Journal of Organometallic Chemistry, 231 (1982) C31—C34
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE HOMOGENEOUSLY CATALYSED SYNTHESIS OF *N*-METHYLDIALKYLAMINES FROM *N*-METHYL AND *N,N*-DIMETHYLALKYLAMINES

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(Received January 21st, 1982)

Summary

N-Methyl and *N,N*-dimethylalkylamines are converted into *N*-methyldialkylamines in good yields when heated at 180°C in the presence of a catalytic amount of $RuCl_2(Ph_3P)_3$.

In previous papers [1,2], we described a convenient method of making symmetrical secondary and tertiary amines starting from primary amines or of producing heterocyclic amines from α,ω-aliphatic diamines by use of the homogeneous catalyst $RuCl_2(Ph_3P)_3$. As a further development we now report a new process for making *N,N*-dialkylmethylamines starting from either secondary *N*-methyl- or tertiary *N,N*-dimethyl-amines and again using $RuCl_2(Ph_3P)_3$ as catalyst. The reactions are as follows:

$$2\,RCH_2NHCH_3 \xrightarrow{cat.} (RCH_2)_2NCH_3 + CH_3NH_2$$

$$2\,RCH_2N(CH_3)_2 \xrightarrow{cat.} (RCH_2)_2NCH_3 + (CH_3)_3N$$

This procedure is of interest because it is very easy to carry out, and is selective and efficient (GLC yields range from 71 to 96%), and so it offers some advantages over previously described methods [3—6]. The reaction is conveniently carried out by heating the starting amine in the presence of a catalytic amount of $RuCl_2(Ph_3P)_3$* at 180°C for 1.5—7 h.

The results are shown in Table 1. The conversion of *N*-methyl- and *N,N*-dimethyl-alkylamines to *N,N*-dialkylmethylamines generally proceeds with satis-

*In experiments on *N,N*-dimethylbenzylamine in the presence of 9 mol% of other catalysts we observed: (i) Pd-black gave *N,N*-dibenzylmethylamine in 50% yield; (ii) the use of 2 mol of Ph_3P/mol of $RuCl_3 \cdot 3H_2O$, as employed elsewhere [2], gave poor and unreproducible results; (iii) $RhCl(Ph_3P)_3$ was practically inactive.

0022-328X/82/0000—0000/$02.75

TABLE 1

CONVERSION OF *N*-METHYL AND *N,N*-DIMETHYLALKYLAMINES INTO *N,N*-DIALKYLMETHYLAMINES: $R^1R^2NCH_3 \rightarrow (R^1)_2NCH_3$

Starting amines $R^1R^2NCH_3$		Reaction conditions			Reaction products (yield %)[a]		B.p. (°C/Torr)[d]	
R^1	R^2	Method[b]	Mol-% cat.[c]	Time (h)	$R^1N(CH_3)_2$	$(R^1)_2NCH_3$	found	lit.
$C_6H_5CH_2$	CH_3	A	9	1.5	5	96 (90)	302–304 (200–202)	161–162/12 (200–201) [7]
		A	7.5	2	29	71		
		B	7.5	7	9	89		
		C	7.5	7	8	92 (90)		
$C_6H_5CH_2$	H	A	9	3	16	78		
		A	9	7	20	58[e]		
		B	7.5	7	11	77		
		B	9	3.5	15	80 (76)		
		C	7.5	7	11	89 (85)		
$n\text{-}C_9H_9$	CH_3	C	3.5	7	9	71 (68)[f]	161–162 (132–134)[g]	
$n\text{-}C_4H_9$	H	C	5	7	10	85 (80)		
$n\text{-}C_6H_{13}$	CH_3	C	3.5	7	12	83 (80)	230–231 (143–145)	121–122/19 (144–145) [8]
$n\text{-}C_6H_{13}$	H	C	5	7	6	75 (72)[f]		
$n\text{-}C_8H_{17}$	CH_3	A	7.5	2	10	82 (78)	301–303 (148–149)	162–165/15 (149–150) [8]
		C	7.5	7	8	89 (85)		
$n\text{-}C_8H_{17}$	H	A	7.5	1.5	13	80 (78)		
		C	7.5	7	11	87 (85)		

[a] Determined by GLC; the yields of isolated products are shown in parentheses. [b] The reaction was performed; A, in open vessel without solvent or B, in open vessel in diphenyl ether, or C, in a sealed glass tube with THF as solvent, (solvent/amine volume ratio 2/1). [c] Based on the amine used. [d] The m.p.'s of the hydrochlorides shown in parentheses. [e] 22% of tribenzylamine was recovered. [f] About 15–20% of trialkylamine was also observed. [g] ^1H NMR and mass spectra confirmed the identity of the material.

