An Exceptionally Mild, Catalytic Homogeneous Method for the Conversion of Amines into Carbamate Esters

Howard Alper* and Frederick W. Hartstock

Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Aromatic amines react at room temperature and atmospheric pressure with carbon monoxide, oxygen, alcohols, and hydrochloric acid, with palladium chloride as the catalyst and copper(II) chloride as re-oxidant to give carbamate esters in fair to quantitative yields.

It has recently been demonstrated that alkenes,[1] alkynes,[2] and allenes[3] undergo regiospecific hydroesterification at room temperature and atmospheric pressure affording saturated or unsaturated carboxylic esters in good yields [*e.g.* reaction (1)]. We now report the application of this process to aromatic amines, heteroatom-bearing substrates lacking the unsaturated functionalities previously investigated. It was expected that amines could be converted into carbamate esters which are valuable from both industrial and academic viewpoints. This communication[4] is prompted by the recent publication of two closely related communications by Fukuoka and co-workers,[5,6] which describe the oxidative carbonylation of amines to carbamate esters catalysed by a palladium group metal and iodide ion at 83 atm and 160—170 °C.

$$R^1CH{=}CH_2 + CO + R^2OH \rightarrow R^1CHMeCO_2R^2 \quad (1)$$

$$\underset{(\mathbf{1})}{ArNH_2} + CO + ROH \rightarrow \underset{(\mathbf{2})}{ArNHCO_2R} \quad (2)$$

Reagents and conditions for both reactions: O_2, HCl, $PdCl_2$, $CuCl_2$, room temp., 1 atm.

Treatment of *p*-toluidine (**1**, Ar = *p*-MeC_6H_4) with carbon monoxide, oxygen, methanol, and hydrochloric acid, with palladium chloride as the catalyst and copper(II) chloride as re-oxidant, at room temperature and atmospheric pressure, gave methyl *N*-*p*-tolylcarbamate (**2**, Ar = *p*-MeC_6H_4, R = Me) in 68% isolated yield [reaction (2)].† Oxygen is beneficial for this reaction since in its absence the yield of carbamate ester decreased to 34% and a small amount of an unidentified product was also isolated. While acetic acid can be used instead of hydrochloric acid, some acid is required, otherwise tars are formed. In terms of metal components, acetates of palladium and copper can be substituted for the corresponding chlorides. Ethanol can also be employed as the alcohol.

This process is applicable to a series of aromatic amines, giving carbamate esters in fair to quantitative yields (see Table 1 for results). Halide, ether, and carbonyl functionalities are unaffected in these reactions. Not only does the reaction have the advantages of occurring under remarkably mild conditions but it is also simple both in execution and work-up. This homogeneously catalysed reaction is therefore clearly superior to known methodology for synthesizing carbamates from amines, including the heterogeneously catalysed reaction of Fukuoka and co-workers[5,6] which requires drastic conditions.

Aromatic carbamate esters are convertible by reaction with formaldehyde into urethanes and/or polyurethanes and are thermally decomposable to isocyanates which are intermediates in the formation of urethanes and polyurethanes by reaction with monohydric alcohols and polyols, respectively. Therefore, the reaction described herein is a viable one for the production of isocyanates and ultimately polyurethanes which avoids the use of phosgene as conventionally employed for converting aromatic amines into isocyanates.

Table 1. Products obtained from the reaction of (**1**) with CO, O_2, ROH, HCl, $PdCl_2$, $CuCl_2$ [reaction (2)].

Ar in (**1**)	R in ROH	% Yield of $ArNHCO_2R$ (**2**)
p-MeC_6H_4	Me	68
p-MeC_6H_4	Me[a]	34[b]
p-MeC_6H_4	Me[c]	91
p-MeC_6H_4	Et	51
Ph	Me	99
Ph	Et	64
p-ClC_6H_4	Me	61[b]
m-$MeCOC_6H_4$	Me	99
2,5-$Me_2C_6H_3$	Me	70
3,5-$Me_2C_6H_3$	Me	23
2,6-$Me_2C_6H_3$	Me	16

[a] No O_2. [b] An unidentified by-product was also formed. [c] With $Pd(OAc)_2$ and $Cu(OAc)_2$.

We are grateful to British Petroleum, and to the Natural Sciences and Engineering Research Council, for support of this research. H. A. is a John Simon Guggenheim Fellow.

Received, 20th May 1985; Com. 695

---

† The following general procedure was used: CO and O_2 were bubbled through the alcohol (60 ml) to which was added in sequence $PdCl_2$ (1.0 mmol), hydrochloric acid (0.1 ml), $CuCl_2$ [0.27 g, (2.0 mmol), and the amine (10 mmol). The mixture was stirred overnight at room temperature and one atmosphere and filtered, and the filtrate was subjected to rotary evaporation. The resulting oil was treated with diethyl ether or acetone and filtered, and concentration of the filtrate gave the carbamate ester. Further purification was effected by thin-layer or column chromatography (silica gel).

References

1 B. Despeyroux and H. Alper, *Ann. N.Y. Acad. Sci.*, 1984, **415**, 148.
2 H. Alper, B. Despeyroux, and J. B. Woell, *Tetrahedron Lett.*, 1983, **24**, 5691.
3 H. Alper, F. W. Hartstock, and B. Despeyroux, *J. Chem. Soc., Chem. Commun.*, 1984, 905.
4 A patent has been filed: U.K. 84 5903.
5 S. Fukuoka, M. Choro, and M. Kohno, *J. Org. Chem.*, 1984, **49**, 1458.
6 S. Fukuoka, M. Choro, and M. Kohno, *J. Chem. Soc., Chem. Commun.*, 1984, 399.