

thracene²² (2.18 g, 6.9 mmoles) in 15 ml of 48% hydrofluoric acid was cooled to -5° and diazotized by portionwise addition of an excess (2.0 g) of finely powdered sodium nitrite. After the 30-min addition period, the resulting yellow suspension was allowed to stir for an additional 15 min, and then poured on an excess of ice. After careful neutralization by addition of sodium hydroxide pellets, the resulting precipitate was collected by suction filtration and washed well with water and finally with 20 ml of cold ethanol, 2.21 g, mp $165-210^{\circ}$. Column chromatography over acid-washed alumina with pentane-benzene elution afforded 0.96 g of colorless prisms from the first 100-ml fraction, mp $224-225^{\circ}$.

Anal. Calcd for $C_{22}H_{38}F$: C, 84.02; H, 9.93. Found: C, 83.84; H, 10.14.

Spectral Measurements. Nmr spectra were recorded using a Varian Associates A-60 spectrometer operating at about 38° .

(22) L. R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672 (1955). The structure was not recognized at the time of this report. See, however, L. R. C. Barclay and E. E. Betts, *J. Am. Chem. Soc.*, **77**, 5735 (1955).

Chemical shift data and coupling constants were measured, except where noted otherwise, in 5% by weight solutions of carbon tetrachloride. Calibrations were made using the usual side-band technique. A Hewlett-Packard Model 524D frequency counter and a Hewlett Packard Model 202C audiooscillator were used for this purpose.

Coupling constants were measured by repetitively sweeping at an expanded sweep width (50 cycles) and taking the average of peak to peak separations.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also wish to thank Dr. David Dreyer, U. S. Department of Agriculture, Pasadena, Calif., for generous allotments of instrument time in the early stages of this work, and Mr. Laurence Armi and Mr. Kenneth Brown for considerable technical assistance.

The Proton Magnetic Resonance Spectra of Olefins.

V. 3-Chloro- and 3-Methoxypropenes

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Received January 27, 1966

Abstract: The high-resolution proton magnetic resonance spectra of allyl chloride, allylidene chloride, allyl methyl ether, and acrolein dimethyl acetal have each been obtained at three or four temperatures in the range -50 to $+130^{\circ}$, and have been analyzed in terms of chemical shifts and [H,H] coupling constants. The magnitude and temperature dependence of the coupling constants indicate which rotamer is the more stable in each case, and an approximate thermodynamic treatment yields limits for ΔH . The values deduced were: allyl chloride, $\Delta H = 100 \pm 30$ cal/mole (H-eclipsed favored); allylidene chloride, $\Delta H = 800 \pm 100$ cal/mole (H-eclipsed favored); allyl methyl ether, $\Delta H = -115 \pm 30$ cal/mole (O-eclipsed favored); acrolein dimethyl acetal, $\Delta H = -110 \pm 30$ cal/mole (O-eclipsed favored).

In a continuation of the study of rotational isomerism in substituted propenes,¹⁻³ we have examined the proton nmr spectra of allyl chloride, allylidene chloride, allyl methyl ether, and acrolein dimethyl acetal at several temperatures.

The expected⁴⁻⁶ geometry of the rotamers of these compounds is depicted in Figure 1.

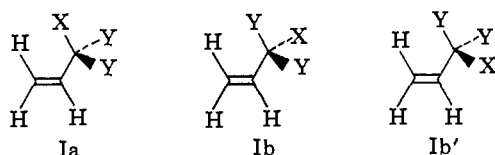


Figure 1. Expected geometry of rotamers of substituted propenes.

(1) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); A. A. Bothner-By, C. Naar-Colin, and H. Günther, *ibid.*, **84**, 2748 (1962).

(2) A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, **34**, 127 (1962).

(3) A. A. Bothner-By, S. Castellano, and H. Günther, *J. Am. Chem. Soc.*, **87**, 2439 (1965).

(4) R. W. Kilb, C. C. Lin, and E. B. Wilson, *J. Chem. Phys.*, **26**, 1695 (1957).

(5) D. R. Herschbach and L. C. Krisher, *ibid.*, **28**, 728 (1958).

(6) E. Hirota, Proceedings, International Symposium on Molecular Structure and Spectra, C 402-1, Tokyo, 1962.

