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## RING EXPANSION REACTIONS OF TRICHLOROMETHYL RADICALS WITH TRIAZOLES AT HIGH TEMPERATURE IN THE VAPOUR PHASE

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The ring expansion reactions of trichloromethyl radicals, generated in the vapour phase from carbon tetrachloride in a flow system at 550° with 1-methyl-1,2,4-triazole and 1-methylbenztriazole, have been investigated separately. The former gave cyanuric chloride as the major ring expansion product while the latter yielded no ring expansion products, only chlorinated benzenes could be obtained as the reaction products.

**Key words:** Reactions, Trichloromethyl radicals, Triazoles.

### Introduction

Previous communications [1-3] described ring expansion reactions of trichloromethyl radicals, generated in the vapour phase from carbon tetrachloride in a flow system at 550°, with N-substituted and C-substituted pyrroles and pyrazoles. This paper presents reactions of 1-methyl-1,2,4-triazole and 1-methylbenztriazole with carbon tetrachloride separately. Ring expansion products could only be obtained from 1-methyl-1,2,4-triazole. The reaction products of these heterocycles with  $CCl_4$  differed markedly from those obtained from chloroform [4]. A solution of the substrate in carbon tetrachloride was pyrolysed.

### Experimental

A Pye series 105 automatic preparative chromatograph, model 15 was used for both analytical and preparative work. All infra-red spectra were recorded on Unicam SP200 spectrometer. The spectrum of a solid sample was examined as a film between sodium chloride plates. Mass spectra were recorded with Perkin-Elmer model 990 chromatograph while NMR spectra were obtained with Varian T 60 spectrometer. The pyrolytic apparatus consisted of nitrogen cylinder, a gas flow-meter containing dibutyl-phthalate as the manometric fluid to measure the flow rate of nitrogen, a preheater made of pyrex glass tube maintained a temperature above the boiling point of the substrate and a horizontal carbolite furnace maintaining a constant temperature of 550°. A reaction tube was inserted into this furnace. The volatile reaction products were then cooled by ice and cardice in the cooling traps.

The pyrolysate from the reaction tube and the cooling traps was treated with 10% hydrochloric acid followed by neutralization with 30% sodium hydroxide. The alkaline solution was extracted with chloroform, and then the solvent removed.

1-methyl-1,2,4-triazole [5] and 1-methylbenztriazole [6] were prepared as described in the literature.

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### 1-Pyrolysis of carbon tetrachloride with 1-methyl-1,2,4-triazoles.

Weight of 1-methyl-1,2,4-triazole = 8.0gm.

Volume of carbon tetrachloride = 52.0 cm<sup>3</sup>.

Weight of the products = 2.5 gm.

### Reaction products.

(i) Cyanuric chloride = 1.0gm. (40%).

(ii) Hexachlorobenzene = 1.5gm. (60%).

The molar ratio of cyanuric chloride to hexachlorobenzene is 2:3, respectively.

**Spectral data of cyanuric chloride.** Colourless solid, m.p. 145-146° IR [7] max<sup>(KBr)</sup> 785 vs.sh(C-Cl str. vib), 3450m. br.cm<sup>-1</sup> MS m/z 187(31), 185(95), 183(95), 148(5), 122(45), 87(100), 61(40), 52(17).

### 2-Pyrolysis of carbon tetrachloride with 1-methylbenztriazole.

Weight of 1-methylbenztriazole = 8.0gm.

Volume of carbon tetrachloride = 35.0 cm<sup>3</sup>

Weight of products = 4.0 gm.

### Reaction products.

(i) 1,2,4,5-tetrachlorobenzene 1.0 gm. 25%

(ii) Pentachlorobenzene 1.0 gm. 25%

(iii) Hexachlorobenzene 2.0 gm. 50%

The molar ratio between 1,2,4,5-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene is 1:1:2 respectively.

**Spectral data of 1,2,4,5-tetrachlorobenzene.** Colourless solid, m.p. 136-137° IR max<sup>(KBr)</sup> 650 vs. sh, 840w (C-Cl or C-H vib), 3100m cm<sup>-1</sup>. NMR S(CDCl<sub>3</sub>) 7.5s, (3-H and 6-H).

**Spectral data of pentachlorobenzene.** Solid, m.p. 81-82° NMR S(C D Cl<sub>3</sub>) 7.4s (1-H).

**Spectral data of hexachlorobenzene.** Colourless crystals, m.p. 288-289° IR max<sup>(KBr)</sup> 700 s.sh, 1640w, 3450m, br. cm<sup>-1</sup> NMR showed no protons.

