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Hypervalent Iodine in Synthesis XL: First Example of Palladium-Catalyzed Coupling Reaction of 1- Hydroxy-1,2-benziodoxol-3(1*H*)-One with Arylboronic Acids and Arylborates

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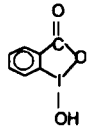
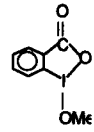
Abstact: Biaryl-2-carboxylic acids have been prepared by palladium-catalyzed coupling reaction of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one with arylboronic acids and arylborates with good yields under mild conditions.

Although hypervalent iodine compounds have been caused focus in organic synthesis recently[1] , heterocyclic iodanes are species which are involved in fewer research. Among all kinds of heterocyclic iodanes, 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (I) is the most important and best investigated one.



(I)



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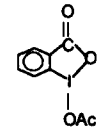

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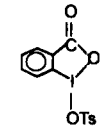

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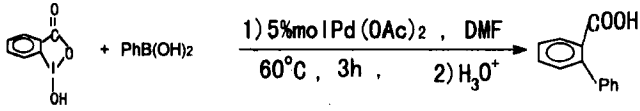
To whom the correspondence should be addressed

Normally, it carry out reactions at I-O bond on the heterocycle and I-O bond outside of the heterocycle, such as the cleavage of phosphates and reactive esters[2] ; as the source to produce other heterocyclic iodane derivatives which can undergo reactions further[3]; reaction with silylate acetylene in the presence of $BF_3{\cdot}Et_2O$ [4] , preparation of *tert*-butylperoxyiodoxol by treatment with *tert*-butyl hydroperoxide which can be used as strong oxidizer toward a variety of organic substrates[5], reaction with trimethylsilyl azide to form azidoiodanes[6] , treatment with cyanotrimethylsilane to produce cyanobenziodoxol which can be served as efficient cyanating reagent[7] , reaction with silaalkynes to provide the sable heterocyclic alkynyliodonium salts[8] , and so on. Recently, Kang and co-workers reported that [hydroxy(tosyloxy)iodo]benzene, i.e.PhI(OH)OTs, could be served as a good substrate to carry out the cross-coupling reaction with organic-boro compounds smoothly to give excellent yields of biaryls under mild conditions[9] . Since structurally, 1-hydroxy-1,2-benziodoxol-3(1*H*)-one(I) is the cyclic analogue to [hydroxy(tosyloxy)iodo]benzene, we proposed that the palladium-catalyzed cross-coupling reaction of (I) with arylboronic acids and arylborates would be realized. To our knowledgement, there has been no report on this aspect [10] .

At first , we took (I) with phenylboronic acid as the sample into investigation. (Scheme I) The reaction was carried out in DMF at 60°C for 3 hours with 5%mol $Pd(OAc)_2$. After acidification and work-up , we gained the expected product of biphenyl-2-carboxylic acid with 83% yield.

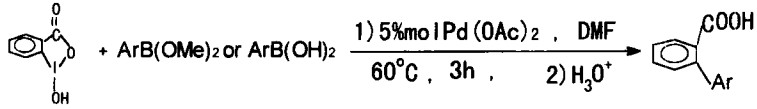


(I)

(Scheme I)

The ligands had obvious effect on the reaction because different derivatives of (I) appeared to have reactivity to different extent . As for the derivatives of 1-hydroxy(I), 1-methoxy(II), 1-acetoxy(III) and 1-tosyloxy-1,2-benziodoxol-3(1*H*)-one(IV) , the order of their reactivity was that OH . OMe > OAc >> OTs . The reaction took place at 60°C for 3 hours with 83% yield , at 60°C for 3 hours with 78% yield and at 60°C for 6 hours with 52% yield , corresponding to OH, OMe, and OAc respectively. When it came to 1-tosyloxy - 1,2-benziodoxol-3(1*H*)-one , the reaction was carried out at 80°C for 7 hours without the expected product of biphenyl-2-carboxylic acid , only recycling the starting substrate almost quantitatively.

We extended the reaction to other arylboronic acids (Scheme 2) . The reaction was smoothly carried out in the same conditions to offer the expected products with good yields (Table 1) .



