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A STUDY OF THE PYROLYSIS OF CYCLOHEXENE AND 2-AMINOPYRIDINE WITH CARBON TETRACHLORIDE

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Reaction of trichloromethyl radical (from carbon tetrachloride in a flow system at 550°) with cyclohexene and 2-aminopyridine, has been investigated. The former gave benzene, chlorobenzene and decomposition products of carbon tetrachloride while the latter yielded cis trans-1, 4-dicyano-1, 3- butadiene.

Key words: Cyclohexene, 2-Aminopyridine, Carbon tetrachloride.

Introduction

We have recently reported [1-3] reaction of trichloromethyl radical generated from carbon tetrachloride at high temperature in the vapour phase with pyrroles, pyrazoles, substituted pyrazoles, imidazoles and triazoles. Ring expansion products were obtained in each case. Herein we report the result of our investigation on the vapour phase reactions of carbon tetrachloride with cyclohexene and 2-aminopyridine.

Results and Discussion

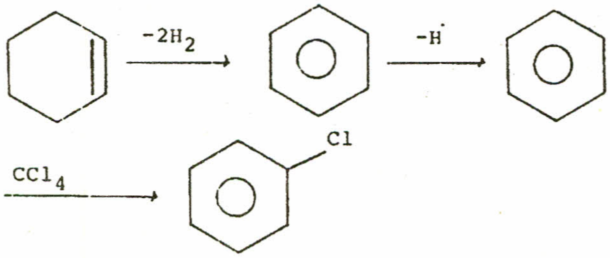
Cyclohexene. Cyclohexene on pyrolysis with carbon tetrachloride afforded:

(i) Benzene (50%), (ii) Chlorobenzene (25%), (iii) Tetrachloroethylene (9%), (iv) Pentachloroethane (10%) and (v) Phenyltrichloroethylene (6%)

Tetrachloroethylene and pentachloroethane are the decomposition products of carbon tetrachloride. The reaction mechanism for the formation of reaction products is explained as:

(i) Benzene. The formation of benzene by dehydrogenation [5,6] of cyclohexene is well documented. So, in this reaction it is believed that benzene results from the dehydrogenation of cyclohexene under high temperature conditions.

(ii) Chlorobenzene. The formation of chlorobenzene is explained by the mechanisms.

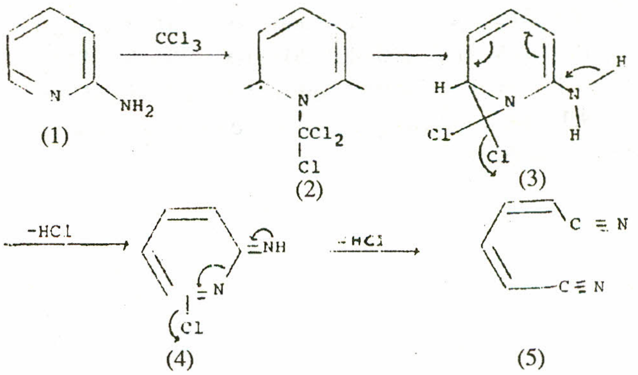


(1)

The possibility involves the formation of benzene by the dehydrogenation of cyclohexene, which by the loss [5,6] of hydrogen atom, yields the radical. The phenyl radical abstracts chlorine from the carbon tetrachloride and forms the chlorobenzene.

The formation of tetrachloroethylene, pentachloroethane and phenyltrichloroethylene can be explained by mechanism similar to those given for other products [7-11].

Reaction mechanism of the reaction of 2-aminopyridine. 2-Aminopyridine when pyrolysed with carbon tetrachloride at 550° yielded a mixture of products consisting of: (i) 2-aminopyridine (75%) and (ii) cis, trans-1, 4-dicyano-1, 3-butadiene (25%). The formation of cis, trans-1, 4-dicyano-1, 3- butadine is described by the mechanism given below:



It seems likely that the trichloromethyl radical generated from carbon tetrachloride attacks the nitrogen atom (1) of the heterocycle forming the radical (2) which by the loss of 1 molecule of hydrogen chloride is converted into the bicyclic system (3). The bicyclic adduct (3) being under strain, opens by eliminating 1 molecule of hydrogen chloride and is transformed into the (4). The (4) is then converted into cis, trans-1, 4- dicyano-1, 3-butadiene (5) by the loss of 1 molecule of hydrogen chloride.

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 SP 200 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 dibuty-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.

Reaction of carbon tetrachloride with cyclohexene. A solution of cyclohexene (8.0gm, 975^{10-4} m.moles) in carbon tetrachloride (52.0 cm^3, 1296^{10-4} m.moles) was pyrolysed and the reaction products were analysed by GLC using carbowax 20M as the stationary phase at 170°. The components were isolated by preparative GLC and the comparison of spectral data with those of respective authentic samples showed the following reaction products: (1) Benzene 50%, (2) Chlorobenzene 25%, (3) Tetrachloroethylene 9%, (4) Pentachloroethane 10%, (5) Phenyltrichloroethylene 6%

Spectral data of phenyltrichloroethylene. NMR $\delta(CDCl_3)$ 7.32m (m, C_6H_5) MS m/z 210 (40), 208 (100), 206 ($M^+, {}^{35}Cl_3$, 100) 171(40), 136 (91), The peak ratio of P, P+2, P+4 and P+6 is 27:27:9:1 which indicates the presence of three chlorine atoms in the molecule.

Reaction of carbon tetrachloride with 2-aminopyridine. A solution of 2-aminopyridine (8.0gm, 851^{10-4} m. moles) in carbon tetrachloride (45.O cm^3, 4237^{10-3} m. moles) was pyrolysed. The reaction mixture (3.0gm) was analysed by GLC using Carbowax 20 M as the stationary phase at 180°. The components were separated by preparative GLC and spectral data were obtained for each component. The spectra and the comparison of retention distance with authentic samples of each component showed cis-trans-1, 4-dicyano-1, 3-butadiene (25%) as the only reaction product while 75% of unreacted starting material was recovered.

Spectral data of cis-trans-1, 4-dicyano-1, 3-butadiene. Colourless solid, m.p.65-66° lit. 65-66° [4] I.R. max$^{(kBr)770s}$ (possibly C-H vib), 1620m (possibly C= C vib), 2200s (C≡N gp) NMR $\delta(CDCl_3)$ 5.7m (2H and 3-H), 7.2m (1-H and 4-H).

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