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CHLORINATION OF TRANS-1,4-DICHLORO-2-BUTENE

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The chlorination of trans-1,4-dichloro-2-butene (tr-DCB-2) in chlorinated hydrocarbon solvents yielded solid and liquid isomers. When methylene chloride (I) was used as a solvent, the solid isomer was obtained in high yield. The ionic pathway dominated in I and was an exclusive trans-addition process.

It has been reported that a mixture of the solid and liquid of isomers of tetrachlorides was given by the chlorination of dichlorobutenes1). It was elucidated that these were the meso isomer and dl isomer, respectively2). It was also reported that the chlorination of trans-2-butene gave two isomers of 2,3-dichlorobutane3),4),5). These were shown by isolation and comparison to authentic samples to be meso and dl 2,3-dichlorobutane3). However, these reports did not refer to the solvent effect.

When tr-DCB-2 was chlorinated in chlorinated hydrocarbon solvent such as I or carbon tetrachloride (II), the ratio of the two isomers varied over a wide range. In an attempt to understand this problem, the effect of the solvent on the chlorination of tr-DCB-2 was investigated with a conventional stirred vessel.

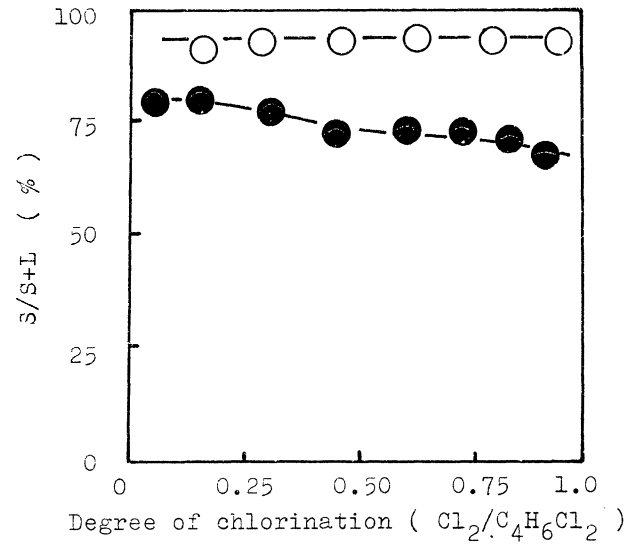

Fig. 1. The effect of the solvent on the selectivity of the solid isomer with nitrogen in the dark.

The chlorination apparatus consisted of 500 ml flask immersed in a thermostated water bath, and was equipped with a stirrer, gas inlet and thermometer pocket. The reaction temperature was maintained at 20°C in all runs of the experiment. Chlorine gas was passed into a mixture of 0.6 mole of tr-DCB-2 and 3.0 mole of I (or II) at the rate of 0.3 mole / hour. The chlorinated products were analyzed by gas-chromatography. Dichlorobutenes were prepared by the chlorination of 1,3-butadiene in II and was fractionated at reduced pressure and the isolated tr-DCB-2 was redistilled. Gas-chromatographic analysis showed that it contained

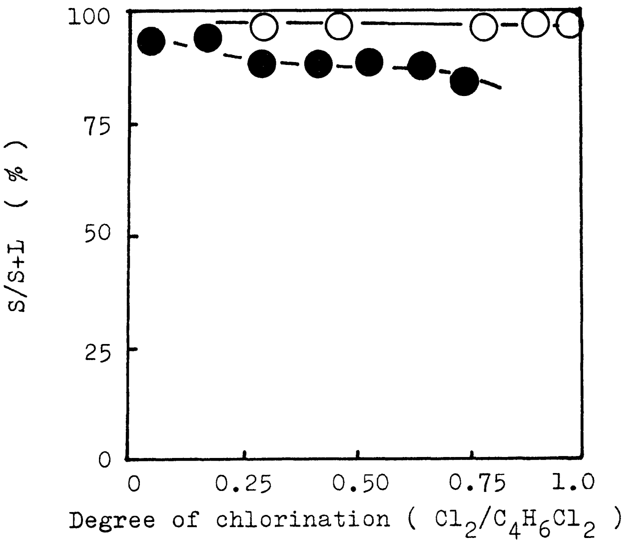

Fig. 2. The effect of cyclohexane on the selectivity of the solid isomer.

