

Reductive carbonylation of 2,4-dinitrotoluene to 2,4-toluendiurethane with palladium(1,10-phenanthroline)₂(hexafluorophosphate)₂, as catalyst, and 1,10-phenanthroline hexafluorophosphate, as cocatalyst.

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Abstract

Reductive carbonylation of 2,4-dinitrotoluene (DNT) affords 2,4-toluendiurethane (TDU) with unprecedented high yield and selectivity when palladium(1,10-phenanthroline)₂(hexafluorophosphate)₂ [Pd(phen)₂(PF₆)₂] is used as catalyst, in combination with free 1,10-phenanthroline (phen) and 1,10-phenanthroline hexafluorophosphate (phenHFP₆), as acid cocatalyst. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Palladium complex; Reductive carbonylation; Dinitroaromatics; Urethanes

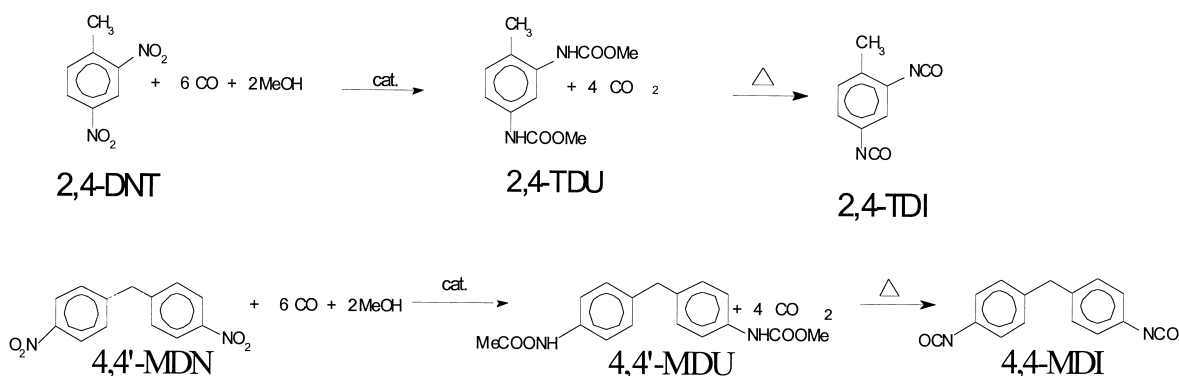
1. Introduction

The catalytic reductive carbonylation of aromatic nitrocompounds to the corresponding carbamates is an important target for the production of 2,4-toluendiisocyanate (TDI) and 4,4'-methylenediisocyanate (MDI) (see Scheme 1), products which are currently manufactured

through the reaction of diamine with the highly toxic phosgene to yield a diisocyanate.

Reductive carbonylation reaction is reported to be catalyzed by group VIII–X transition metals such as Ru, Rh and Pd [1–7]. Among these, promising catalysts are based on palladium complexes of nitrogen chelating ligands (phenanthroline, bipyridine and their substituted derivatives) [8–11]. Although these reactions are reported to be very effective with aromatic mononitrocompounds, the conversion of the commercially important dinitrosubstrates is more difficult [12–14].

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Scheme 1. Reductive carbonylation of aromatic dinitroderivates into diisocyanates.

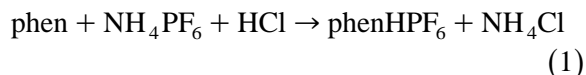
Recently, carbonylations of dinitroderivatives catalyzed by Pd(1,3-bis-diphenylphosphino-propane)Cl₂-potassium carbonate, montmorillonite-(bipyridil)palladium acetate and Pd(phen)₂(triflate)₂, have been reported [12–14]. The good yield reported in the carbonylation of dinitroderivatives into the corresponding dicarbamates can be ascribed either to the low value of the substrate/palladium catalyst molar ratio or to the high concentration of the acid cocatalyst.

Here we report the astonishing effect of the non conventional acid phenanthroline hexafluorophosphate (phenHPF₆) used as cocatalyst, with Pd(phen)₂(PF₆)₂ as the catalyst in the reductive carbonylation of DNT to TDU.

2. Results and discussion

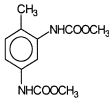
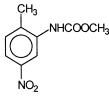
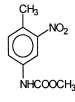
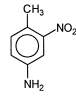
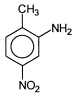
The choice of this combination arises from the fact that Pd(phen)₂(PF₆)₂ was previously reported as an active catalyst in the carbonylation of nitrobenzene [8] and that, moreover, many authors have realized the importance of the presence of a non-esterifiable (by the alcoholic solvent) acid cocatalyst whose conjugated base is a weakly coordinating anion (e.g., 2,4,6-trimethylbenzoic acid, 2-chlorobenzoic acid, *p*-toluensulfonic acid and so on) [7,8,11, 15,17]. The phenHPF₆ cocatalyst meets both these requirements being composed from the

acid phenH⁺ (p*K*_a = 4.86) and from the weakly coordinating counterion, PF₆⁻. This cocatalyst is prepared in a very simple way by reaction of phenanthroline with ammonium hexafluorophosphate, in acidic medium, according to Eq. (1) [16]:



