

or D-O<sub>2</sub> separations.<sup>31</sup> When the quenching efficiencies of O<sub>2</sub> and NO are compared, as the interactions in the A and F states are weak, the change of the acceptor will mainly affect the charge transfer state. As  $E_{NO}$  is lower than  $E_{O_2}$ , the potential curve for the C·T state of D-NO will lie about 0.4 e.v. higher

than that for the D-O<sub>2</sub> pair. The results of Porter and Wright<sup>32</sup> indicate that in spite of the rise in the C·T state potential curve, the <sup>2</sup>F→<sup>2</sup>CT radiationless transitions for NO quenching are not activation controlled, proceeding at every encounter as in the case for the <sup>3</sup>F→<sup>3</sup>CT radiationless transitions for O<sub>2</sub> quenching.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE, SOUTH HADLEY, MASSACHUSETTS]

## Substituent Effects on Nuclear Magnetic Resonance Coupling Constants and Chemical Shifts in a Saturated System: Hexachlorobicyclo[2.2.1]heptenes<sup>1</sup>

BY KENNETH L. WILLIAMSON

RECEIVED AUGUST 30, 1962

The coupling constants between protons on adjacent saturated carbon atoms have been found to depend on the electronegativity of the substituent adjacent to the coupling protons in a series of monosubstituted hexachlorobicyclo[2.2.1]heptenes. Assuming a  $\cos^2$  dependence of the coupling constant on dihedral angle, these coupling constants are shown to be remarkably similar to those observed for the corresponding ethylene compounds. The internal chemical shifts,  $\delta_X - \delta_A$  and  $\delta_X - \delta_B$  between the X and A or B protons in this rigid ABX system have been found to depend on both the electronegativity of the substituent and on the dihedral angle between the CX bond and those bonds involving the adjacent (A or B) protons.

### Introduction

The purpose of the work reported herein was to determine the effect of various substituents on the coupling constants between protons on adjacent carbon atoms in a rigid saturated system. Karplus has demonstrated theoretically that the coupling constants of protons on adjacent carbon atoms are functions of the dihedral angles between the protons governed by the relationship<sup>2</sup>

$$J = \begin{cases} 8.5 \cos^2\phi - 0.28, & 0^\circ \leq \phi \leq 90^\circ \\ 9.5 \cos^2\phi - 0.28, & 90^\circ \leq \phi \leq 180^\circ \end{cases}$$

This relationship has been shown experimentally to apply to a wide variety of compounds<sup>3</sup> with varying degrees of precision.

In an analysis of the X portion of the ABX system found in six isomeric  $\alpha$ -acetoxy ketones in the A-ring of a steroid, we found it necessary to revise the constants of the Karplus equation in order to obtain mutually consistent values for the dihedral angles between the coupling protons in these compounds.<sup>4</sup> It is not surprising, in view of the approximations involved in Karplus' theoretical calculations, that such a revision should be necessary. However, our revised equation did not give mutually consistent values for calculated dihedral angles when applied to similar compounds with different substituents adjacent to the coupling protons.<sup>4</sup> In short, the magnitude of the observed coupling constants in this system seemed to vary, not according to changes in the dihedral angle between the coupling protons, but according to the nature of the substituent adjacent to the coupling protons. In view of the conformational flexibility of the A-ring of the steroid molecule such a conclusion must, of necessity, be regarded as tenuous. Furthermore because the

AB lines of the ABX pattern are not clearly resolved from the lines due to the many other protons in the molecule, a complete ABX analysis is impossible.

Substituent effects on the couplings between protons on saturated carbon atoms have been remarked upon by previous workers. In a study of some cyclopropane carboxylic acids, Hutton and Schaefer<sup>5f</sup> indicated that the difference between their observed coupling constants and those calculated from the Karplus equation may depend on the electronegativity of the substituent, although they did not rule out distortion of the ring system by the large substituents. By way of contrast Graham and Rogers<sup>5</sup> in a recent study of a series of cyclopropane derivatives, including some cyclopropanecarboxylic acids, concluded that substituent effects were not important in the consideration of the proton-proton coupling constants.

