[Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia]

Proton Magnetic Resonance in Substituted Propenes. II. 2,3-Disubstituted Propenes

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Results from analysis of the 40 megacycle n.m.r. spectra of nine 2,3-disubstituted propenes are summarized and compared with previously reported values for 2-substituted propenes. Of particular interest is the variation of long-range coupling constants with solvent which is observed for some of these systems and is attributed to conformational effects arising from hindered rotation about the =C–C bond.

Introduction

In the first paper of this series, hereafter referred to as I, we described the proton magnetic resonance spectra of a number of β-substituted propenes, $H_2C{=}CY{-}CH_3$, in dilute solution in inert solvents.[2a] Similar measurements are here reported for some disubstituted propenes of the general type $H_2C{=}CY{-}CH_2Z$, and the changes in the spectra produced by allylic substitution are considered by comparison with the data in I.

Analysis of Spectra.—Samples were prepared by diluting with 20 volumes of cyclohexane or tetramethylsilane in 5 mm. Pyrex sample tubes, freezing in Dry Ice-acetone and sealing under an atmosphere of dry N_2. Spectra were obtained at 40 megacycles on the Varian Model 4300B spectrometer and were calibrated by interpolation using audio side bands from the solvent averaged over several alternating sweep directions. The shifts are expressed in p.p.m. relative to an external H_2O (liq.) reference for the cyclohexane solution, using empirical frequency corrections of + 58.0 c.p.s. (cyclohexane) and + 201.5 c.p.s. (TMS).[2a]

With the exception of the methallyl halides, the spectra all belong to the general class[3] ABX_2, the analysis of which follows simply from an extension of the ABX_N equations tabulated in I to the $N = 2$ case. Detailed descriptions of the analysis of two compounds in this group are given elsewhere.[4–6] In virtually all cases the AB spin states were inappreciably mixed, so that the spectra could be interpreted from first order splittings but the relative signs of the coupling constants were not determined. This was also true of the methallyl halides, which belong to the more complicated class ABM_2X_3. A typical spectrum in this group was illustrated in I, where the parameters involving the methyl group also were listed. These are omitted in the present discussion and the remaining variables discussed as an ABX_2 system.

In accord with previous practice, protons A and B are specified according to $|J_{AX}| > |J_{BX}|$ in the belief that this order is more consistent with the molecular assignments than one based on the relative chemical shifts. (This results in a reversal of the labelling of the vinyl protons in the methallyl halides in I, where the methyl protons are used as the basis for labelling.) The weight of evidence, much of which will be subsequently published,[7] supports the assignment of proton A as *cis* to the methylene group, *i.e.*, $|J_{cis}| > |J_{trans}|$ for 1,3 couplings in propenes. This was the order inferred from medium effects in 2-substituted propenes,[2a] and the methallyl halide spectra show that the vinyl proton coupled strongest to the methyl group has the weaker interaction with the halomethyl group and *vice versa.* A number of precedents for this order also are reported in the literature.[8]

Discussion of Results

It is immediately apparent from the chemical shifts in Table I that substituent effects are greater at the 2-position than the 3-position for all proton shieldings. While this is not surprising in the case of the vinyl protons, the rather effective "damping" of the methylene proton shifts against variation of the allylic substituent is in rather curious contrast to the regular decreases with increasing substituent electronegativity observed in alkyl[9] and propargyl[2b] halides. A reverse trend was reported for isopropyl halides, however,[9] so that the effect in the allylic systems is not unique.

