The palladium–phenanthroline catalyzed carbonylation of nitroarenes to diarylureas: Effect of chloride and diphenylphosphinic acid

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Abstract

The application of the palladium–phenanthroline catalytic system to the carbonylation of nitrobenzene in the presence of aniline to afford diphenylurea has been investigated. The reaction is best performed with equimolar amounts of the two reagents. Use of higher concentrations of either aniline or nitrobenzene or an increase in temperature in the range 120–170 °C leads to the formation of higher amounts of azo- and azoxybenzene. The latter were found to contain exclusively the aryl moiety deriving from nitrobenzene, with no inclusion of that derived from aniline. The addition of a small amount of diphenylphosphinic acid doubles the conversion and improves the selectivity in diphenylurea, but the effect is attenuated for larger amounts of acid. Small amounts of chloride, of the order of 10–30 mol% with respect to palladium, improve both rate and selectivity, but only inhibiting effects are detected when chloride is added to the reaction mixture for the carbonylation of 2,4-dinitrotoluene to dimethyl 2,4-toluenedicarbamate. The data obtained and that previously reported in the literature has been analyzed in the context of a unifying mechanism and an explanation for some apparent contradictions has been given.
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1. Introduction

The carbonylation of organic nitro compounds is a process with a high potential synthetic and industrial interest, since many products can be obtained from nitro compounds and CO, including isocyanates, carbamates and ureas [1–3]. Ureas and carbamates are important final products and intermediates in the synthesis of pesticides and fertilizers and mono- and diisocyanates are important intermediates in the manufacturing of pesticides, polyurethane foams plastics, synthetic leather, adhesives, and coatings.

The classical method for the production of isocyanates requires the intermediate reduction of the nitro compound to amine, followed by reaction with phosgene. However, phosgene is a very toxic and corrosive material and an enormous effort has been applied to the development of phosgene-free routes to isocyanates. Among these, the catalytic carbonylation of nitro compounds, particularly of aromatic ones, represents one of the most interesting alternatives, but the direct carbonylation of nitro compounds to the corresponding isocyanates has proved to be a difficult reaction. However, in the presence of an alcohol, carbamates can be obtained more easily and with a high selectivity (Eq. (1)):

$$ArNO_2 + ROH + 3CO \overset{cat.}{\rightarrow} ArNHCOOR + 2CO_2 \qquad (1)$$

If no alcohol is added, but at least an equimolar amount of aromatic amine with respect to the nitroarene is present, diarylureas are produced (Eq. (2))

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$$ArNO_2 + ArNH_2 + 3CO \xrightarrow{cat.} ArNHC(O)NHAr + 2CO_2 \quad (2)$$
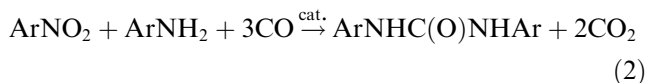
Moreover, it has been shown that, at least in the case of ruthenium-catalyzed reactions, diarylureas are intermediately formed during the reaction even when alcohols are present [4–6]. Both carbamates and ureas are important industrial products themselves, but can also be thermally cracked to the corresponding isocyanates, thus providing a phosgene free route to these important intermediates [7].

In recent years, the catalytic system based on palladium–phenanthroline complexes has emerged as the most active and promising for a possible industrial application [8–40]. We have recently much improved the activity of this catalytic system in the production of carbamates by the addition of phosphorus acids [38–40]. Since diarylureas appeared to be intermediates in the reaction, we decided to investigate more closely their formation with the dual aim of improving their synthesis from nitroarenes and gaining more information on the mechanism of the carbonylation reaction even when carbamates are the final products. Since some apparently contradictory results had been earlier reported on the effect of chloride anion on the palladium–phenanthroline catalyzed carbonylation of nitrobenzene to methyl phenylcarbamate, we also decided to investigate more in depth this aspect and the results of this study are also reported in this paper.

Before describing our results, it must be mentioned that, in addition to that reported in Eq. (2), a second stoichiometry has been proposed for the production of diarylureas from nitroarenes and anilines (Eq. (3)) [1–3,23]:

$$ArNO_2 + 5ArNH_2 + 3CO \xrightarrow{cat.} 3ArNHC(O)NHAr + 2H_2O \quad (3)$$
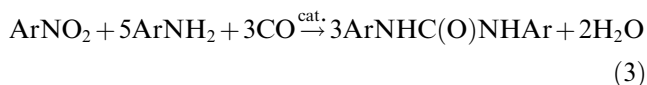
In this process, more aniline is consumed than nitroarene and water is also formed. We have recently shown [5,6] that both processes in Eqs. (2) and (3) play a role when the combination $Ru_3(CO)_{12}/Cl^-$ is employed as catalyst. For simplicity, in the following we will refer to the processes in Eqs. (2) and (3) as the 1:1 and 1:5 process, respectively.

2. Results

2.1. Formation of azo- and azoxybenzene

The main byproducts of the carbonylation reaction of nitrobenzene and aniline are azo- and azoxybenzene, the latter being always more abundant than the first. Since it was an aim of this work to investigate the stoichiometry of the process, it was important to trace their origin. It is well known from the organic chemistry that azoarenes

can be obtained by reaction of aromatic amines with nitrosoarenes [41]. The latter are well established intermediates in the reductive carbonylation of nitroarenes.

To definitely set the problem of the origin of azo derivatives, we run several reactions between pentadeuterated nitrobenzene and undeuterated aniline, in the presence of palladium trimethylbenzoate/phenanthroline or $[Pd(Phen)_2][BF_4]_2$ as catalysts. A longer series of these experiments is still in progress, but here it suffices to mention that in all reactions, independent of the catalyst, the solvent and other promoters, only decadeuterated azo- and azoxybenzene could be detected by GC–MS analysis of the solutions after the catalytic reactions. Only very small amounts of nona- and octadeuterated products derived from incomplete deuteration of the starting nitrobenzene were also detected, but no pentadeuterated or non-deuterated azo- and azoxybenzene were ever detected. Thus, these derivatives do not involve aniline in any way. Their formation can be accounted for by the reactions described in Eqs. (4) and (5), although we will see in the discussion that another alternative may exist.

$$2ArNO_2 + 3CO \xrightarrow{cat.} ArN(O)=NAr + 3CO_2 \quad (4)$$

$$ArN(O)=NAr + CO \xrightarrow{cat.} ArN=NAr + CO_2 \quad (5)$$
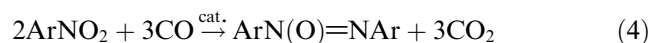
2.2. Effect of reaction conditions and diphenylphosphinic acid in the synthesis of diphenylurea

The most active palladium/phenanthroline catalysts for the carbonylation of nitroarenes to methyl phenylcarbamates in methanol as solvent have formulation $[Pd(Phen)_2][X]_2$, where X^- is a non-coordinating anion (e.g., BF_4^- or PF_6^-). However, this complex is inactive in polar non-protic, coordinating solvents, and is completely insoluble in medium to low polarity solvents such as toluene. In order to study the synthesis of ureas, we thus employed palladium 2,4,6-trimethylbenzoate, $Pd(TMB)_2$, as catalyst, in the presence of phenanthroline. This compound has already been shown by Mestroni and us to be suitable catalyst precursor even in toluene as solvent [15]. Note that palladium trimethylbenzoate and phenanthroline immediately react in solution to afford $Pd(Phen)(TMB)_2$ [15].

