

## MASS SPECTRAL STUDIES OF SOME CYCLOHEXENE-DERIVED POLYHALOGENOALKANES

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**Abstract.** The mass spectral studies of dichloromethylcyclohexane (I), 1-dichloromethyl-2-chlorocyclohexane (II) and dichloromethylcyclohexane (III) have been described. The pattern of mass fragmentation of the above compounds show a regular order.

Cyclohexene-derived polyhalogenoalkanes are formed in the reaction between amines and polyhalogenoalkanes when cyclohexene was added to the reaction mixture.<sup>1,2</sup> The studies of combined glc-mass spectrometry on these compounds are reported in detail in the present communication. The mass spectrum of dichloromethylcyclohexane (I) shows molecular ion peak at  $m/e$  166, 168, 170 in the ratio of 9:6:1 indicating the presence of two chlorine atoms. The compound I undergoes fragmentation following two routes with the loss of 36 and 83 mass units corresponding to the molecule of hydrogen chloride and dichloromethyl radical. The loss of hydrogen chloride occurs due to elimination of hydrogen from a carbon  $\alpha$  or  $\beta$  (or a proton on any other position) to the dichloromethyl linkage and a chlorine on the dichloromethyl group, thus forming an olefin or a norcarane ring,  $m/e$  130, 132 in the ratio 3:1; indicating the presence of single chlorine in the species. This is then followed by the loss of a chlorine atom resulting a charged species  $m/e$  95. This readily loses 28 mass units ( $C_2H_4$ ) giving rise to another ionic species  $m/e$

67 which is then followed by a loss of 26 mass units ( $C_2H_2$ ).

The initial loss of dichloromethyl radical with mass units 83 gives rise to a mass ion  $m/e$  83. Further loss of 26 mass units gives another species at  $m/e$  55. Three metastable peak at  $m_1^*$  47.3,  $m_2^*$  25.1 and  $m_3^*$  36.4 are produced in these fragmentations and are illustrated in the above scheme. All these ionic species are outlined in Chart 1 and its mass plate given in Fig. 1.

The mass spectrum of 1-dichloromethyl-2-chlorocyclohexane (II) show a molecular ion peak at  $m/e$  200, 202, 204, 206 in the ratio 27:27:9:1, which shows that three chlorine atoms are present in the compound. The compound II by losing 36 mass units corresponding to the molecule of hydrogen chloride gives a mass ion at  $m/e$  164, 166, 168 in the ratio of 9:6:1. The loss occurs due to the elimination of chlorine substituted at a carbon adjacent to the carbon on which dichloromethyl-linkage is attached and a hydrogen from the carbon  $\alpha$  to the dichloromethyl group thus giving rise to an olefin or a loss of proton on the dichloromethyl-linkage successively giving rise to a norcarane ring at  $m/e$  164, 166, 168 in the ratio 9:6:1. This charged ion corresponds to 1-dichloromethylcyclohexene or equivalent (a). The charged ion (a) undergoes fragmentation by two routes with the loss of 35 and 83 mass units corresponding to a chlorine atom and dichloromethyl radical respectively. The elimination of a single chlorine gives ion (b) at  $m/e$  129:131 with ratio 3:1 indicating the presence of only one chlorine. Further fragmentation of this ion occur

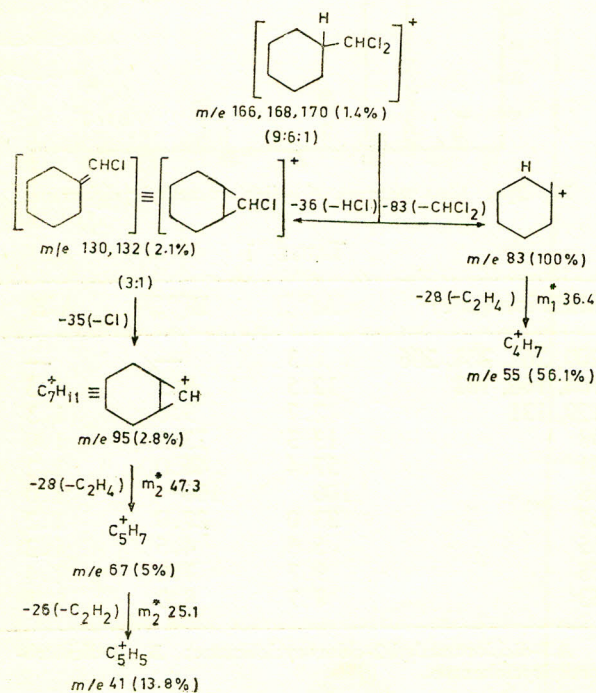


Chart. 1. Mass fragmentation pattern of dichloromethylcyclohexane.