The effects of the 2-substituents on the various chemical shifts are not substantially different from those observed in I where allylic substitution is absent; nor do they vary significantly as the allylic substituent is altered. To illustrate, the change in shift at vinyl proton A produced by replacing a chlorine with a bromine atom in the 2-position is − 0.46 ± 0.01 p.p.m. over the series Z = H, Cl, Br in the allylic substituent. The corresponding change in shift at vinyl proton B is − 0.24 ± 0.02 p.p.m. over the same series, and the effect in the X group is − 0.13 ± 0.04 p.p.m. The behavior is slightly less regular when a halogen is replaced by a methyl group in the 2-position, particularly in comparisons involving isobutylene (Z = H). The difference between the methyl shift in the systems $H_2C{=}CH{-}CH_3$ and the methylene shifts in the corresponding allyl bromides, $H_2C{=}CY{-}CH_2Br$, appears to depend on the Y substituent, values of $\Delta\delta_X = -1.86$, -1.91, and -2.11 being obtained

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[2] (a) E. B. Whipple, J. H. Goldstein and Leon Mandell, This Journal, **82**, 3010 (1960); (b) E. B. Whipple, J. H. Goldstein, Leon Mandell, G. S. Reddy and G. R. McClure, *ibid.*, **81**, 1321 (1959).

[3] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959.

[4] W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

[5] F. S. Mortimer, *J. Mol. Spec.*, **3**, 335 (1959).

[6] A. D. Cohen and N. Sheppard, *Proc. Roy. Soc.* (*London*), **A252**, 488 (1959).

[7] J. H. Goldstein, J. P. Kokko and E. B. Whipple, to be published.

[8] S. Alexander, *J. Chem. Phys.*, **28**, 358 (1958). See, however, reference 5, where an opposite order is suggested.

[9] A. A. Bothner-By and C. Naar-Colin, This Journal, **80**, 1728 (1958).

TABLE I

CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] IN 2,3 DISUBSTITUTED PROPENES, $H_2C{=}CY{-}CH_2X$[c]

X Substituent	$\delta_{A\infty}$	$\delta_{B\infty}$	$\delta_{X\infty}$	J_{AX}	J_{BX}	J_{AB}
			1. Y = Cl Series			
—I	−0.44	−0.17	1.05	0.7	...	1.4
—Br	− .45	− .25	1.08	0.9	...	1.5
—Cl	− .48	− .27	1.01	1.2	0.6	1.5
—OH	− .38	− .19	0.96	1.5	1.0	1.4
			2. Y = Br Series			
—Br	−0.91	−0.51	0.96	1.1	...	2.0
—Cl	−0.94	−0.51	0.92	1.5	0.9	1.9
			3. Y = CH_3 Series			
—I	−0.09	0.24	1.25	0.8	...	1.5
—Br	.01	.20	1.25	0.9	...	1.5
—Cl	.05	.20	1.16	1.0	...	1.6

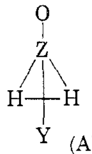
[a] In p.p.m. relative to an H_2O (liq.) external reference for the dilute solution in cyclohexane. [b] In c.p.s. [c] Parameters listed according to ABX_2 notation with A proton defined by $|J_{AX}| < |J_{BX}|$.

for Y = $-Cl$, $-Br$, $-CH_3$, respectively. The corresponding difference between propylene and allyl bromide yields $\Delta\delta_x = -2.13$ for Y = H.[10]

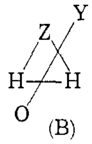
The spin couplings between the vinyl protons on the terminal carbon are about the same as observed for the corresponding 2-substituted propenes, although the experimental uncertainties are greatest in these parameters so that variations on the order of ±0.2 c.p.s. could escape detection. Since the values also correspond in magnitude to those in vinyl halides,[10,11] they are probably of like sign and hence opposite from the larger 1,2 couplings across C=C bonds. Similar reasoning in all probability applies to the long-range couplings in chloropropenes[5,6] and bromopropenes.[7] These interactions are smaller in magnitude than observed in the absence of the allylic substituent and decrease regularly in the order Z = H, Cl, Br, I. The difference between *cis* and *trans* couplings is, as before, rather constant at about 0.6 c.p.s.