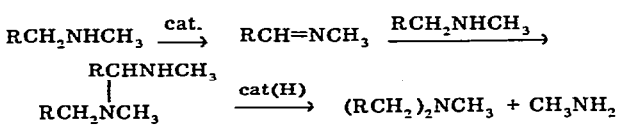
factory yields when the reaction is carried out with more than 3 mol-% of catalyst over a short reaction time (1.5—2 h). Preliminary experiments with *N,N*-dimethylbenzylamine in open vessel and in absence of solvent led to the following observations: (i) with 2.5 mol-% of catalyst, the yield of *N,N*-dibenzylmethylamine reaches a maximum of 60% after 5 h, then decreases to 45% after 12 h; (ii) longer reaction times or higher catalyst concentrations favour tribenzylamine formation (15% after 12 h with 2.5% of catalyst and 40% after 7 h with 7.5% of catalyst); (iii) the amount of this side-product can be reduced to below 5% using diphenyl ether as solvent (see Table 1).

Similar behaviour was observed with *N,N*-dimethyloctylamine, which unexpectedly gave both di- and tri-octylamine: these products were obtained in 15 and 30% yield, respectively, after 12 h with 2.5% of catalyst, and in 25 and 30% yield after 7 h with 7.5% of catalyst. However, both byproducts are almost absent if the reaction is performed in THF as solvent.

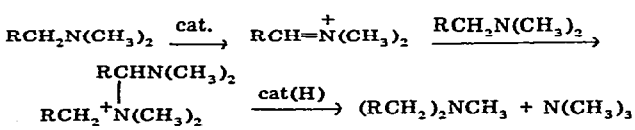
The *N,N*-dialkylmethylamines can also be obtained in good yields (72—88%) starting from a mixture of *N,N*-dimethylalkylamine and *N*-methylalkylamine under the same reaction conditions. The results starting from secondary *N*-methylalkylamines can be rationalized by assuming a reaction path similar to that already proposed for the synthesis of tertiary amines [1] which involves an intermediate Schiff-base (Scheme 1). In support of this interpretation, *N*-methylbenzylamine (with 2—3 mol.% of catalyst) gave some benzylidenemethylamine (always detected in about 5—10% during the reaction) and CH_3NH_2 which was recovered as its hydrochloride (m.p. 230—232°C).

In contrast, with tertiary *N,N*-dimethylalkylamines, the mechanism might be similar to that suggested for the Pd-black catalyzed amine exchange reaction of tertiary amines [3], which involves an iminium ion complex as key intermediate (Scheme 2). This mechanistic hypothesis is in agreement with the following findings in experiments with *N,N*-dimethylbenzylamine: (i) Pd-black, as mentioned above, gave *N,N*-dibenzylmethylamine, although in poor yield; (ii) some $(CH_3)_3N$ (isolated as the hydrochloride; m.p. 280—284°C) was formed; (iii) no benzylidenemethylamine was ever observed during the reaction.

SCHEME 1



SCHEME 2



General procedure. A mixture of the starting amine (6 mmol), a two-fold volume of solvent (when one was used), and $RuCl_2(Ph_3P)_3$ (0.21—0.45 mmol) was heated at 180°C for 1.5—7 h. The reaction was carried out in a sealed

glass tube for amines boiling below 180°C, but in open vessel (with stirring under nitrogen) for amines boiling above 180°C. The products were analyzed by GLC by comparison with authentic samples and the yields were determined by use of an internal standard method. The best results obtained for every amine were confirmed in experiments using double quantities of the reactants. The products, which were isolated by distillation or by chromatography on alumina with hexane/ether as eluent, were identified by their b.p.'s and their IR and ^{1}H NMR spectra and their purities were checked by GLC on the following columns: 2m × 2mm, SE 52 (5%) on Chromosorb W (for *N,N*-dibenzylmethylamine) and 2m × 2mm, Versamid 900 and NaOH (0.5%) on Chromosorb G (for other *N,N*-dialkylmethylamines).

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