Palladium Complex–Potassium Carbonate-catalysed Reductive Carbonylation of Mono- and Di-nitroaromatic Compounds

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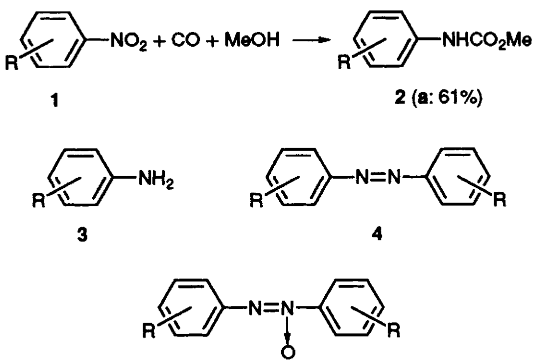
Mono- and di-nitroaromatic compounds react with carbon monoxide in benzene containing methanol, with catalytic quantities of 1,3-bis(diphenylphosphino)propanepalladium dichloride and potassium carbonate as the base, to give urethanes in reasonable yields.

Mono- and di-urethanes (carbamates) are industrially important products as they are not only useful agricultural chemicals or pesticides but also precursors for isocyanates which in turn are intermediates for high-performance plastics, polyurethanes, elastomers, adhesives, *etc.* The existing commercial production of isocyanates involves the reaction of highly poisonous and corrosive phosgene gas with the corresponding amines. One of the most promising ways[1–3] to circumvent the difficulties in the phosgene route is the direct preparation of isocyanates as well as urethanes by the transition metal-catalysed oxidative carbonylation of amines[2,4] or reductive carbonylation of nitro compounds.[5] Most of the previously reported catalytic systems for the reductive carbonylation of nitro compounds usually require corrosive Lewis acids[6–9] and/or a base[6,7,9] such as pyridine or triethylamine in excess amounts. For example, supported palladium is inactive in the absence of a Lewis acid even in the presence of an excess of pyridine,[7] whereas $PdCl_2$ exhibits good activity in the absence of Lewis acids but requires excess of base.[10] Palladium(II) complexes of the type $[Pd(py)_2Cl_2]$ (py = pyridine) can catalyse the reaction at low py : Pd ratio but the method requires promoters such as $FeCl_3$ or $MoCl_5$ and aprotic solvents such as chlorobenzene.[11] On the other hand, catalysis of the reductive carbonylation of nitro compounds by palladium anchored to montmorillonite,[5] supported Pd–1,10-phenanthroline derivatives in the presence of a Brønsted acid,[12] Pd^{II} complexes with 1,10-phenanthroline derivatives[13] and Pd-heteropolyanion[14] are recent approaches to this problem.[15] In pursuing new methods for the development of catalytic systems for the synthesis of carbamates, we found that a catalytic amount of K_2CO_3 can promote the Pd-catalysed reductive carbonylation of mono- as well as di-nitro aromatic compounds in the presence of methanol under comparatively mild conditions, to give mono- and di-urethanes in good yields.

Treatment of a mixture of *p*-nitrotoluene **1a**, (2 mmol), 1,3-bis(diphenylphosphino)propanepalladium dichloride, $[Pd(dppp)]Cl_2$ (0.04 mmol), K_2CO_3 (0.06 mmol), methanol (1 ml) and benzene (4 ml) with CO (300 psi) at 155–160 °C for 24 h gave the carbamate **2a** in 61% yield. The ratio of **2a**, amine **3a**, azo compound **4a** and azoxy compound **5a** was 89 : 7 : 3 : 1 (Scheme 1).



1 **2** (**a**: 61%) **3** **4** **5**

a: R = *p*-Me
b: R = *o*-Me
c: R = *p*-OMe
d: R = *o*-OMe
e: R = *p*-Cl
f: R = H

Scheme 1 *Conditions:* $[Pd(dppp)]Cl_2$, K_2CO_3, C_6H_6, 155–160 °C, 24 h

The striking feature of the present catalytic system is the use of K_2CO_3 as a cocatalyst. There was virtually no conversion of **1a** in the absence of K_2CO_3. Under identical conditions (Scheme 1), an increase or decrease of the amount of K_2CO_3 or the use of other bases such as Na_2CO_3 and NEt_3 affected the yield and selectivity of **2a**. With Na_2CO_3, although **1a** was completely consumed, the yield of **2a** decreased to 53% (**2a** : **3a** : **4a** : **5a** = 85 : 7 : 8 : 0) and, with NEt_3, the conversion of **1** was only 27% (**2a** : **3a** : **4a** : **5a** = 52 : 34 : 3 : 11). The catalytic system is sensitive to the temperature and the amount of methanol. In the presence of excess of methanol or at higher temperatures, the reaction favours the formation of the amine **3a**.