The observed<sup>6</sup> coupling constants in three-membered rings containing the heteroatoms oxygen, nitrogen, and sulfur do not agree well with Karplus' predictions. Hutton and Schaefer<sup>5f</sup> again noted that the deviations from the predicted values parallel the differences in electronegativity between the heteroatoms and carbon, from which they conclude that the coupling constants in these heterocyclic compounds depend not only on angular factors but also on the electronegativity of the heteroatom.

**The Hexachlorobicyclo[2.2.1]heptene System.**—In order to determine the effect of substituents of varying electronegativity and magnetic anisotropy on the magnitude of the coupling constant between protons on adjacent saturated carbon atoms, it is necessary to have a system in which the stereochemistry of the coupling protons remains fixed and known. Only in this way can the effect of the substituent on the coupling constant be separated from the known dependence<sup>2,3</sup> of  $J$  on the dihedral angle between the coupling protons. Furthermore the system must have a minimum number of coupling protons to facilitate complete, unambiguous analysis of the spectra and, finally, it must be possible to introduce a variety of groups of differing magnetic anisotropy and electronegativity. For these reasons we have chosen to examine the n.m.r. spectra of Diels-Alder adducts formed from hexachlorocyclopentadiene and a series of monosubstituted ethylenes.

(1) This work was presented at the 142nd Natl. Meeting of the American Chemical Society at Atlantic City, N. J., September, 1962. This investigation was supported in part by PHS research grant GM 10224-01 from the Division of General Medical Sciences.

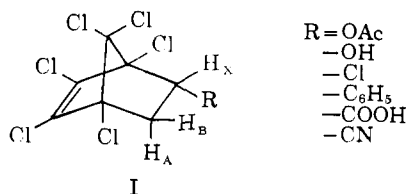
(2) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(3) See *inter alia* (a) R. U. Lemieux, R. K. Kullnig and R. Y. Moir, *J. Am. Chem. Soc.*, **80**, 2237 (1958); (b) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *ibid.*, **80**, 6098 (1958); (c) C. D. Jardtzy, *ibid.*, **84**, 62 (1962); (d) R. U. Lemieux, *Can J. Chem.*, **39**, 116 (1961); (e) F. A. L. Anet, *ibid.*, **39**, 789 (1961); (f) H. M. Hutton and T. Schaefer, *ibid.*, **40**, 875 (1962); (g) R. J. Abraham, K. A. McLauchlan, L. D. Hall and L. Hough, *Chem. and Ind.* (London), 213 (1962).

(4) K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 4623 (1961).

(5) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962).

(6) F. S. Mortimer, *J. Mol. Spectroscopy*, **5**, 199 (1960).



Some of the best evidence for the conformational rigidity of this bicyclo-[2.2.1]-heptene system lies in a recent X-ray analysis of 2-bromo-2-nitrocamphane.<sup>7</sup> In this compound the C<sub>2</sub>-C<sub>1</sub>-C<sub>7</sub> angle is found to be 101° while the C<sub>6</sub>-C<sub>1</sub>-C<sub>7</sub> angle is 98° and even this small distortion is attributed to the bulky halogen interacting with the methyl group on the bridge carbon atom,<sup>7</sup> an interaction not found in the hexachloro system considered here. Furthermore, it seems reasonable to suppose that the chlorobicycloheptene system, by virtue of its C<sub>1</sub>-C<sub>2</sub> double bond, would be more rigid than the saturated camphane ring system.