The DNT carbonylation catalyzed by the system Pd(phen)₂(PF₆)₂ and phenHPF₆ at a molar ratio of [Pd]/[phenH⁺] = 1/8 has been studied at different temperatures (Table 1). At 115°C (run 1) the DNT conversion is 98%, but the TDU yield (I) is only 6%. In this case, yields in monocarbamates (II + III) of 86% and in nitroanilines (IV + V) of 7% are obtained, with no other detectable byproducts. An increase of the reaction time from 2 to 5 h (run 2 vs. 1) allows a complete conversion of the substrate with a TDU yield of 40%. This value and a 40% yield in monocarbamates (II + III) take into account for the 80% of the converted substrate. The remaining 20% of the products is mainly constituted of a complex mixture of isomeric azo and azoxy derivatives (see Scheme 2). The same reaction carried out at 135°C (run 3) affords again a complete conversion of the substrate, with a TDU yield of 32%. The monocarbamates yield (46%) is lower than in run 1

Table 1
Reductive carbonylation of DNT to TDU at various temperatures

Run	T (°C)	DNT Conv. (%)					
			(I) yield (%)	(II) yield (%)	(III) yield (%)	(IV) yield (%)	(V) yield (%)
1	115	98	6	31	55	1	6
2	115 ^a	100	40	10	30	0	1
3	135	100	32	10	30	0	1
4	160	100	75	0	0	0	1

Reaction conditions: [DNT] = 0.71 M, [Pd] = 1.44×10^{-3} M, [DNT]/[Pd]/[PhenH⁺] = 520:1:8, MeOH 100 ml, 2,2'-dimethoxypropane (DMP) 1 ml; 60 bar CO; 2 h.

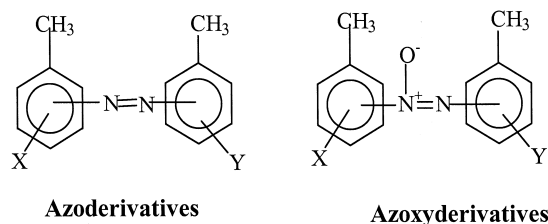
^aFive hours.

and the nitroanilines almost disappear. The remaining products (19%) are isomeric azo and azoxy derivatives. The catalytic system is active and selective at 160°C (run 4) with a TDU yield of 75%. However, in this case 23% of azo and azoxy byproducts are also present. These results show that, contrary to other catalytic systems, even a low ratio acid cocatalyst/palladium provides an efficient catalytic system.

The effects of the variation of molar ratio in Pd(phen)₂(PF₆)₂/phenH⁺ and of the addition of some free ligand in carbonylation of DNT at 135°C are collected in Table 2. The TDU yield increases with the concentration of the acid cocatalyst (runs 1–3) and the substrate is completely converted within 2 h. The product yield is 32%, at a molar ratio of [Pd]:[phen]:[phenH⁺] = 1:0:8 (run 3). The total monocarbamates yield is 46%, whereas the nitroanilines disappear with the increase in acidity. In the presence of added phenanthroline (runs 4, 5 and 6, Table 2), the conversion of the substrate is complete and the selectivities to the dicarbamate increase monotonically with the phen/palladium molar ratio. At [Pd]:[phen]:[phenH⁺] molar ratio of 1:4:8 (run 5) a 72% TDU yield is obtained. Only trace amounts of monocarbamates and nitroanilines are detected. Finally, at [Pd]:[phen]:

[phenH⁺] molar ratio of 1:8:8 (run 6) the yield dicarbamate rises to 82%. In this case, the monocarbamates yield accounts for 8%, while the azo and azoxy byproducts are 10%. The TDU yield has to be compared with the value of 31% previously obtained with Pd(phen)₂(OTf)₂ and 4-chlorobenzoic acid catalytic system [14].

The crucial peculiarity of this system is the contemporary presence of phenH⁺ and phen, which act as a buffer, releasing an equilibrate and dosed concentration of protons and free ligand during the reaction. The acid avoids the formation of nitroso intermediates, which can probably lead to azo and azoxy derivatives [17–20], while the free ligand stabilizes the catalyst against decomposition to palladium metal.

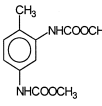
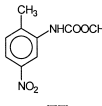
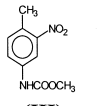
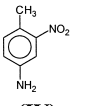
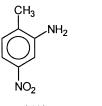


X and Y = -NO₂ and/or -NHCOOMe

Scheme 2. Isomeric azo and azoxy byproducts structure.