● carbon tetrachloride
○ methylene chloride

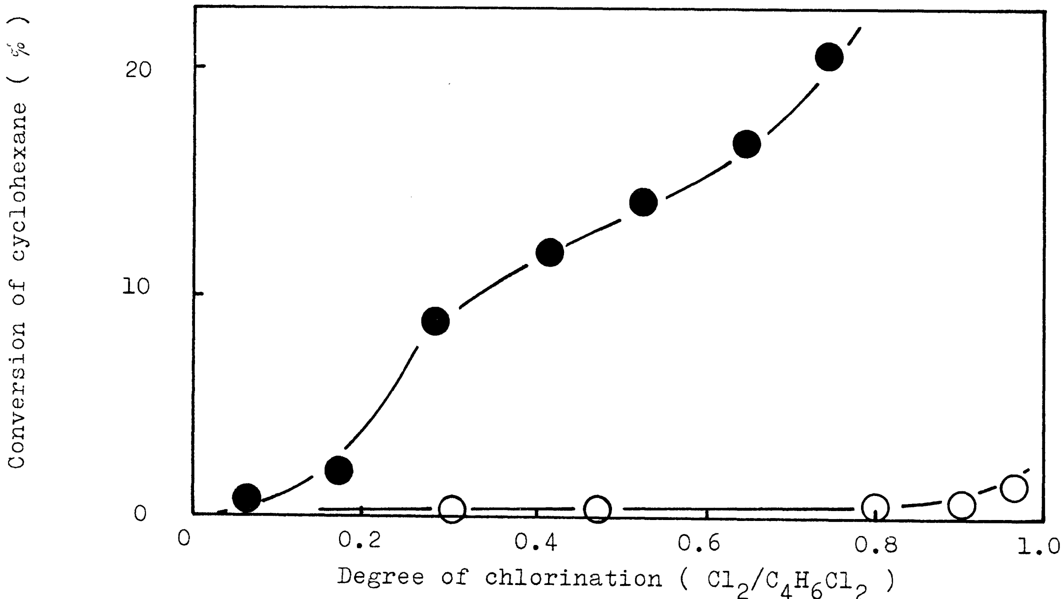

Fig. 3. The effect of the solvent on the formation of cyclohexyl chloride.

● carbon tetrachloride
○ methylene chloride

less than 5 % of the cis isomer and 3,4-dichloro-1-butene as impurities. The results of the chlorination with nitrogen in the dark are shown in Fig. 1. The solid isomer to the solid and liquid isomers (S/S+L) was not less than 90% with use of I as a solvent. When II was used as a chlorination solvent, both trans and cis addition to double bond occurred at the same time and the liquid isomer was also formed. In contrast with II, I was favorable to the formation of the solid isomer.

0.6 mole of cyclohexane was added into the solution of tr-DCB-2 and I (or II). This solution was chlorinated in the dark. The experimental results are shown in Fig. 2. The value of S/S+L was higher than that with nitrogen in the dark.

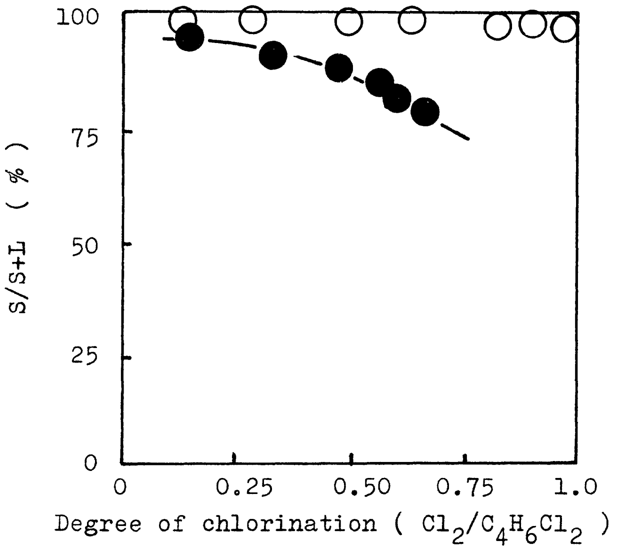

Fig. 4. The effect of oxygen on the selectivity of the solid isomer.

● carbon tetrachloride
○ methylene chloride

Fig. 3 indicates the formation of cyclohexyl chloride in the chlorination of tr-DCB-2.

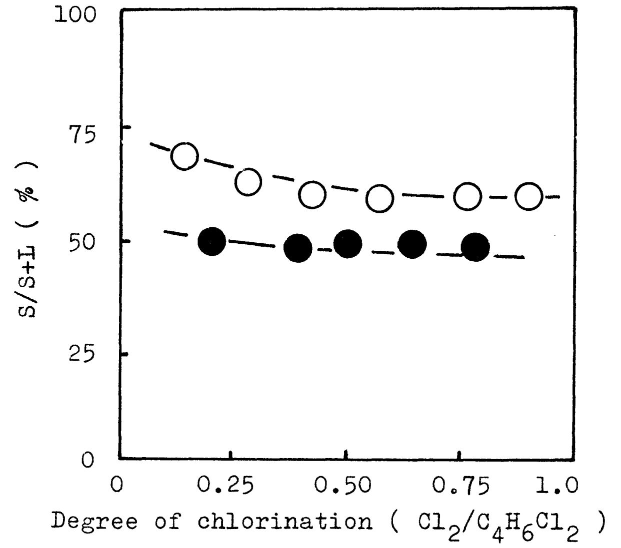

Fig. 5. The effect of the light on the selectivity of the solid isomer.

● carbon tetrachloride
○ methylene chloride

A chlorine atom attacked on cyclohexane and cyclohexyl chloride was formed by the abstracting a hydrogen atom from cyclohexane. It was a proof that the radical reaction took place considerably that cyclohexane was chlorinated into cyclohexyl chloride in the case of II.

Fig. 4 shows the effect of oxygen on the selectivity of the solid isomer. The flow rate of oxygen gas was 0.05 mole / hour. The values of S/S+L had a same tendency to the results of cyclohexane.

The results of the chlorination under nitrogen with external illumination are shown in Fig. 5. S/S+L was lowered in the case of I as well as II. It was confirmed that the radical pathway was undesirable for the formation of the solid isomer.

The main conclusion to be drawn from these results is as follows.
The ionic pathway dominated in I and was an exclusive trans-addition. On the other hand, the nature of the products and the attack on cyclohexane showed the ionic pathway was considerably replaced in II by the radical pathway.

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