#### N.M.R. SPECTRUM OF DIELS-ALDER ADDUCT, 60 MC.

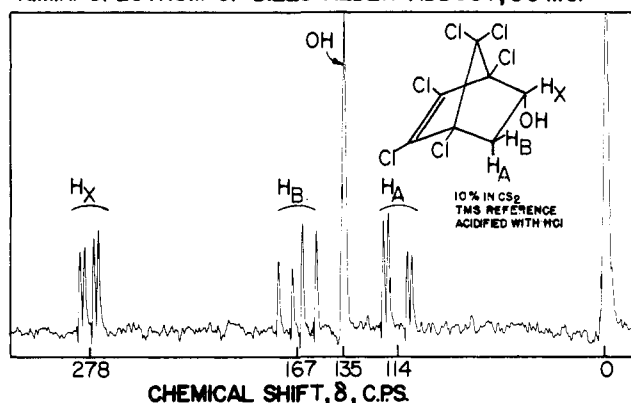


Fig. 1.—N.m.r. Spectrum of Diels-Alder adduct, 60 Mc.

All six of the compounds employed in this study are assumed, in accordance with the rule of Alder and Stein,<sup>8</sup> to be the *endo*-isomers. The dihedral angles between the coupling protons are assumed to be 0 and 120°.

If the assumption is made that a perfectly symmetrical bicycloheptene ring system exists in these compounds, then the coupling constants calculated from the Karplus equation<sup>2</sup> would be  $J_{AX} = 2.1$  and  $J_{BX} = 8.2$  c.p.s. corresponding to dihedral angles of 120° and 0°, respectively.

### Results

**Coupling Constants.**—In this series of six compounds,  $J_{AX}$  varies from 2.4 to 4.6 c.p.s. and  $J_{BX}$  varies from 7.4 to 9.3 c.p.s. (Table I). These coupling constants were in each case calculated by an ABX analysis<sup>9</sup> of the spectrum, although for the chloro, hydroxy, and acetoxy derivatives, the calculated couplings are the

TABLE I  
COUPLING CONSTANTS AND CHEMICAL SHIFTS

Substituent: R	$J_{AX}$	$J_{BX}$	$J_{AB}$	$\delta_A$	$\delta_B$	$\delta_X$	$\delta_X -$		Electronegativity <sup>12</sup>
							$\delta_A$	$\delta_B$	
CN	4.6	9.3	-12.6	129	162	204	75	42	2.49
COOH	4.4	8.5	-12.6	146	163	217	71	54	2.60
C <sub>6</sub> H <sub>5</sub>	4.2	8.9	-12.7	143	172	232	89	60	2.75
Cl	3.2	8.0	-13.2	133	185	283	150	98	3.25
OH	2.4	7.4	-12.6	114	167	278	164	110	3.43
OAc	2.5	7.6	-13.3	114	177	330	215	152	3.80

(7) D. A. Brueckner, T. A. Hamor, J. Monteath Robertson and G. A. Sim, *J. Chem. Soc.*, 799 (1962).

(8) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(9) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 132.

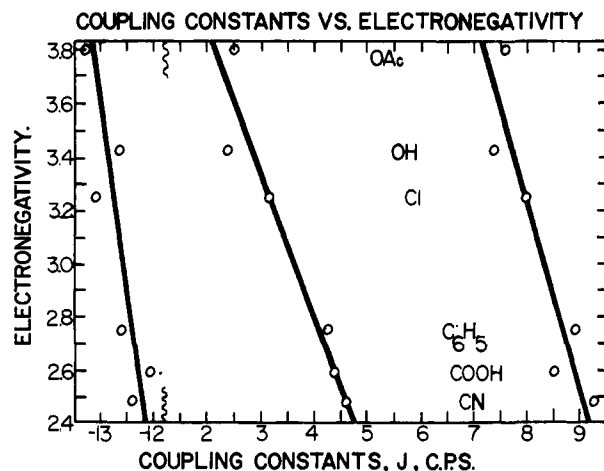


Fig. 2.—Coupling constants vs. electronegativity.

same within experimental error as those obtained by direct measurement, because the chemical shifts between the coupling protons are so large. The lines for each proton in all spectra were very well resolved (Fig. 1) allowing assignments and line positions to be measured without ambiguity.<sup>10</sup>

