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**NOVEL PRODUCTS  
FROM  
PENTACHLOROCYCLOPROPANE:  
A  
SYNTHETIC AND STRUCTURAL  
INVESTIGATION**

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A Thesis Submitted in Partial Fulfilment of the Requirements  
for the Degree of  
Doctor of Philosophy in Chemistry  
University of Auckland

1996

## ABSTRACT

Primary and secondary amines react with pentachlorocyclopropane to form a variety of novel products. Amidines, allyl and cyclopropenyl cations are easily reached by these reactions. The 1,1,3,3-*tetra*-aminoallyl cations of this series can be reversibly protonated at C(2) to give diamidinium ions. Action of KOH on the diamidinium species  $\text{CH}_2[\text{C}(\text{NHBu}^i)_2]_2^{2+}$  produces the diamidine  $\text{CH}_2[\text{C}(\text{NBu}^i)(\text{NHBu}^i)]_2$  which hydrolyses to the formamidine  $\text{CH}(\text{NBu}^i)(\text{NHBu}^i)$ . *Bis*- and *tris*-amino substituted cyclopropenylium ions are formed by the action of secondary amines on pentachlorocyclopropane.

The cations of this study are stabilised by electron back-donation from nitrogen atoms of substituent groups. The subject of back-bonding was probed in several ways. Crystallographically determined structures of representative salts afforded bond length data from which deductions about back-bonding were made. The measurement of barriers to bond rotation is another way that this effect was investigated. Using the technique of variable temperature NMR, VT-NMR, spectroscopy, energies of activation about unsaturated bonds of allyl, amidinium and cyclopropenylium cations were found. UV-spectra provided additional information concerning bonding in these species.

Tautomerism of N,N'-disubstituted amidines was investigated by VT-NMR spectroscopy. Individual tautomers were identified in NMR spectra ( $^{13}\text{C}$ ,  $^1\text{H}$ ).

*Tris*-alkylaminocyclopropenylium ions were oxidised to form intensely coloured radical dications. The first Raman spectrum of a cyclopropenyl radical dication was determined. Using the technique of pulse radiolysis we were able to reduce the cyclopropenylium cation,  $[\text{C}_3(\text{NEt}_2)_3]^+$ , to the molecular radical. Further, pulse experiments enabled standard reduction potentials of representative  $[\text{C}_3(\text{NR}_2)_3]^{2+}$  and allyl radical dications to be measured and compared.

In general, tertiary amines reacted with pentachlorocyclopropane to generate product mixtures. Reaction of *para*-dimethylaminopyridine, DMAP, on pentachlorocyclopropane was a case in exception. The novel allylide product is the same as that formed via an alternative route.

The direct reaction of ammonia on pentachlorocyclopropane produced several products including the formamidine  $\text{NC-N}=\text{CH-NH}_2$ .

A polyamide was prepared from the hydrolysis of a diamidinium ion. The mechanism of formation and the characterisation of this glossy, thermoplastic material is discussed.

## ACKNOWLEDGEMENTS

I would like to thank my supervisor, Assoc. Prof. Michael Taylor for his invaluable assistance throughout the course of this work. I wish him well on his retirement from teaching and look forward to future opportunities for research collaboration. Many thanks go to Assoc. Profs. George Clark and Cliff Rickard for solving the x-ray crystal structures of this project. Special thanks go to Assoc. Prof. John Packer and Dr Robert Anderson for introducing me to the technique of pulse radiolysis. Many thanks are also expressed to Drs Penny Brothers and David Ware for their assistance and helpful advice. A special thank you goes to Dr Melvyn Kilner of Durham University for advice and encouragement. Thanks also goes to my room mates, L-J Baker and Ian Laban for their friendship and support.

Thank you Christine for your support, love and commitment to me. A big thank you is also due to my family for the love, advice and support that you have given me.

I am indebted to the University of Auckland and the William Georgetti scholarship trust for providing financial assistance throughout the course of this work.

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