Thus if we know or can choose a value of n and A we can calculate the ratio E^*/E_m for our system.

Having calculated the ratio (E^*/E_m), one then uses eq 29 and 30 with $\Delta E_m/RT \sim (n-1)^{1/2}$ to calculate E_m at any given temperature.[35] This is done numerically, explicit solutions not being possible.

With Stirling's approximation for $(n-1)!$ we have from eq 29 and 30

$$k = \frac{k_w}{2\sqrt{2\pi}}\left[\frac{eE_m}{(n-1)RT}\right]^{n-1}\exp\left(-\frac{E_m}{RT}\right) \quad (35)$$

which permits us to solve for E_m from the observed value of k and the appropriate value of n.

When the high-pressure Arrhenius parameters A and E^* are known, as is often the case, n is the only unknown parameter and it can be determined accurately.

We have used eq 35 in our theoretical estimates for the rate of decomposition of *i*-PrI.

[35] This approximation for ΔE_m is obtained by use of the method of steepest descents for the integration of eq 29.

A Nuclear Magnetic Resonance Study of Steric Effects in *cis*- and *trans*-1,4-Dichloro-2-butene[1]

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Abstract: The 60-Mc nmr spectra of *cis*- and *trans*-1,4-dichloro-2-butene are reported and analyzed. A population analysis based upon the observed vicinal couplings indicates that the steric interaction between $-CH_2Cl$ groups in the *cis* isomer is at least 170 cal mole^{-1} larger when the chlorine atom is oriented *trans* with respect to the adjacent vinyl proton.

The nuclear spin–spin coupling between vicinal protons in HC–CH groups of ethane and ethylene-type molecules has been found to be dependent upon the dihedral angle.[3] Since internal rotational energy barriers about carbon–carbon single bonds are low, only an average coupling is observed in many cases, but such an average can still be useful to determine which is the more stable rotamer.

The analysis of the complex nmr spectra of *cis*- and *trans*-1,4-dichloro-2-butene was undertaken since the coupling constants obtained from these spectra can be used to infer the conformation of the CH_2Cl groups about the carbon–carbon single bonds. Our primary objective was to see if we could determine the extent of the steric interaction of these groups in the *cis* compound.

The basis for our conformational study rests upon the following considerations. Figure 1 shows the anticipated stable conformation of *trans*-1,4-dichloro-2-butene.[4-6] It is assumed that in this case a certain average vicinal coupling between the methyl protons (H_a) and the adjacent vinyl proton (H_b) will be observed, the magnitude of which is determined by the energy difference between the conformation of Figure 1 and others obtained by rotations about the carbon–carbon single bonds. If the same *trans* orientation of an H_a proton with respect to the adjacent H_b proton persisted in the *cis* isomer, we would expect to observe a rather strong steric interaction between the H_a protons of the different $-CH_2Cl$ groups. Of course with the chlorine atoms *trans* with respect to H_b, the steric effect would be even more pronounced. Because of these interactions, conformational stability requirements are altered, and these changes should be reflected in the average proton couplings observed.

This unsaturated system may be regarded as an allylic system, since there is spin–spin coupling between protons separated by one double bond and three single bonds, and also as a homoallylic system, where the coupling between protons is over five bonds with the protons symmetrically placed about the carbon–carbon double bond, *i.e.*, H—C—C═C—C—H.[7]

Karplus,[8] through a valence bond treatment, has had most success in correlating experimental results with theoretical calculations, with respect to both the sign and magnitude of couplings in allylic and homoallylic systems. The proposed mechanism involves hyperconjugation determined by σ–π configuration interaction.

From the theoretical point of view, the allylic coupling constants are negative in sign with the coupling being transmitted mainly through the π-electron system.[8] The magnitudes of the allylic coupling constants have been found to vary between 0 and 3 cps.[9] These coupling constants attain a maximum of approximately 3 cps when the azimuthal angle is 90°, and a minimum when the azimuthal angle is 0 or 180°.

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In the homoallylic system the coupling also involves the $\sigma-\pi$ configuration interaction mechanism.[8] The theory predicts the sign to be reversed, but there should be no change in the magnitude of the coupling constants on replacing the fragment C=C by C=C—CH. The same stereochemical limitations should apply as for the allylic case.

Experimental Section

Preparation of Compounds. *trans*-1,4-Dichloro-2-butene was obtained from K and K Laboratories Inc. as a 98% pure compound. *cis*-1,4-Dichloro-2-butene was synthesized following the procedure of Babbit, Amundsen, and Steiner.[10] Attempts to purify these compounds by distillation and fractional crystallization were unsuccessful, but through the courtesy of Dr. G. Perkins, Jr., of Continental Oil Co., both compounds were finally purified using gas chromatography.[11] The chromatogram indicated that the *trans* compound was contaminated with about 18% of impurities before purification.