These observed variations in coupling constants are too large to be accommodated by changes in the geometry of the molecule. A torsional deformation of the bicyclic ring system would produce a change in the dihedral angles between coupling protons. If, for instance, steric interactions were to push the substituent group, R, by 5° toward the *exo* configuration then the dihedral angle between the A and X protons would be 125° and the angle between the B and X protons would be 5°. These angles would give rise to  $J_{AX} = 3.1$  and  $J_{BX} = 8.1$  c.p.s. Very large (and unlikely) distortions of this bicyclic system would thus be necessary to account for the variations in  $J$  noted in these six compounds.

The coupling constants between the protons on adjacent carbon atoms of the six compounds studied do, however, correlate with the electronegativities of the substituent groups (Fig. 2) and are in the order expected from these electronegativities. As noted by Banwell and Sheppard<sup>11</sup> in their study of the coupling constants in vinyl compounds, a substituent atom of high electronegativity would be expected to reduce the electron density around the nearby coupling protons which in turn should lead to less interaction between nuclear and electron spins and therefore to lower coupling constants.

The electronegativity values are taken from the work of Cavanaugh and Dailey and are derived from the expression: Electronegativity =  $0.0114\delta_{\text{internal}} + 1.78$ , where  $\delta_{\text{internal}}$  is the internal chemical shift in c.p.s. at 60 Mc. between the methyl and methylene protons for a series of substituted ethyl derivatives.<sup>12</sup>

A correlation has previously been made between the coupling constants and electronegativities for a series of monosubstituted vinyl derivatives.<sup>11,13-16</sup> It has been noted for these vinyl compounds that a

(10) We have also prepared the compounds where R = SiCl<sub>3</sub> and Si(OCH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> in order to extend our series to very low substituent electronegativities; however, the chemical shifts between the coupling protons in these compounds are so small that ABC spectra which contain only nine resolvable lines result. These spectra are still in the process of analysis.

(11) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

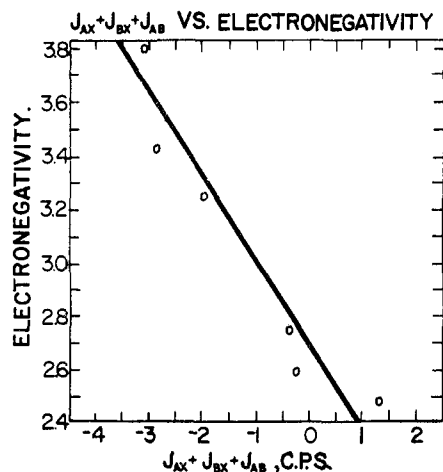
(12) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).

(13) C. N. Banwell, N. Sheppard and J. J. Turner, *Spectrochim. Acta*, **16**, 794 (1960).

(14) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

(15) J. S. Waugh and S. Castellano, *J. Chem. Phys.*, **35**, 1900 (1961).

(16) J. Feeney, A. Ledwith and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1962).

Fig. 3.— $J_{AX} + J_{BX} + J_{AB}$  vs. electronegativity.

linear correlation exists between the individual coupling constants and the electronegativities of the substituents<sup>11,13,15</sup> as well as between the algebraic sum of the coupling constants and electronegativities.<sup>14</sup> It was noted some time ago by Glick and Bothner-By<sup>17</sup> that the coupling constants for a series of ethyl derivatives could be fitted within experimental error by the equation  $J_{CH_2-CH_3} = 8.4 - 0.4$  electronegativity. In the present work if the assumption is made<sup>18</sup> that  $J_{AB}$  is negative or at least opposite in sign from  $J_{AX}$  and  $J_{BX}$  as seems probable from the work of Fraser, Lemieux and Stevens<sup>19</sup> and Kaplan and Roberts,<sup>20</sup> then a correlation exists between the sum of the coupling constants and the electronegativities of the substituents (Fig. 3).

