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A FACILE SYNTHESIS OF SYMMETRICAL SECONDARY AMINES FROM PRIMARY AMINES PROMOTED BY THE HOMOGENEOUS CATALYST $RuCl_2(Ph_3P)_3$

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Summary

Primary amines bearing an α-hydrogen atom are quantitatively converted to symmetrical secondary amines by heating at 185°C for 5 h in the presence of a catalytic amount of $RuCl_2(Ph_3)_3$.

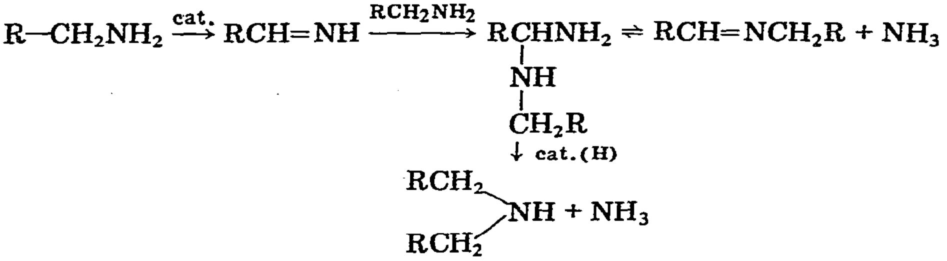
It has been reported that heterogeneous catalysts such as nickel [1,2] or palladium [3,4] can convert primary amines to the corresponding secondary amines in absence of hydrogen, but Greenfield [5] reports only a 3% conversion of mono- to di-cyclohexylamine on treatment with 5% Ru on carbon under hydrogen pressure.

In the course of an exploration of the catalytic effect of Group VIII metal ions on this type of reaction, we have achieved practically quantitative yields of symmetrical secondary amines simply by heating primary amines, bearing an α-hydrogen atom, in the presence of a catalytic amount of $RuCl_2(Ph_3P)_3$ at 185°C for 5 h in homogeneous phase. We are not aware of any other example of homogeneous catalysis of this reaction, and our procedure looks very attractive because of its ease and the high yields obtained.

The reaction of a long chain amine (n-dodecylamine) and of α-substituted amines (cyclohexyl and isopropylamine) affords poorer yields, but these are improved by use of either a larger amount of catalyst or of tetrahydrofuran as solvent (THF/amine volume ratio 1/1).

Experiments with benzylamine showed the importance of some parameters: (i) the concentration of the catalyst must not exceed certain limits if formation of tertiary amines is to be avoided: use of 5 mol % of the catalyst gives a mixture of mono- (11%), di- (75%) and tri-benzylamine (12%). (ii) If the reaction is carried out for a shorter time (1 to 3 h) or at a lower temperature (in the range 140—175°C) n-benzylidenebenzylamine is formed. The latter is the main product (73%) when the reaction is carried out in an open vessel with a slow stream of nitrogen to remove NH_3 from the reaction mixture.

The evidence leads us to favour a mechanism for the ruthenium complex catalyzed reaction which closely resembles that proposed previously for catalysis by palladium [3] or nickel [1,6] metal.



$$R{-}CH_2NH_2 \xrightarrow{cat.} RCH{=}NH \xrightarrow{RCH_2NH_2} RCH(NH_2)NHCH_2R \rightleftharpoons RCH{=}NCH_2R + NH_3$$

$$RCH(NH_2)NHCH_2R \xrightarrow{cat.(H)} (RCH_2)_2NH + NH_3$$

General procedure. A mixture of primary amine (10 mmol) and 0.1 to 0.3 mmol of $RuCl_2(Ph_3P)_3$ [7] was heated in a sealed glass tube for 5 h at 185°C. The dark-blue solution turned orange. The tube was cooled, then carefully opened and the catalyst was precipitated with diethyl ether and filtered off. After solvent evaporation the products were identified by GLC and IR by comparison with authentic samples. The yields were determined by GLC using internal standards. The best results obtained for every amine were confirmed by using five fold amounts of reactants; the products were isolated by distillation and then identified by b.p. and IR spectra. The purity, >99%, was checked by GLC on suitable columns. The results are summarized in Table 1.

TABLE 1

CONVERSION OF PRIMARY TO SECONDARY AMINES BY $RuCl_2(Ph_3P)_3$

Primary amine RNH_2	% Mol of catalyst	% Recovered RNH_2 [a]	Secondary amine R_2NH			
			Yield (%)		B.p. (°C/torr)	
R			a	b	found	reported [8]
A. Without solvent						
1 n-butyl	1	—	99	94	160	159
2 n-hexyl	1	9	90			
3 n-dodecyl	1	22	76			
4 n-butyl	2	—	96 [c]			
5 n-hexyl	2	—	98	90	193—195	192—195
6 n-dodecyl	2	—	98	95 [d]	205—206 [e]	207—208[9]
7 benzyl	2	—	99	92	119—120/0.5	125—127/1
8 cyclohexyl	2	8	90			
9 isopropyl	2	88	10			
B. In tetrahydrofuran						
10 benzyl	2	—	96 [c]			
11 cyclohexyl	3	—	99	92	144—146/14	121/11
12 isopropyl	3	26	72			

[a] Determined by GLC using the following columns: 2 m × 2 mm, Versamid 900 (4%) and NaOH (0.5%) on Chromosorb G (entries 1, 2, 4, 5, 8, 11); 1 m × 2 mm, SE 52 (2%) on Chromosorb G (entries 3, 6); 2 m × 2 mm, SE 52 (5%) on Chromosorb W (entries, 7, 10); 2 m × 2 mm, Poropack Q (entries 9, 12). [b] Determined on distilled amine. [c] About 2% of tertiary amine is also present. [d] Determined on the crude hydrochloride salt. [e] M.p. of hydrochloride salt crystallized from THF.

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