ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 11, pp. 1683–1689. © Pleiades Publishing, Inc. 2006.
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Urea as Ammonia Equivalent in Aryl Halides Amination Catalyzed by Palladium Complexes

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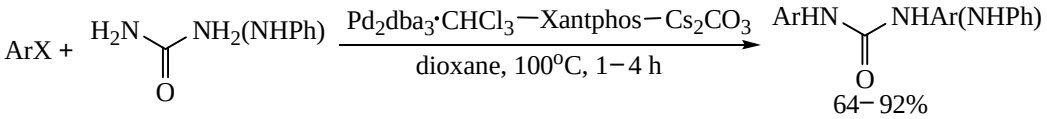
Received March 9, 2006

Abstract—Urea reaction with nonactivated aryl bromides and chlorides under catalysis with palladium complexes led to the formation in 65–95% yield of triarylamines from *para*- and *meta*-substituted aryl halides and of diarylamines from *ortho*-isomers.

DOI: 10.1134/S1070428006110133

Reactions catalyzed by palladium complexes are nowadays extensively exploited in the aryl halides amination (Buchwald–Hartwig reaction). However, the existing procedure has no direct approach to the synthesis of primary aromatic amines. Therefore a number of nitrogen-containing compounds was introduced as ammonia equivalent in order to solve the problem of primary aryl amines preparation (benzophenone imine, hexamethyldisilazane salts, allyl- and diallylamines, complexes formed *in situ* from molecular nitrogen and a system Ti(OPr-*i*)$_3$–Me$_3$SiCl–Li) [2–9]. The synthesis of secondary and tertiary aromatic amines by Pd-catalyzed reactions is already well developed now [1]. However, according to our information the only known method for one-step preparation of symmetrical di- and triarylamines directly from aryl halides is arylation of lithium amide. Therewith the *meta*- and *para*-substituted aryl halides led to the formation of triarylamines (75–82%), the *ortho*-substituted aryl halides gave diarylamines (86–95%) [8].

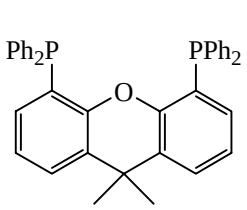
We have developed a new convenient method for preparation of symmetrical di- and triarylamines using as ammonia equivalent a cheap and available reagent, namely, urea. In previous studies we developed an efficient method of synthesis of *N*,*N*'-diaryl- and *N*-aryl-*N*'-phenylureas by reaction of aryl halides with urea and phenylurea in the presence of a system Pd$_2$dba$_3$·CHCl$_3$–Xantphos–Cs$_2$CO$_3$ in dioxane.



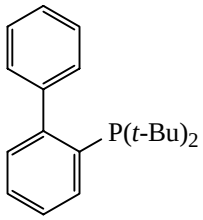
X = I, Br.

However, the applicability of this procedure did not go beyond aryl halides containing electron-withdrawing groups [10]. The problem of using nonactivated aryl bromides in the palladium-catalyzed urea arylation was partly solved by employing a ligand based on Xantphos with thrifluoromethyl substituents in phenyl groups [11]. Yet the way of activating aryl chlorides and deactivated aryl bromides under the said conditions remained unsettled.

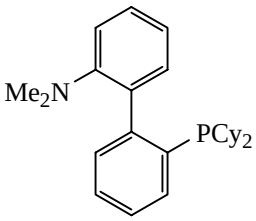
We attemptet to vary bases and ligand by an example of reaction between *p*-bromotoluene and urea. In the presence of the catalytic system Pd$_2$dba$_3$·CHCl$_3$–Xantphos–Cs$_2$CO$_3$ in dioxane the conversion of *p*-bromotoluene in this reaction reached 62%, but the yield of *N*,*N*'-ditolylurea was only 7%[10]. On replacing Xantphos with bulky alkylphosphines L_1, L_2, and *t*-Bu$_3$P we attained the complete conversion of the *p*-bromotoluene in the reaction (Table 1), but it turned out that the process took quite other direction and resulted in formation of di- and triarylamines. The quantitative conversion of *p*-bromotoluene was obtained only at the use of *t*-BuOK, weaker bases (Cs$_2$CO$_3$, *t*-BuONa) were much less efficient.