The results of a series of reactions run in the absence of promoters or in the presence of diphenylphosphinic acid are reported in Table 1. In the same table, we also reported the ratio, R, between the molar amounts of aniline and nitrobenzene reacted. Since azo- and azoxybenzene exclusively derive from nitrobenzene, each consuming two equivalents of nitrobenzene to be produced, we also calculated a ratio R^* in which the nitrobenzene amount which has been consumed to produce azo derivatives has been subtracted, that is (Eq. (6))

Table 1
Effect of temperature, reagent amounts, and addition of diphenylphosphinic acid[a]

Run	T (°C)	t (h)	PhNO$_2$/Pd mol ratio	PhNH$_2$/Pd mol ratio	Acid/Pd mol ratio	PhNH$_2$ conversion (%)[b]	PhNO$_2$ conversion (%)[c]	PhNHC(O)NHPh selectivity (%)[d]	PhN(O)=NPh selectivity (%)[e]	PhN=NPh selectivity (%)[e]	R	$R*$	TOF[f]
1	120	1	300	300	–	19.8	15.9	70.4	7.9	<0.1	1.22	1.34	47.7
2	120	2	300	300	–	31.4	27.0	81.6	12.2	<0.1	1.16	1.28	40.5
3	120	3	300	300	–	39.4	36.8	82.0	14.7	1.1	1.07	1.29	36.8
4	120	2	300	600	–	20.9	27.4	64.5	15.5	<0.1	1.52	1.79	41.1
5	120	2	300	900	–	23.7	31.8	53.1	20.9	1.5	2.24	2.84	47.7
6[g]	120	2	150	300	–	25.2	50.1	80.0	11.9	<0.1	0.98	1.11	38.3
7[g]	120	2	225	300	–	29.4	38.1	83.9	16.1	<0.1	1.01	1.20	43.2
8[g]	120	2	300	300	–	34.0	31.4	83.0	22.0	1.6	1.05	1.37	47.3
9[g]	120	2	450	300	–	32.4	20.7	73.1	36.6	2.0	1.01	1.64	46.9
10[g]	120	2	300	225	–	39.7	30.6	83.5	20.2	<0.1	0.98	1.22	46.1
11	135	1	300	300	–	33.7	31.1	77.3	19.3	1.1	1.08	1.37	31.1
12	150	1	300	300	–	35.9	32.7	69.4	31.9	1.4	1.10	1.64	32.7
13	170	1	300	300	–	45.0	42.5	59.4	46.8	2.0	1.06	2.08	42.5
14[h]	120	2	600	600	–	19.6	15.7	71.2	22.7	<0.1	1.25	1.61	47.1
15	120	2	300	300	4.4	63.6	63.5	94.7	1.2	1.0	1.00	1.03	95.3
16	120	2	300	300	8.8	55.8	56.7	96.2	2.3	1.9	0.98	1.03	85.1

[a] Experimental conditions: Pd(TMB)$_2$ = 0.030 mmol; mol ratio Phen/Pd = 4, P_{CO} = 40 bar, in toluene (8 ml).
[b] Calculated with respect to the starting aniline.
[c] Calculated with respect to the starting nitrobenzene.
[d] Calculated with respect to the sum of reacted nitrobenzene and aniline.
[e] Calculated with respect to the reacted nitrobenzene.
[f] TOF = turnover frequency = mol PhNO$_2$ reacted/mol Pd × h.
[g] Reactions 6–10 were performed at a more than one year distance from the others and by a different person. Runs 2 and 8 correspond to the same experimental conditions. Although there is a good qualitative agreement between the two reactions, small differences are present and comparisons should be made within the individual series.
[h] Pd(TMB)$_2$ = 0.015 mmol; mol ratio Phen/Pd = 8:1.

$$R^* = (\text{mol PhNH}_2\text{consumed})/[\text{mol PhNO}_2\text{consumed}$$
$$- 2(\text{mol PhN(O)}{=}\text{NPh} + \text{mol PhN}{=}\text{NPh formed})]$$
$$(6)$$

By examining the stoichiometries in Eqs. (2) and (3) (the 1:1 and 1:5 processes), it is immediately evident that if only the 1:1 process is operating, R^* should be 1, whereas if only the 1:5 is active, R^* should be 5. Any intermediate value indicates that both processes are operating in competition.

It should be noted that we intentionally operated as to have low conversions, to avoid that the complete consumption of one of the reagents may alter the kinetics of the reaction or the relative weigh of the two stoichiometries.

After all reactions, partial decomposition of the catalytic system to give metallic palladium was observed.

A few trends emerge from the analysis of the data.