Interconversion between rotamers is rapid at temperatures down to -60° , so that only weighted-average values of the chemical shifts and coupling constants are observed. Thus

$$J_{HX} = p_a J_{HX}^t + (1 - p_a) J_{HX}^g \quad (1)$$

where J_{HX} is the observed coupling constant, p_a is the fractional population in form Ia, J_{HX}^t and J_{HX}^g are the (H,X) coupling constants characteristic of form Ia and Ib (or Ib'), respectively. Solving for p_a , and substituting in

$$\Delta F = -RT \ln K_{eq} = -RT \ln 2p_a/(1 - p_a) \quad (2)$$

one obtains

$$\Delta F = -RT \ln 2(J_{HX} - J_{HX}^g)/(J_{HX}^t - J_{HX}^g) \quad (3)$$

Similarly

$$\Delta F = -RT \ln (J_{HY}^t + J_{HY}^g - 2J_{HY})/(J_{HY} - J_{HY}^g) \quad (4)$$

In some other studies of rotational isomerism,⁷⁻¹² it has been found or assumed explicitly that $\Delta S \sim 0$.

(7) S. I. Mizushima, "Structure of Molecules and Hindered Rotation," Academic Press Inc., New York, N. Y., 1956.

(8) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 39 (1961).

Following this lead we substitute ΔH for ΔF in eq 3 and 4. It should be recognized, however, that this may lead to some error.¹³ Especially in the cases of allyl methyl ether and acrolein dimethyl acetal, it seems quite possible that rotation about the various C-O bonds might be hindered to different extents in the two rotamers. We think it unlikely, however, that this effect could reverse the conclusions reached in this paper.

The procedure adopted in the present work was to measure J_{HX} (or J_{HY}) for a given compound at three or four temperatures, then to search for a set of values of J^g and J^t which would cause the right-hand side of eq 3 or 4 to be independent of temperature. To facilitate this search a short computer program was written which evaluated the expressions for $\Delta F (= \Delta H)$ at the experimental points for chosen arrays of values of J^g and J^t . From the tabulated results, the optimum values of J^g and J^t could be read off, and an estimate of the determinacy of the system formed.¹⁴

Experimental Section

Materials. Allyl chloride and acrolein dimethyl acetal were of commercial origin, and were used as received.

Allylidene chloride was prepared by the method of Andrews and Kepner;¹⁵ it was separated from the 1,3-dichloro isomers by spinning-band column distillation. The material used had bp 59.8° (402 mm); n_D^{25} 1.4482; it was 97.6% pure as judged by vapor phase chromatography.

Allyl methyl ether was prepared by the reaction of sodium allylate (1 mole) with methyl iodide (1 mole) in excess allyl alcohol. The product, isolated by fractional distillation, boiled at 41–43° (lit.^{16,17} bp 46°, 42.5–43° (757 mm)).

In each case the nmr spectrum exhibited only lines which were attributable to the substance in question; the absence of extraneous peaks was taken as a sufficient criterion of purity.

Spectra. Samples were degassed on the vacuum line, and sealed into 5-mm sample cells together with 1% of tetramethylsilane to serve as an internal reference. Spectra were obtained on the Varian A-60 spectrometer fitted with a variable temperature probe. Temperatures were calibrated using the methanol or ethylene glycol thermometers.¹⁸ Spectra were recorded at 50-cps full scale. The scale was calibrated by means of audio side bands. At least six spectra were recorded in each case, and average peak positions were used in analyzing the spectrum.

Analysis of Spectra

First-order assignments were made in each case by inspection and introspection. In the cases of allylidene chloride, this task was complicated somewhat by the small difference in chemical shifts between protons 1 and 4 (numbering of protons; see Table I). Use of the iterative program LAOCOON II on the basis of these assignments, however, gave rapid convergence and excellent fitting of the spectra. In each case the root

(9) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **37**, 1466 (1962).

(10) H. S. Gutowsky, *Rev. Pure Appl. Chem.*, **7**, 93 (1963).

(11) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Proc. Roy. Soc. (London)*, **A282**, 559 (1964).

(12) H. Finegold, *J. Chem. Phys.*, **41**, 1808 (1964).

(13) R. A. Newmark and C. H. Sederholm, *ibid.*, **39**, 3131 (1964).

(14) If the coupling constant does not change with temperature, then the system is completely indeterminate—either $\Delta F = 0$, $J_{HX} = \frac{1}{2}(J^t + 2J^g)$, with any consistent set of values of J^t and J^g , or $\Delta F > 2$ kcal or $\Delta F > -2$ kcal, and $J_{HX} = J^t$ or J^g .