### Discussion

After pyrolysing pyrroles, pyrazoles and imidazoles, it was thought worthwhile to investigate the nature of reaction products caused by increasing the number of nitrogen atoms in



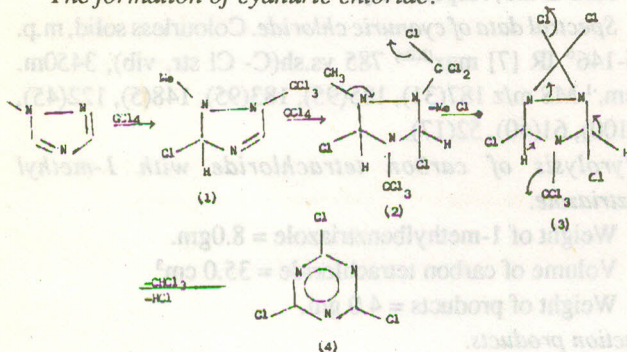
the heterocycle from two to three. For this purpose, 1-methyl-1,2,4-triazole was chosen for study.

1-methyl-1,2,4-triazole is an interesting heterocycle as it has features in common with both pyrazoles and imidazole which have N-atoms in 1,2- and 1,3-positions, respectively. It was envisaged that reaction of the triazole with carbon tetrachloride might involve competition between pyrazole-like reactions and imidazole-like reactions. If a pyrazole-like reaction had occurred, then chlorinated-1,3,5-triazine would have been formed, on the other hand, the imidazole-type reaction would lead to the formation of chlorinated-1,2,5-triazine.

**Reaction of 1-methyl-1,2,4-triazole.** 1-methyl-1,2,4-triazole on pyrolysis with carbon tetrachloride afforded a mixture of two products consisting of. (i) Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) (40%); (ii) Hexachlorobenzene (60%); whereas 1,2,4-triazole [4] with chloroform gave no product and only the unreacted starting material was recovered. In the latter case, it was thought that some reaction had indeed occurred, but that the products formed were not isolated because of their volatility.

The formation of the reaction products from 1-methyl-1,2,4-triazole can be explained by the mechanisms:-

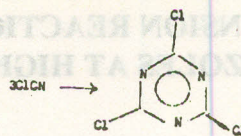
*The formation of cyanuric chloride:*



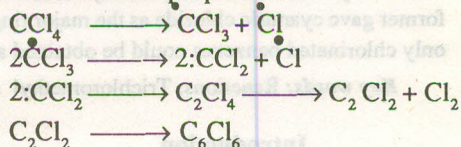
It seems probable that in this case, two molecules of carbon tetrachloride attack one molecule of 1-methyl-1,2,4-triazole. The preferential site for attack by the trichloromethyl radicals seem to be 2- and 4-nitrogen atoms which are pyridine like and are electron rich. The trichloromethyl and chlorine radicals attack the 2- and 5-positions, respectively, forming the adduct (1), which in turn is attacked by another pair of trichloromethyl and chlorine radicals this time at the 4- and 3-positions, respectively, making the complex adduct (2). The adduct affords the bicyclic intermediate (3) by the loss of methyl chloride, which in turn yields the cyanuric chloride (4) by eliminating one molecule of hydrogen chloride and chloroform.

Another possibility is the formation of cyanogen chloride by decomposition of the triazole nucleus, presumably after loss of aromaticity caused by attack of carbon tetrachloride (or radicals derived from  $\text{CCl}_4$ ), and the cyanogen chloride then

trimerises to give cyanuric chloride.



**Hexachlorobenzene.** The formation of hexachlorobenzene [8] results by the direct decomposition of carbon tetrachloride involving the generation of trichloromethyl radical. The reaction mechanism proposed is:-



The trichloromethyl radical gives dichlorocarbene by the loss of a chlorine atom which in turn is converted into dichloroacetylene via the intermediate tetrachloroethylene. The dichloroacetylene then trimerizes to yield the product, hexachlorobenzene.

**Reaction of 1-methylbenzotriazole.** Pyrolysis of 1-methylbenzotriazole in carbon tetrachloride gave a mixture of chlorinated benzenes consisting of.

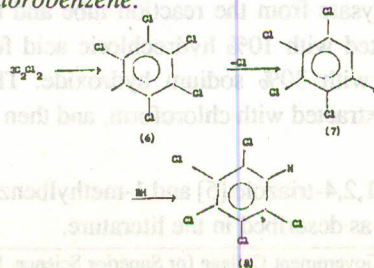
- (i) 1,2,4,5-tetrachlorobenzene (25%)
- (ii) Pentachlorobenzene (25%), and
- (iii) Hexachlorobenzene (50%)

Whereas benzotriazole with chloroform [4] gave no isolable products though only 10% of the benzotriazole was recovered. It seems that the chlorinated benzenes are the direct result of the decomposition of carbon tetrachloride [8] under high temperature conditions of the reactions.