(1) As the reaction proceeds, its rate decreases (runs 1–3). By plotting $\log([\text{PhNO}_2]_0/[\text{PhNO}_2]_f)$ (where $[\text{PhNO}_2]_0$ and $[\text{PhNO}_2]_f$ are the nitrobenzene concentration, respectively, at the beginning and at the end of reactions 1–3 in Table 1) against the reaction time, a straight line is obtained ($R^2 = 0.997$) which is indicative of a first order dependence of the rate on nitrobenzene concentration. Since aniline and nitrobenzene consumptions run almost parallel in runs 1–3, it should be considered that an apparent first-order consumption of nitrobenzene may instead derive from a first order dependence of the rate on aniline concentration. This possibility is discounted by the fact that an overall threefold increase in the initial aniline amount (runs 2, 4 and 5) results only in a small variation in the nitrobenzene consumption, which is at the limits of experimental error between runs 2 and 4, despite a doubling of the aniline amount in the second reaction. Such small variations may just be due to a solvent effect, since the aniline volume is not completely negligible and affects both the volume and the polarity of the reaction medium. However, it must also been considered that catalyst deactivation is observed and we are also looking at the overall result of two different stoichiometries. Thus, a clean first order dependence on nitrobenzene concentration cannot be claimed, although it is evident that nitrobenzene concentration has an effect on the reaction rate. To gain more information on the kinetics of this reaction, a further series of reactions (runs 6–10) was performed by varying the initial nitrobenzene amount. Reactions 6–10 were performed at a more than one year distance from the others and by a different person. Runs 2 and 8 correspond to the same experimental conditions. Although there is a good qualitative agreement between the two reactions, small differences are present and comparisons should be made within the individual series. The turnover frequencies of the reactions run with a nitrobenzene/Pd ratio 450 or 300 (runs 8 and 9) are indistinguishable within the experimental error. This is a clear evidence of zero order dependence of the rate on nitrobenzene concentration. When the catalytic ratio is further lowered, the TOF decreases. However, the activities observed for runs 6 and 7 are not consistent with a first-order kinetics in nitrobenzene. Overall, these experiments indicate that we are operating in a transition area in which neither a clean zero nor a clean first order in nitrobenzene concentration are observed. By increasing the nitrobenzene amount, the rate approaches zero order dependence, whereas it approaches first order as the nitrobenzene concentration decreases, as it occurs while the reaction is proceeding. Run 10 confirms the independence of the rate on aniline concentration.

(2) By increasing the amount of aniline at constant temperature (runs 2, 4 and 5) the aniline consumption and the R^* value increase, indicating a shift towards the 1:5 process. This effect also explains why a higher R^* value is observed in run 1 with respect to runs 2 and 3. Indeed the aniline concentration lowers as the reaction proceeds and the corresponding lowering of R^* will result in a lower global R^* value, although differences are at the limits of the experimental error. A comparison of the R^* values for runs 6–9 shows that the R^* value also rises when the nitrobenzene concentration increases.

(3) In general, the selectivity in diphenylurea decreases if either the nitrobenzene or the aniline concentrations increases, while more azo- and azoxybenzene are formed.

(4) By increasing the reaction temperature up to 170 °C (runs 1 and 11–13), the conversion increases, although irregularly, but the selectivity in diphenylurea markedly decreases. The R^* value and the azoxybenzene selectivity rise steadily. It should be noted that an increase in the azoxybenzene selectivity with temperature had been earlier observed even when the reaction is performed in methanol and in the absence of added aniline [38,39]. In any case, temperatures higher than 135 °C appear to be unsuitable for the production of ureas, although the ideal temperature for the formation of carbamates is 170 °C [38,39]. At the end of these reactions, increasing amounts of metallic palladium were observed as the temperature was increased. Clearly, the catalytic system is deactivating faster at higher temperatures and this explains the irregularity in the rate increase.

(5) When the palladium amount is halved (runs 2 and 14), the conversion decreases, but does not halve, indicating that the catalyst deactivates more slowly when its concentration is lower, an effect already observed in several cases, including the synthesis of carbamates by the same catalytic system [38,39]. Selectivities are different in runs 2 and 14, but it is more instructive to compare run 14 with run 1, where the reaction was performed with a double amount of catalyst and for half the time. The outcome of the two reactions is very

similar, indicating that nitrobenzene and aniline concentrations are more important than palladium concentration and reaction time in determining the reaction rate and selectivity.

(6) The addition of diphenylphosphinic acid (run 15) in a 4.4 acid/Pd mol ratio more than doubles the nitrobenzene conversion (from 27.0, run 2, to 63.5%) and markedly increases the diphenylurea selectivity. Quite importantly, very little azoxybenzene is formed and the $R*$ is almost unity, indicating that the contribution of the 1:5 process becomes negligible. A further increase in the acid amount results in a slower reaction, but the selectivity in urea is further enhanced to 96.2%. The mechanistic implications of these results will be discussed in a later paragraph, together with the trends in the R value, but the important result from a synthetic point of view is that the addition of phosphorus acids is strongly beneficial not only in the synthesis of carbamates, but also of ureas.

2.3. Effect of chloride on the synthesis of diphenylurea

Several years ago, Mestroni and co-workers [11] reported that the presence of small amounts of chloride in the palladium–phenanthroline catalytic system increased the rate of the carbonylation reaction, in methanol, of nitrobenzene to methyl phenylcarbamate, despite the fact that the use of palladium chloride as catalyst was ineffective. Later, Lee and co-workers [42] reported a positive effect of chloride on the carbonylation of nitrobenzene to diphenylurea when palladium catalysts with monodentate phosphines as ligands were employed. When chelating phosphines were employed [43], an inhibiting effect was observed instead. Finally, van Leeuwen and co-workers [17] reported that the addition of a 1:1 molar amount of chloride with respect to palladium to a catalytic system very similar to that reported by Mestroni was sufficient to decrease the catalytic activity.

At this point, it was important to investigate more quantitatively the promoting effect of chloride and its possible role in addressing the reaction stoichiometry. Indeed, it should be noted that the 1:5 process can be envisioned as an oxidative carbonylation reaction of aniline, with nitrobenzene acting as the oxidant in place of oxygen, and chloride is known to have a profound effect on the latter reaction when palladium is employed as catalyst [1]. For reasons of solubility and stability, an organic countercation, PPN^+ ($PPN^+ = (PPh_3)_2N^+$), was employed. This specific salt was chosen because it is more chemically stable than other quaternary ammonium and phosphonium chlorides and, moreover is not hygroscopic. It is our experience that small amounts of water can almost completely inhibit the activity of chloride in an organic solvent, likely because of the formation of strong hydrogen bonds.

The addition of increasing amounts of [PPN][Cl] (from 10 to 30 mol% with respect to palladium) led to an increase in conversion from 39% to 50% and to lowering of the amount of azoxybenzene formed and of the $R*$ value (Table 2, runs 1–3, to be compared to run 3 in Table 1). The best results were obtained at a ratio Cl^-/Pd = 0.2, but the results at Cl^-/Pd = 0.3 are essentially indistinguishable. Higher amounts of chloride (60–100 mol% with respect to palladium) gradually decreased the conversion to approximately the initial value, but the selectivity in urea remained higher than in the absence of chloride (Table 2, runs 4 and 5, and Table 1, run 3).