Table 2

Reductive carbonylation of DNT in the presence of phenH⁺PF₆⁻ and free phenanthroline

Run	[Pd]/[Phen]/[PhenH ⁺] Molar ratio	DNT Conv. (%)	 (I) yield (%)	 (II) yield (%)	 (III) yield (%)	 (IV) yield (%)	 (V) yield (%)
1	1/ 0/ 1	98	4	39	22	1	2
2	1/ 0/ 4	98	11	38	20	0	0
3	1/ 0/ 8	100	32	33	13	1	0
4	1/ 2/ 8	100	53	1	11	0	0
5	1/ 4/ 8	100	72	0	4	0	2
6	1/ 8/ 8	100	82	1	7	0	0

Reaction conditions: [DNT] = 0.71 M, [Pd] = 1.44×10^{-3} M, [DNT]/[Pd] = 520, MeOH 100 ml, 2,2'-dimethoxypropane (DMP) 1 ml; 135°C, 60 bar CO; 2 h.

In conclusion, we have demonstrated that the combination Pd(phen)₂(PF₆)₂, phenanthroline and phenHPF₆ constitute really a powerful catalytic system for reductive carbonylation of dinitrotoluene to afford TDU in high yield and selectivities.

3. Experimental

All the chemicals were purchased from Aldrich and Acros and used as received, except for the DNT, which was crystallized from methanol before the use. Pd(phen)₂(PF₆)₂ [7] and phenHPF₆ [16] were prepared according to the literature. Carbon monoxide was purchased from Rivoriva.

All the reactions were carried out in a Hastelloy C autoclave (500 ml), equipped with a mechanical stirrer, a manometer and a heating mantle. A teflon-coated thermocouple allowed the internal temperature to be measured.

The results of the experiments were analysed by HPLC on a Hewlett Packard apparatus mod. 1060, with a LiChrospher 100 RP 18 nm 250 × 4 mm endcapped.

4. General procedure for reductive carbonylation

In a typical reaction run, the reaction mixture constituted by 13 g of DNT (71.4 mmols), 84 mg of the palladium catalyst Pd(phen)₂(PF₆)₂ (0.137 mmols), the desired amount of acid phenHPF₆, the free ligand, 1,10-phenanthroline, in 100 ml of methanol and 1 ml of 2,2'-dimethoxypropane (DMP), added as a dehydrating agent for methanol, was charged into the autoclave, and, after passing three times with CO, was again filled with CO at 60 bar and heated at the required temperature. At the end of the reaction, the reactor was depressurized and the reaction mixture after dilution with methanol required volume was analyzed by HPLC.

Acknowledgements

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References

- [1] T. Mizuno, H. Alper, *J. Mol. Catal.* 121 (1997) 119.
- [2] S. Cenini, C. Crotti, M. Pizzotti, F. Porta, *J. Org. Chem.* 53 (1988) 1248.
- [3] W.J. Gladfelter, J.D. Gargulak, *A.C.S. Symp.* 557 (1995) 47, and references therein.
- [4] F. Ragaini, S. Cenini, A. Fumagalli, C. Crotti, *J. Organomet. Chem.* 428 (1992) 401.
- [5] S.P. Gupte, R.W. Chaudari, *J. Mol. Catal.* 24 (1984) 197.
- [6] F. Ragaini, S. Cenini, *La Chimica e l'Industria* 78 (1996) 421, and references therein.
- [7] E. Drent, *Pure Appl. Chem.* 62 (1990) 61.
- [8] A. Bontempi, E. Alessio, G. Chanos, G. Mestroni, *J. Mol. Catal.* 42 (1987) 67.
- [9] E. Drent, P.E. Prillwitz, *EP Appl.* 225, 673 (1987); *C.A.*: 108, 55671y.
- [10] P. Wehman, V.E. Kaasjager, W.G.J. De Lange, F. Hartl, P.J. Kamer, P.W.N.M. Van Leeuwen, J. Fraanje, K. Goubitz, *Organometallics* 14 (1995) 3751.
- [11] P. Wehman, G.C. Dol, E.R. Moorman, P.J. Kamer, P.W.N.M. Van Leeuwen, J. Fraanje, K. Goubitz, *Organometallics* 13 (1994) 4856.
- [12] P.R. Nagavelli, N.P. Reddy, A.M. Masdeu, B.E. Ali, H. Alper, *J. Chem. Soc., Chem. Commun.* (1994) 863.
- [13] V.L.K. Valli, H. Alper, *J. Am. Chem. Soc.* 115 (1993) 3778.
- [14] P. Wehman, P.J. Kamer, P.W.N.M. Van Leeuwen, *Chem. Commun.* (1996) 217.
- [15] S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni, E. Alessio, *J. Mol. Catal.* 64 (1991) 179.
- [16] R. Santi, A.M. Romano, F. Panella, G. Mestroni, A. Sessanta O Santi, *Dom. Brev. It.* 5738 (1996).
- [17] P. Wehman, L. Borst, P.C.J. Kamer, P.W.N.M. Van Leeuwen, *J. Mol. Catal.* 112 (1996) 23.
- [18] S.J. Skoog, W.L. Gladfelter, *J. Am. Chem. Soc.* 119 (1997) 11049.
- [19] S.J. Skoog, J.P. Campbell, W.L. Gladfelter, *Organometallics* 13 (1994) 4137.
- [20] P. Leconte, F. Petit, F. Metz, A. Mortreux, J.A. Osborn, F. Paul, A. Pillot, *J. Chem. Soc., Chem. Commun.* (1990) 1616.