strong withdrawing groups, the regiochemistry of the alkyne in the seven-membered azacycle **B** is similar to the five-membered azacycles proposed in the reductive-coupling reaction between imines and alkynes.[8d,e]



Scheme 2. Synthesis of pyridinium salts from (*Z*)-3-iodo-3-phenylacrylaldehyde, *p*-toluidine, and alkyne derivatives.

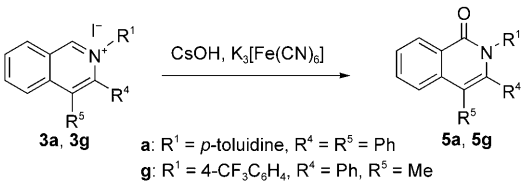


4 A B

Similarly, greater regio-selectivity was observed with terminal aryl alkynes than with internal aryl alkynes.

The nature of the nickel and palladium benzaldimine cyclometalated complexes reflects the difference in catalytic activity between the two metal complexes for the present isoquinolinium salt formation. It is known that nickel complexes are much more susceptible than palladium complexes to ligand-substitution reactions, and thus are also more susceptible to alkyne-coordination and insertion reactions.[9] On the other hand, the high stability and the inertness of the benzaldimine cyclopalladated halo dimer (see Scheme 1) probably explain the fact that palladium complexes do not catalyze the reaction.

An interesting application of the isoquinolinium salts prepared by the above method is the transformation of these salts into isoquinolinones.[1,2,6] Thus, isoquinolinium iodides **3a** and **3g** were converted to **5a** and **5g** in the presence of CsOH and $K_3[Fe(CN)_6]$ in a mixture of CH_3CN, H_2O, and MeOH in yields of 80 and 89%, respectively (Scheme 3),

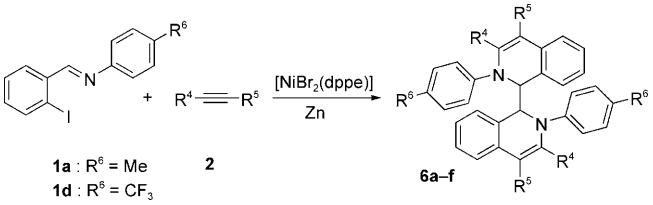


Scheme 3. Synthesis of isoquinolinone derivatives from the corresponding isoquinolinium salts by using CsOH and $K_3[Fe(CN)_6]$.

through a modified reported procedure.[10] The transformation reaction probably involves the addition of a hydroxide ion at the C_1 carbon of the isoquinolinium salt followed by the oxidation of the resulting 1-hydroxy-dihydroisoquinoline species with a ferric cyanide ion.

Another interesting property of isoquinolinium salts **3** is their easy reductive dimerization to give **6** in the presence of zinc powder as the reducing agent (Scheme 4).[11] For example, when **3a** was treated with zinc in acetonitrile at 80°C for 40 min, the corresponding dimer **6a** was obtained in 96% yield. Compound **6a** can also be prepared by treating **1a** with **2a** in the presence of $[NiBr_2(dppe)]$ and Zn at 80°C. No isoquinolinium salt was observed under the reaction conditions, but **6a** was isolated in 93% yield (Table 2,

Table 2. Catalytic synthesis of isoquinoline dimers **6** by using aldimine **1a** and alkynes.[a]

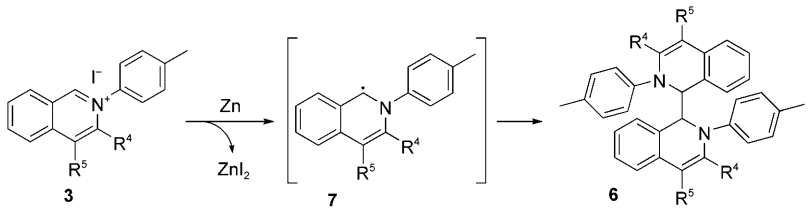


Entry	Imine	2	Product	Yield [%][b]
1	**1a**	Ph—≡—Ph	**6a** ($R^4=R^5=$Ph)	93
2	**1a**	Et—≡—Et	**6b** ($R^4=R^5=$Et)	87
3	**1a**	Ph—≡—Et	**6c** ($R^4=$Ph, $R^5=$Et)	85
4	**1a**	Ph—≡—CO_2Me	**6d** ($R^4=$Ph, $R^5=CO_2$Me)	82
5	**1a**	Me—≡—CO_2Me	**6e** ($R^4=$Me, $R^5=CO_2$Me)	74[c]
6	**1b**	≡—Ph	**6f** ($R^4=$Ph, $R^5=$H)	91