To check if the addition of chloride was modifying the kinetic order with respect to nitrobenzene, two further experiments were run, employing different initial

Table 2
Effect of the addition of chloride in the synthesis of diphenylurea[a]

Run	P (bar)	PhNO$_2$/Pd mol ratio	Cl$^-$/Pd mol ratio	PhNH$_2$ conversion (%)[b]	PhNO$_2$ conversion (%)[c]	PhNHC(O)NHPh selectivity (%)[d]	PhN(O)=NPh selectivity (%)[e]	PhN=NPh selectivity (%)[e]	R	$R*$	TOF[f]
1	40	300	0.10	48.9	44.8	89.7	12.2	1.3	1.09	1.24	44.8
2	40	300	0.20	50.2	49.4	93.6	3.7	<0.1	1.02	1.06	49.4
3	40	300	0.30	47.6	48.2	94.5	3.4	<0.1	0.99	1.02	48.2
4	40	300	0.60	41.0	38.6	91.2	4.5	<0.1	1.06	1.10	38.6
5	40	300	1.00	42.3	41.7	89.8	3.7	<0.1	1.01	1.05	41.7
6	40	225	0.20	44.9	60.4	95.0	2.7	<0.1	1.01	1.02	45.7
7	40	600	0.20	51.8	29.1	93.7	8.7	<0.1	0.89	0.94	58.2
8	30	300	0.20	42.3	47.0	97.1	5.8	<0.1	0.90	0.95	47.0
9	60	300	0.20	40.1	43.9	98.2	3.4	<0.1	0.91	0.95	43.9

[a] Experimental conditions: Pd(TMB)$_2$ = 0.03 mmol; mol ratios PhNH$_2$/Phen/Pd = 300:4:1, T = 120 °C, in toluene (8 ml) for 3 h.
[b] Calculated with respect to the starting aniline.
[c] Calculated with respect to the starting nitrobenzene.
[d] Calculated with respect to the sum of reacted nitrobenzene and aniline.
[e] Calculated with respect to the reacted nitrobenzene.
[f] TOF = turnover frequency = mol PhNO$_2$ reacted/mol Pd × h.

amounts of nitrobenzene (runs 6 and 7). A comparison of the turnover frequencies observed in these reactions with that of run 2 shows a situation analogous to that in the absence of chloride. A dependence of the rate on nitrobenzene concentration is clearly observable, but it is lower than that expected for a first-order kinetics. Thus, again an intermediate kinetic regime is observed.

We finally also investigated the influence of CO pressure (runs 2, 8 and 9). The results of the three reactions are close, with a bell-shaped effect on nitrobenzene conversion, at variance with the results previously obtained for the related carbonylation to give methyl phenylcarbamate, where a clean first order dependence of the rate on CO pressure was observed [38,39].

2.4. Synthesis of diphenylurea in methanol as solvent

Several pieces of evidence in the literature show that when the carbonylation of nitroarenes is performed in the presence of alcohols, diarylureas are intermediately formed. Only at a later stage, these react with the alcohol to produce the finally observed carbamate. An equivalent of aromatic amine is regenerated at the same time, which re-enters the catalytic cycle [4–6]. In order to evidence if this is the case even when palladium–phenanthroline catalytic systems are employed, we performed a few reactions. First, the uncatalyzed alcoholysis of diphenylurea in methanol (Eq. (7)) was investigated.

$$PhNHC(O)NHPh + MeOH \rightarrow PhNHCOOMe + PhNH_2 \tag{7}$$
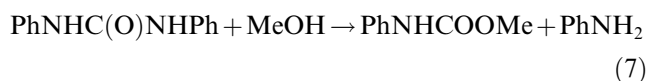
The reaction proceeded with a rate increasing with the temperature at temperatures higher or equal 120 °C, but was very slow at 110 °C. This temperature was thus selected for the carbonylation experiments because possibly formed urea would not be significantly alcoholyzed and should be detectable. Both $Pd(TMB)_2$ and $[Pd(Phen)_2][BF_4]_2$ were tested in order to further strengthen the analogy between the synthesis of carba-

mates and ureas. The results of two experiments are reported in Table 3.

The results clearly show that with both catalysts only a trace amount of carbamate is formed, the main product being diphenylurea. This confirms that diphenylurea is indeed intermediately formed even in the presence of methanol and that the presence of a carboxylate ligand is not necessary. The tetrafluoborate catalyst is inactive in toluene for solubility reasons, but can produce ureas when dissolved in a suitable solvent. The comparison also confirms other expected features. The presence of coordinating anions is known to decrease the activity of the catalytic system [18], in accord with the lower conversion of run 2. Moreover, the addition of carboxylate anions has been reported to increase the amount of azoxybenzene [19], which is also confirmed by the present results.

A comparison with the results reported in Table 1, also shows that the catalytic system is much more active in methanol, but the effect of the presence of a large amount of aniline is also more negative on the selectivity than in toluene.

2.5. Effect of chloride on the carbonylation of 2,4-dinitrotoluene to dimethyl 2,4-toluenedicarbamate

The first problem which is encountered when dealing with the carbonylation of 2,4-dinitrotoluene is the large number of possible intermediates and byproducts. Apart from the desired dicarbamate (**1**), there are two nitrocarbamates (**2a,b**), two aminocarbamates (**3a,b**), two nitrotoluidines (**4a,b**), diaminotoluene (**5**) (Scheme 1) and a virtually unlimited number of azo- and azoxyarenes, and ureas. In a very recent work [40], we have independently synthesized all the nitro- and aminocarbamates reported in Scheme 1, so that it is possible to analyze them quantitatively. The experimental conditions for the synthesis of the dicarbamate **1** had also been optimized. The experiments in the presence of chloride are reported in Table 4, together with a reference reaction under optimized conditions. Note that in this case

Table 3
Synthesis of diphenylurea in methanol as solvent[a]

Run	Catalyst	$PhNH_2$ conversion $(\%)$[b]	$PhNO_2$ conversion $(\%)$[c]	PhNHC(O)NHPh selectivity $(\%)$[d]	PhN(O)=NPh selectivity $(\%)$[e]	PhN=NPh selectivity $(\%)$[e]	PhNHCOOMe selectivity $(\%)$[d]	R	R^*
1	$[Pd(Phen)_2][BF_4]_2$	23.2	21.0	67.1	46.9	1.3	1.9	1.10	2.14
2	$Pd(TMB)_2$	17.7	13.8	53.5	64.0	<0.1	2.9	1.28	3.56

