# REACTIONS OF TERMINAL ACETYLENES WITH ARYL IODIDES CATALYZED BY PALLADIUM COMPLEXES UNDER INTERFACIAL CONDITIONS

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The reaction of aryl iodides with Cu acetylenides [1, 2] and with terminal acetylenes in the presence of $K_2CO_3$, CuI [3, 4], or powdered Cu [5] occurs under severe conditons (boiling in pyridine or dimethylformamide (DMF) for 6-16 h). In the presence of additions of halo-Pd complexes, cross-coupling of Cu acetylenides with aryl iodides could be carried out under extremely mild conditons (20°C for 0.3-3 h) with quantitative yields [6]. An analogous effect was observed in reactions of terminal acetylenes with aryl iodides in the presence of bases and CuI with the addition of Pd complexes [7]. Secondary or tertiary amines, which simultaneously act as a solvent, are usually used as the base [8-11]. Previously we showed that these reactions can be carried out in $C_6H_6$, $CHCl_3$, DMF, or tetrahydrofuran (THF) in the presence of 1.5-2 equivalents of the amine [12, 13]. Reactions of terminal acetylenes with aryl, vinyl, and heteryl halides [14, 15] were also carried out in the interfacial system $C_6H_6$—aqueous alkali—$PhCH_2\overset{+}{N}Et_3Cl^-$ in the presence of Pd complexes and CuI additions.

We studied the possibility of using in these reactions solid bases (alkali or potash) in the interfacial system solid base—liquid organic phase. It was shown that phenylacetylene (I) does not react with p-nitroiodobenzene (II) in the presence of powdered alkali and a Pd complex in THF. However, when 10 mole % 18-crown-6 was added to the reaction mixture, p-nitrotolan (III) was formed in quantitative yield, even in the absence of CuI, in 3 h.

$$\mathrm{PhC{\equiv}CH} + p\text{-}\mathrm{NO_2C_6H_4} \xrightarrow[\text{18-crown-6, THF, 20°, 3 h}]{\mathrm{PhPdI(PPh_3)_2,\ NaOH_{so}}} \underset{\text{(III)}\quad 100\%}{p\text{-}\mathrm{NO_2C_6H_4C{\equiv}CPh}} \qquad (1)$$

In going to aryl iodides containing substituents that were less electron-accepting, the reaction rate decreased significantly. For example, whereas the reaction of (I) with p-iodobenzonitrile under the conditions of (1) afforded 71% p-cyanotolan in 9 h, under the same conditons p-chloroiodobenzene gave only 23% p-chlorotolan (Table 1). We should note the high selectivity of these reactions even in the case of p-carbomethoxyiodobenzene, containing a $CO_2Me$ group sensitive to the effect of the alkali.

The duration of reaction (1) could be halved by adding 1 mole % CuI (Table 1). Under these conditons, $C_6H_6$ could be used as the solvent instead of THF.

Arylation of the terminal acetylenes could also be carried out with potash as the base. For example, in the reaction of (I) with (II) in the presence of 5 equivalents of $K_2CO_3$, 1 mole % CuI, and $PdCl_2(PPh_3)_2$ and also an interfacial catalyst (10 mole % 18-crown-6 and 10 mole % $Bu_4NBr$) in DMF, (III) was formed in nearly quantitative yield.

$$\mathrm{PhC{\equiv}CH} + p\text{-}\mathrm{NO_2C_6H_4I} \xrightarrow[\substack{\text{18-crown-6, Bu}_4\text{NBr, DMF} \\ \text{50°, 1.5 h}}]{\mathrm{PdCl_2(PPh_3)_2,\ K_2CO_3,\ CuI}} \underset{95\%}{\text{(III)}} \qquad (2)$$

The reaction was significantly accelerated when the amount of CuI was increased to 10 mole % (Table 2). Reaction (2) occurred somewhat slower in THF than in DMF.

It was shown that in the absence of an interfacial transfer agent in the reaction of $K_2CO_3$ with a mixture of (I) and CuI (1:1) in DMF, copper phenylacetylenide was formed in 85% yield in 1 h.

$$\mathrm{PhC{\equiv}CH} + \mathrm{CuI} \xrightarrow[\text{DMF, 20°, 1h}]{\mathrm{K_2CO_3}\text{ (2 eq.)}} \underset{85\%}{\mathrm{PhC{\equiv}CCu}\downarrow} \qquad (3)$$

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TABLE 1. Reactions of PhC≡CH with ArI Catalyzed by 1 Mole % $PhPdI(PPh_3)_2$ in the Presence of Solid NaOH (10 equivalents), 18-Crown-6 (10 Mole %), 20°C, and $C_0$ = 0.25 M

| ArI | Solvent | Time, h | ArI conversion, % | Product | Yield, %[a] |
|---|---|---|---|---|---|
| p-$NO_2C_6H_4$ | $C_6H_6$[b] | 2 | 2 | p-$NO_2C_6H_4C≡CPh$ | 0 |
| » | $C_6H_6$[b,c] | 1 | 1 | Ditto | 0 |
| » | THF | 3 | 100 | » | 100 |
| » | THF[c] | 1,5 | 100 | » | 95 |
| » | $C_6H_6$[c] | 3 | 91 | » | 90 |
| p-$CNC_6H_4I$ | THF | 9 | 76 | p-$CNC_6H_4C≡CPh$ | 71 |
| p-$MeO_2CC_6H_4I$ | Ditto | 9 | 40 | p-$MeO_2CC_6H_4C≡CPh$ | 37 |
| p-$ClC_6H_4I$ | » | 9 | 23 | p-$ClC_6H_4C≡CPh$ | 21 |
| PhI | » | 9 | – | PhC≡CPh | 41 |
| p-$MeOC_6H_4I$ | » | 9 | 20 | p-$MeOC_6H_4C≡CPh$ | 19 |

