position would yield biphenyl and palladium(0).[15] The pattern of reactivity observed in these experiments also suggests that phenylpalladium(II) acetate is oxidized to an unstable phenylpalladium(IV) compound in the presence of dichromate ion. The thermal decomposition of this intermediate provides phenyl acetate and regenerates the electrophilic catalyst. The reaction path shown in eq 1 well accommodates the observations obtained under the conditions of these experiments.

$$\mathrm{(C_6H_5)_2Pd(II)} \xleftarrow{\mathrm{C_6H_6}} \mathrm{C_6H_5Pd(II)OAc} \xrightarrow{\mathrm{[OX]}} \mathrm{C_6H_5Pd(IV)OAc_3} \rightarrow \mathrm{C_6H_5OAc + Pd(II)OAc_2} \quad (1)$$

Registry No. Palladium(II) acetate, 3375-31-3; 2-chlorophenyl acetate, 4525-75-1; 2-methylphenyl acetate, 533-18-6; 3-chlorophenyl acetate, 13031-39-5; 3-methylphenyl acetate, 122-46-3; 3-*tert*-butylphenyl acetate, 13189-51-0; 4-chlorophenyl acetate, 876-27-7; 4-methylphenyl acetate, 140-39-6; 4-*tert*-butylphenyl acetate, 3056-64-2; chlorobenzene, 108-90-7; toluene, 108-88-3; *tert*-butylbenzene, 98-06-6; benzene, 71-43-2; phenyl acetate, 122-79-2; biphenyl, 92-52-4; benzene-d_6, 1076-43-3; 1,1′-biphenyl-*2,2′,3,3′,4,4′,5,5′,6,6′*-d_{10}, 1486-01-7; biphenyl-*2,3,4,5,6*-d_5, 20637-23-4.

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[14] Unger, M. O.; Fouty, R. A. *J. Org. Chem.* **1969**, *34*, 18.

[15] Decomposition of diarylpalladium(II) compounds has been described by Calvin and Coates[16] and that of dialkylpalladium(II) compounds has been reported by Gillie and Stille.[17]

[16] Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960**, 2008.

[17] Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

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Cyclization of α,ω Aliphatic Diamines and Conversion of Primary Amines to Symmetrical Tertiary Amines by a Homogeneous Ruthenium Catalyst

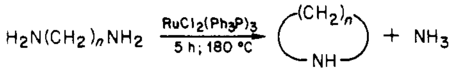
Summary: α,ω Aliphatic diamines were cyclized to heterocyclic amines by being heated at 180 °C for 5 h with $RuCl_2(Ph_3P)_3$ in diphenyl ether. Primary amines having an α-hydrogen atom are converted to symmetrical tertiary amines by being heated at 185 or 235 °C for 8 h with $RuCl_3{\cdot}3H_2O$ and Ph_3P in THF solution.

Sir: In a previous paper[1] we reported a convenient method of obtaining secondary amines by heating primary amines in the presence of the homogeneous catalyst $RuCl_2(Ph_3P)_3$.

As a development of this method we tried to synthetize some heterocyclic amines starting from α,ω aliphatic diamines. The best yields were achieved by heating the α,ω-diamines in a sealed, glass tube at 180 °C for 5 h in the presence of the catalyst $RuCl_2(Ph_3P)_3$ and using diphenyl ether as solvent (see the Table I).

We further developed experimental conditions to obtain tertiary amines from aliphatic primary amines. For this purpose primary amines having an α-hydrogen atom were reacted under an inert atmosphere in a sealed, glass tube at 185 or 235 °C for 8 h in presence of a catalytic amount of $RuCl_2(Ph_3P)_3$ or, more simply, with $RuCl_3{\cdot}3H_2O$ in THF solution. Preliminary experiments, performed on benzylamine and employing other solvents, gave poorer results. In fact, in dioxane (distilled from sodium) a mixture of dibenzylamine (20%) and tribenzylamine (75%) resulted, while in benzene solution dibenzylamine (65%), tribenzylamine (10%), and benzylidenebenzylamine (25%) were obtained. In acetic acid a quantitative formation of benzylacetamide was observed, while in a basic solvent such as pyridine only a poor conversion to benzylidenebenzylamine (25%) was obtained. We remark that there is no need to prepare the Ru catalyst in advance and that 2 mol of Ph_3P/mol of $RuCl_3{\cdot}3H_2O$ is sufficient to produce a good catalytic effect.