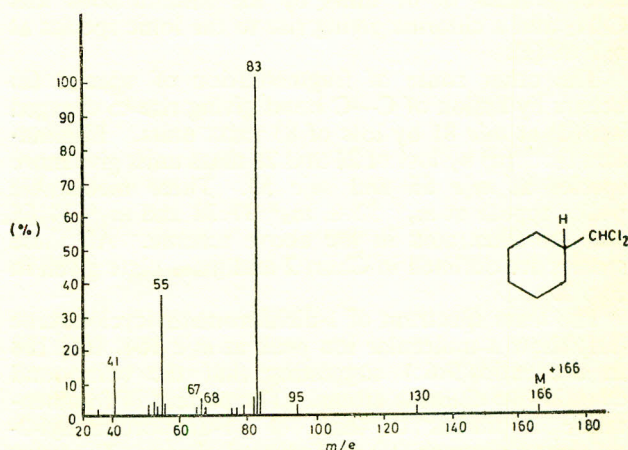


Fig. 1. Mass spectrum of dichloromethylcyclohexane.

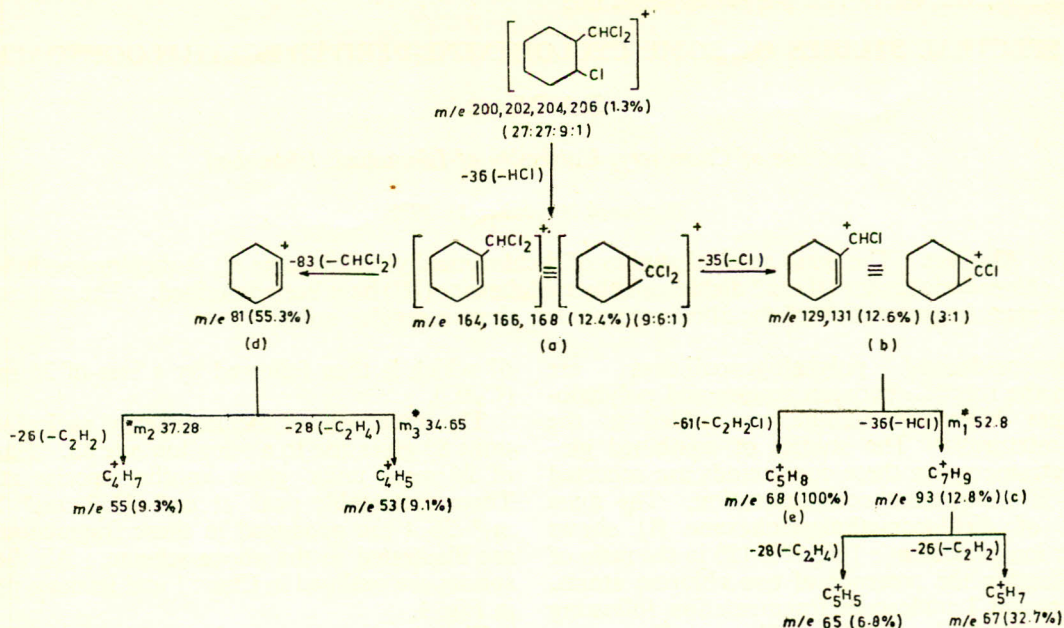


Chart. 2. Mass fragmentation pattern of dichloromethyl-2-chlorocyclohexane.

