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DEPENDENCE OF STERIC COURSE OF NITROSYL CHLORIDE ADDITION TO CYCLOHEXENE ON SOLVENTS

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Recent investigation of the stereochemical course of the addition of nitrosyl chloride to olefins have shown that the addition mechanism of nitrosyl chloride to double bonds depends upon the structure of olefins. The additions to norbornene[1)] and 3, 4, 6-tri-0-acetyl-D-glucal[2, 3)] follow cis stereochemical courses while that to Δ^9-octalin follows a trans one.

In order to use these reactions for a synthetic purpose, we have studied the addition of nitrosyl chloride to cyclohexene, which is one of the most common cycloolefins, and found that the steric course depends upon solvents. This communication describes the results of such a study.

The addition of nitrosyl chloride to cyclohexene in liquid sulfur dioxide[4)] afforded an adduct (I), in 60 - 80% yield, showing m.p. 152 - 153° after recrystallization from ethanol . (Anal. Calcd. for $C_{12}H_{20}N_2O_2Cl$: C, 48.9 ; H, 6.79 ; N, 9.5 ; Cl, 24.1 ; M. W., 295. Found : C, 48.82 ; H, 6.76 ; N, 9.16 ; Cl, 23.80 ; M. W., 298). On the other hand, the same reaction in methylene chloride, chloroform or preferably trichloroethylene afforded an adduct (II), in 10 - 24% yield, showing m.p. 133 - 135° after recrystallization from ethanol[5]. (Anal. Found : C, 49.01 ; H, 6.87 ; N, 9.15 ; Cl, 24.2 ; M. W., 295) .

Both of the adducts I and II were confirmed to be bis (2-chloro-1-nitrosocyclohexane) by the elemental analysis and molecular weight determination, but distinguished each other clearely by the depression of the mixed melting point and spectral evidences.

The geometrical configuration of adducts I and II about the N-N bond was assigned to trans by the N-O stretching frequencies, 1195 - 1222 and 1208 cm^{-1}, respectively, by comparing with those of known C-nitroso-dimers[6, 7].

Therefore, the adducts I and II must be geometrical isomers of cyclohexane ring.

The infrared spectrum of I shows an absorption at 745 cm^{-1} characteristic of an equatorial C-Cl bond[8], but that of II shows no absorption at 740 - 750 cm^{-1} but at 685 cm^{-1},[9] suggesting the presence of an axial C-Cl bond.

Evidences to establish the stereochemistry of the adducts were provided with the nuclear magnetic resonance spectra as shown in Figs. 1 and 2.

The n.m.r. spectrum of I shows proton signals at 4.51 τ (1 H), 5.68 τ (1 H), and 8.18 τ (8H). The signals at 4.51 and 5.68 τ showed the same splitting pattern (a triplet with J= 11 cps further divided into doublet with J=3.5 cps) and were assigned to protons at C_1 and C_2 , respectively, by comparison with C_1 protons of bis (nitrosocyclohexane)

(5.0τ) and chlorocyclohexane (6.04τ).

The strong coupling indicates trans conformation of the protons at C_1 and C_2 in a chair form and the splitting patterns are well consistent with those expected from the first approximation[10] as shown in Fig. 1. Therefore, the configurations of nitroso group and chlorine atom must be equatorial and I is a trans adduct.

The n.m.r. spectrum of II is very different from that of I in the region of tertiary hydrogens, showing proton signals at 4.80 τ (0.5 H), 4.95τ(1.5H) and 8.15τ (8H). The signals can reasonably be explained by considiering cis conformation of the protons at C_1 and C_2 in a chair form. The axial proton at C_1 couples strongly with axial proton at C_6 (J=12 cps) and weakly with two equational protons at C_2 and C_6 (J= 3.3 cps), and half of it appears at 4.80 τ and the rest of it falls at the same place as an equatorial proton at C_2 which couples with neighboring three protons. Therefore, the configurations of nitroso group and chlorine atom must be equatorial and axial, respectively, and II is a cis adduct.

The finding of the dependence of addition of nitrosyl chloride to cyclohexene on solvent will serve to apply the reaction to olefins of natural products and it should be mentioned that the stereochemistry of nitrosyl chloride addition is a sensitive function not only of olefin structure but also of solvent.

