

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. Sharts¹ briefly described the conversion of *NN*-dichloro-*t*-butylamine into isobutylene (>80%) on reaction with AgF in refluxing MeCN .

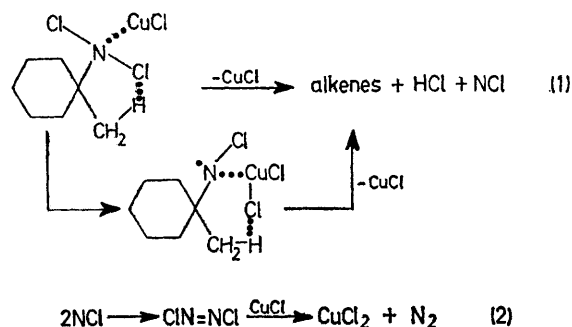
We have found that a similar technique can be used for other *NN*-dichloro-tertiary-alkyl primary amines. Treatment of *NN*-dichloro-1-methylcyclohexylamine (1) with CuCl in Me_2SO at room temperature afforded 1-methylcyclohexene (2), and methylenecyclohexane (3) in a combined yield of 96%. Other *NN*-dichloro-tertiary-alkyl

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 predominated¹ with R_3CHNX_2 ($\text{X} = \text{F}$ or Cl) and CsF .

TABLE

Products from tertiary- RNCl_2 and CuCl		
R		Products (% yield)
1-Methylcyclohexyl	..	(2) (64); (3) (32)
$\text{Bu}^n\text{C}-$	$\text{Pr}^n\text{CH}=\text{CBu}^n$ (65-71)
$\text{PhCH}_2\text{C}(\text{Me})-$	$\text{PhCH}_2\text{C}(\text{Me})=\text{CH}_2$ (49-62)
		$\text{PhCH}=\text{CMe}_2$ (24-31)
$\text{PhC}(\text{Me})-$	$\text{PhC}(\text{Me})=\text{CH}_2$ (68-79)

In a typical reaction, (1)² (12.5 mmol) was added dropwise to a rapidly stirred mixture of Me₂SO (30 ml) and



purified CuCl (12.5—25.0 mmol) under N₂ 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.

An ionic pathway³ 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 radicals⁴ 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 FeCl₃).⁵ Alternatively, an *E*₂ or *E*_{1cB} 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 acid⁶ in alternative procedures are avoided since essentially a single pathway is involved.

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