[a] Experimental conditions: Catalyst 0.020 mmol, mol ratios $PhNO_2/PhNH_2/Phen/Pd$ = 730:730:6:1 (in the case of run 1, the ratio Phen/Pd = 6 includes the amount of phenanthroline already coordinated to palladium in the starting complex), T = 110 °C, P_{CO} = 60 bar, in methanol (10 ml) for 1.5 h.
[b] Calculated with respect to the starting aniline.
[c] Calculated with respect to the starting nitrobenzene.
[d] Calculated with respect to the sum of reacted nitrobenzene and aniline.
[e] Calculated with respect to the reacted nitrobenzene.
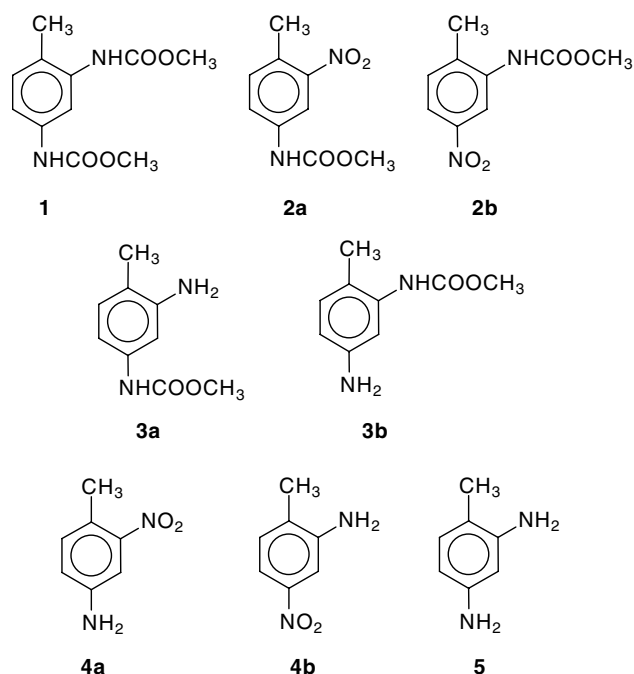
Scheme 1. Numbering scheme for the products derived from 2,4-dinitrotoluene.

phenylphosphonic acid was employed in place of diphenylphosphinic acid because the former had been found to give superior results in the synthesis of carbamates.

From the data in Table 4 it is immediately evident that, under these conditions, chloride always inhibits the formation of the dicarbamate, the effect increasing with an increase in the chloride amount. The effect is remarkable if we consider that even at the highest amount investigated, its concentration is only 5×10^{-4} M.

3. Discussion

3.1. Synthetic aspects

In this paper, we have examined the influence of several experimental variables and of the promoting effect of diphenylphosphinic acid and chloride anion on the palladium–phenanthroline catalyzed carbonylation of nitrobenzene to diphenylurea and the effect of chloride anion on the carbonylation by the same type of catalyst of 2,4-dinitrotoluene to the corresponding dicarbamate. The strongly promoting effect of phosphorus acids on the palladium–phenanthroline catalyzed carbonylation of nitroarenes to carbamates had already been evidenced by us in previous papers [38–40]. The synthetically relevant conclusions that can be drawn from the results reported in Tables 1–4 are the following:

(1) The palladium–phenanthroline catalytic system can be employed to produce diphenylurea with a high selectivity, but the activity is lower than in the corresponding carbonylation reaction to afford carbamates. This is likely mostly due to the fact that the catalytic system deactivates to give metallic palladium quite rapidly.

(2) Although aniline is a reagent in the synthesis of diphenylurea, its amount should not exceed that of nitrobenzene, otherwise selectivity is shifted towards the formation of azo derivatives.

(3) An increase in temperature in the range 120–170 °C is also detrimental to the selectivity, whereas the CO pressure is little influential in the range 30–60 bar.

(4) The addition of a small amount (4.4-fold that of palladium) of diphenylphosphinic acid results in a doubling of the reaction rate and an increase in selectivity towards diphenylurea, but a further increase in the acid amount gave an attenuated effect. Although the positive effect on rate and selectivity was also observed in the synthesis of carbamates, in that case much larger amounts of acid were tolerated before the effect flattened and only a small decrease in activity was observed at very high acid loadings. Note that phosphoric or phenylphosphonic acids, which are the best promoters in the case of the synthesis of carbamates were not tested in the synthesis of ureas because of solubility/miscibility problems with the toluene solvent.

Table 4
Effect of chloride on the carbonylation of 2,4-dinitrotoluene to dimethyl 2,4-toluenedicarbamate (**1**)[a]

Run	Cl⁻/Pd mol ratio	**1** selectivity (%)[b]	**2a** selectivity (%)[b]	**2b** selectivity (%)[b]	**3a** selectivity (%)[b]	**3b** selectivity (%)[b]
1[c]	–	77.6	1.1	–	2.6	0.8
2	0.5	68.4	1.5	1.9	2.3	0.7
3	1	63.7	3.8	3.5	2.5	1.1
4	2	55.7	3.6	3.6	2.2	0.7

[a] Experimental conditions: Catalyst [Pd(Phen)$_2$][BF$_4$]$_2$ = 3.2 mg, 5.0×10^{-3} mmol, mol ratios 2,4-dinitrotoluene/**4b**/phenylphosphonic acid/Phen/Pd = 2920:400:330:32:1, 2,2-dimethoxypropane = 1.0 ml, P_{CO} = 100 bar, T = 170 °C, in methanol (20 ml), for 3.5 h. Conversion of dinitrotoluene and **4b** was complete in all cases. No **4a,b** or **5** was detected at the end of the reaction. Chloride was added as [PPN][Cl].
[b] Calculated with respect to the sum of reacted **4b** and dinitrotoluene.
[c] Data from [40].

(5) Small amounts of chloride have been confirmed to have a positive role on nitrobenzene conversion in the synthesis of diphenylurea, with a bell-shaped concentration/activity relationship, but only inhibiting effects were detected in the synthesis of carbamates. It is important to note that, in the case of the synthesis of diphenylurea, not only an increase in rate, but also in selectivity was observed and the last persisted even at chloride levels where the activity decreases. A positive effect of chloride on the selectivity of a palladium–phenanthroline catalyzed carbonylation reaction of a nitroarene had never been reported before.

Other trends are either self-evident or are of more relevance to the reaction mechanism and will be discussed in the next paragraph.

3.2. Reaction mechanism

The data collected and a comparison with previously reported results pose several mechanistic questions and give some hints as to how solve them.

