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Preliminary communication

CLEAVAGE OF C—N BONDS OF TERTIARY AMINES AND CARBONYLATION OF ORGANIC HALIDES WITH PALLADIUM COMPLEXES AS CATALYSTS LEADING TO FORMATION OF TERTIARY AMIDES

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Summary

The C—N bond of tertiary amines was cleaved with a palladium complex as catalyst in the presence of an organic halide and carbon monoxide, and tertiary amides were obtained.

The carbonylation reaction of organic halides in the presence of heteroatom nucleophiles, such as alcohols and primary or secondary amines, is a useful preparative method for esters and amides [1,2] (eq. 1). Recently we reported that dialkyl ethers also act as nucleophiles in the carbonylation of organic halides to give esters via C—O bond cleavage [3] (eq. 2). We have found that even tertiary amines are cleaved in carbonylation reactions of organic halides using palladium complexes as catalysts to give tertiary amides (eq. 3).

$$RX + CO + YH \rightarrow RCOY + HX \quad (1)$$

$$RX + CO + R'OR' \rightarrow RCOOR' + R'X \quad (2)$$

$$RX + CO + R'_3N \rightarrow RCONR'_2 + R'X \quad (3)$$

Tertiary amines are known to be cleaved by acyl halides or anhydrides to give amides in some cases [4—6] and palladium-catalyzed reactions of tertiary amines which involve C—N bond cleavage are also reported [7,8]. In this communication, we report that the C—N bond of several tertiary amines is cleaved with palladium complexes as catalyst in the presence of organic halides and carbon monoxide to give tertiary amides.

The typical procedure of the reaction is as follows. In a 27-ml stainless steel autoclave, iodobenzene (3.0 mmol), triethylamine (1.5 ml, 10.2 mmol, as reactant and solvent), and iodophenylbis(triphenylphosphine)palladium

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(1.88×10^{-2} mmol) were placed under a nitrogen atmosphere. The vessel was charged with carbon monoxide (20 atm at room temperature), and heated in an oil bath at 120°C till the gas absorption ceased. After 64 h, the vessel was cooled and the reaction mixture was analyzed by GLC, which showed that *N*,*N*-diethylbenzamide was the sole volatile product. After filtration of the ammonium salt, distillation of the reaction mixture gave pure *N*,*N*-diethylbenzamide (73.9% yield, b.p. 150°C/15 Torr, Kugelrohr distillation apparatus, lit. [9] b.p. 150–151°C/15 Torr). NMR analysis of the precipitate showed that the salt consisted of Et_3NHI [10] and Et_4NI [11] in about 1/3 ratio. Although the proton in Et_3NHI may be derived from the cleaved ethyl group, ethylene was not detected by GLC analysis of the gas phase.

TABLE 1

AMIDE FORMATION FROM ORGANIC HALIDE, CARBON MONOXIDE AND TERTIARY AMINE IN THE PRESENCE OF PALLADIUM COMPLEX CATALYSTS [a]

Tertiary amine	Organic halide	Catalyst	Reaction time (h)	Amide	Yield [b] (%)
Et_3N	PhI	$(Ph_3P)_2PhPdI$	64	$PhCONEt_2$	73.9
Pr_3N	PhI	$(Ph_3P)_2PhPdI$	67	$PhCONPr_2$	23.9
Bu_3N	PhI	$(Ph_3P)_2PhPdI$	90	$PhCONBu_2$	10.7
Et_2NPh	PhI	$(Ph_3P)_2PhPdI$	139	PhCONEtPh	41.7
				EtCONEtPh	9.2
Et_2NPh	EtI	$(Ph_3P)_2PhPdI$	69	EtCONEtPh	75.0
Et_3N	PhCH=CHBr	$PdCl_2(dppf)$ [c]	12	$PhCH{=}CHCONEt_2$	43.5

[a] Amine 1.5 ml, halide 3.0 mmol, catalyst 1.88×10^{-2} mmol, $P(CO)$ 20 atm, temperature 120°C
[b] Isolated yields after distillation or preparative TLC
[c] dppf, 1,1′-bis(diphenylphosphino)ferrocene

The results are summarized in Table 1, and show that the alkyl group of the tertiary amines seriously influences the yield of amide. When tributylamine was used in place of triethylamine, the formation of tarry material increased at the expense of the amide.

The reaction of *N*,*N*-diethylaniline with iodobenzene unexpectedly gave *N*-ethyl-*N*-phenylpropanamide besides *N*-ethyl-*N*-phenylbenzamide (eq. 4, 5). The former might not arise from the direct carbonylation of *N*,*N*-diethylaniline.

$$\mathrm{PhI + CO + Et_2NPh \xrightarrow{[Pd]} PhCONEtPh + EtI} \tag{4}$$

$$\mathrm{EtI + CO + Et_2NPh \xrightarrow{[Pd]} EtCONEtPh + EtI} \tag{5}$$

$$\mathrm{EtI + Et_2NPh \rightarrow Et_3NPhI} \tag{6}$$

Direct carbonylation of tertiary amines in the presence of Co or Ni catalysts was reported in patent claims [12], but in our study, an organic halide was

$$\mathrm{Et_2NPh + CO \xrightarrow[190^\circ C,\ 700\ atm]{[Co]} EtCONEtPh}$$

essential. In the absence of organic halides, *N*,*N*-diethylaniline was not carbonylated by use of iodophenylbis(triphenylphosphine)palladium as the catalyst even at 150°C for 24 h.

References

1 A. Schoenberg, I. Bartoletti and R.F. Heck, J. Org. Chem., 39 (1974) 3318.
2 A. Schoenberg and R.F. Heck, J. Org. Chem., 39 (1974) 3327.
3 M. Tanaka, M. Koyanagi and T. Kobayashi, Tetrahedron Lett., 22 (1981) 3875.
4 G. Drefahl, H. Lückert and W. Köhler, J. Prakt. Chem., 11 (1960) 341.
5 Ya.L. Gol'dfarb, R.M. Ispiryan and L.I. Belen'kii, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 923.
6 P. Caubère and J.C. Madelmont, C.R. Acad. Sci. Paris, 275 (1972) 1305.
7 S.-I. Murahashi, T. Hirano and T. Yano, J. Am. Chem. Soc., 100 (1978) 348.
8 F.R.S. Clark, R.O.C. Norman and C.B. Thomas, J. Chem. Soc. Perkin I, (1975) 121.
9 C.R. Hauser and H.G. Walker, Jr., J. Am. Chem. Soc., 69 (1947) 295.
10 T. Kagiya, S. Narisawa, T. Maeda and K. Fukui, Kogyo Kagaku Zasshi, 69 (1966) 732.
11 W.A. Henderson, Jr. and C.J. Schults, J. Org. Chem., 27 (1962) 4643.
12 BASF, Ger. 948,056: Chem. Abstr., 53 (1959) 4207e.
BASF, Ger. 863,800: The contents of this patent were summarized by W. Reppe; Ann., 582 (1953) 1.