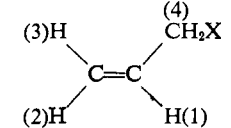
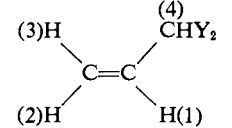
(15) L. J. Andrews and R. E. Kepner, *J. Am. Chem. Soc.*, **70**, 3456 (1948).

(16) L. Henry, *Ber.*, **5**, 455 (1872).

(17) J. C. Irvine, J. L. A. MacDonald, and C. W. Soutar, *J. Chem. Soc.*, 349 (1915).

(18) Varian Publication No. 87–100–110. The curves reported in this publication were checked and found to be reproducible to within 1–2°.

Table I. Nmr Parameters for 3-Chloro- and 3-Methoxypropenes at Various Temperatures

					
Temp, °C		+80	+37	–50	
Allyl Chloride					
$\nu(1)^a$		355.66	355.68	355.94	
$\nu(2)$		307.97	308.58	309.89	
$\nu(3)$		317.25	317.74	318.75	
$\nu(4)$		238.40	239.24	241.53	
$J(1,2)$		10.14	10.11	10.04	
$J(1,3)$		16.89	16.87	16.85	
$J(1,4)$		6.48	6.56	6.75	
$J(2,3)$		1.22	1.24	1.32	
$J(2,4)$		–0.95	–0.93	–0.83	
$J(3,4)$		–1.42	–1.41	–1.35	
Temp, °C		+90	+37	–50	
Allylidene Chloride					
$\nu(1)$		366.47	366.67	367.51	
$\nu(2)$		311.52	312.28	313.37	
$\nu(3)$		325.49	325.41	325.06	
$\nu(4)$		367.47	368.67	370.82	
$J(1,2)$		10.21	10.13	10.06	
$J(1,3)$		16.76	16.72	16.82	
$J(1,4)$		6.75	7.07	7.81	
$J(2,3)$		0.24	0.26	0.25	
$J(2,4)$		–0.86	–0.72	–0.62	
$J(3,4)$		–1.02	–1.01	–0.81	
Temp, °C		+90 ^b	+37	–50	
Allyl Methyl Ether					
$\nu(1)$		350.60	350.45	350.38	
$\nu(2)$		303.74	304.63	305.80	
$\nu(3)$		311.35	312.27	314.16	
$\nu(4)$		230.24	230.34	230.24	
$J(1,2)$		10.55	10.50	10.49	
$J(1,3)$		17.32	17.27	17.29	
$J(1,4)$		5.40	5.38	5.23	
$J(2,3)$		1.95	2.01	2.11	
$J(2,4)$		–1.41	–1.42	–1.49	
$J(3,4)$		–1.66	–1.67	–1.74	
Temp, °C		+130	+90	+37	–50
Acrolein Dimethyl Acetal					
$\nu(1)$		344.65	344.47	344.40	345.05
$\nu(2)$		310.68	311.69	313.21	316.35
$\nu(3)$		318.68	319.45	320.63	323.32
$\nu(4)$		281.51	282.19	283.32	286.92
$J(1,2)$		10.78	10.76	10.79	10.75
$J(1,3)$		17.53	17.50	17.50	17.47
$J(1,4)$		4.37	4.36	4.34	4.15
$J(2,3)$		1.79	1.82	1.86	1.94
$J(2,4)$		–1.26	–1.26	–1.30	–1.29
$J(1,4)$		–1.33	–1.35	–1.36	–1.41

^a All chemical shifts reported as cps from tetramethylsilane at 60 Mcps. $\tau_x = 10.0 - (\nu_x/60)$. Coupling constants reported in cps.

^b Average of two separate determinations.

mean square (rms) error in line fitting was 0.07 cps or less when all observable lines were assigned. In one case (allyl methyl ether at +90°) two separate complete determinations were performed as above. The difference in the deduced chemical shifts averaged 0.045 cps; in the coupling constants, 0.018 cps.

Results

The parameters obtained in the analyses are summarized in Table I.

Chemical Shifts. The changes observed in the chemical shifts are all small and exhibit the same general trend that has been observed previously:³ less shielding (relative to TMS) at lower temperature. Proton 3 in allylidene chloride shows a reverse trend, and this suggests that the chlorines are substantially further from proton 3 on the average at lower temperatures, *i.e.*, that form Ia (X = H) is preferred.

