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Homocoupling of Substituted Benzenes to Symmetrical Biaryls with Mercury(II) in the Presence of Cerium(IV)†

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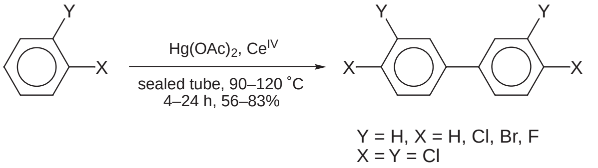
Homocoupling of substituted benzenes to symmetrical biaryls is achieved with different cerium(IV) compounds such as cerium(IV) triethylammonium nitrate (CTEAN), cerium(IV) pyridinium nitrate (CPN) and $Ce(OTf)_4$ in the presence of Hg^{II} in good to high yields.

Carbon–carbon bond formation through coupling of aromatic compounds encounters problems which are familiar to many organic chemists.[1] Biaryls, especially functionalized symmetrical biaryls, have found interesting applications as precursors of rigid liquid crystals[2] and as semiconducting complexes.[3] In addition to the classical methods for homocoupling of arenes,[1,4–6] modified methods using compounds of Tl^{III},[7] Pd^{II}[1,7b,8a] and N^{II}[9] have been widely reported. Homocoupling of organomercuryII[8b] and bismuths[8c] by Pd^{II} and Ni^{II} under reducing conditions[10,11] and desulfonylative homocoupling of arenesulfonyl chlorides[12] by Pd^{II} in the presence of an excess of Ti^{IV} were also reported.

Recently, catalytic oxidative homocoupling of organostannans,[13] and organolead[14] having electron donating groups (*e.g.* Me, MeO) to biaryls with $Pd^{(II)}$ and also cross-coupling of organolead and organoboranes[15] have been reported. These methods have not been applied for the synthesis of biaryls substituted with halides. Another problem encountered with these later methods[13–15] is that the organometallic compounds should be prepared first and then in a separate reaction converted into their coupled products.

Since Ce^{IV}[16] has been widely used for oxidation of organic compounds, we studied the possibility of using its compounds such as cerium(IV) triethylammonium nitrate (CTEAN),[17] cerium(IV) pyridinium nitrate (CPN)[18] and $Ce(OTf)_4$[19] for the coupling reaction of different substituted benzenes in the presence of mercury(II) salts (Scheme 1).



Scheme 1

The coupling reaction of toluene was studied in the presence of an equimolar amount of $Hg(OTf)_2$ or $Hg(OAc)_2$ and different cerium(IV) compounds using toluene as both reagent and solvent under reflux conditions, or using equimolar amounts of toluene in a sealed tube at 100 °C. The results obtained are presented in Table 1.

Comparison of the results shows that combination of CPN and $Hg(OAc)_2$ in sealed tube gives the best yield and the lowest reaction time for the formation of 4,4′-bitolyl in the above mentioned reactions. GC and NMR analysis of the crude reaction mixture showed also the formation of the 2,2′ isomer in 10–12% yield together with a mixture of other isomers in 4–5% yields. The formation of different regioisomers is also reported for the mercuriation of toluene with $Hg(OAc)_2$ under different acidic conditions.[20].

We also studied this reaction with benzene, chloro-, bromo-, fluoro- and 1,2-dichlorobenzene using equimolar amounts of different cerium(IV) compounds and $Hg(OAc)_2$ in sealed tubes. The results are shown in Table 2. The reaction times for the coupling of arenes carrying halogens are longer than those observed for benzene and toluene, but the process is regioselective and only 4,4′-isomers were obtained after purification.

The formation of biaryls in these reactions could occur through the formation of biarylmercury followed with the subsequent coupling reaction in the presence of Ce^{IV}. In order to have some evidence in support of this proposal, we performed a reaction between biphenylmercury and CPN in a sealed tube at 90 °C for 4 h. The corresponding

Table 1 Coupling of toluene to bitolyl with different mercury(II) and cerium(IV) salts

$Ce^{IV\,a}$	Hg^{II}	Conditions	t/h	Yield(%)[b]
CPN	$Hg(OTf)_2$	Reflux	24	74
CTEAN	$Hg(OTf)_2$	Reflux	24	60
$Ce(OTf)_4$	$Hg(OTf)_2$	Reflux	24	40
CPN	$Hg(OAc)_2$	Reflux	24	78
CTEAN	$Hg(OAc)_2$	Reflux	24	65
$Ce(OTf)_2$	$Hg(OAc)_2$	Reflux	24	50
CPN	$Hg(OAc)_2$	Seald, 100 °C	4	80
CTEAN	$Hg(OAc)_2$	Seald, 100 °C	4	77
$Ce(OTf)_2$	$Hg(OAc)_2$	Seald, 100 °C	4	70

[a] CPN = $Ce(NO_3)_6(C_5H_5NH)_2$, CTEAN = $Ce(NO_3)_6[(C_2H_5)_3NH)]_2$.
[b] Yield refers to isolated product. In the case of those reactions in which toluene is used as solvent, the yield is based on $Hg(OAc)_2$.

Table 2 Coupling of arenes to biaryls with equimolar amounts of $Hg(OAc)_2$ and cerium(IV) salts in sealed tubes

Arene	$Ce^{IV\,a}$	T/°C	t/h	Yield(%)[b]
Benzene	CPN	90	4	65
Benzene	$Ce(OTf)_4$	90	4	70
Chlorobenzene	CPN	110	10	65
Chlorobenzene	$Ce(OTf)_4$	110	10	83
Bromobenzene	$Ce(OTf)_4$	110	10	70
Bromobenzene	CPN	110	10	78
Fluorobenzene	$Ce(OTf)_4$	110	24	46
Fluorobenzene	CPN	110	24	58
1,2-Dichlorobenzene	$Ce(OTf)_4$	110	24	50
1,2-Dichlorobenzene	CPN	110	24	68

[a] CPN = $Ce(NO_3)_6(C_5H_5NH)_2$, CTEAN = $Ce(NO_3)_6[(C_2H_5)_3NH)]_2$.
[b] Yield refers to isolated product after purification.

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biphenyl was obtained from this reaction. This observation shows the possibility of formation of biarylmercury during the reaction.

Experimental

Products were characterised by comparison of their physical data with those of known samples. All yields refer to isolated products. IR spectra were recorded on Perkin-Elmer 781 and Pye Unicam 8725 spectrometers and NMR spectra on a Bruker DPX 250.

Coupling of Toluene with $Hg(OAc)_2$ *and CPN: Typical Procedure.*—A sealed tube containing 1 mmol of toluene, 1 mmol of $Hg(OAc)_2$, and 1 mmol of CPN was heated at 100 °C for 4 h in an oil-bath. After cooling the tube, it was opened and chloroform was added. The reaction mixture was washed with water several times to remove any pyridine and pyridinium acetate which are formed during the reaction. The organic solution was dried with Na_2SO_4 and evaporated. Chromatography of the crude product on silica gel eluted with *n*-hexane–CH_2Cl_2 (6 : 1) gave the pure bitolyl in 80% yield, mp 122 °C (lit.,[7b] 123–124 °C).

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