Xantphos



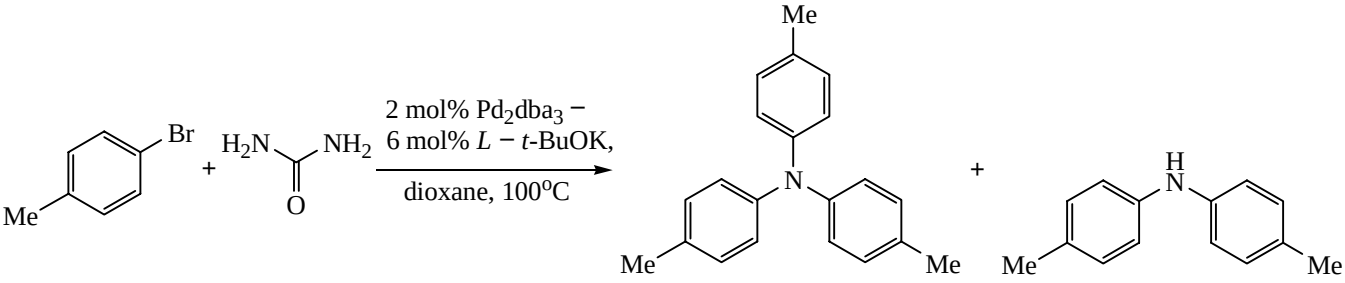
L_1



L_2

The analysis of the products obtained under these conditions from urea and *p*-bromotoluene showed that in the presence of ligands L_1 and L_2 formed a mixture of di- and triarylamines with the latter prevailing in the case of ligand L_2, and only at the use of *t*-Bu_3P was selectively generated tri-*p*-tolylamine in 80% yield (Table 2, runs nos. *1*–*3*).

The conditions developed (2 mol% $Pd_2dba_3 \cdot CHCl_3$, 6 mol% *t*-Bu_3P, *t*-BuOK, dioxane) were exploited for preparation of triarylamines from various aryl bromides and urea. As seen from Table 2, application of aryl halides containing electron-donor substituents in the *meta*- and *para*-position of the phenyl ring led to the formation of triarylamines in high yields. For instance, the amination



of bromobenzene, *p*- and *m*-bromotoluenes occurred with 80–85% yields (runs nos. *3*, *4*, and *6*), somewhat lower yield of the product was obtained from the less active *p*-bromoanisole (65%) (run no. *5*).

We demonstrated that these conditions are also suitable for amination of aryl chlorides. On reacting urea with chlorobenzene and *p*-chlorotoluene triarylamines were obtained in 80–95% yields (Table 2, runs nos. *7*–*9*). Note that the reactions with aryl chlorides are significantly slower than with aryl bromides, but the yields of products are comparable or even higher (cf. runs nos. *3*, *7* and *6*, *9*).

The reactivity of *ortho*-substituted aryl halides is unlike that of *meta*- and *para*-isomers: For instance, the reactions with urea of *o*-bromotoluene and *o*-bromoanisole result in selective formation of diarylamines in 66–70% yields (Table 2, runs nos. *10* and *11*). Aryl halides with two *ortho*-substituents also enter into the reaction. Thus the

Table 1. Variation of bases and ligands in the reaction of *p*-bromotoluene with urea

Run no.	Ligand	Base	Time, h	Conversion of *p*-bromotoluene, %
1	Cy_3P	Cs_2CO_3	20	0
2	*t*-Bu_3P	Cs_2CO_3	18	9
3	L_1	Cs_2CO_3	18	0
4	L_1	*t*-BuONa	14	31
5	L_2	*t*-BuONa	14	39
6	*t*-Bu_3P	*t*-BuOK	21	100
7	L_1	*t*-BuOK	14	100
8	L_2	*t*-BuOK	14	100

Table 2. Prepartion of di- and triarylamines by reaction of urea with aryl halides[a]

