equilibrium mixtures of two conformers with predominance of the less polar rotamers, in which the plane of the aromatic ring eclipses the C-H bond.

2. Graphical methods for the conformational analysis of spin-spin coupling constants on the basis of  $J_1^{HH}-J_j^{HH}$  data and of the electric and magnetic birefringence constants (mK-mC) have been proposed.

#### LITERATURE CITED

- 1. A. N. Vereshchagin, Polarizability of Molecules [in Russian], Nauka, Moscow (1980).
- S. G. Vul'fson, V. F. Nikolaev, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2296 (1983).
- 3. V. G. Dashevskii, Conformations of Organic Molecules [in Russian], Khimiya, Moscow (1974).
- 4. A. J. Gordon and R. A. Ford, A Chemist's Companion: A Handbook of Practical Data, Techniques, and References, Wiley-Interscience, New York (1973).
- 5. S. G. Vul'fson, O. M. Dianova, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 1552 (1986).
- 6. S. G. Vul'fson and O. M. Dianova, Izv. Akad. Nauk SSSR, Ser. Khim., 2269 (1984).
- 7. H. Bilth, Liebigs Ann. Chem., 296, 263 (1897).
- 8. H. Greenfield, S. Meltin, and M. Orchin, J. Am. Chem. Soc., 74, 4079 (1952).
- 9. Beilstains Handbuch der Organischen Chemie, fourth edn., B (1956).
- 10. E. Erdmann, Liebigs Ann. Chem., 216, 179 (1882).
- 11. O. A. Osipov, V. I. Minkin, and A. D. Garnovskii, Handbook of Dipole Moments [in Russian], Vyssh. Shk., Moscow (1971).
- 12. W. F. Reynolds and D. J. Wood, Canad. J. Chem., 49, 1209 (1971).
- A. N. Vereshchagin and S. G. Vul'fson, in: Conformational Analysis of Organometallic Compounds [in Russian], Nauka, Moscow (1983), pp. 6-46.
- 14. P. J. D. Park, R. A. Pethrick, and B. H. Thomas, in: W. J. Orville-Thomas (ed.), Internal Rotation of Molecules, Wiley-Interscience, London-New York (1974).
- 15. C. A. G. Haasnoot, F. A. A. M. Leeuw, and G. Altona, Tetrahedron, 36, 2783 (1980).
- 16. V. E. Kataev, S. G. Vul'fson, O. M. Dianova, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2014 (1986).

STERIC STRUCTURE AND ORBITAL INTERACTIONS IN  $\alpha$ -Chlorovinyl ethers

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 $\alpha$ -Chlorovinyl ethers, first obtained in 1945 [1], have been studied insufficiently. At the same time, the combination of different functional groups in these molecules makes their investigation promising [2]. In  $\alpha$ -chlorovinyl ethers, there is the possibility of  $\eta$ - $\pi$  interaction of the unshared electron pair of oxygen with the  $\pi$  system of the vinyl fragment, significantly determining the properties of vinyl ethers [3], and  $\eta$ - $\sigma$  interaction of the unshared electron pair of oxygen with orbitals of the C-Cl bond, characteristic of  $\alpha$ -chloro ethers [4]. The orbital interactions of both types are stereospecific:  $\eta$ - $\pi$  interactions are optimal when the dihedral angle of C=COC ( $\tau$ ) is equal to 0 or 180°, and the  $\eta$ - $\sigma$  interaction is maximum when the angle of ClCOC ( $\phi$ ) is equal to 90°.

In haloalkyl vinyl and haloalkyl aryl ethers [3, 5, 6], in which the competition of  $\eta - \pi$ and  $\eta - \sigma$  interactions is also possible, the angles  $\tau$  and  $\phi$  could change independently, which made it possible for both types of orbital interactions to occur simultaneously, although to different degrees. If the vinyl fragment in  $\alpha$ -chlorovinyl alkyl ethers is planar, the dihedral angles are related by the correlation  $\tau = \phi -180^{\circ}$ . In practice this means that the effective  $\eta - \sigma$  interaction weakens to a minimum of  $\eta - \pi$  interaction involving the same unshared electron pair and vice versa.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Physicotechnical Institute, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 106-109, January, 1987. Original article submitted June 10, 1985. To elucidate the priority of the orbital interactions, in the present paper we investigated the steric structure and  $^{35}$ Cl NQR spectra of 1-chlorovinyl alkyl ethers CH<sub>2</sub>=CCl-O-R with R=Me(I), Et (II), i-Pr (III).