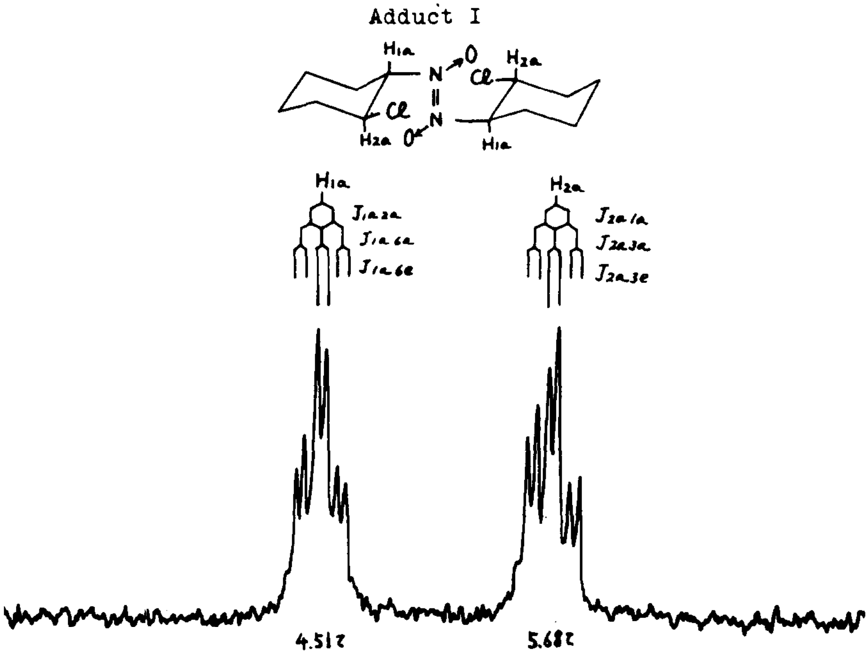

Fig. [illegible]. The NMR Spectrum of Tertiary Hydrogens of Adduct I in $CDCl_3$ (100 Mc, TMS as an internal standard).

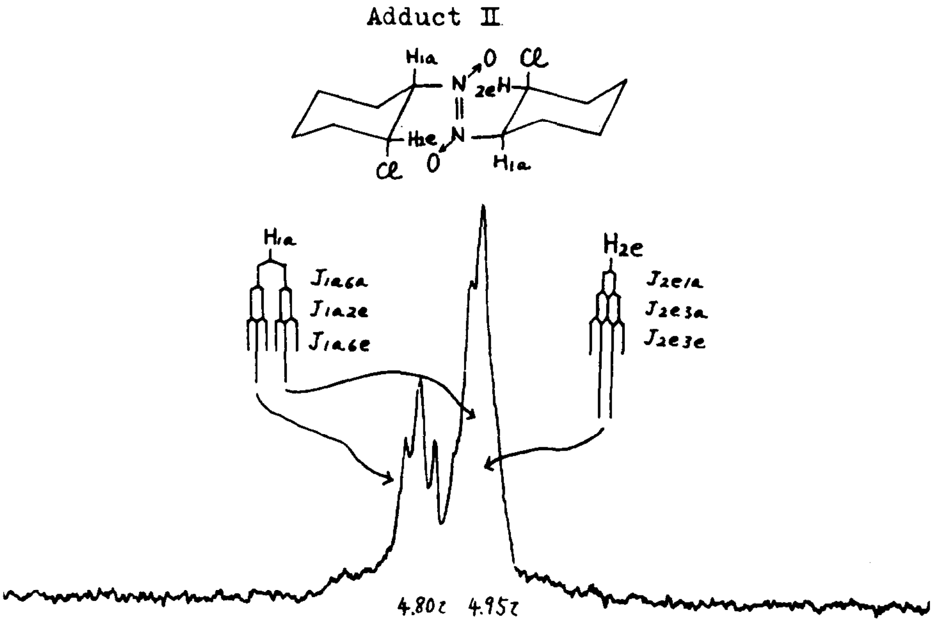

Fig. 2. The NMR Spectrum of Tertiary Hydrogens of Adduct II in $CDCl_3$
(100 Mc , TMS as an internal standard).

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(5) A blue oil was accompanied in 30 - 40% yield and proved to be 1, 2-dichloro-1-nitrosocyclohexane.

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(9) The C-N bending absorption of bis (nitrosocyclohexane) appears at 690 cm^{-1} and the C-Cl bending absorption of chlorocyclohexane appears at 742 and 688 cm^{-1}. Therefore, the conformation of adduct I and II can not be definitely decided by the infrared spectra alone.

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