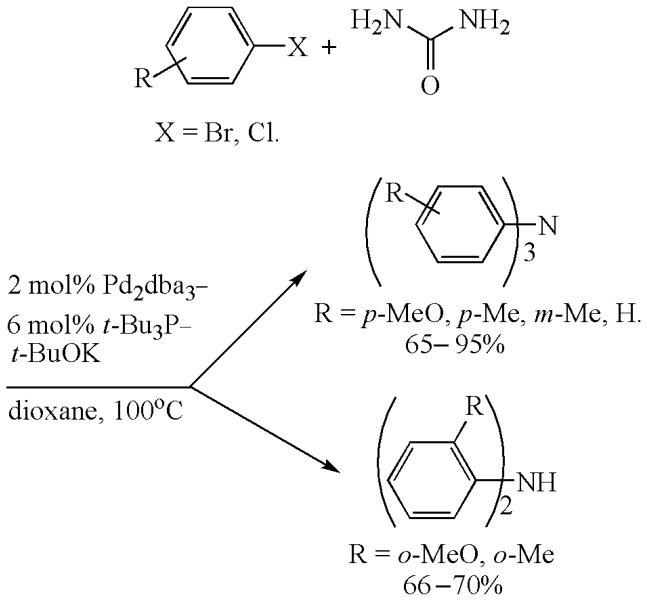
Run no.	R	X	Ligand	Time, h	Conversion, %	Yield, %		Reduction products
						Ar_3N	Ar_2NH	
1	*p*-Me	Br	L_1	21	100	32	41	*p*,*p*'-di(tolyl), 4%
2	*p*-Me	Br	L_2	19	100	73	7	*p*,*p*'-di(tolyl), 2%
3	*p*-Me	Br	*t*-Bu_3P	18	100	80	–	
4	*m*-Me	Br	*t*-Bu_3P	21	100	85		
5	*p*-MeO	Br	*t*-Bu_3P	21	100	65		anisole, 10%[d]
6	H	Br	*t*-Bu_3P	19	100	83		
7	*p*-Me	Cl	*t*-Bu_3P	44	85	80		
8	H	Cl	*t*-Bu_3P	20	72	60	5	
9	H	Cl	*t*-Bu_3P	46	100	95	trace	
10	*o*-Me	Br	*t*-Bu_3P	8	100		70	
11	*o*-MeO	Br	*t*-Bu_3P	20	100		66	anisole, 10%[d]
12	2,4,6-Me	Cl	*t*-Bu_3P	46	78		60	mesitylene, 4%[d]
13[b]	2,4,6-Me	Cl	*t*-Bu_3P	45	90		87	mesitylene, 12%[d]
14[c]	*n*-Me	Br	*t*-Bu_3P	48	100	94	–	*p*,*p*'-di(tolyl), 25%, toluene, 25%[d]

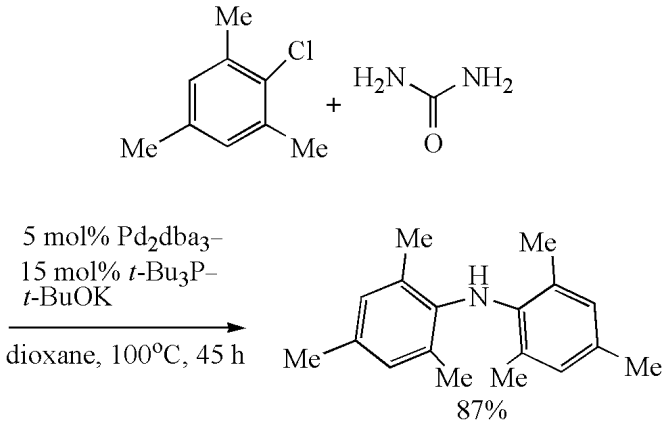
[a] Reaction was carried out under an argon atmosphere at 100°C in the presence of 1.65 mmol of aryl halide, 0.5 mmol of urea, 2.9 mol % of *t*-BuOK, 2 mol % of $Pd_2dba_3{\cdot}CHCl_3$ (4 mol % Pd), and 6 mol % of ligand in 6 ml of dioxane.

[b] 5 mol % of Pd_2dba_3 in $CHCl_3$ (10 mol % Pd) and 15 mol % of ligand was used.

[c] Reaction was carried out under an argon atmosphere in the presence of 2.99 mmol of *p*-bromotoluene, 0.516 mmol of urea, 5 mmol of *t*-BuOK, 6.23×10^{-2} mmol of $Pd_2dba_3{\cdot}CHCl_3$, and 18.5×10^{-2} mmol of *t*-$Bu_3PH^+{\cdot}BF_4$ in 6.5 ml of dioxane.

[d] Determined by GLC.