## Experimental Part

<u>1-Chlorovinyl Methyl Ether (I).</u> We placed 7.3 g (0.13 mole) of methoxyacetylene stabilized with a small amount of hydroquinone into a carefully dried flask purged beforehand with dry Ar. The flask was equipped with a gas-delivery tube reaching to the bottom of the flask and with a reflux condenser cooled with a mixture of solid CO<sub>2</sub> and butanol. The flask was cooled with ice, and a mixture of dry Ar and HCl was passed for 2 h; the HCl was obtained from 8.6 g (0.16 mole) of NH<sub>4</sub>Cl and conc. H<sub>2</sub>SO<sub>4</sub>. Careful distillation in a dry inert atmosphere gave 6.48 g of a fraction with bp 64-68°C,  $n_D^{25}$  1.4060,  $d_4^{25}$  1.0367, containing >80% (I). Proton NMR spectrum ( $\delta$ , ppm): 3.64 singlet (3H, CH<sub>3</sub>O), 4.23 singlet (2H,=CH<sub>2</sub>).

<u>1-Chlorovinyl Ethyl Ether (II)</u>. According to [1], from 5.45 g of ethoxyacetylene we obtained 3.2 g of a fraction with bp 93°C,  $n_D^{25}$  1.4131,  $d_4^{25}$  0.9961 (bp 88-90°C [1],  $n_D^{20}$  1.4163 [7],  $d_4^{20}$  1.0037 [1]), containing >80% (II).

<u>1-Chlorovinyl Isopropyl Ether (III).</u> Similarly, from 11 g of isopropoxyacetylene we obtained 9.02 g of a fraction with bp 98-99°C,  $n_D^{25}$  1.4150, d<sub>4</sub><sup>25</sup> 0.9551, containing >95% (III). Proton NMR spectrum ( $\delta$ , ppm): 1.25 doublet (6H, CH<sub>3</sub>), 4.35 multiplet (1H, HCO), 4.33 singlet (2H,=CH<sub>2</sub>).

The samples of (I)-(III) contained as impurities alkyl acetates  $ROC(0)CH_3$  and alkyl dichloroethyl ethers  $ROCCl_2CH_3$  the amounts of which were determined according to the integrated intensities of the singlet signals in the proton NMR spectra of the protons of  $CH_3C(0)O$  in acetates (1.90-1.93 ppm),  $CH_3CCl_2$  in dichloro ethers (2.33-2.35 ppm), and  $H_2C=CC1$  in vinyl ethers. In all the cases, the ratio of the chloro ether and the acetate was 1:3.

An impurity of ethyl acetate and dichloroethyl ethyl ether in specimens of (II) was also noted previously [7]. Just as we, Heslinga et al. [7] could not purify the chlorovinyl alkyl ethers further.

The proton NMR spectra were recorded on a Varian T-60 instrument (60 MHz), and the IR spectra of the pure liquids and solutions in  $CS_2$  were recorded on a UR-20 spectrophotometer. The dipole moments and molar Kerr constants were determined for dilute solutions in  $CCl_4$  at 25°C. The <sup>35</sup>Cl NQR spectra were recorded on an IS-3 pulsed spectrometer at 77 K. The obtained characteristics are given in Table 1.

# Discussion of the Obtained Results

Steric Structure of 1-Chlorovinyl Alkyl Ethers. Compounds (I)-(III) were analyzed first by the dipole-moments method. The presence of impurities in the samples changed insignificantly the values of the experimentally determined dipole moments, which can be illustrated by (I). The orientation polarization (P<sub>0</sub>) determined experimentally for solutions of (I) is 86.80 (P, cm<sup>3</sup>). Using the additivity of the polarization and determining  $P_{\infty}$  (81.84) of methyl acetate, the main impurity in (I), we can find P<sub>0</sub> = 90.76 and dipole moment = 2.11 D for 1chlorovinyl methyl ether. Thus, the presence of the impurities distorts insignificantly the results of the dipole-moment measurements.

The conformation of (I) is determined only by the rotation about the  $C_{sp2} - 0$  bond because the rotation about the  $C_{sp2}-0$  bond leads to degenerate structures. In the IR spectra of (I) from +30 to -80°C there is no disappearance or redistribution of the band intensities, which suggests conformational homogeneity for it. (The second possibility, the coexistence of

Alkyl	Ethers	$CH_2 = CC$	STOR		
Ether		R	μ, Ď	$m^{K \cdot 10^{12}}$ , esu	v <sup>35</sup> Cl, MHz (signal/noise)

 $69 \pm 13$ 

 $51 \pm 12$ 

 $13 \pm 11$ 

34.810(15)

34,925 (15)

34.812(15)

 $2.09 \pm 0.08$ 

 $2.09\pm0,10$ 

 $2.17\pm0.08$ 

Me

 $\operatorname{Et}$ 

i-Pr

(ÌĪ)

(İII)

TABLE 1. Physical Characteristics of 1-Chlorovinyl Alkyl Ethers CH<sub>2</sub>=CC10R

several conformers with close enthalpies, contradicts, for example, the data of the dipolemoments method given below.)