A quite interesting fact concerning the long-range couplings in the dihalopropenes is that they show a decided variation with the solvent, the trend being toward smaller couplings in the more polar media. This probably accounts for most of the small discrepancies between the data in Table I, measured in non-polar media, and earlier results for the couplings in 2,3-dichloropropene[4,5] and 2,3-dibromopropene[3] measured in the neat liquids. This has been confirmed in the event of the latter. Table II shows a representative set of data obtained for 2-bromo-3-chloropropene in a mixed acetone–cyclohexane solvent of varying proportions. The medium effects are absent in 2-bromopropene and methallyl chloride, however, so that both the 2- and 3-substituents evidently are involved.

Since there is both theoretical basis[12] and experimental evidence[13] for a variation of nuclear spin couplings with dihedral angle, the solvent effect is most plausibly interpreted in terms of restricted rotation about the $=C{-}CH_2{-}$ bond. This is particularly so in view of infrared and Raman evidence for the existence of two distinct forms of the closely analogous systems,[14] $O{=}CY{-}CH_2Z$, which were argued to have the structures (A) and (B), the former being the more stable form. Raman evidence for the existence of distinct conformers in chloropropenes[15] is inconclusive except in the case of the highly substituted system, *cis*-1,2,3,3-tetrachloropropene-1, although unexplained doubling of $C{=}CH_2$ stretching bonds in less highly substituted members is reported.



(A)



(B)

TABLE II

LONG-RANGE PROTON SPIN COUPLINGS IN 2-BROMO-3-CHLOROPROPENE-1 IN MIXED ACETONE–CYCLOHEXANE SOLUTIONS[a]

Acetone, % vol.	J_{AX}	J_{BX}	ω_X[b]
0	1.5	0.9	−106.7
2.5	1.4	.7	−108.4
5.0	1.4	.7	−109.4
10.0	1.3	.6	−110.7
20.0	1.2	.6	−112.0
50.0	1.2	.4	−116.1
90.0	1.0	.3	...

[a] Solute concentration 10% vol. [b] Methylene shift in c.p.s. at 40 m.c. from cyclohexane internal reference.

It has been shown further in the case of the related carbonyl system, chloroacetone ($Y = CH_3$) that two conformers also exist[16] and that the abundance of the *cis* form (B) varies considerably more with medium polarity than does the corresponding system with Y = Cl.

At the present time it is only possible to speculate regarding the conformations in the dihalopropenes, but one is impressed by the fact that the behavior toward solvent polarity with Y = halogen and $Y = CH_3$ apparently is opposite between the isoelectronic systems $H_2C{=}CY{-}CH_2Z$ and $O{=}CY{-}CH_2Z$. In the latter case, Mizushima, *et al.*,[16] argue that steric hindrance favors the more stable conformation (A) while electrostatic repulsion favors (B), and in the case of polar Y substituents the polarity difference between the two conformations becomes less important, so that the (B)/(A) ratio is less dependent on the medium. In the case of (C) and (D), an opposite balance of effects might be expected, *i.e.*, steric effects are favorable toward (D) while electrostatic repulsion favors (C), and increasing the polarity of Y would increase the sensitivity toward the medium. Since (D) is

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(10) E. B. Whipple and J. H. Goldstein, unpublished results.

(11) H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

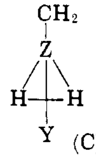
(12) M. Karplus, *ibid.*, **30**, 11 (1959).

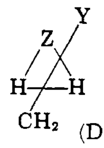
(13) R. E. Richards and T. Schaffer, *Proc. Roy. Soc. (London)*, **A246**, 429 (1958).

(14) I. Nakagawa, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **20**, 1720 (1952).

(15) H. Gerding and H. G. Haring, *Rec. trav. chim.*, **74**, 957 (1955).

(16) S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).


(C)


(D)

the more polar form with Y = halogen, this argument would imply that its proportion increased in solvents of high dielectric constant and that the long-range couplings become smaller as the methylene group is *trans* to the allylic substituent.