3.2.1. Origin of azo- and azoxyarenes

Azo- and, especially azoxyarenes are the most ubiquitous byproducts during the carbonylation reactions of nitroarenes with a variety of catalysts [1]. It has long been known in the literature that reaction of aromatic amines with nitrosoarenes, catalyzed by both acids and bases, affords azoarenes even under mild conditions [41]. Since nitrosoarenes are well recognized intermediates in the reduction of nitroarenes by CO and aromatic amines are also often added or generated in the reaction mixture, it has been proposed that at least part of the produced azoarenes may derive from such a coupling reaction. Although such assumption appears to be very reasonable, our data on the deuteration level of azo- and azoxybenzene in reactions between deuterated nitrobenzene and undeuterated aniline shows unequivocally that reaction of aniline with nitrosobenzene plays no detectable role in the production of azobenzene, at least with the palladium–phenanthroline catalytic system. Azobenzene can also derive from a deoxygenation reaction of azoxybenzene and, since in most experiments its amount is very low and only increases at long reaction times, it is likely that this process is indeed the only one relevant to its production. Several possibilities, on the other hand, exists for the formation of azoxybenzene, but the data reported in this paper do not allow to make any choice among them, so we will postpone the discussion of this aspect until we can give a clearer answer to this problem.

The absence of aniline-derived aryl moieties in azo- and azoxybenzene was quite surprising even because it has been observed in a number of reports [1,20], including the present one, both with palladium/phenanthroline and other metals catalysts, that the addition of large amounts of aniline to the reaction mixture for the carbonylation of nitroarenes to carbamates much increases the amount of azo derivatives formed. Since it has also been reported that bases have an analogous effect [1], it is now clear that the effect of aniline in the formation of azo derivatives is due to its basicity and not to a direct involvement into the product formation.

3.2.2. Role of chloride

As previously mentioned, small amounts of chloride have been reported to be beneficial to the carbonylation reactions of nitroarenes under certain conditions [11,42], but to inhibit it in others [17,43]. Since non-coordinating anions give better catalytic systems, the origin of the inhibiting effect can be immediately identified. We also recall that Pd(Phen)Cl$_2$ is very stable and insoluble in any solvent that does not displace phenanthroline. The origin of the positive effect is, on the other hand, less obvious. In review articles [1,23], we have earlier proposed that the promoting effect may be due to the formation of an anionic palladium(0) complex having a coordinated chloride anion (Scheme 2).

The idea had been prompted us by a series of papers by Amatore, Jutand, and Co-workers [44] in which these authors analyzed the products of the electrochemically induced reduction of PdX$_2$(PPh$_3$)$_2$ (X = Cl, Br), possibly in the presence of added n-Bu$_4$NX, and showed them to be an equilibrium mixture of [Pd(PPh$_3$)$_2$X]$^-$, [Pd(PPh$_3$)$_2$(μ-X)]$_2^{2-}$, and [Pd(PPh$_3$)$_2$X$_2$]$^{2-}$ with the first largely predominating in the absence of added halide and the last becoming increasingly important as the concentration of X$^-$ increases. From the point of view of the reactions presently discussed, it is particularly important that the polarographic oxidation wave potential of a solution of Pd^0(PPh$_3$)$_4$ decreased by as much as 0.3 V when n-Bu$_4$NCl was also added [45]. Since the first step of the nitro compound reduction is almost surely an electron transfer from a Pd^0 complex to the nitro compound [1,23], a similar shift of the oxidation potential of the complex should markedly accelerate it. The addition of halides increased the rate of oxidative addition of ArI [45] and ArOTf [46] to Pd(PPh$_3$)$_4$.
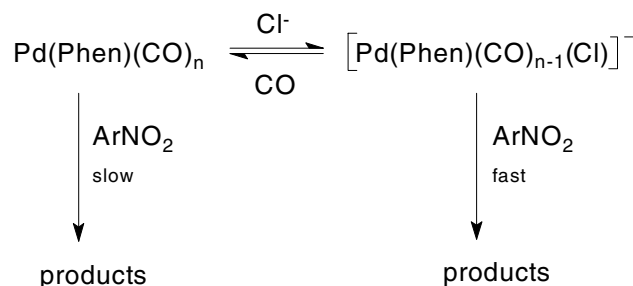
Scheme 2.

The explanation we proposed can be correct only in case the activation of the nitroarene is the slow step of the reaction. This implies that the kinetics should be dependent on the nitroarene concentration. The experimental data reported in this paper shows that this is indeed the case when the synthesis of diphenylurea is concerned, which is also the system in which we detected a positive effect. On the contrary, van Leeuwen and coworkers [18] showed the kinetics to be approximately zero order in nitrobenzene under the same conditions in which the negative effect of chloride was detected [17]. We have also found a zero-order rate dependence on nitrobenzene concentration under conditions [38,39] very similar to the ones in which the experiments in Table 4 were performed and the available data on the carbonylation of dinitrotoluene [40] strongly suggests that its initial activation is not the rate determining step of the reaction, although a detailed kinetic study was not performed. Thus, the apparent contradiction between the data obtained in different conditions, both in the literature and in the present paper, can be easily solved. A positive effect is to be expected, and is indeed observed, when the activation of the nitroarene is slow, whereas should not be present, and is indeed not observed, when it is fast. Since chloride can also have an inhibiting effect when coordinated to a palladium(II) intermediate, this will be the only effect detectable when no positive effect occurs. In his original experiments, Mestroni did not measure the kinetics of the reaction, but extension of the discussion above suggests that the activation of nitrobenzene was not a fast process under his conditions.

It may be noted that carboxylate anions can also coordinate to palladium(0) complexes [47] and play a similar role to chloride. However, it has been shown by van Leeuwen and co-workers [19] that the addition of excess carboxylate anions to the palladium–phenanthroline catalytic system not only slows down the reaction, but also results in higher amounts of azoxybenzene. Although the effect of very small amounts of carboxylates was not investigated and it is not possible to say if an accelerating effect would be observed, the effect on selectivity is clearly opposite to that here observed for chloride. Since carboxylate anions are basic, whereas chloride is not, and a large body of accumulating evidence [1,19] shows that the presence of bases results in an increase of azoderivatives formation in the carbonylation reactions of nitroarenes, it is clear that the basicity effects of carboxylate prevail on any possible positive effect. That chloride has also a positive effect on selectivity and not only on activity is an unprecedented and unexpected feature. At the moment, our knowledge of the detailed reaction mechanism is insufficient to allow an explanation supported by experimental data and we prefer not to make any unsupported speculation.

3.2.3. Kinetics

Before discussing the kinetics of the process, it is useful to recall the possible alternative mechanisms for the reaction (Scheme 3).

