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STRUCTURE OF BIS-(2-CHLORO-1-NITROSOCYCLOHEXANE)

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Bis-(2-chloro-1-nitrosocyclohexane) (I) was first synthesized by A. Baeyer (1), but no report has been appeared as to the structure of this compound. The compound (I) was synthesized according to the method of U.S.P. 2,485,180 and its structure was determined chemically as well as spectroscopically.

Thirty grams of nitrosylchloride was introduced to a solution of 41 g. of cyclohexene in 175 ml. of liquid sulfur dioxide at -50°C. The solid formed was (I), m.p. 137-8°(decomp.), yield 76%. The infrared spectrum of (I) was measured on a Japan Spectroscopic Model DS-402G high resolution infrared spectrophotometer, in crystalline state. Stretching vibrations of C-Cl were observed at 742 cm^{-1} and 687 cm^{-1} (Fig. 1).

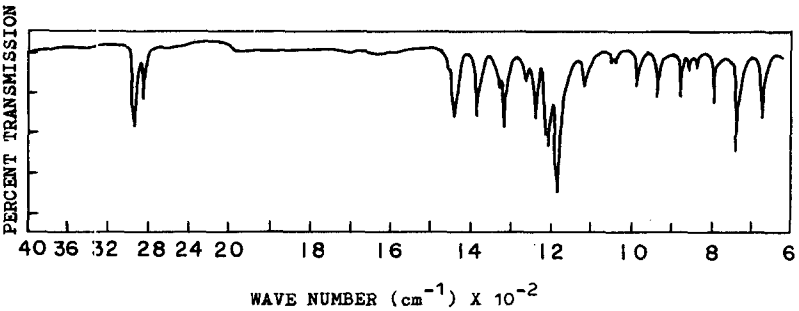

FIG. 1

Infrared spectrum of bis-(2-chloro-1-nitrosocyclohexane)

It is well known that equatorial substituents usually show typical infrared absorptions at higher frequencies than axial substituents (2). For example, in chlorocyclohexane derivatives, infrared absorption band due to equatorial C-Cl stretching is at 736-856 cm^{-1} and that due to axial C-Cl stretching is 646-730 cm^{-1} (3). Therefore absorption bands at 742 cm^{-1} and 687 cm^{-1} were assigned to the equatorial and the axial C-Cl stretching vibrations respectively. Generally, preferred conformation of trans-1,2-disubstituted cyclohexane is diequatorial form. For example, trans--1,2-dimethylcyclohexane is almost entirely (99%) in the diequatorial form at room temperature (4).

Accordingly the fact that chloro substituent in (I) is both axial and equatorial leads us to the idea of cis addition of nitrosyl chloride to cyclohexene. However, (I) was reduced to give cyclohexylamine and trans-2-chlorocyclohexylamine with $LiAlH_4$ in tetrahydrofuran. No cis-2-chlorocyclohexylamine was obtained. Therefore configuration of nitroso and chloro groups of (I) is trans, because inversion of configuration may not occur in the process of reduction. Configuration of the dimer is trans, because characteristic absorption band of trans-nitroso dimer was observed at 1190 cm^{-1}. On the basis of these data, it seems reasonable to assume that the structure (configuration and conformation) of (I) is as follows.

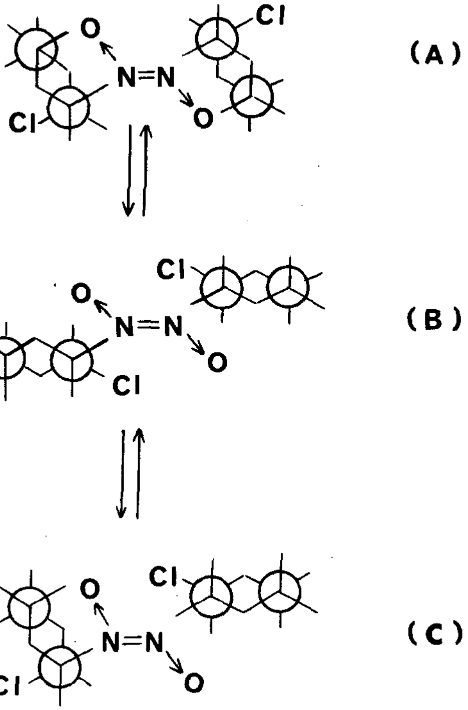

FIG. 2

Structure of bis-(2-chloro-1-nitrosocyclohexane)

It seems that diaxial form is less stable than diequatorial form because of 1,3-diaxial interaction, but dipole repulsion between nitroso and chloro group in diequatorial form is much greater than in diaxial form.

As a result, difference of stability between diaxial form and diequatorial form is little. Probably fraction of conformers A, B and C is comparable in magnitude.

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