STUDIES ON SOME COMPOUNDS OF PROBABLE INSECTICIDE EFFECTS

A THESIS

In Partial Fulfilment of the Requirements of M. Sc. Degree

By

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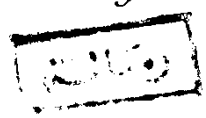
B. Sc. (Honour)



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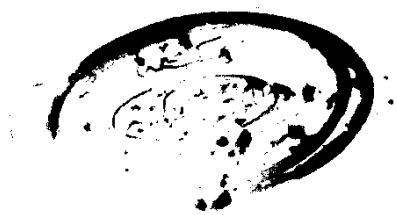

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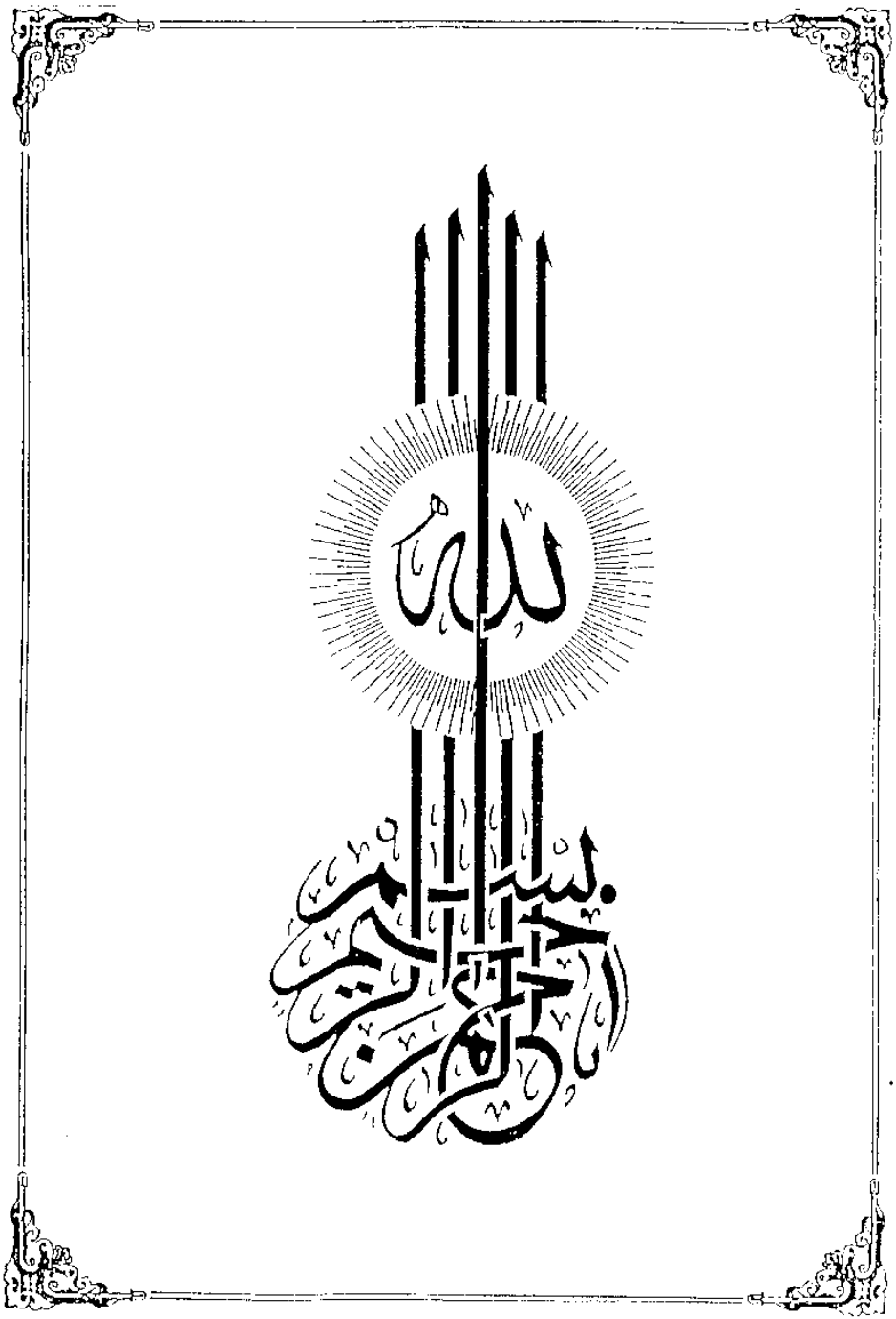

A C K N O W L E D G E M E N T

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The author should like to express her deepest gratitude to Prof. Dr. W.I. Awad, D.Sc., Professor of Organic Chemistry, University College for Women, Ain Shams University and to Dr. M.A. El Deek, Lecturer of Organic Chemistry, Department of Industrial Midicine, Faculty of Medicine, Ain Shams University, not only for suggesting the subjects investigated but also for continuous advice and valuable criticism.

N O T E

Besides the work carried out in this thesis, the candidate has attended postgraduate courses for one year in organic chemistry including the following topics.