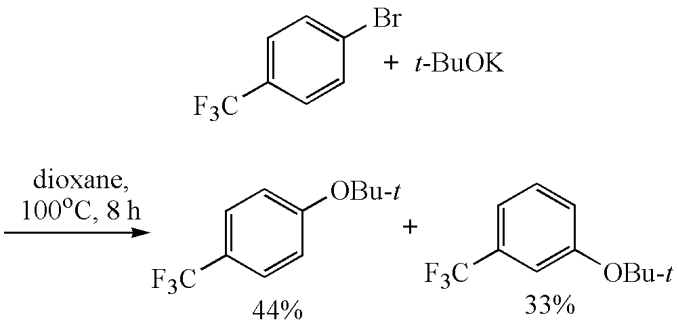




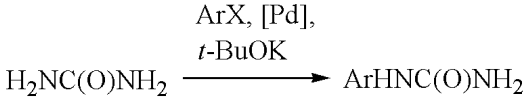
amination of chloromesitylene gave rise to dimesitylamine in 87% yield (run no. *12*, *13*).

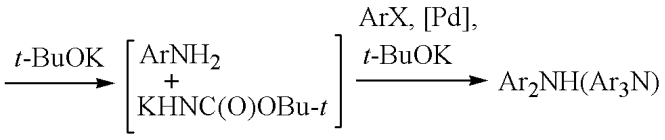
Apparently further arylation of diarylamines under the reaction conditions is hampered by sterical reasons. Presumably the triarylamines with an *ortho*-substituent in each phenyl ring cannot be obtained at all by amination in the presence of palladium complexes. The same pattern was observed in the palladium-catalyzed arylation of

lithium amide: The *ortho*-substituted aryl halides gave only diarylamines, and *para*- and *meta*-isomers, triarylamines[8]. Arylation of anilines in the presence of Pd_2dba_3–L_1 provides a possibility to prepare triarylamines containing a single *ortho*-substituent [12].



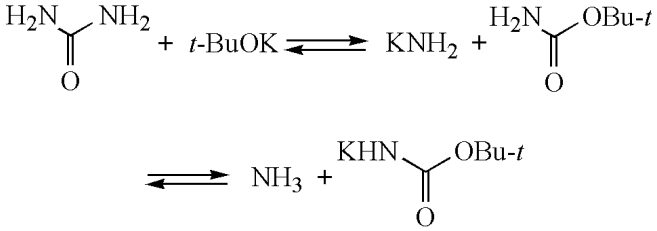
Regretfully, the applicability of this reaction is limited to nonactivated aryl halides. The reactions with activated aryl halides often give rise to the corresponding aryl *tert*-butyl ethers, for instance, from *p*-bromobenzotrifluoride and urea under these conditions a mixture of *p*- and *m*-(trifluoromethyl)phenyl *tert*-butyl ethers formed in overall yield 77%. A similar result was obtained in reaction without the catalyst. Evidently here a reaction of nucleophilic substitution by aryne mechanism took place.

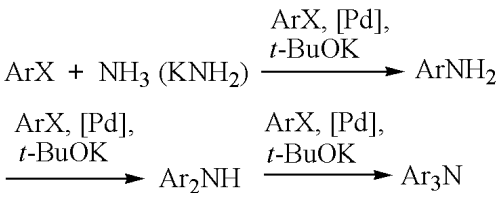




Two ways of di- and triarylamines formation from urea and aryl halides are presumable. First one consists in urea arylation followed by its cleavage into aniline and carbamate which is then successively arylated into di- and triarylamines.

However, the catalytic system Pd_2dba_3–L_1–*t*-BuOK proved to be inefficient for arylation of amides: On heating to 100°C *p*-bromotoluene with *p*-tolyamide for 29 h we

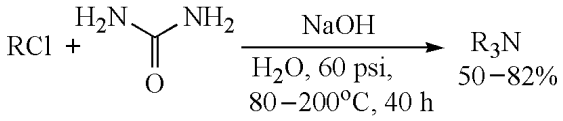




did not find any considerable amount of the amide N-arylation product. Therefore we believe that the second route is more probable involving urea dissociation to ammonia followed by arylation of ammonia or potassium amide.

Actually, the ligands L_1, L_2, and *t*-Bu_3P are known to be very efficient in amines arylation [13, 14]. The catalytic system Pd_2dba_3–L_1–*t*-BuONa was used in amines arylation at room temperature [13] and also, as already mentioned, in arylation of lithium amide [8].

