Dealkylation of Tertiary-alkyl Primary Amines *via* their *NN*-Dichloro-derivative and Copper(I) Chloride

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Summary Compounds of the type tertiary-$RNCl_2$ are dealkylated in high yield to alkene products by copper(I) chloride in Me_2SO at room temperature.

SEVERAL methods are commonly used for dealkylation of primary amines, including Hofmann and Cope eliminations, or treatment with nitrous acid. Sharts[1] briefly described the conversion of *NN*-dichloro-t-butylamine into isobutylene (>80%) on reaction with AgF in refluxing MeCN.

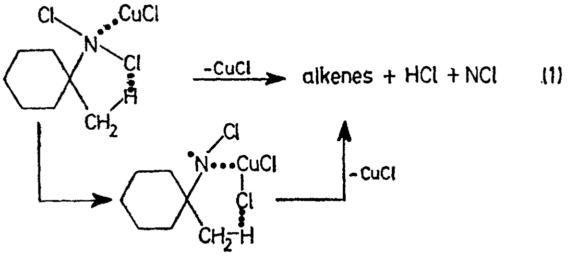
We have found that a similar technique can be used for other *NN*-dichloro-tertiary-alkyl primary amines. Treatment of *NN*-dichloro-1-methylcyclohexylamine (**1**) with CuCl in Me_2SO at room temperature afforded 1-methylcyclohexene (**2**), and methylenecyclohexane (**3**) in a combined yield of 96%. Other *NN*-dichloro-tertiary-alkyl primary amines behaved analogously (Table), providing the corresponding alkenes in good yields. This approach is apparently limited to trialkyl primary carbinamines since *NN*-dichlorohexylamine gave hexanenitrile (60%), along with small amounts of hex-1-ene, hexanal, and hexylamine. In addition, dehydrohalogenation predominated[1] with R_2CHNX_2 (X = F or Cl) and CsF.

TABLE

Products from tertiary-$RNCl_2$ and CuCl

R	Products (%yield)
1-Methylcyclohexyl	(**2**) (64); (**3**) (32)
$Bu^n{}_3C$–	$Pr^nCH{=}CBu^n{}_2$ (65—71)
$PhCH_2C(Me_2)$–	$PhCH_2C(Me){=}CH_2$ (49—62) $PhCH{=}CMe_2$ (24—31)
$PhC(Me_2)$–	$PhC(Me){=}CH_2$ (68—79)

In a typical reaction, (**1**)[2] (12·5 mmol) was added dropwise to a rapidly stirred mixture of Me_2SO (30 ml) and purified CuCl (12·5—25·0 mmol) under N_2 at room temperature. After 30—60 min the mixture was stirred with water and filtered. Extraction with pentane or light petroleum provided (**2**) and (**3**). Yields were determined by g.l.c. analysis after workup or directly on the reaction mixture. Products were identified by i.r. and n.m.r. spectra, as well as comparison with authentic materials.



$$2NCl \longrightarrow ClN{=}NCl \xrightarrow{CuCl} CuCl_2 + N_2 \qquad (2)$$

An ionic pathway[3] is unlikely based on product isomer distribution. The absence of methylcyclohexane, dimers, and 1-chloro-1-methylcyclohexane, as well as little influence on yield by the presence of oxygen, suggests that free radicals[4] are not involved. A concerted mechanism might be operative [equations (1) and (2)]. In an analogous system, nitrogen-centred radicals have been proposed in the addition of *N*-chloroamines to olefins in redox systems (CuCl or $FeCl_2$).[5] Alternatively, an E_2 or $E1cB$ elimination may be involved.

This two-step method, using mild conditions, has advantages over the Cope or Hofmann eliminations which require 3—5 steps, and the competing reactions resulting from the use of nitrous acid[6] in alternative procedures are avoided since essentially a single pathway is involved.

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