In compounds (II) and (III), the rotation about the  $C_{sp3}$ -0 bond can lead to different conformers, but in a first approximation the dipole moment in this case is also determined by the rotation about the  $C_{sp2}$ -0 bond. In calculating the theoretical relation of the dipole moments of (I)-(III) to the dihedral angle  $\tau$  ( $\tau = 0^{\circ}$  with shielding of the C-O and C=C bonds) we used group dipole moments and molar Kerr constants m of (Alk-O) determined from data for ethers [8] and dipole moments of the bonds  $C_{sp2}$ -Cl = 0.36 and  $C_{sp2}$ -O = -0.13 D determined from the data for compounds of 1,4-dioxene derivatives which are close in nature [9]. The theoretical dipole moments increase monotonically from the minimum values of 0.47 D for (I) and (II) and 0.62 D for (III) at  $\tau = 180^{\circ}$ , reaching a maximum of 2.09 D for (I) and (II) and 2.20 D for (III) at  $\tau = 0^{\circ}$ . The good agreement of the latter values with the experimental data indicates that the main conformation for  $\alpha$ -chlorovinyl alkyl ethers is the s-cis conformation or one close to it.

The data on the polarizability of molecules (I)-(III) do not contradict this conclusion. In the calculation of the theoretical Kerr constants, the following values  $(A^3)$  were used as the semiaxes of the polarizability ellipsoids of the bonds: C=C  $b_{L} = 2.80$ ,  $b_{T} = 0.73$ ,  $b_{V} =$ 0.77; C--Cl  $b_L$  = 3.99,  $b_T$  =  $b_V$  = 1.85 (a given polarizability ellipsoid for C--Cl was used in the determination of the polarizability ellipsoid of C=C in the 1,1-dichloroethylene molecule [10]);  $C_{sp_3} - 0 b_L = 0.89$ ,  $b_T = b_V = 0.46$ ;  $C_{sp_2} - 0 b_L = 1.78$ ,  $b_T = -0.97$ ,  $b_V = 0.87$  (from the data for anisole [9]). The theoretical Kerr constants for the s-cis conformation were 39, 28, and 20.10<sup>-12</sup> esu for (I), (II), and (III), respectively; the average values of the Kerr constants for all the possible alternate conformations of the Alk-O fragment are given for the latter two compounds. The calculation conveys correctly the general tendency of the decrease of the Kerr constants in the series and, on the whole, agrees satisfactorily with the experimental data. In [11] and [12], it was ascertained experimentally and theoretically [12-14] that the planar s-cis and nonplanar gauche conformations with dihedral angle  $\tau \sim 140\text{--}170^\circ$  correspond to the energy minimums for methyl vinyl ether. The nonplanar conformation is less favorable with respect to enthalpy ( $\Delta H \approx 2$  kcal/mole), but has a doubled statistical weight. In the gas phase, the fraction of the gauche conformer is  $\sim 1\%$  [12]. The planar s-cis conformer also predominates in the case of other alkyl vinyl ethers, except for ethers with tertiary alkyl radicals [3, 15, 16]. The effective participation of the C-Cl bond in 1-chlorovinyl alkyl ethers in  $\eta$ - $\sigma$  orbital interaction should lead to stabilization of the gauche conformer, which is characteristic of saturated  $\alpha$ -chloro ethers. On the other hand, the experimentally observed preponderant predominance of the s-cis conformation for a-chlorovinyl ethers makes it possible to consider the Cl atom in these compounds as a relatively neutral bulky substituent additionally destabilizing the gauche conformer so much that even in compound (III) the fraction of the gauche conformer is insignificant.

Thus, the steric structure of compounds (I)-(III) can serve as an argument in favor of the predominance of  $\eta - \pi$  interaction in them.

<u>Chlorine-<sup>35</sup>NQR Spectra.</u> An anomalous decrease of the <sup>35</sup>Cl NQR frequencies is characteristic of  $\alpha$ -chloro ethers in which there is  $\eta$ - $\sigma$  electron transfer [4, 17]. The NQR frequencies of compounds (I)-(III) (see Table 1) should be compared with the frequency in CH<sub>2</sub>=CHCl, 33.411 MHz [17]. As is evident, under the effect of the alkoxy group in (I)-(III), there is not a decrease, but an increase of the frequency, on the average, of 1.4 MHz.