Urea was used as ammonia source in [15] in the synthesis of trialkylamines from alkyl, allyl, and benzyl chlorides.



R = Alk, Bn, Allyl, Metallyl, Crotyl.

Under sufficiently severe conditions (60 psi, 200°C) used in this process the urea hydrolyzed to give two ammonia molecules. Under our conditions a single equiv of ammonia takes part. It is confirmed by the findings that reaction carried out with 3 or 6 mol of aryl bromide results in the same yield of triarylamine (Table 2, runs nos. *3* and *14*).

EXPERIMENTAL

^{1}H NMR spectra (400 MHz) were registered on a spectrometer Bruker Avance-400, chemical shifts were measured from the signals of residual protons of deuterated solvent or from TMS. Mass spectra were measured on Finnigan SSQ 7000 instrument (electron impact ionization, 70 eV). GLC was carried out on chromatographs Agat-9 equipped with a flame-ionization detector, column 2500 × 5 mm packed with Inerton Super 160–200 μm, stationary phase OV-17, carrier gas helium. The conversion in reaction was estimated with the use of internal reference (durene). Preparative column chromatography was performed on silica gel Fluka 40-65.

Purification and drying of dioxane was carried out by standard procedure, and it was maintained over benzophenone ketyl in a vacuum, ethyl acetate and petroleum ether (65–68°C) were subjected to distillation. Urea was recrystallized from ethanol and dried in a vacuum at 80°C (10^{-2} mm Hg). *p*-Toluamide was subjected to chromatography on silica gel (Merck 60, 40–63 μm) with ethyl acetate as eluent. Cesium carbonate was dried in a vacuum at 200°C, potassium *tert*-butylate was sublimed. Sodium *tert*-butylate (Lancaster), 2-di(*tert*-butyl)-phosphinobiphenyl, 2-di-methylamino-2'-dicyclohexyl-phosphinobiphenyl (Strem), and *t*-$Bu_3P{\cdot}HBF_4$ (Limited Liability Co "DAlKHIM Ltd") were used without further purification. Palladium complex $Pd_2dba_3{\cdot}CHCl_3$[16] and 9,9-dimethyl-4,5-bis-(diphenylphosphino)xanthene (Xantphos) were obtained by procedures from [17].

General procedure of di- and triarylamines preparation from urea and aryl halides. Into a reactor filled with argon was charged 1.6–1.7 mmol of aryl halide (10–20% exess), 0.5 mmol of urea, 2.1–2.5 mmol of a base, 2 mol% of $Pd_2dba_3{\cdot}CHCl_3$(4 mol% Pd), 6 mol% of a ligand, and 5–6 ml of dioxane saturated with argon. The reaction mixture was degassed, then the reactor was filled with argon. The reaction was carried out at 100°C while stirring till complete disappearance of initial aryl halide within an interval mentioned in Table 2, then the reaction mixture was cooled, diluted with 30 ml of ethyl acetate, the solution was filtered through a Celite bed and evaporated on silica gel. The residue obtained was subjected to chromatography on silica gel Merck 60 (40–63 μm).

Arylation of urea with *p*-bromotoluene in the presence of L_1 (Table 2, run no. *1*). From 293 mg (1.713 mmol) of *p*-bromotoluene, 31 mg (0.517 mmol) of urea, 31 mg (3.0×10^{-2} mmol) of $Pd_2dba_3{\cdot}CHCl_3$, 27 mg (9.06×10^{-2} mmol) of ligand L_1, 280 mg (2.50 mmol) of *t*-BuOK, and 6 ml dioxane 46 mg (32%) of tri(*p*-tolyl)amine and 40 mg (41%)of di(*p*-tolyl)amine was obtained. Eluent petroleum ether, then a mixture ethyl acetate–petroleum ether, 1:40, finally 1:20. Tri(*p*-tolyl)amine, mp 100°C* (102–103°C[18]). ^{1}H NMR spectrum, δ, ppm: 7.06 d (6H, *J* 8.5 Hz), 6.89 d (6H, *J* 8.5 Hz), 2.27 s (9H). Mass spectrum, *m/z* (I_{rel}, %): 287 (100) $[M]^+$, 271 (7) $[M–CH_3–H]^+$, 194 (4) $[M – C_6H_4CH_3–H]^+$, 180 (8) $[C_{13}H_{10}N]^+$. Di(*p*-tolyl)amine, mp 73–75°C (79°C [20]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.08 d (4H, *J* 8.4 Hz), 6.97 d (4H, *J* 8.4 Hz), 5.50 br.s (1H), 2.31 s (6H). Mass spectrum, *m/z* (I_{rel}, %): 197 (100) $[M]^+$, 180 (10) $[C_{13}H_{10}N]^+$, 91 (4) $[C_7H_7]^+$.