Ar= Ph, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *o*-$CH_3OC_6H_4$, *o*-$CH_3C_6H_4$, *p*-ClC_6H_4, 1-naphthyl

(Scheme II)

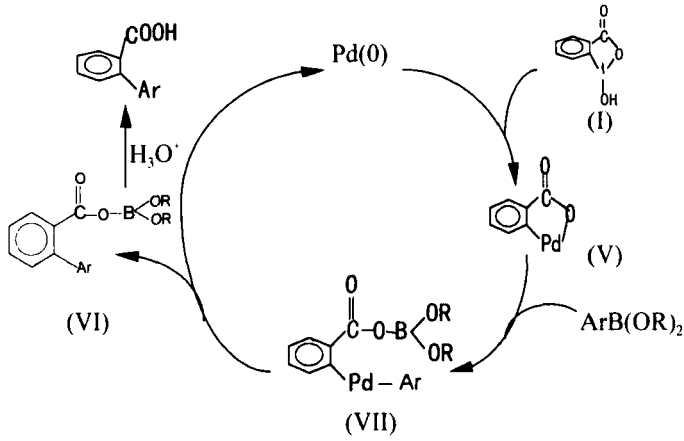
As shown in the Table 1 , the yields could decrease in the cases when arylboronic acids bore *ortho-* groups. The reason lay in the fact that the existence of *orth-* groups world come up with the steric hindrance during the oxidation-addition step. Apart from arylboronic acids, arylborates could also undergo the reaction under the same conditions with good yields. As we know, Suzuki-type palladium-catalyzed coupling reactions need an added base to make sure the completion of the reactions[12]. In our case, however, added base was unnecessary become carboxylic group took the role of internal base to continue the reaction. Once we put a few drops of diluted hydrochloric acid into the reactive mixture, there was no reaction taken place and expected products could not be obtained.

Table 1. Palladium-Catalyzed Coupling Reaction of 1-Hydroxy-1,2-benziodoxol- 3(1*H*)-one with Arylboronic Acids and Arylborates [a]

Entry	$ArB(OR)_2$	Product	Yield(%)[b]
1	$PhB(OH)_2$	Biphenyl-2-carboxylic Acid	83
2	*p*-$CH_3C_6H_4B(OH)_2$	4'-Methylbiphenyl-2-carboxylic Acid	80
3	*o*-$CH_3OC_6H_4B(OH)_2$	2'-Methoxybiphenyl-2-carboxylic Acid	67
4	*o*-$CH_3C_6H_4B(OH)_2$	2'-Methylbiphenyl-2-carboxylic Acid	72
5	*p*-Cl $C_6H_4B(OH)_2$	4'-Chlorobiphenyl-2-carboxylic Acid	79
6	α-$C_{10}H_7B(OH)_2$	2-(1-Naphthyl)-benzoic Acid	63
7	*p*-$CH_3OC_6H_4B(OH)_2$	4'-Methoxybiphenyl-2-carboxylic Acid	87
8	$PhB(OMe)_2$	Biphenyl-2-carboxylic Acid	81
9	*p*-$CH_3C_6H_4B(OMe)_2$	4'-Methylbiphenyl-2-carboxylic Acid	80
10	*o*-$CH_3OC_6H_4B(OMe)_2$	2'-Methoxybiphenyl-2-carboxylic Acid	65

a. The reaction as carried out with 1mmol arylboronic acid or arylborate, 1.2 mmol 1-hydroxy-1,2- benziodoxol- 3(1*H*)-one and 5% mol $Pd(OAc)_2$ in 10 ml DMF at 60°C for 3 hours; b. Isolated yields

We assumed the mechanism of the reaction might be as the following : Firstly , $Pd(OAc)_2$ was reduced to complexible Pd (0) species , then the oxidation-addition took place at C-I bond on the heterocycle to form the five-member palladium intermediate (V) . Thus , the cross-coupling reaction was carried out between the intermediate(V) and arylboronic acid/arylborate to give the intermediate (VII) which took place reductive elimnation to offer the intermediate(VI) and to regenerate Pd(0). Then, the product of biaryl-2-carboxylic acid was obtained by acidification of the intermediate(VI).