Without entering into the details, two main alternatives exist. In the first, path A in Scheme 3, nitrobenzene is intermediately reduced to aniline, while a palladium(II) complex is formed (step (a)). Only in the following step (step (b)) does this palladium complex react with aniline to afford phenylisocyanate. This is in turn trapped by excess aniline to afford diphenylurea. When the reaction is run in methanol and at temperatures higher than 110 °C, alcoholysis of the urea generates methyl phenylcarbamate and an equivalent of aniline. The identity of the intermediate palladium complex is not relevant at this stage of the description. When methanol is present, it is likely to be $Pd(Phen)(COOMe)_2$ [1,19,23,37,47], but in the present system it may be $Pd(Phen)(TMB)_2$. In any case, it is known that many palladium(II) compounds reacts with amines under a CO atmosphere to give ureas. It is important to recall that it has been found that the reaction of $Pd(Phen)(COOMe)_2$ with amines is accelerated by the presence of acids [48] and we have very recently found that the reaction is also very sensitive to the concentration of CO in solution [49]. Moreover, even the reaction of $Pd(Phen)(TMB)_2$ with aniline is accelerated by acids.

A second alternative (path B) involves the formation of a metallacyclic intermediate [29–33]. This can decompose to yield phenylisocyanate, which will be trapped by aniline as in path A. Quite importantly, even the decomposition of this metallacycle has been reported to be accelerated by acids (specifically trimethylbenzoic acid) [29]. This second pathway can provide urea without aniline being intermediately formed.

Since both pathways consume equal amounts of nitrobenzene and aniline, it is obvious that at least a third pathway should operate in order to justify the different consumption of the two reagents. We will deal with this in one of the following paragraphs.

In this paper, we have unequivocally shown that diphenylurea is indeed intermediately formed during the carbonylation of nitrobenzene even when methanol is employed as solvent. This allows a comparison of the results obtained in the synthesis of ureas with those previously obtained for the synthesis of carbamates. We have previously provided strong evidence that in the synthesis of methyl phenylcarbamate catalyzed by palladium–phenanthroline complexes path A in Scheme 3 is either the only operating or, more likely, the strongly prevailing pathway for the reaction [38,39]. The kinetics is zero order in nitrobenzene, first order in CO pressure and accelerated by an increase in the concentration of aniline (a clean first order dependence is not observed because of the different equilibria in which this compound is involved). A strong acceleration by acids was

Scheme 3.
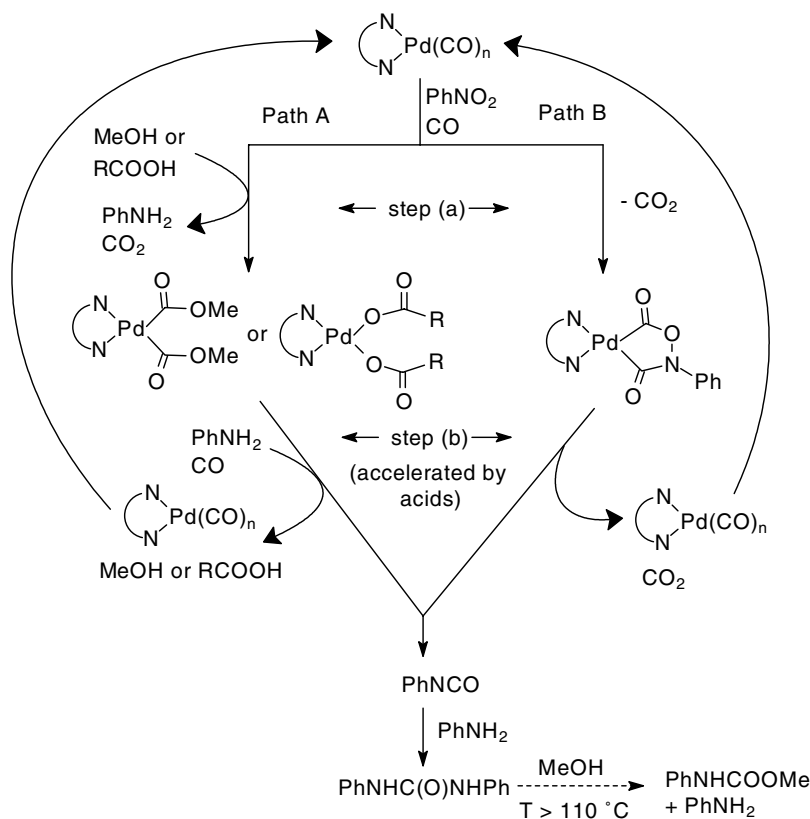
observed. Since the rate of the step (b) depends on the aniline concentration, but that of step (a) does not, it is reasonable to assume that by gradually increasing the aniline amount we may reach the point at which the rate of the nitrobenzene activation and aniline carbonylation become comparable or the latter is even faster than the former. The kinetic data reported in this paper indicate that we have indeed reached this limit. Under these conditions, either a first order dependence of the rate on nitroarene concentration (if the rate of step (a) is markedly slower than step (b)) or a complex kinetic rate (if the two rates are comparable), is expected and is indeed observed. If step (a) is rate determining, the kinetics should also become independent from both aniline and CO concentrations (CO coordination to a palladium(0) complex should be easy), which is also in accord with the kinetic data.

The role of the acid is more difficult to quantify, because it is apparently involved at several stages of the reaction and because of the possible involvement of the process in path B. If we suppose that the main effect of the acid is to accelerate the reaction between the intermediate palladium(II) complex and aniline (step (b) in path A), a small acceleration by the acid should still be observable if the rate of step (a) and (b) are comparable, but this should rapidly flatten. Indeed, as the rate of step (b) is accelerated, it will become faster than step

(a) and any further acceleration will not be kinetically observable. This is in agreement with the experimental data.

Note that the reaction associated with path B can surely contribute to the overall process because we have previously reported that when the Pd(TMB)$_2$/Phen catalytic system is employed under very similar conditions, but in the absence of aniline, phenylisocyanate is formed [15]. In the absence of added aniline, path B is likely to be dominant because the small amounts of aniline produced during the reaction would be mostly trapped by phenylisocyanate to give diphenylurea and the rate of step (b) in path A would be strongly decreased. However, by the same token, a large amount of aniline, such as that employed in this work, should increase the importance of path A at the expense of path B.