No ring expansion products were isolated from the reaction of 1-methylbenzotriazole and carbon tetrachloride. This non-formation of the ring expansion products can be attributed to the presence of the benzene ring in the molecule, which being a deactivating group, reduces the reactivity of the triazole ring present in the molecule. The formation of the chlorinated benzenes can be explained by the mechanism.

**Hexachlorobenzene.** Hexachlorobenzene may result from the direct decomposition of carbon tetrachloride [8] via trichloromethyl radical. The mechanism is similar to that given earlier for the formation of hexachlorobenzene in the reaction of 1,2,4-triazole and carbon tetrachloride.

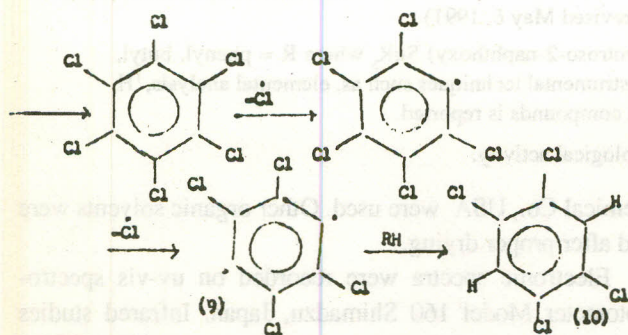
**Pentachlorobenzene.**





It seems likely that hexachlorobenzene formed from dichloroacetylene, one of the decomposition products of carbon tetrachloride, is an intermediate for the formation of pentachlorobenzene. Hexachlorobenzene eliminates one chlorine atom and forms the intermediate radical (7) which abstracts a hydrogen atom from the benzotriazole and is transformed into pentachlorobenzene (8).

1,2,4,5-tetrachlorobenzene



1,2,4,5-tetrachlorobenzene possibly results again by the partial dehalogenation of hexachlorobenzene. Hexachloroben-

zene eliminates two chlorine atoms from 3- and 6- positions forming a diradical (9) which in turn abstracts hydrogens from the 1- methylbenzotriazole and is converted into 1,2,4,5-tetrachlorobenzene (10).

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These complexes are quite stable, high molecular weight crystalline solids having sharp melting points. Chloro derivatives showed higher melting point than phenyl and butyl derivatives which is probably due to increased ionic character of the chlorine bond in these compounds. All these compounds are soluble in most of the common organic solvents. The infrared spectra of the synthesized complexes were compared with their precursors to assess the extent of any structural changes resulting from complexation. The prominent infrared bands are shown in Table 3. Stretching vibrations due to  $\nu_{C-Cl}$  and  $\nu_{N=O}$  are the most important bands and provide conclusive evidence of complexation. The bands in  $440-480\text{ cm}^{-1}$  region, characteristic of the  $\nu_{C-O}$  bond, [15-16] have not undergone any appreciable

change. The use of organotin in various fields is dependent on both the nature and number of organic groups bonded with tin atoms. For example, mono and diorganotin compounds are primarily used as heat and light stabilizers in PVC [1,2]. Whereas triorganotin have biological activity against various species. A number of investigators [3] have shown that several classes of organotin possess antimutagenic activity against P-388 lymphocytic leukemia in mouse cell. Eng and Farkis [4] synthesized diamine-tin complexes of the halides and found that toxicity of these compounds was too high to use them as anticancer agents. Barbic et al. [5] studied in detail anticancer activity of tin derivatives of amino acids and correlated activity with structures of these complexes. Giclen and coworkers [6-8] synthesized a number of organotin (IV) complexes of various donor ligands and studied their activity in vivo and in vitro against P-388 and L-1210 leukemias. Due to diverse applications of organotin compounds, we were tempted to synthesize new organotin complexes and investigate their antibacterial activity. We wish to report the synthesis of 1-amino-2-naphthol complexes of tin tetrachloride, tributyltin chloride and triphenyltin chloride. These complexes have been characterized by elemental analysis, thermal analysis, proton nmr, electronic and infrared studies. Their biological activity has been studied against bacteria *Staphylococcus aureus*, *Salmonella typhosa* and *Bacillus subtilis* using streptomycin sulphate as a standard.