Arylation of urea with *p*-bromotoluene in the presence of L_2 (Table 2, run no. *2*). From 276 mg (1.614 mmol) of *p*-bromotoluene, 30.5 mg (0.508 mmol) of urea, 30.6 mg (2.96×10^{-2} mmol) of $Pd_2dba_3{\cdot}CHCl_3$, 36 mg (9.13×10^{-2} mmol) of ligand L_2, 290 mg (2.59 mmol) of *t*-BuOK, and 5 ml of dioxane 105 mg (73%) of tri(*p*-tolyl)amine and 6.5 mg (7%) of di(*p*-tolyl)amine was obtained. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:40, finally 1:20.

Tri(*p*-tolyl)amine. *a.* From *p*-bromotoluene in the presence of *t*-Bu_3P (Table 2, run no. *3*). From 274 mg (1.602 mmol) of *p*-bromotoluene, 31.5 mg (0.525 mmol) of urea, 31 mg (3.00×10^{-2} mmol) of $Pd_2dba_3{\cdot}CHCl_3$, 27.9 mg (9.62×10^{-2} mmol) of *t*-$Bu_3PH^+{\cdot}BF_4^-$, 295 mg (2.63 mmol) of *t*-BuOK, and 5 ml of dioxane 115 mg (80%) of tri(*p*-tolyl)amine was obtained. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:40, finally 1:20.

***b*. From *p*-chlorotoluene in the presence of *t*-Bu_3P (Table 2, run no. *7*).** From 214 mg (1.690 mmol) of *p*-chlorotoluene, 31 mg (0.517 mmol) of urea, 33 mg (3.19×10^{-2} mmol) of $Pd_2dba_3{\cdot}CHCl_3$, 28.5 mg (9.82×10^{-2} mmol) of *t*-$Bu_3PH^+{\cdot}BF_4^-$, 310 mg (2.77 mmol) of *t*-BuOK, and 6.3 ml dioxane was obtained 115 mg (80%) of tri(*p*-tolyl)amine. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:40, finally 1:20.

***c*. From *p*-bromotoluene in the presence of *t*-Bu_3P (Table 2, run no. *14*).** From 512 mg (2.99 mmol) of *p*-bromotoluene, 31 mg (0.516 mmol) of urea, 64.4 mg (6.23×10^{-2} mmol) of $Pd_2dba_3{\cdot}CHCl_3$, 53.5 mg (18.5×10^{-2} mmol) of *t*-$Bu_3PH^+{\cdot}BF_4^-$, 500 mg (5 mmol) of *t*-BuOK, and 6.5 ml of dioxane 136 mg (94%) of tri(*p*-tolyl)amine and 35 mg (25%) of di(*p*-tolyl)amine are obtained. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:40, finally 1:20.

Tri(*m*-tolyl)amine (Table 2, run no. *4*). From 282 mg (1.652 mmol) of *m*-bromotoluene, 30.8 mg (0.513 mmol) of urea, 31.5 mg (3.04×10^{-2} mmol) of $Pd_2dba_3{\cdot}CHCl_3$, 25.2 mg (8.69×10^{-2} mmol) of *t*-$Bu_3PH^+{\cdot}BF_4^-$, 325 mg (2.90 mmol) of *t*-BuOK, and 6 ml of dioxane was obtained 122 mg (85%) of tri(*m*-tolyl)amine. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:40, finally 1:20. mp 66°C (64–65°C [8]). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.14 t (3H, *J* 7.7 Hz), 6.77–6.87 m (9H) 2.23 s (9H). Mass spectrum, *m/z* (I_{rel}, %): 287 (100) $[M]^+$, 271 (12)

* In some expreiments (p-$MeC_6H_4)_3N$ with mp 117°C (117°C [19]) was obtained.

