A Novel Catalytic Synthesis of Carbamates by Oxidative Alkoxycarbonylation of Amines in the Presence of Palladium and Iodide

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Palladium and iodide catalyse the oxidative carbonylation of amines by CO, O_2, and alcohols to give carbamates in high yields.

Carbamates are important compounds not only as agricultural chemicals or pesticides, but also as precursors of isocyanates, because carbamates can be thermally decomposed to give isocyanates in good yields. Carbamates are usually prepared by the reaction of alcohols with isocyanates manufactured by phosgenation of the corresponding amines. Few methods for the high yield catalytic preparation of carbamates directly from amines are known.†

We now report that the catalyst system comprising metallic palladium and iodide is very effective for preparing carbamates directly from amines, CO, O_2, and alcohols (equation 1).

$$R^1NH_2 + CO + R^2OH + 1/2\ O_2 \rightarrow R^1NHCO_2R^2 + H_2O \quad (1)$$

The reaction is illustrated by the preparation of ethyl *N*-phenylcarbamate (R^1 = Ph, R^2 = Et). A 200 ml autoclave internally lined with titanium was charged with aniline (50 mmol), EtOH (50 ml), Pd black (0.3 mg-atom), and NaI (0.6 mmol). After the air inside the autoclave had been replaced with CO, CO was pressurized into the autoclave to 80 kg/cm^2 and then O_2 was introduced, to a total pressure of 86 kg/cm^2. The reaction was carried out at 160—170 °C for 2 hours with stirring, and subsequently the cooled reaction mixture was filtered. G.l.c. and h.p.l.c. analyses of the clean pale yellowish filtrate showed that the conversion of aniline was 95% and the yield of ethyl *N*-phenylcarbamate was 93% with a selectivity of 98%, and the yield of *N,N'*-diphenylurea, an intermediate, was 0.5%. *N*-Ethylaniline and diethylcarbonate were scarcely detected. The Pd black was collected completely on the filter paper and was not detected in the filtrate by atomic absorption spectrometry. The NaI was also recovered completely by hot water extraction of the residue obtained after removal of the EtOH from the filtrate.

When the procedure described above had been repeated 20 times reusing the Pd black and the NaI recovered each time, ethyl *N*-phenylcarbamate was obtained in a yield of 92—94% with a selectivity of 96—98% in each case.

Results of other experiments under similar conditions using several substrates and catalyst systems are summarized in Table 1. The combination of Pd and I^- shows excellent catalytic activity, (neither Pd nor I^- alone catalyse the reaction). Of course, the reaction does not proceed in the absence of oxygen.

The reaction seems to proceed *via* heterogeneous catalysis by the metallic Pd with the aid of I^- because the Pd is not dissolved into the medium during the reaction. Carbamoyl palladium species [RNHCO–Pd] which would be formed on the surface of Pd are presumed to be the active species.‡ Alcoholysis and aminolysis of these species would give carbamate and *N,N'*-disubstituted urea respectively. *N,N'*-

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† Only two methods have been hitherto proposed for preparing carbamates by oxidative alkoxycarbonylation of amines. (a) One method uses Se and bases, ref. 1. (b) The other uses $PdCl_2$ and a Lewis acid. The Lewis acid must contain a metal capable of undergoing redox reactions, such as $CuCl_2$, $FeCl_3$, FeOCl, ref. 2. In this case, the reaction seems to proceed by the Wacker type redox reaction. In fact, Pd^0, Pd^{2+}, Fe^0, and Fe^{3+} were present in the reaction mixture when $PdCl_2$ and $FeCl_3$ were used. In our catalyst system such metal species are not required and so a different type of mechanism is presumed to operate.

‡ Carbamoyl metal complexes are known to be intermediates in the homogeneous reaction of amines with CO. (a) R_2NCO–$Co(CO)_3PPh_3$ has been isolated, ref. 3. (b) Li[Me_2NCO–$Ni(CO)_3$] has been reported, and this complex is available as a nucleophilic carbamoylation reagent, ref. 4. Few alkoxycarbonyl palladium species [ROCO–Pd] seem to be formed under these conditions, since dialkylcarbonate was scarcely produced even after all of the amine had been converted.

Table 1. Pd–I$^-$ catalysed carbamate synthesis. Oxidative alkoxycarbonylation of amines by oxygen.[a]

Iodide	Amine	Carbamate	% Yield[b]
None	$PhNH_2$	$PhNHCO_2Et$	3
NaI (No Pd)	$PhNH_2$	—	0
LiI	$PhNH_2$	$PhNHCO_2Et$	75(94)
KI	$PhNH_2$	$PhNHCO_2Et$	95(97)
RbI	$PhNH_2$	$PhNHCO_2Et$	94(97)
CsI	$PhNH_2$	$PhNHCO_2Me$[c]	95(98)
CsI	Bu_2NH	$Bu^n{}_2NCO_2Et$	85(90)
KI	p-$Me_2NC_6H_4NH_2$	p-$Me_2NC_6H_4NHCO_2Et$	90(95)
NH_4I	$PhNH_2$	$PhNHCO_2Et$	90(95)
Et_4NI	$PhNH_2$	$PhNHCO_2Me$[c]	94(98)
$[Me_3NPh]I$	$PhNH_2$	$PhNHCO_2Et$	95(97)
$[Ph_3PMe]I$	$PhNH_2$	$PhNHCO_2Et$	90(96)
$[Ph_3AsMe]I$	$PhNH_2$	$PhNHCO_2Et$	90(95)
Me_4NI	Cyclohexyl–NH_2	Cyclohexyl–$NHCO_2Et$	95(97)
Me_4NI	$H_2N[CH_2]_6NH_2$[d]	$EtOCONH[CH_2]_6NHCO_2Et$	89(94)
$\vdash CH_2NMe_3]I$[e]	$PhNH_2$	$PhNHCO_2Et$	92(95)
Me_4NI	$PhNH_2$	$PhNHCO_2Et$[f]	94(97)
CsI	$PhNH_2$	$PhNHCO_2Me$[c,g]	92(96)
NaI	$PhNH_2$	$PhNHCO_2Me$[c,h]	90(96)

[a] See text for conditions [amine (50 mmol), I$^-$ (0.6 mmol), Pd (0.3 mg-atom), and EtOH (50 ml)] unless otherwise stated. [b] Based on amine used. Yields in parenthesis were calculated based on amine reacted, and they show selectivities. [c] 50 ml of MeOH was used. [d] 15 mmol of diamine was used. [e] Macroreticular type anion exchange resin was used after exchanging the –OH anion with iodide anion by treating with aq. HI. The reaction was carried out at 150 °C. [f] 5 weight % of Pd on activated carbon was used. [g] 5 weight % of Pd on $CaCO_3$ was used. [h] 0.5 weight % of Pd on Al_2O_3 was used.

Disubstituted urea is alkoxycarbonylated further to give carbamates. This was confirmed by the fact that *N,N'*-diphenylurea was converted into ethyl *N*-phenylcarbamate quantitatively under similar conditions (equation 2).

$$PhNH\text{–}CO\text{–}NHPh + CO + 2EtOH + 1/2\ O_2 \xrightarrow[CsI]{Pd} \underset{(98\%)}{2\,PhNHCO_2Et} + H_2O \qquad (2)$$

Thus this simple Pd–I$^-$ system has excellent catalytic activity for oxidative carbonylation of nitrogen containing compounds.

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