Table I. Conversion of α,ω Aliphatic Diamines to Heterocyclic Amines



n for diamine	mol % of catalyst	solvent	% yield[a]	bp, °C (torr) found	bp, °C (torr) lit.[6]
4	2		62	89	88.5–89
4	2	*b*	81		
5	2		79	106	106
5	2	*b*	90		
6	2.5		68	142 (760)	138 (749)
6	2.5	*b*	78		

[a] Yield of isolated product. [b] The solvent was $(C_6H_5)_2O$.

Tertiary amines were obtained as the main product (GLC yields ranging from 51% to 98%) along with secondary amines; the amount of unreacted primary amines was negligible. The low yields obtained from octyl-, dodecyl-, and cyclohexylamine were improved either by using a larger amount of the catalyst or by raising the reaction temperature to 235 °C (see Table II). The reaction therefore appears more sensitive to the steric bulk around the nitrogen atom than we found in the synthesis of secondary amines.[1] This feature is also reported for the addition of secondary amines to ethylene in the presence of $RhCl_3{\cdot}3H_2O$.[2]

In the absence of other evidence, it is reasonable to suppose that the secondary amine formed during the reaction adds to an intermediate imine through a reaction path similar to that already proposed for the secondary amines synthesis (ref 1 and references therein) or for the Pd[3] or the copper–chromium oxide[4] catalyzed alkylation of secondary amines by alcohols:

$$\mathrm{(RCH_2)_2NH + RCH{=}NH} \rightleftharpoons \mathrm{RC(N(CH_2R)_2)HNH_2} \xrightarrow{\text{catalyst (H)}} \mathrm{(RCH_2)_3N + NH_3}$$

The ammonia formation was ascertained in an experiment performed with benzylamine: 93% of the stoichiometric amount of gaseous ammonia was found at the end of the reaction by titration with 0.1 N HCl according to the equation $3RNH_2 \rightarrow R_3N + 2NH_3$.

The general procedure for heterocyclic amine synthesis was as follows. A mixture of α,ω aliphatic diamine (6

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[1] Bui-The-Khai, Carlo Concilio, and Gianni Porzi, *J. Organomet. Chem.*, **208**, 269 (1981).

[2] D. R. Coulson, *Tetrahedron Lett.*, 429 (1971).

[3] S. I. Murahashi, T. Shimamura, and I. Moritani, *J. Chem. Soc., Chem. Commun.*, 931 (1974).

[4] A. Baiker and W. Richarz, *Tetrahedron Lett.* 1937 (1977).

[5] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

[6] "Handbook of Chemistry and Physics", 56th ed., CRC Press, Cleveland, OH, 1975–1976.

[7] G. S. Hiers and R. Adams, *J. Am. Chem. Soc.*, **49**, 1099 (1927).

Table II. Conversion of Primary Amines to Tertiary Amines

$$3RNH_2 \xrightarrow[\Delta,\ THF,\ 8\ h]{RuCl_3/Ph_3P} (R)_3N + 2NH_3$$

no.	R for RNH_2	mol % of catalyst[a]	temp, °C	% yield[b] of amine		mp or bp (torr), °C	
				secondary	tertiary	found	lit.[6]
1	benzyl	5	185		97 (87)	89-91	91-92
		5[c]	185	75	12		
		5[d]	185		90		
2	n-butyl	4	185		89 (81)	216 (760)	213 (760)
		4[d]	185		86		
3	n-hexyl	4	185		98 (89)	264-265 (760)	263-264 (760)
4	n-octyl	4	185	51	47		
		6	185	21	72 (58)	252-253[e]	
5	n-dodecyl	4	185	67	30		
		6	185	50	49		
		6	235	26	70 (52)	78-79[f]	
6	cyclohexyl	6	185	92	5		
		6	235	42	51 (40)	225-226[g]	225-226[7]