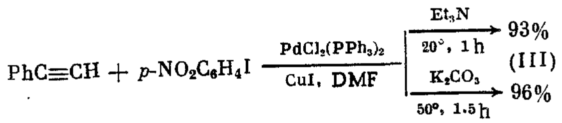
[a] The yield was determined by thin-layer chromatography and UV spectroscopy.
[b] In the absence of 18-crown-6.
[c] In the presence of CuI (1 mole %).

TABLE 2. Reactions of PhC≡CH with ArI Catalyzed by 1 Mole % $PdCl_2(PPh_3)_2$ in DMF in the Presence of $K_2CO_3$ (5 equivalents) and CuI (10 mole %), 50°C, $C_0$ = 0.25 M

| ArI | Time, h | Yield, % | | Yield, %[a] | |
|---|---|---|---|---|---|
| | | PhC≡CAr | ArI | PhC≡CAr | ArI |
| p-$NO_2C_6H_4I$ | 40 min[b] | | | 92 | 8 |
| Ditto | 1.5[b] | 96 | 0 | 95 | 0 |
| » | 0,3 | | | 100 | 0 |
| » | 1.5[b,c] | | | 45 | 53 |
| p-$CNC_6H_4I$ | 0.5 | 82 | 16 | 80 | 0 |
| p-$ClC_6H_4I$ | 0.5 | | | 60 | 33 |
| PhI | 1.5 | | | 60 | – |
| p-$MeOC_6H_4I$ | 1,5 | 35 | 63 | 40 | 43 |

[a] In the presence of 18-crown-6 (10 mole %) and $Bu_4NBr$ (10 mole %).
[b] In the presence of 1 mole % CuI.
[c] In THF, 25°C.

Under these conditions (5 equivalents of $K_2CO_3$, 10 mole % CuI, DMF, 50°C) the reaction of (II) with ArI catalyzed by $PdCl_2(PPh_3)_2$ occurred at the same rate as in the presence of the interfacial catalyst (Table 2), but the selectivity of these reactions was somewhat higher (the conversion of aryl iodide was approximately equal to the yield of the corresponding tolan). A comparison of the results obtained when $Et_3N$ [12] and potash were used as the base showed that reactions of terminal acetylenes with aryl iodides catalyzed by Pd complexes can be carried out successfully in the presence of available $K_2CO_3$ with slight heating. For example, the reaction of (I) with (II) catalyzed by 1 mole % $PdCl_2(PPh_3)_2$ and CuI in the presence of 2 equivalents of $Et_3N$ gave 93% (III) in 1 h, and in the presence of 5 equivalents of $K_2CO_3$ the yield of (III) was 96% in 1.5 h.



$$PhC{\equiv}CH + p\text{-}NO_2C_6H_4I \xrightarrow[\text{CuI, DMF}]{PdCl_2(PPh_3)_2} \left| \begin{array}{l} \xrightarrow[20°,\ 1\,h]{Et_3N} 93\% \\ \qquad\qquad (III) \\ \xrightarrow[50°,\ 1.5\,h]{K_2CO_3} 96\% \end{array} \right. \qquad (4)$$

In going from (II) to p-iodoanisole, we observed the decrease in the reactivity of aryl iodides which is usual for these reactions (Table 2).

## EXPERIMENTAL

<u>Reactions of (I) with ArI in the Presence of NaOH and $PhPdI(PPh_3)_2$.</u> Into a two-necked flask equipped with a magnetic stirring device were placed 2 ml of THF, 0.051 g (0.5

mmole) of (I), 0.115 g (0.5 mmole) of p-$CNC_6H_4I$, 0.20 g (5 mmoles) of powdered NaOH, 13 mg (0.05 mmole) of 18-crown-6, and 4.2 mg (0.005 mmole) of $PhPdI(PPh_3)_2$. The reaction was carried out at ~ 20°C in an Ar atmosphere. After 9 h, the yields of p-cyanotolan (71%) and p-iodobenzonitrile (24%) were determined by thin-layer chromatography on Silufol UF-254 UV spectroscopy.

Reactions of (I) with ArI in the Presence of $K_2CO_3$, CuI, and $PdCl_2(PPh_3)_2$. Into a thermostated vessel filled with Ar were placed successively 0.1245 g (0.5 mmole) of (II), 0.345 g (2.5 mmoles) of freshly calcined $K_2CO_3$, 16.1 mg (0.05 mmole) of $Bu_4NBr$, 13.2 mg (0.05 mmole) of 18-crown-6, 2 ml of DMFA, 0.06 ml (0.55 mmole) of (I), and then 3.5 mg (0.005 mmole) of $PdCl_2(PPh_3)_2$ and 9 mg (0.05 mmole) of CuI. The reaction was carried out with stirring at 50°C in an argon atmosphere. After 40 min, the yield of (III) was determined as 92% by thin-layer chromatography and UV spectroscopy.

## CONCLUSIONS

It was shown that in reactions of aryl iodides with terminal acetylenes catalyzed by palladium complexes, potash or alkali can be used as a base in the interfacial system.

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