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Mixed Polarization in an Electronic Transition by the Method of Polarized Photoöxidation[1]

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The detailed polarization of the near ultraviolet band of N,N,N′,N′-tetramethyl-*p*-phenylenediamine is investigated by the method of polarized photoöxidation. The theory of this method, previously developed, is applied to translate the observed orientation of the photo-product, Wurster's Blue, into relative transition probabilities along the two in-plane axes of the parent molecule. The near ultraviolet band is thus analyzed at 5 mμ intervals and it is found that while in the low energy region short axis absorption is dominant, at the higher energies of the same band there is a reversal and long axis absorption predominates. Evidence indicates that this mixed polarization is not due to the overlap of two different electronic transitions but more likely represents the breakdown of selection rules based on nuclear coördinate independent electronic wave functions.

Introduction

Recently[2] the method of polarized photoöxidation has been employed to determine the gross polarization of certain electronic transitions in N,N,N′,N′ - tetramethyl - *p* - phenylenediamine (TMPD) and Wurster's Blue (WB). In that investigation work was directed toward answering the question: In which direction is a given electronic transition polarized? Such a question is prompted by theory based on equilibrium configuration electronic wave functions. Thus[3,4] to a first approximation the integrated intensity of a single electronic transition is related to the square of the transition moment

$$\mathfrak{M}^0_{g,k} = \int \Theta_g^0 \, m_e \, \Theta_k^0 \, dx \qquad (1)$$

where m_e is the electronic part of the electric moment operator and both electronic wave functions Θ_g^0 (ground state) and Θ_k^0 (excited state k) are normally prescribed for the fixed equilibrium nuclear configuration of the ground electronic state. The integral is over the electron space only, x symbolizing electron coördinates. Group-theoretical analysis of the integrand leads to a prediction of the polarization of absorption (the direction of m_e) given the symmetry properties of the combining wave functions. Conversely an observation of the polarization leads to predictions concerning the symmetry properties of the electronic functions. In the earlier investigation[2] (hereafter referred to as I) every transition studied revealed at least a predominant direction of polarization. On the basis of eq. 1 any deviation from perfect polarization must be regarded as anomalous (for molecules not too high in symmetry). Failure to obtain pure polarization was attributed either to inherent defects of the method or in one obvious case to the overlap of oppositely polarized bands. However, one set of observations never yielded to this sort of explanation. Polarized photoöxidation in the near ultraviolet band of TMPD gave good orientation only when illumination was confined to the low energy region of the band. Whenever the entire band was illuminated essentially no orientation was observed. These qualitative observations lead one to conclude that either this band consists of two strongly overlapped bands having opposite polarization or that the selection rules based on Eq. 1 have broken down.

In the present paper a detailed polarized absorption analysis of the near ultraviolet band of TMPD is presented. A reversal of polarization is found on going from the low to the high energy region. Evidence is marshalled indicating that the observed anomalous mixed polarization apparently implies the breakdown of the selection rules of Eq. 1. Such mixed polarization, however, is predictable on the basis of nuclear coördinate dependent electronic wave functions.[4]

Experimental

a. **Materials.**—TMPD was obtained from the Eastman Kodak preparation of its dihydrochloride salt. Purification of the salt was achieved by two recrystallizations from a 2-propanol solution saturated with HCl. A dilute solution of triethylamine (Eastman Kodak, white label) in 1-propanol was used as described below to obtain the free base. Isopentane (Phillips Petroleum, pure grade) was used with 1-propanol in making the rigid media. The 1-propanol (Eastman Kodak, white label) was rendered spectroscopically pure by one treatment with norite at elevated tempera-

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[1] (a) This work was supported in part by the National Science Foundation. (b) Presented in part before the Symposium on Molecular Structure and Spectroscopy, the Ohio State University, Columbus, Ohio, June, 1958.

[2] A. C. Albrecht and W. T. Simpson, THIS JOURNAL, **77**, 4454 (1955).

[3] R. S. Mulliken and C. A. Rieke, *Repts. Progr. in Phys.*, **8**, 231 (1941).

[4] For a detailed discussion of the problem treated here (and notation) see a paper entitled "Forbidden Character in Allowed Electronic Transitions," by A. C. Albrecht, *J. Chem. Phys.*, **33**, in press (1960).