[a] Reaction conditions: *o*-iodobenzaldimine (0.20 mmol), alkyne (0.25 mmol), acetonitrile (3.0 mL), $[NiBr_2(dppe)]$ (0.011 mmol), and Zn (0.60 mmol) at 80°C for 1.5 h. [b] Isolated yields. [c] A mixture of regioisomers was isolated.

entry 1). We think that isoquinolinium salt **3a** was formed during the catalytic reaction, but was then quickly reduced to dimer **6a**. In a similar manner, symmetrical (**2b**), unsymmetrical (**2l**, **2m**, and **2n**), and terminal alkynes (**2f**) reacted with **1a** and **1b** to afford the corresponding dimers **6b–f** in good to excellent yields (Table 2, entries 2–6). Based on the ^{1}H NMR spectroscopy data, products **6a–f** consist of a mixture of *meso* and D,L isomers with a ratio of these diastereomers of approximately 2:1. The structure of the *meso* diastereoisomers of **6d** and **6e** were further verified by single-crystal X-ray diffraction. In all of the mass spectra of **6**, the corresponding molecular ions did not appear, but only the ions with mass values equivalent to the monomeric form **7** were observed.

In conclusion, we have demonstrated for the first time a general method for the synthesis of *N*-aryl and *N*-alkyl isoquinolinium salts by using readily available starting materials. A vast number of functionalities can be introduced to the salts. The application of this methodology is illustrated by the facile transformation of the salts to other structures such as isoquinolinones **5** and reductive dimerization products **6**. Isoquinolinone is an important core structure for a vast number of natural products. Application of this methodology in the total synthesis



Scheme 4. Mechanism for the formation of isoquinoline dimer **6**.

of isoquinolinone-based natural products is in progress.

Experimental Section

Procedure for the preparation of isoquinolinium salt 3a: A screw-cap sealed tube fitted with a septum containing 2-iodobenzaldehyde (0.20 mmol) and *p*-toluidine (0.20 mmol) was evacuated and purged with nitrogen gas three times. The tube was charged with $[Ni(cod)_2]$ (0.011 mmol, 3.0 mg) and P(*o*-Tol)$_3$ (0.023 mmol, 7.0 mg) inside a glove box. The tube was then kept under an atmosphere of nitrogen on a dual-manifold Schlenk line. Alkyne **2a** (0.25 mmol) was dissolved in acetonitrile (3.0 mL) and was added to the stirred mixture through a syringe. The septum was quickly exchanged for a screw cap and the reaction mixture was stirred at 80 °C for 1.5 h. At the end of the reaction, the reaction mixture was diluted with CH_2Cl_2 and then filtered through a silica-gel pad by using methanol as the eluent (~20 mL). The combined filtrate was concentrated in vacuo and the residue was carefully washed with ethyl acetate and hexane to afford the desired pure product **3a** in 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.19$ (s, 3H), 6.94 (d, $J = 7.5$ Hz, 2H), 6.97 (d, $J = 6.5$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 2H), 7.11 (d, 7.0 Hz, 2H), 7.22–7.24 (m, 5H), 7.52 (d, $J = 7.5$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.87 (t, $J = 7.0$ Hz, 1H), 7.97 (t, $J = 7.5$ Hz, 1H), 8.77 (d, $J = 7.5$ Hz, 1H), 10.16 ppm (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 21.0$, 126.3, 126.4, 126.8, 127.6, 128.1, 128.4, 128.9, 129.7, 130.1, 130.8, 130.9, 131.1, 131.7, 133.0, 137.4, 138.6, 139.1, 139.4, 140.4, 144.1, 149.8 ppm; IR (KBr): $\tilde{\nu} = 1250$, 1440, 1718, 2933, 2959 cm^{-1}.

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