Pyrolytic Eliminations with *NN*-Dichloroalkylamines

By JOHN T. ROBERTS and PETER KOVACIC*
(*Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin* 53201)
JOHN A. TONNIS
(*Department of Chemistry, University of Wisconsin-La Crosse, La Crosse, Wisconsin* 53601)
and FRANCIS V. SCALZI
(*Department of Chemistry, Hiram College, Hiram, Ohio* 44234)

Summary *NN*-Dichloroalkylamines ($RNCl_2$) undergo thermal decomposition in gas chromatography at 215—260 °C giving products in high yield: alkenes from tertiary R groups, alkenes and *N*-chloroimines, from secondary, and nitriles predominantly, with a minor amount of alkenes, from primary.

THE pyrolysis of many organic compounds containing various functional groups has been investigated.[1–3] We report the first examples of thermal decomposition, in gas chromatography, of simple *NN*-dichloroalkylamines. The reactions proceed during short times and at relatively low temperatures, 215—260 °C; the minimum possible temperature has not yet been ascertained. The type of product formed depends upon the R group in $RNCl_2$: alkene from tertiary; alkene and *N*-chloroimine from secondary; and nitrile predominantly, with a minor amount of alkene, from primary. In all cases, the total yields of organic products were high (>90%) (Table); inorganic byproducts were not determined.

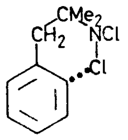
The effect of structural variation was further studied with phenyl substituted compounds on a Dow Corning 710 (20% Chromosorb P) column; column temp., 210 °C; injector port temp., 240 °C; detector temp., 245 °C; He flow rate, 24 ml min^{-1}, 2·25 mmol $RNCl_2$ in CH_2Cl_2. For $PhCMe_2NCl_2$, the yield of α-methylstyrene was *ca.* 60%. No alkene ($PhCH{=}CMe_2$ or $PhCH_2CMe{=}CH_2$) was detected

TABLE. Pyrolysis products from *NN*-dichloroalkylamines[a]

$RNCl_2$[b]	Products[c] (% yield)	
1-Methyl-*NN*-dichlorocyclohexylamine	1-Methylcyclohexene	(*ca.* 80)
	Methylenecyclohexane	(*ca.* 20)
NN-Dichlorocyclohexylamine	Cyclohexene	(*ca.* 48)
	Chloroiminocyclohexane	(**1**) (*ca.* 52)
NN-Dichlorohexylamine	Hex-1-ene	(7)
	Hexanenitrile	(88)

[a] Copper column, 6 ft by ¼ in; 15% SE-30 on Chromosorb W; injection temp. 260 °C; column temp., 70 °C; He flow rate, 150 ml min^{-1}; injected neat. [b] Prepared according to P. Kovacic and S. S. Chaudhary, *Org. Synth.*, 1968, **48**, **4**. [c] Identified by comparison of g.l.c. retention times and mass spectra with those of authentic materials: Aldrich Chemical Co.; (**1**) G. H. Alt and W. S. Knowles, *Org. Synth.*, 1975, Col. Vol. V, 208.

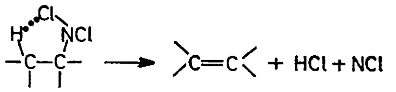
in the case of $PhCH_2CMe_2NCl_2$. Higher temperatures might be required for the best results with these substrates of higher molecular weight. Also, intramolecular, nuclear chlorination[4] may be a competing process, as depicted in (**2**).



(2)

In a consideration of the reaction pathway for 1,2-elimination leading to *N*-chloroimine or nitrile, a comparison can be made with the pyrolysis of alkyl chlorides.[1,2] With thermal dehydrohalogenation, carried out at appreciably higher temperatures (usually 300—500 °C), decomposition can be a complex process following various routes. In the unimolecular reaction for RCl, most of the results can be rationalized on the basis of a highly polar transition state, or an ion pair, which yields the product directly. A closer analogy is provided by comparison with *gem*-dihalides. Studies with 1,1-dichloroethane[5] (365—453 °C) and 1,1-dichloropropane[6] (425 °C) demonstrated that the reaction was limited essentially to elimination of one mole of hydrogen chloride, with negligible quantities of alkyne being produced. Furthermore, acetylene was generated[5] in $<10\%$ yield from vinyl chloride at 444 °C for 14 min. Hence, it is evident that *N*-chloroimines undergo dehydrohalogenation with much greater facility than vinyl chlorides. The following results for loss of HCl from alkyl chlorides also show that this reaction is slow: 24% HCl loss for ethyl chloride after 57 min at 438 °C, and 47% for 1,1-dichloroethane after 10 min at 444 °C.[5] For *NN*-dichloroamines the low bond energy of N–Cl (47·7 kcal mol^{-1})[7] compared with C–Cl (78·5 kcal mol^{-1}) is probably important in leading to a ready reaction under mild conditions.

Alkene formation may be viewed mechanistically in several ways. There is a resemblance in some respects to thermolysis (90—105 °C) of Bu^tSO_2Cl which yields isobutene, t-butyl chloride, sulphur dioxide, and hydrogen chloride.[8] The most plausible pathways entailed a cyclic, intramolecular transition state or a heterogeneous, nonchain process. A principal difference is the fact that effectively no t-RCl was obtained from t-$RNCl_2$. A cyclic transition state for the thermolyses reported here would lead to the pathway in equation (1). Recent work supports the view that a number of gas-phase processes are actually surface-catalysed, involving stabilization of charge separation in the transition state.[9]



(1)

If the NCl_2 group behaves as a pseudohalogen,[10] then generation of alkene might also occur by 1,2-elimination.

The processes (alkene, *N*-chloroimine, and nitrile formation) which are described herein for $RNCl_2$ have counterparts in liquid-phase systems.[4,10] Under thermal conditions, certain *NN*-dichloroamines, *e.g.* perfluoroalkyl[11] and aryl,[12] are reported to provide azo compounds.

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