1) Reaction mechanisms.
2) Electronic, Infrared, Raman, N.M.R. and Mass spectral studies of organic compounds.
3) Advanced topics in organic chemistry.
4) Organic Microanalysis.
5) Quantum chemistry.
6) Chemistry of hetero-cyclic compounds.

She has successfully passed an examination in these topics.

Prof. Dr. S.M. Abdel Wahab

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C O N T E N T S

SUMMARY

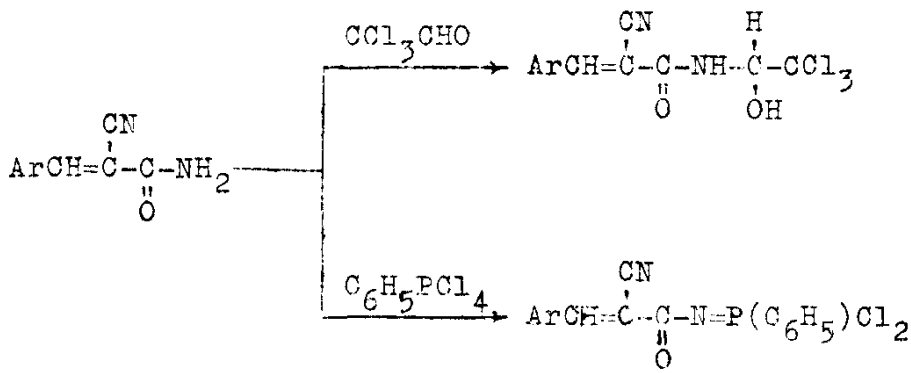
S U M M A R Y

This thesis includes three parts; the first of which is an introduction to the different methods of preparation and the chemical properties of aryltetrachlorophosphoranes and phosphazoacyls, as well as the behaviour of chloral towards different classes of organic compounds.

The second part discusses the author's work which is a comparative study between the reaction of arylidene-cyanoacetamides, $ArCH{=}C(CN)-CONH_2$, with phenyltetrachloro-phosphorane, $C_6H_5PCl_4$ and chloral.

Three centres in arylidenecyanoacetamides are expected to react with, $C_6H_5PCl_4$, or with chloral, namely, the amide group, the nitrile group, and the ethylenic hydrogen.

Under different experimental conditions, only the amide group was found to react with chloral or $C_6H_5PCl_4$ to give N-(2,2,2-trichloroethyl)arylidenecyanoacetamides and dichloro-phenylphosphazoarylidenecyanoacetyls respectively.



It has been found that in case of chloral the reaction was carried out at 120-150°C for about 12 hrs., while in case of $C_6H_5PCl_4$ the reaction time was only 30-40 min., at 80°C.

The structure of these compounds was established by studying their i.r. and U.V. spectra.

The i.r. spectra showed strong bands between 1560-1610cm^{-1} and between 1660-1700 cm^{-1} which were associated with the C=C & C=O respectively.

The introduction of the chloral moeity causes a bathochromic shift in both the carbonyl and the double bond absorptions between 10-25 cm^{-1}, while the phosphorimidic dichloride moeity, $N=P(C_6H_5)Cl_2$, has a higher effect, 20-30 cm^{-1}.

The chloral adducts are stable to moisture in contrast to that of $C_6H_5PCl_4$ which are easily hydrolysed in air. The phosphazo compounds are hydrolysed with quantitative amounts of water to give the corresponding phosphonamide derivatives. The latter compounds can be obtained by formolysis or acetolysis

$$ArCH{=}\overset{CN}{\overset{|}{C}}{-}CON{=}P(C_6H_5)Cl_2 + (H_2O,\ HCOOH \text{ or } CH_3COOH) \longrightarrow$$

$$ArCH{-}\overset{CN}{\overset{|}{C}}{-}CONH{-}\overset{O}{\overset{\|}{P}}(C_6H_5)Cl$$

The chloral adducts are hydrolysed with boiling dil. alkali to give chloroform, ammonia and the starting aldehydes.

The third part of the thesis is devoted to the experimental work and the thesis ends with biblography of 119 references.

INTRODUCTION

A- HALOGENOPHOSPHORANES AND PHOSPHAZOACYL COMPONDS

I- METHODS OF PREPARATION OF TETRACHLOROPHOSPHORANES

Chlorine combines with phosphonous dichlorides, $RPCl_2$, and phosphinous chlorides, R_2PCl_2, to form tetrachlorophosphoranes and trichlorophosphoranes respectively. The reactions are exothermic and are generally conducted in inert solvents. The products, yellow crystalline solids which generally resemble phosphorus pentachloride in appearance and reactivity, are isolated by filtration. A few mixed chlorobromophosphoranes have been prepared[1] by the addition of bromine to phosphonous dichlorides or phosphinous chlorides.