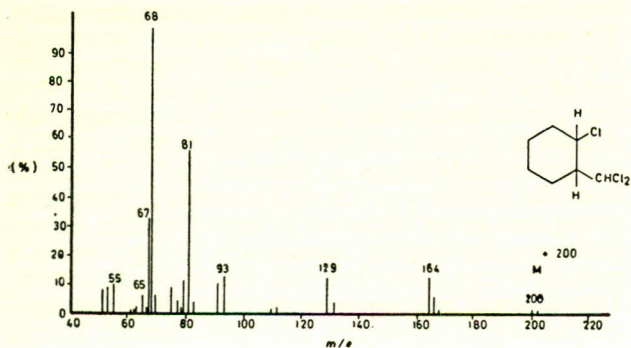


Fig. 2. Mass spectrum of 1-dichloromethyl-2-chlorocyclohexane.

by two routes. The loss of hydrogen chloride gives mass ion (c) at  $m/e$  93. Its further degradation gives two more ionic species at  $m/e$  65 and  $m/e$  67 by loss of 28 and 26 mass units respectively. Species (b) also loses a mass of 61 units by the simultaneous loss  $C_2H_2$  and a chlorine giving rise to the ionic species at  $m/e$  68 (e).

The other route of fragmentation of species (a) occurs by fission of C—C bond giving rise to charged ion (d) at  $m/e$  81 by loss of 83 mass units. Elimination from (d) by loss of 26 and 28 mass units give more species at  $m/e$  55 and  $m/e$  53. Three metastable peaks appear at  $m_1^*$  52.8,  $m_2^*$  37.38 and  $m_3^*$  34.65 and are illustrated in the above scheme. All these species are outlined in Chart 2 and mass plate given in Fig. 2.

The mass spectrum of 1-dichloromethylcyclohexene (III) show a molecular ion peak at  $m/e$  164, 166, 168 in the ratio 9:6:1 suggesting that the compound contain two chlorine atoms. The pattern of fragmentation is similar to that of 1-dichloromethyl-2-chlorocyclohexane (II) as discussed above. The mass plate (Fig. 2a) is illustrated for comparison. It

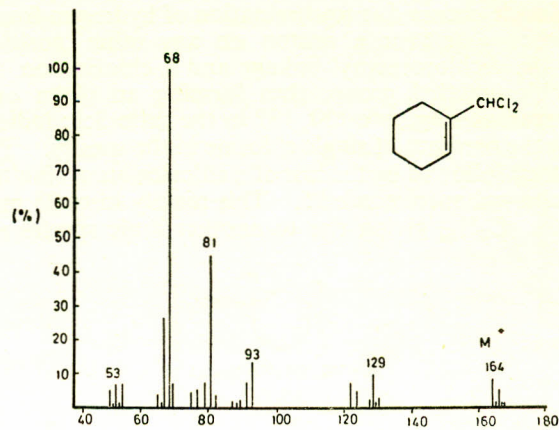


Fig. 2(a). Mass spectrum of 1-dichloromethylcyclohexane.

TABLE 1

Mass ion ( $m/e$ )	A(%)	B(%)	A/B
200, 202, 204, 206	1.3	—	—
164, 166, 168	12.5	8.5	1.5
129, 131	12.7	9.6	1.3
93	13.3	13.2	1.0
81	57.4	46.0	1.2
68	100	100	1.0
67	33.0	27.0	1.2
65	5.6	4.5	1.2
55	9.7	7.0	1.4
53	8.7	8.0	1.1

A, 1-dichloromethyl-2-chlorocyclohexane; B, 1-dichloromethylcyclohexane.

seems that a definite pattern is followed in which a halogen fragment break-up from the parent compound

in at least two forms resulting ions with lower mass units. The major mass ion peaks are only composed of carbon-hydrogen skeleton. Comparisons of the mass fragments of 1-dichloromethyl-2-chlorocyclohexane and dichloromethyl-cyclohexene (Table 1) reveal that the intermediate mass ions possess nearly the same per cent fragmentation and mass units. The ratio of the same species from two different sources is near unity and indicate that both the fragmentation patterns follow a common route.

#### Experimental

Mass spectra were determined on an AE1 MS 12 mass spectrometer. This instrument was also used coupled to a Pye-104 gas chromatograph for combined gas-liquid chromatography-mass spectrometry to

ensure purity of the sample under study. The Pye instrument with a flame ionisation detector was connected to RE-511 Georze Servoscribe recorder. The glass column (I.D. 4 mm) used was 2.4m in length packed with 20% Apiezon L on Celite (100-120 mesh).

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#### References

1. J.R. Lindsay Smith and Z.A. Malik, *J. Chem. Soc.*, 617B (1970).
2. J.R. Lindsay Smith and Z.A. Malik, *J. Chem. Soc.*, 920B (1970).