Before observing the nmr spectra of the liquid samples of *cis*- and *trans*-1,4-dichloro-2-butene, these samples were degassed by flushing with nitrogen gas in standard thin-walled cells. Sealed capillaries of benzene were inserted into the sample tubes for use as an external reference standard. There were no bulk susceptibility corrections made.

Instrumentation. The nmr spectra were recorded on a Varian A-60 spectrometer operating at room temperature. The line positions were measured at total peak height with a probable error of ±0.05 cps.

The spectra were calculated using a computer program written for an IBM 1620 Model II computer having a disk pack. The computer program was written in FORTRAN II following the procedure given by Pople, Schneider, and Bernstein.[12] Values for the chemical shift for each proton plus the coupling constants between the various protons in the molecule are used as parameters to calculate the spectrum. By varying these parameters the experimental spectrum was fairly well reproduced. The probable error for the calculation of the frequencies and intensities is 0.05 to 0.1 cps. Thus we feel that the chemical shifts and coupling constants determined in this way are accurate to at least ±0.1 cps.

Results

The calculated chemical shifts and coupling constants for the *cis* and *trans* isomers as determined by the methods discussed above are found in Tables I and II, respectively. The results are illustrated in Figures 2 and 3. The field is calibrated in cycles per second from the benzene external standard.

The results obtained are in agreement with the theory as well as with the results obtained by other investigators.[7] The small but significant differences in the allylic, vicinal, and long-range coupling constants for the two isomers can be used to discuss conformational effects. Since the vicinal coupling is the more straightforward, we will limit our subsequent discussion to it.

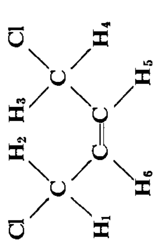
A complete conformational analysis is complicated by the fact that much less experimental data are available in the case of orientations about a carbon–carbon single bond which involves sp^3 hybridization on one end and sp^2 hybridization on the other. However, both theoretical[13] and experimental[6,14] indications are that the angular dependence of the vicinal coupling constant closely parallels that found for sp^3–sp^3 hybridization.

Table I. Chemical Shifts and Coupling Constants for *cis*-1,4-Dichloro-2-butene

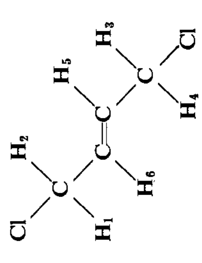
Chemical shifts from benzene, cps						Coupling constants, cps														
$\nu(1)$	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$	$\nu(6)$	J_{12}	J_{13}	J_{14}	J_{15}	J_{16}	J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
141.8	141.8	141.8	141.8	40.0	40.0	. . .	0.53	0.53	−1.1	7.9	0.53	0.53	−1.1	7.9	. . .	7.9	−1.1	7.9	−1.1	10.2

Table II. Chemical Shifts and Coupling Constants for *trans*-1,4-Dichloro-2-butene

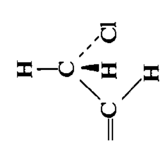
Chemical shifts from benzene, cps						Coupling constants, cps														
$\nu(1)$	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$	$\nu(6)$	J_{12}	J_{13}	J_{14}	J_{15}	J_{16}	J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
147.0	147.0	147.0	147.0	34.0	34.0	. . .	0.9	0.9	−1.5	7.1	0.9	0.9	−1.5	7.1	. . .	7.1	−1.5	7.1	−1.5	17.0



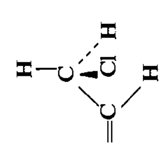
cis



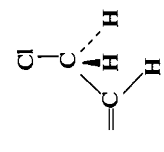
trans



I



II



III

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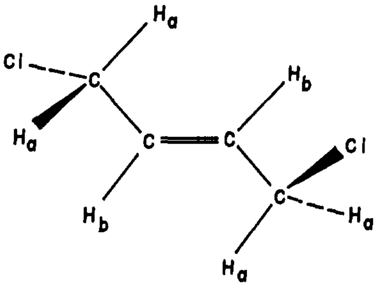

Figure 1. Assumed conformation of *trans*-1,4-dichloro-2-butene.