$[M - CH_3 - H]^+$, 257 (4) $[M - 2CH_3]^+$, 180 (5) $[C_{13}H_{10}N]^+$.

Tri(*p*-anisyl)amine (Table 2, run no. *5*). From 299 mg (1.604 mmol) of *p*-bromoanisole, 30 mg (0.500 mmol) of urea, 31.2 mg (3.01×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 27.2 mg (9.38×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 320 mg (2.86 mmol) of *t*-BuOK, and 6.5 ml of dioxane 109 mg (65%) of tri(*p*-anisyl)amine was obtained. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:6, finally 1:1. mp 92–93°C (95°C [21]). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 6.88–6.93 m (6H), 6.77–6.85 m (6H), 3.74 s (9H). Mass spectrum, *m/z* (I_{rel}, %): 335 (100) $[M]^+$, 320 (59) $[M - CH_3]^+$, 198 (6) $[C_{13}H_{12}NO]^+$, 167 (18) $[C_{12}H_9N]^+$, 92 (11) $[C_7H_8]^+$, 77 (13) $[C_6H_5]^+$.

Triphenylamine. *a.* From bromobenzene in the presence of *t*-Bu_3P (Table 2, run no. *6*). From 261 mg (1.656 mmol) of bromobenzene, 30.7 mg (0.512 mmol) of urea, 31 mg (3.00×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 28.5 mg (9.82×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 320 mg (2.86 mmol) of *t*-BuOK, and 5 ml of dioxane 102 mg (83%) of triphenylamine was obtained. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:40. mp 126°C (publ.: mp 127°C [20]). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.25–7.33 m (6H), 7.00–7.07 m (9H).

***b*. From chlorobenzene in the presence of *t*-Bu_3P (Table 2, run no. *8*).** From 188 mg (1.680 mmol) of chlorobenzene, 30 mg (0.500 mmol) of urea, 31.2 mg (3.01×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 27.6 mg (9.52×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 315 mg (2.81 mmol) of *t*-BuOK, and 6 ml of dioxane 72 mg (60%) of triphenylamine and 4.4 mg (5%) of diphenylamine was obtained.

***c*. From chlorobenzene in the presence of *t*-Bu_3P (Table 2, run no. *9*).** From 188 mg (1.662 mmol) of chlorobenzene, 31 mg (0.517 mmol) of urea, 32 mg (3.09×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 27 mg (9.31×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 320 mg (2.86 mmol) of *t*-BuOK, and 6 ml of dioxane 117 mg (95%) of triphenylamine and traces of diphenylamine are obtained.

Di(*o*-tolyl)amine (Table 2, run no. *10*). From 284 mg (1.661 mmol) of *o*-bromotoluene, 31.6 mg (0.527 mmol) of urea, 31.6 mg (3.05×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 27.8 mg (9.59×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 295 mg (2.63 mmol) of *t*-BuOK, and 6 ml of dioxane 69 mg (70%) of di(*o*-tolyl)amine was obtained. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:20, finally 1:40. mp 50°C (52–53°C [20]). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.19 d (2H, *J* 7.5 Hz), 7.08 t (2H, *J* 7.5 Hz), 6.87 t (2H, *J* 7.5 Hz), 6,83 d (2H, *J* 7.5 Hz), 6.06 br.s (1H), 2.25 s (6 H). Mass spectrum, *m/z* (I_{rel}, %): 197 (18) $[M]^+$, 180 (29) $[C_{13}H_{10}N]^+$, 167 (27) $[M - 2CH_3]^+$, 91 (76) $[C_7H_7]^+$, 65 (100) $[C_5H_5]^+$.

Di(*o*-anisyl)amine (Table 2, run no. *11*). From 309 mg (1.647 mmol) of *o*-bromoanisole, 31 mg (0.517 mmol) of urea, 34 mg (3.29×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 30 mg (10.34×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 310 mg (2.768 mmol) of *t*-BuOK, and 6 ml of dioxane 76 mg (66%) of di(*o*-anisyl)amine was obtained. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:6, finally 1:1, oily substance (publ.: oily substance [8]). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.34 d.d (2H, *J* 7.5, *J* 2 Hz), 6.99 d.d (2H, *J* 7.5, *J* 2 Hz), 6.81–6.91 m (4H), 6.59 br.s (1H), 3.89 s (6H). Mass spectrum, *m/z* (I_{rel}, %): 229 (23) $[M]^+$, 214 (46) $[M-CH_3]^+$, 199 (16) $[M - 2CH_3]^+$, 182 (62) $[M-CH_3O-CH_3H]^+$, 106 (46) $[C_7H_8N]^+$, 91 (24) $[C_7H_7]^+$, 78 (100) $[C_6H_6]^+$.