In [6], Bredikhin et al. give a correlation equation relating the  ${}^{35}$ Cl NOR frequencies of RCH<sub>2</sub>Cl compounds to the  $\sigma_{\rm I}$  constants of the R substituent:  $\nu^{35}$ Cl (MHz) = 9.35  $\sigma_{\rm I}$  + 32.77. The frequency for alkyl chloromethyl ethers calculated according to this equation ( $\sigma_{\rm I}$  (O-Alk) = 0.3) in 35.5 MHz, which is 1.5 MHz higher than  $\nu^{35}$ Cl in CH<sub>3</sub>Cl (34.029 MHz). Thus, the purely inductive effect of the alkoxy group should lead to an increase of the frequency in the NOR of the geminal Cl atom by 1.5 MHz, on the average. The close correspondence of this evaluation to the value observed for 1-chlorovinyl ethers suggests that the interaction of the OCCl triad in these compounds has a predominantly inductive nature, and specific  $\eta$ - $\sigma$  transfer is absent. The conclusion concerning the absence of  $\eta$ - $\sigma$  interaction was also drawn previously in an investigation of structurally close cyclic  $\alpha$ =chlorovinyl ethers [18].

It is interesting to note that also in the case of cyclic molecules the appearance of a geminal 0 atom leads to an increase of v <sup>35</sup>Cl by  $\sim$ 1.4 MHz: let us compare the NQR frequencies of 34.464 MHz in 5-chloro-2,3-dihydropyran, 35.833 MHz in 2-chloro-1,4-dioxene, 35.506 MHz in 5,6-dichloro-2,3-dihydropyran, and 37.0 MHz (average) in 2,3-dichloro-1,4-dioxene [18].

Taking into account the above-mentioned stereospecificity of the orbital interactions, we can assume that the closeness of such characteristics, sensitive to them, as the NQR frequencies in cyclic and acyclic a-chloro vinyl ethers, serves as an indication of the closeness of their steric structure. The half-chair conformation, occurring for derivatives of 2,3-dihydropyran and 1,4-dioxene, is close to the s-cis conformation of acyclic vinyl ethers. Thus, the conclusion concerning the predominance of the s-cis conformation for compounds (1)-(III) can also be drawn on the basis of NQR data.

## Conclusions

1-Chlorovinyl alkyl ethers exist predominantly in the s-cis conformation.

2. In 1-chlorovinyl alkyl ethers there is no specific  $\eta - \sigma$  interaction of the unshared electron pair of the oxygen atom and the antibonding orbital of the C-Cl bond.

## LITERATURE CITED

- 1. A. E. Favorskii and M. N. Shchukina, Zh. Obshch. Khim., 15, 394 (1945).
- 2. M. A. Kazankova and I. F. Lutsenko, Vestn. Mosk. Univ., Ser. 2, Khim., <u>24</u>, 315 (1983).
- 3. B. A. Trofimov, Heteroatomic Derivatives of Acetylene [in Russian], Nauka, Moscow (1981), 319 pp.
- 4. Z. Ardalan and E. A. C. Lucen, Helv. Chim. Acta, 56, 1715 (1973).
- 5. A. A. Bredikhin, V. L. Polushina, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2720 (1985).
- 6. A. A. Bredikhin, V. L. Polushina, A. I. Andreeva, I. A. Safin, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 1195 (1985).
- 7. L. Heslinga, Q. J. Katerberg, and J. F. Arens, Rec. Trav. Chim., 76, 982 (1957).
- 8. A. A. Bredikhin, V. L. Polushina, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 1320 (1985).
- 9. A. A. Bredikhin, V. L. Polushina, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 1753 (1985).
- 10. J. R. Bromley, C. G. LeFevre, R. J. W. LeFevre, and B. P. Rao, J. Chem. Soc., 1183 (1959).
- 11. J. R. Durig and D. A. C. Compton, J. Chem. Phys., 69, 2028 (1978).
- 12. W. Pyckhout, P. van Nuffel, C. van Alsenoy, and L. van den Enden, J. Mol. Struct., 102, 333 (1983).
- 13. R. H. Nobes, L. Radom, and N. L. Allinger, J. Mol. Struct., 85, 185 (1981).
- M. Klessinger and A. Zywietz, J. Mol. Struct., <u>90</u>, 341 (1982). J. R. Durig and D. J. Gerson, J. Mol. Struct., <u>71</u>, 131 (1981). 14.
- 15.
- 16. H. Friege and M. Klessinger, J. Chem. Res. (S), 208 (1977); H. Friege and M. Klessinger, Chem. Ber., <u>112</u>, 1614 (1978).
- G. K. Semin, T. A. Babushkina, and G. G. Yabobson, Use of Nuclear Quadrupole Resonance 17. in Chemistry [in Russian], Khimiya, Leningrad (1972).
- 18. A. A. Bredikhin, A. I. Andreeva, I. A. Safin, and A. N. Vereshchagin, Izv. Akad. Nauk SSSR, Ser. Khim., 2204 (1985).