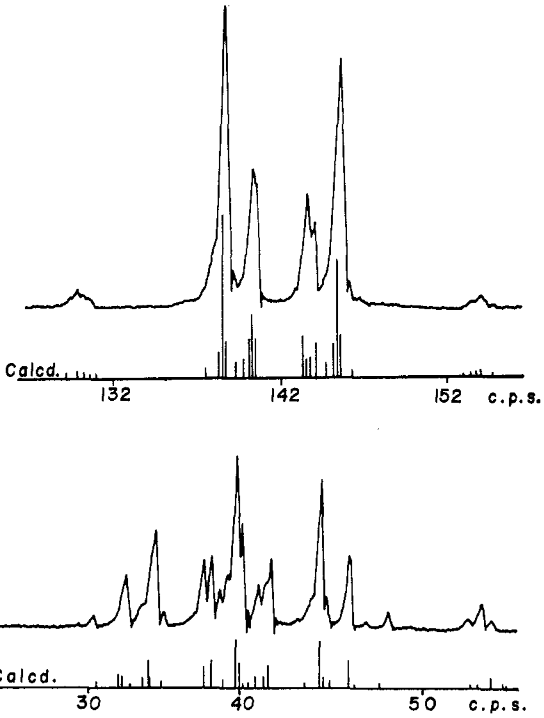

Figure 2. The experimental and calculated 60-Mc nmr spectrum of *cis*-1,4-dichloro-2-butene.

A population analysis based upon the three conformations I–III leads to an average vicinal coupling constant

$$J = p_{\mathrm{I}}J_{\mathrm{t}} + (1 - p_{\mathrm{I}})J_{\mathrm{g}}$$

where J_{t} and J_{g} are the *trans* and *gauche* couplings, and the fractional populations are p_{I}, p_{II}, and p_{III} ($p_{\mathrm{I}} = p_{\mathrm{II}}, p_{\mathrm{I}} + p_{\mathrm{II}} + p_{\mathrm{III}} = 1$).

We assume the values of $J_{\mathrm{t}} = 13.4$ cps and $J_{\mathrm{g}} = 2.4$ cps reported by Bothner-By, *et al.*,[15] for the vicinal *trans* and *gauche* couplings in allyl chloride. Then we find for the *trans* configuration ($J = 7.1$ cps) $p_{\mathrm{I}} = 0.427$, and for the *cis* configuration ($J = 7.9$ cps) $p_{\mathrm{I}} = 0.500$. If we assume, as is usually done,[15] that $\Delta S = 0$, then the energy difference in the conformers I or II and III is

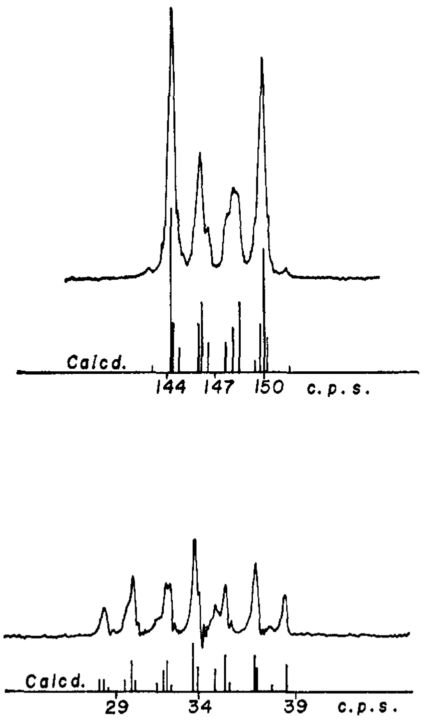

Figure 3. The experimental and calculated 60-Mc nmr spectrum of *trans*-1,4-dichloro-2-butene.

$$\Delta H = -RT \ln K_{\mathrm{eq}} = -RT \ln \frac{2p_{\mathrm{I}}}{1 - p_{\mathrm{I}}}$$

We find in this way that $\Delta H_{trans} = -237$ cal mole^{-1} and $\Delta H_{cis} = -411$ cal mole^{-1}. The difference, $\sim$170 cal mole^{-1}, represents a lower limit to the difference in energy of interaction of a proton and a chlorine atom in the *trans* orientation (with respect to the vinyl proton) with the average potential of a $-CH_2Cl$ group oriented *cis* (with respect to the other $-CH_2Cl$ group).

The fact that this figure is but a lower limit is shown by the value of $p_{\mathrm{I}} = 0.5$ for the *cis* compound, which means that $p_{\mathrm{III}} = 0$ and $J = (J_{\mathrm{t}} + J_{\mathrm{g}})/2$. Obviously, all that we can determine is the least amount of interaction energy which is required to drive the system to this limit. It is also possible that there may be some skewing of the stable conformation due to the steric interaction, similar to that reported by Woolfenden and Grant[16] for *o*-methyl groups in aromatic systems. Whether or not this effect is significant should be revealed by a study of the parent compounds, *i.e.*, the *cis*- and *trans*-2-butenes, where no population effects are involved. Such a study is being pursued by us at the present time.

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