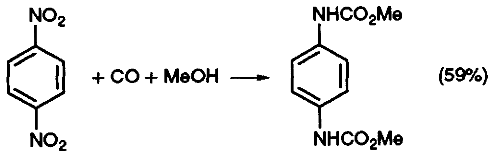
Other palladium catalysts gave **2a** in lower selectivity and yield as shown in the Table 1. The bidentate ligand dppp is essential for the complete conversion of **1a** and good yields of urethane. No conversion of **1a** was observed in the presence of $[Pd(PPh_3)_2]Cl_2$. However, addition of 1 equiv. of dppp relative to $[Pd(PPh_3)_2Cl_2$ gave the urethane in approximately the same yield as with $[Pd(dppp)]Cl_2$. In combination with $[Pd(PPh_3)_2]Cl_2$, 1,2-bis(diphenylphosphino)ethane or 1,4-bis(diphenylphosphino)butane did not significantly promote the reaction.[16]

Various nitrobenzenes **1a–f** were subjected to reductive

Table 1 Pd-catalysed reductive carbonylation of nitroaromatic compounds[a]

Substrate	Catalyst[b]	Conversion of **1** (%)	Yield of **2** (%)[c]	**2** : **3** : **4** : **5**[d]
1a	A	100	61[e]	89 : 7 : 3 : 1
a	B + 1 equiv. dppp	70	35	70 : 20 : 5 : 3
a	C	0	—	—
a	C + 1 equiv. dppp	100	64[e]	89 : 1 : 1 : 9
b	A	86	42	50 : 36 : 4 : 10
c	A	100	76	90 : 10 : 0 : 0
d	A	100	58	60 : 40 : 0 : 0
e	A	96	53	70 : 22 : 8 : 0
f	A	100	51	58 : 10 : 8 : 24

[a] Reaction conditions: **1** (2 mmol), Pd complex, (0.04 mmol) K_2CO_3 (0.06 mmol), MeOH, (1 ml), benzene (4 ml) P_{CO}, 20 atm; *T* 155–160 °C; *t* 24 h. [b] = $[Pd(dppp)]Cl_2$; B = $Pd(OAc)_2$; C = $[Pd(PPh_3)_2]Cl_2$. [c] NMR yields unless otherwise mentioned. [d] GLC ratio; all compounds were identified by spectroscopic methods and/or by comparison with authentic compounds. [e] Isolated yield.



Scheme 2 *Conditions:* $[Pd(dppp)]Cl_2$, K_2CO_3, C_6H_6, 155–160 °C, 7 h

carbonylation in the presence of [Pd(dppp)]Cl_2 as catalyst to give the corresponding urethanes in moderate to good yields. A relatively low yield of urethane was obtained with *o*-nitrotoluene.

The catalytic system also worked well in the case of dinitroaromatics to give the diurethanes in good yields. Surprisingly, the reaction of 1,4-dinitrobenzene was relatively rapid to give 59% of diurethane (Scheme 2). The reaction of 4,4′-dinitrobiphenyl (for 24 h) and 2,4-dinitrotoluene (for 50 h) gave the corresponding diurethanes in 53 and 47% yield respectively. In all the reactions of dinitro compounds a large amount of insoluble material was obtained.† ^{1}H NMR studies of the soluble portion showed the presence of diurethane and almost negligible amounts of byproducts such as monocarbamates and amines. The catalytic system, however, could not catalyse the reaction of 1,5-dinitronaphthalene.

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Footnote

† The insoluble material is believed to be a polymeric mixture resulting from the amine-containing byproducts. The reaction mixture was filtered and washed with acetone and the diurethanes were recrystallized from chloroform or chloroform–hexane.

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