[a] $RuCl_3 \cdot 3H_2O/Ph_3P$ in a 1:2 molar ratio unless stated otherwise. [b] Determined by GLC; in parentheses are the yields of isolated product. [c] Reaction performed in absence of solvent. [d] $RuCl_2(Ph_3P)_3$ complex prepared as reported in ref 5. [e] Melting point of hydrobromide salt which agrees with that of an authentic sample. [f] Melting point of hydrochloride salt which agrees with that of an authentic sample. [g] Melting point of hydrobromide salt.

mmol) and $RuCl_2(Ph_3P)_3$ (0.12–0.15 mmol) in 0.5 mL of $(C_6H_5)_2O$ was heated at 180 °C for 5 h in a glass tube sealed under a nitrogen atmosphere. The reaction products were then isolated by distillation and identified by their IR and NMR spectra and boiling points. The purity (higher than 99%) was checked by GLC on the following columns: 2 m × 2 mm, SE-52 (5%) on Chromosorb W or 2 m × 2 mm, Versamid 900 (4%) and NaOH (0.5%) on Chromosorb G.

The general procedure for tertiary amine synthesis was as follows. A mixture of primary amine (6 mmol), $RuCl_3 \cdot 3H_2O$ (0.24–0.36 mmol), and Ph_3P (2 mmol/mmol of Ru salt) in 1.5 mL of THF in a glass tube sealed under a nitrogen atmosphere was heated at 185 or 235 °C for 8 h. Diethyl ether was then added to the reaction mixture, and after filtration the solvent was evaporated. The residue was analyzed by GLC and compared with authentic samples of amines, and the yields were determined by the internal standard method. The following chromatographic columns were used: 2 m × 2 mm, SE-52 (5%) on Chromosorb W (entries 1, 3, 4, 6); 1 m × 2 mm, SE-52 (2%) on Chromosorb G (entry 5); 2 m × 2 mm, Versamid 900 (4%) and NaOH (0.5%) on Chromosorb G (entry 2). The tertiary amines obtained with best yields (entries 1–3) were isolated as hydrochloride salts and identified by their melting or boiling points after reconversion to the free amine. The other tertiary amines (entries 4–6) were isolated by elution with hexane/ether through an alumina column and converted to hydrochloride or bromide salts (the melting points are reported in Table II).

Registry No. 1,4-Butanediamine, 110-60-1; 1,5-pentanediamine, 462-94-2; 1,6-hexanediamine, 124-09-4; pyrrolidine, 123-75-1; piperidine, 110-89-4; hexahydro-1*H*-azepine, 111-49-9; benzylamine, 100-46-9; *n*-butylamine, 109-73-9; *n*-hexylamine, 111-26-2; *n*-octylamine, 111-86-4; *n*-dodecylamine, 124-22-1; cyclohexylamine, 108-91-8; dibenzylamine, 103-49-1; di-*n*-octylamine, 1120-48-5; di-*n*-dodecylamine, 3007-31-6; dicyclohexylamine, 101-83-7; tribenzylamine, 620-40-6; tribenzylamine HCl, 7673-07-6; tri-*n*-butylamine, 102-82-9; tri-*n*-butylamine HCl, 6309-30-4; tri-*n*-hexylamine, 102-86-3; tri-*n*-hexylamine HCl, 21339-34-4; tri-*n*-octylamine, 1116-76-3; tri-*n*-octylamine HBr, 4221-96-9; tri-*n*-dodecylamine, 102-87-4; tri-*n*-dodecylamine HCl, 2486-89-7; tricyclohexylamine, 7335-09-3; tricyclohexylamine HBr, 76630-83-6; $RuCl_2(Ph_3P)_3$, 15529-49-4.

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