In summary, we report the first example of palladium-catalyzed coupling reaction of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one with arylboronic acids and arylborates to give biaryl-2-carboxylic acids with good yields under mild conditions so as to extend the application of hypervalent iodine compounds in organic synthesis. Our reaction shows 1-hydroxy-1,2-benziodoxol-3(1*H*)-one is an useful *o*-carboxylphenyl cation synthon and its application in other aspects of synthesis will be reported in due course.

Experimental Section:

General Procedure for the preparation of biaryl-2-carboxylic acids:

Under N_2 , added 10ml DMF to the mixture of 1mmol arylboronic acid or arylborate,1.2mmol 1-hydroxy-1,2-benziodoxol-3(1*H*)-one and 5%mol $Pd(OAc)_2$. The resulting mixture was stirred at 60°C for 3 hours . After cooling to room temperature , 10ml 10% HCl was added to acidify the solution. The organic layer was washed with 10ml water after extracting with 2×5 ml ether . The ether layer

was dried over anhydrous $MgSO_4$, then removed the solvent to give the residue which was purified by TLC (silicon gel) with *n*-hexane/EtOAc (2:1) as developer to provide the product which was recrystallized from appropriate solvent.

entry 1 and entry 8: m.p. 107-109°C (recrystallized from aq. EtOH) Lit. m.p.[12] 112°C ^{1}H-NMR(60Hz,$CDCl_3$/ppm) 7.23(s,8H), 7.72(m,1H), 11.20(s,1H) I.R.(KBr/cm^{-1}) 3400-2400 (br), 1700,1600, 1450, 1300, 930, 800, 775, 750, 700, 650

entry 2 and entry 9: m.p. 146-148°C (recrystallized from benzene) Lit. m.p. [13]147-149°C ^{1}H-NMR(60Hz, $CDCl_3$/ppm) 2.39(s,3H), 7.17-7.94(m,8H), 11.20(s,1H) I.R.(KBr/cm^{-1}) 3350-2450(br),1700, 1605, 1440, 1300, 930, 835, 750

entry 3 and entry10: m.p. 149-152°C (recrystallized from aq. EtOH) Lit. m.p.[14] 150-152°C ^{1}H-NMR(60Hz,$CDCl_3$/ppm)3.66(s,3H),6.70-8.00(m,8H),11.30(m,1H) I.R.(KBr/cm^{-1}) 3330-2450(br), 1705, 1600, 1450, 1305, 1250, 1120, 930, 750

entry 4: m.p. 100-102°C(recrystallized from aq. MeOH) Lit. m.p.[15] 104-105°C ^{1}H-NMR(60Hz, $CDCl_3$/ppm) 2.38(s,3H), 7.15-8.05(m,8H), 11.30(s,1H) I.R.(KBr/cm^{-1}) 3350-2500(br), 1700, 1600, 1440, 1300, 930, 750

entry 5: m.p. 163-165°C (recrystallized from aq. EtOH) Lit. m.p. [16]165-166°C ^{1}H-NMR(60Hz, $CDCl_3$/ppm) 7.00-8.15(m,8H), 11.35(s,1H) I.R.(KBr/cm^{-1}) 3300-2500(br) , 1705, 1600, 1430, 1305, 930, 830, 750

entry 6: m.p. 157-158°C (recrystallized from aq. EtOH) Lit. m.p.[17] 161°C ^{1}H-NMR(60Hz, $CDCl_3$/ppm) 7.21-8.23(m,11H),11.30(s,1H) I.R.(KBr/cm^{-1}) 3400-2500(br), 1705, 1605, 1440, 1300, 930, 790, 770, 750

entry 7: m.p. 202-204°C (recrystallized from aq. EtOH) Lit. m.p.[18] 206°C ^{1}H-NMR(60Hz, $CDCl_3$/ppm) 3.70(s,3H), 6.64-8.05(m,8H), 11.33(s,1H) I.R.(KBr/cm^{-1}) 3300-2500(br), 1700, 1600, 1430, 1350, 1250, 1125, 930, 830, 750

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