Di(*o*-mesityl)amine. *a.* (Table 2, run no. *12*). From 255 mg (1.649 mmol) of chloromesitylene, 31.7 mg (0.528 mmol) of urea, 31.7 mg (3.06×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 27 mg (9.31×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 325 mg (2.902 mmol) of *t*-BuOK, and 6.5 ml of dioxane 80 mg (60%) of dimesitylamine was obtained. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:40. mp 124°C (122–123°C [22]). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 6.74 s (4H), 5.38 br.s (1H), 2.18 s (6H), 1.94 s (12H). Mass spectrum, *m/z* (I_{rel}, %): 253 (100) $[M]^+$, 236 (18) $[M - CH_3 - 2H]^+$, 222 (15) $[M - 2CH_3 - H]^+$, 208 (4) $[M - 3CH_3]^+$, 132 (12) $[C_9H_{10}N]^+$, 91 (4) $[C_7H_7]^+$.

***b*. (Table 2, run no. *13*).** From 232 mg (1.500 mmol) of chloromesitylene, 30.1 mg (0.502 mmol) of urea, 76.3 mg (7.37×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 65.7 mg (22.7×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 335 mg (2.902 mmol) of *t*-BuOK, and 6 ml of dioxane 110 mg (87%) of dimesitylamine was obtained.

Reaction of *p*-toluamide with *p*-bromotoluene in the presence of *t*-Bu_3P. A mixture of 96 mg (0.561 mmol) of *p*-bromotoluene, 68 mg (0.504 mmol) of *p*-toluamide, 10.6 mg (1.02×10^{-2} mmol) of $Pd_2dba_3\cdot CHCl_3$, 9.7 mg (3.34×10^{-2} mmol) of *t*-$Bu_3PH^+\cdot BF_4^-$, 125 mg (1.116 mmol) of *t*-BuOK, and 4 ml of dioxane was stirred at 100°C for 20 h. We recovered 59 mg (87%) of initial *p*-toluamide and obtained 4 mg (1.5%) of

p-$MeC_6H_4CONHC_6H_4Me$-*p* (identical by R_f with an authentic sample). Conversion of initial aryl halide was 97%. Eluent petroleum ether, then a mixture EtOAc–petroleum ether, 1:20, finally 1:40.

Reaction of urea with *p*-bromotrifluoromethylbenzene in the presence of L_2. A mixture of 337 mg (1.50 mmol) of *p*-bromotrifluoromethylbenzene, 31.1 mg (0.517 mmol) of urea, 8.03 mg (7.75×10^{-3} mmol) of $Pd_2dba_3\cdot CHCl_3$, 8.87 mg (2.25×10^{-2} mmol) of L_2, 335 mg (2.98 mmol) of *t*-BuOK, and 4 ml of dioxane was heated at 100°C for 23 h. Conversion of initial aryl bromide was 92%. Yields (according to ^{1}H NMR spectra): 44% of *p*-(trifluoromethyl)phenyl *tert*-butyl ether and 33% of *m*-(trifluoromethyl)phenyl *tert*-butyl ether. The same products formed in a blank experiment on heating at 100°C for 16 h a mixture of *p*-bromotrifluoromethylbenzene with *t*-BuOK in dioxane. ***p*-(Trifluoromethyl)phenyl *tert*-butyl ether**. ^{1}H NMR spectrum (dioxane), δ, ppm: 7.56 d (2H, *J* 8.5 Hz), 7.08 d (2H, *J* 8.5 Hz), 1.38 s (9H). ***m*-(Trifluoromethyl)phenyl *tert*-butyl ether**. ^{1}H NMR spectrum (dioxane), δ, ppm: 7.39 t (1H, *J* 8 Hz), 7.35 d (1H, *J* 7.5 Hz), 7.26 s (1H), 7.18 d (1H, *J* 8 Hz), 1.36 s (9 H).

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