Coupling Constants. The effects of rotational isomerism should be most pronounced on the coupling constants $J_{1,4}$, $J_{2,4}$, and $J_{3,4}$. In the four cases studied these coupling constants all varied monotonically with temperature. Furthermore, in a given compound they either increase or decrease algebraically together, in accord with previous studies^{1-3,19} which have indicated that $J_{1,4}$ is positive and is largest in that conformation where H₁ and H₄ are *trans* oriented, while $J_{2,4}$ and $J_{3,4}$ are usually negative and are smallest in magnitude in the same conformation (X = H, form Ia).

Small effects on the coupling constants within the vinyl group might also be anticipated; the changes with temperature of the calculated values of $J_{1,2}$, $J_{1,3}$, and $J_{2,3}$ are in fact rather small in all cases, and follow an apparently random pattern.

Calculations were performed as described above using the calculated value of $J_{1,4}$ as a measure of rotamer population. The values of J^g and J^t giving the most nearly constant ΔH are given in Table II.

Table II. J^g , J^t , and ΔH for Chloro- and Methoxypropenes

Compd	J^g , cps	J^t , cps	J^∞ , cps	ΔH , cal
CH ₂ =CHCH ₂ Cl	2.4	13.4	6.1	100
CH ₂ =CHCHCl ₂	2.5	9.6	4.9	800
CH ₂ =CHCH ₂ OCH ₃	2.8	11.5	5.7	-115
CH ₂ =CHCH(OCH ₃) ₂	1.8	10.3	4.6	-110

Reasonable values of J^g and J^t are obtained in each case. The treatment determines $(2J^g + J^t)/3$ rather better than J^g or J^t separately. This is the predicted high-temperature limit of the observed J , and is given in Table II as J^∞ . The values appear reasonable from the point of view of electronegativity effects on vicinal coupling constants.^{20,21}

(19) A review of the pertinent studies has been made by S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

It is interesting to compare the results reported to date for the 1-substituted and 3-substituted propenes. In the case of the 1-substituted propenes, *cis-trans* isomerism is possible, and in a few cases it has been established that the *cis* isomer is the more stable. A list of the propenes, in which either the rotamer with an eclipsed (X in form Ia) or the *cis,trans* isomer with the *cis*-1 substituent is more stable, includes allyl methyl ether, acrolein dimethyl acetal, allyl cyanide,^{2,22} crotononitrile,²³ allyl fluoride,³ 1-chloropropene,²⁴ and 1-bromopropene;²⁵ conversely the *gauche* substituent (X in form Ib) or *trans* isomer is preferred in allylidene fluoride,³ allyl chloride, allylidene chloride, allyl bromide,² allyl iodide,² and 1- and 3-alkylpropenes¹ with bulky alkyl groups.

Consideration of models suggests that this is reasonable, if it be postulated that a small attractive (van der Waals) force is operative at larger separations. In this way, for example, even if the chlorine and adjacent methyl proton in *cis*-chloropropene are on the repulsive limb of the potential energy curve, the *trans* compound may be at a higher potential energy. Such considerations also explain the opening out of the valence angles deduced from the microwave spectrum of allyl fluoride.⁶

The change in ΔH on going from allyl chloride to allylidene chloride is parallel to that in going from allyl fluoride to allylidene fluoride, and may arise from the same cause,³ decreased C-X bond polarity in the allylidene derivative.

The couplings found in a series of allyl ethers and amines by Martin, Martin, and Caubère²⁶ are in accord with those reported here. That the values of $J_{1,4}$ reported for γ -alkoxy-*trans*-crotonic acids (3.7-4.0 cps) are smaller than those for the corresponding *cis* acids (4.7-4.8 cps) is expected from the reduced steric hindrance for eclipsed alkoxyl in the *trans* acids.

Acknowledgments. This work was supported in part by an Air Force Office of Scientific Research grant, AF 199-63. Computation was performed with partial support by the National Science Foundation.

(20) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1963).

(21) S. Ebersole, S. M. Castellano, and A. A. Bothner-By, *J. Phys. Chem.*, **68**, 3430 (1964).

(22) R. C. Hirst, quoted by M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

(23) J. N. Butler and R. D. McAlpine, *Can. J. Chem.*, **41**, 2487 (1963).

(24) R. A. Beaudet, *J. Chem. Phys.*, **40**, 2705 (1964).

(25) P. S. Skellin and R. G. Allen, *J. Am. Chem. Soc.*, **80**, 5997 (1958).

(26) M. L. Martin, G. J. Martin, and P. Caubère, *Bull. Soc. Chim. France*, 3066 (1964).