Chlorophosphoranes are frequantly prepared by chlorination of phosphonic[2] or phosphinic[3] and their chlorides or esters with phosphorus pentachloride.

$$RPCl_2 \xrightarrow{Cl_2} RPCl_4 \xleftarrow{PCl_5} RP(O)(OH)_2$$

$$R_2PCl \xrightarrow{Cl_2} R_2PCl_3 \xleftarrow{PCl_5} R_2P(O)(OH)$$

Crystalline compounds having the composition R_3PX_2 (X = Cl, Br, I) are formed by the addition of halogen

to tertiary phosphines. The compounds are insoluble in non-polar media but soluble in solvents such as acetonitrile and nitrobenzene. Formulation as ionic solids $(R_3PX)^+X^-$ (halogenophosphonium halides), is indicated by their solubility behaviour, by their high melting points, by electrical conductivity in nitrobenzene solution and from infrared spectroscopy of $(CH_3)_3PX_2$.[4]

Pseudohalogens such as cyanogen bromide and triphenylphosphine react to form Ph_3PCNBr[5,6].

I.1- Chlorination of phosphonic dichlorides:

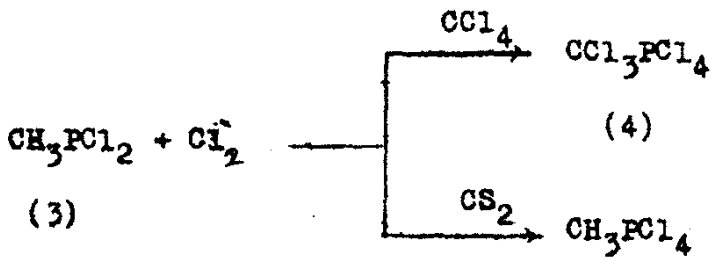
Chlorination of alkylphosphonic dichlorides (1) which are formed when alkyl chlorides are added, with cooling and stirring to mixtures of phosphorus trichloride and aluminium trichloride. The rapidly formed alkyltrichlorophosphonium tetrachloroaluminates (2), are easily chlorinated to give the corresponding tetrachlorophosphorane[7-10].

$$RCl + AlCl_3 \xrightarrow{PCl_3} \underset{(2)}{RPCl_3^+ AlCl_4^-} \xrightarrow{\text{Reduction}}$$

$$NaAlCl_4 + \underset{(1)}{RPCl_2} \downarrow Cl_2$$

$$RPCl_4$$

It is interested to record that chlorination of methylphosphonic dichloride (3) in carbon tetrachloride to give trichloromethyltetrachlorophosphorane (4), while chlorination in carbon disulfide gives methyltetrachlorophosphorane (5)[11,12].



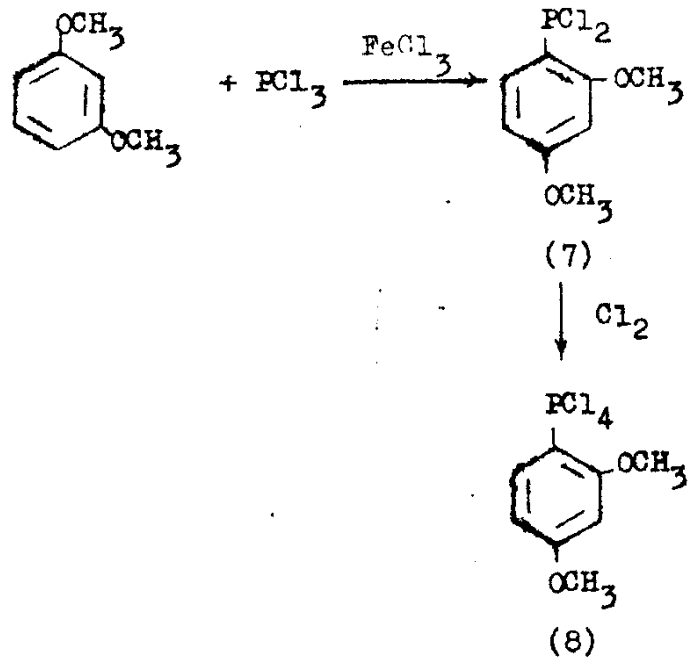
Aryldichlorophosphines similarly reacted with chlorine in carbon tetrachloride but at a higher temperature e.g. p-tolyldichlorophosphine reacted with chlorine at 140°C to give p-trichlorotolyltetrachlorophosphorane (6)[13].

$$p\text{-}CH_3C_6H_4PCl_2 \xrightarrow[140°C]{Cl_2} p\text{-}CCl_3C_6H_4PCl_4$$

(6)

It is interested to report that m-dimethoxybenzene reacted with phosphorus trichloride in the presence of anhydrous ferric chloride to give the corresponding phosphonic

dichloride (7) which on chlorination gives 2,4-dimethoxy-phenyltetrachlorophosphorane (8).



I.2- <u>From unsaturated compounds</u>:

Ethylene was found to react with phosphorus trichloride in the presence of aluminium chloride and potassium chloride to give chloroethylphosphonic dichloride (9). The required phosphorane (10) can be prepared from (9) by the reaction with chlorine[14].

$$C_2H_4 + PCl_3 + AlCl_3 \xrightarrow{KCl} ClCH_2CH_2PCl_2$$

(9)