Finally, it can be noted that the scenario described above also explains why catalyst deactivation is much faster during the synthesis of ureas than during that of carbamates. Formation of metallic palladium clearly derives from aggregation of insufficiently stabilized palladium(0) complexes. Under the conditions in which the synthesis of carbamates is performed, at least in our group and the one of van Leeuwen, the oxidation of the palladium(0) complex to palladium(II) is a fast reaction (zero-order kinetics with respect to nitrobenzene) and the resting state of the catalyst is a palladium(II)

complex, which cannot aggregate to metallic palladium. However, as the aniline concentration is increased, the rate of the reduction of palladium(II) increases and can even become higher than that of its formation. Under these conditions (first-order kinetics in nitrobenzene) a palladium(0) will become the resting state of the catalytic cycle, thus explaining the easy deactivation.

3.2.4. Reaction stoichiometry

Based on the literature precedents and on our finding that azoderivatives only originate from nitrobenzene, in the Results section we have interpreted the observed reagents consumption as deriving from the two stoichiometries described in Eqs. (2) and (3), respectively (the 1:1 and 1:5 processes). However, an examination of the data reported in Tables 1–3 clearly shows that with few exceptions, the most outstanding of which corresponding to reactions in which a very high concentration of aniline was present, the molar amounts of aniline and nitrobenzene consumed are always very similar. In most cases the ratio is so close to one that the difference is well within the experimental error. This occurs despite the amount of azoxybenzene, only deriving from nitrobenzene (Eq. (4)), varies widely. The major process, that described by Eq. (2), consumes equal amounts of the two reagents, so that the larger inclusion of aniline-derived moieties in the produced urea should derive from the 1:5 process. However, that two completely independent reactions, the synthesis of azoxybenzene (Eq. (4)) and the 1:5 process (Eq. (3)), exactly compensate each other to give an overall 1:1 consumption of aniline and nitrobenzene may coincidentally occur in one case, but it is extremely unlikely to occur in most reactions. The only reasonable explanation is that under most of the conditions employed in this study, one only process, rather than two independent ones, is operating. Such process should have the stoichiometry shown in Eq. (8):

$$2PhNO_2 + 2PhNH_2 + 3CO \rightarrow PhN(O){=}NPh \\ + PhNHC(O)NHPh + 2CO_2 + H_2O \quad (8)$$
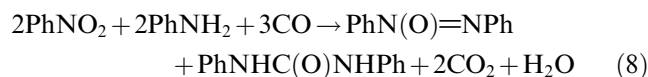
To the best of our knowledge, no process of this kind has ever been described or proposed in the literature and we are now trying to provide an experimental basis for its occurrence. The process must clearly be a multistage one and the only information we can give on it at the moment, based on the selectivity data reported in the literature and collected here, is that it appears to be favored by the presence of bases and inhibited by both acids and chloride anion. Since formation of azo derivatives as byproducts is at the moment the main obstacle to commercialization of a technology based on carbonylation of nitroarenes, understanding the mechanism of their formation is of outmost importance for the development of this field.

4. Conclusions

Carbonylation of nitroarenes is a complex reaction. Even when an apparently simple catalytic system is employed, such as that based on palladium–phenanthroline complexes, several reaction pathways and even different reaction stoichiometries are clearly involved. This has led to apparently contradictory results from several laboratories. We have started several years ago to investigate more deeply this reaction and, although a complete picture is still far to be reached, several pieces of information begins to fit a general scheme. In this paper, we have shown that some apparently contradictory results on the effect of chloride are probably all correct and an explanation can be given for this. Some new findings were also discussed, which also restrict the range of possible mechanisms and will constitute the basis for further investigations.

5. Experimental

5.1. General procedure

All solvents were dried by standard procedures, distilled and stored under dinitrogen before use. Pd(trimethylbenzoate)$_2$ [15] and [Pd(Phen)$_2$][BF$_4$]$_2$ [11,50] were prepared as reported in the literature. Compounds **2a,b** and **3a,b** were prepared as previously reported [40]. Nitrobenzene was purified by shaking with 10% H$_2$SO$_4$, washing with water, and drying with Na$_2$SO$_4$, followed by distillation under dinitrogen and storage under an inert atmosphere. Aniline was distilled and stored under dinitrogen before use. 2,4-Dinitrotoluene was recrystallized from methanol to remove water. All other reagents were commercial products and were employed as received.

5.2. Catalytic reactions

In a typical catalytic reaction, the catalyst, Phen, PhNO$_2$, and, when required, PhNH$_2$ and the acidic promoter or [PPN][Cl] were weighed in a glass liner. The liner was placed inside a Schlenk tube with a wide mouth under dinitrogen and was frozen at −78 °C with dry ice, evacuated and filled with dinitrogen, after which the solvent was added. After the solvent was also frozen, the liner was closed with a screw cap having a glass wool-filled open mouth which allows gaseous reagents to exchange and rapidly transferred to a 200 ml stainless steel autoclave with magnetic stirring. The autoclave was then evacuated and filled with dinitrogen three times. CO was then charged at room temperature at the required pressure and the autoclave was immersed in an oil bath preheated at the required temperature; the autoclave took about 15 min to fully equilibrate at

the final temperature. Other experimental conditions are reported in the captions to the tables and figures. At the end of the reaction the autoclave was cooled with an ice bath and vented.

5.3. Products analysis

5.3.1. Synthesis of diphenylurea

At the end of the reaction, most of the produced diphenylurea precipitated out of the solution. Naphthalene (GC internal standard) and benzophenone (HPLC internal standard) were added to the reaction mixture and dissolved. Then the suspension was filtered through a glass frit and the solid washed with additional toluene. The solid was dried under vacuum and weighed. It is pure diphenylurea and no trace of contaminants could be detected by any spectroscopic or chromatographic analysis. The solution was analyzed by HPLC (RP-18 column, methanol/water 55:45 as eluent) to quantify the diphenylurea still remained in solution, and by gas chromatography (Dani 8610 gas chromatograph, equipped with a PS 255 column) for nitrobenzene, aniline, azo- and azoxybenzene. Aniline and nitrobenzene were also quantified by HPLC analysis. The obtained value are in good agreement with the values obtained by GC analysis, but were affected by a larger standard deviation and only the GC data have been employed.

5.3.2. Synthesis of dimethyl 2,4-toluenedicarbamate

At the end of the reaction, part of the dicarbamate (**1**) was present as a precipitate. Naphthalene (GC internal standard) and benzophenone (HPLC internal standard) were added to the reaction mixture and enough THF was added to dissolve any solid. The solution was then analyzed by HPLC (RP-18 column, methanol/water 55:45 as eluent; for 2,4-dinitrotoluene, **1**, **2a,b**, **3a,b**) and gas chromatography (PS 255 column; for **4a,b** and **5**).

Acknowledgements

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