**Comparison of Coupling Constants in Saturated and Unsaturated Systems.**—Bothner-By and Naar-Colin<sup>21</sup> have postulated that the coupling constant for the H-C-C-H system depends primarily on the dihedral angle, and that the change in hybridization of the carbons from  $sp^3$  to  $sp^2$  introduces only a small perturbation on the form of the functional dependence. This is substantiated by their analysis of propene<sup>21</sup> as well as by Elvidge and Jackman's work on muconic esters.<sup>22</sup> If this postulate is of general applicability then one should find some correspondence between the *cis* coupling constants in ethylenes and  $J_{BX}$  for the corresponding bicyclic derivatives since both sets of compounds have dihedral angles of  $0^\circ$  between the coupling protons. As can be seen from the data in Table II, there is a rough correspondence in these values. If one assumes a  $\cos^2$  dependence of the coupling constant on the dihedral angle, then the *trans* coupling constants ( $J_{trans}$ ) ( $\phi = 180^\circ$ ) for the same ethylene derivatives can be compared to  $J_{AX}$  ( $\phi = 120^\circ$ ) in the corresponding bicyclic compounds by simply multiplying  $J_{trans}$  by 0.25 since  $\cos^2 180^\circ = 1$  and  $\cos^2 120^\circ = 0.25$ . Somewhat better agreement is obtained for this comparison at  $120^\circ$  (Table II) than for  $0^\circ$ . This would seem to further substantiate the postulate that coupling of adjacent protons takes place through the  $\sigma$  bond and is therefore independent of the hybridization of the carbon atoms and the carbon-carbon bond distance.

In a study of substituted methanes, Barfield and Grant<sup>23</sup> indicated that in those compounds with

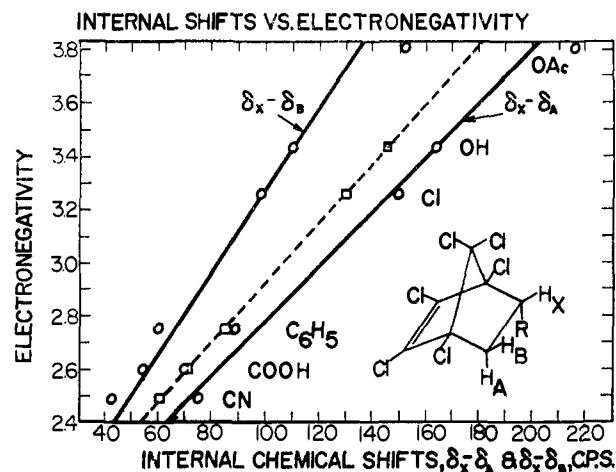


Fig. 4.—Internal shifts vs. electronegativity.

substituents containing  $\pi$  electrons, larger geminal coupling constants are found than predicted by the treatment of the angular dependence by Gutowsky, Karplus and Grant.<sup>24</sup> This increase in the geminal coupling constant was explained in terms of hyperconjugation of the methyl or methylene group with the adjacent  $\pi$  electrons. In the present work if the HCH angle of  $C_8$  is assumed to remain constant in these

TABLE II  
COMPARISON OF COUPLING CONSTANTS FOR BICYCLIC AND ETHYLENE COMPOUNDS

R	$\phi = 0^\circ$		$\phi = 120^\circ$	
	Ethylene $J_{cis}$	Bicyclic $J_{BX}$	Ethylene $0.25 J_{trans}$	Bicyclic $J_{AX}$
CN	11.3	9.3	4.6	4.6
COOH	10.2	8.5	4.3	4.4
$C_6H_5$	11.0	8.9	4.5	4.2
Cl	7.3	8.0	3.4	3.2
OAc	6.3	7.6	3.5	2.5

bicyclic compounds, then the small increase in  $J_{gem} = J_{AB}$  (Fig. 2 and Table I) in proceeding from substituents of low to high electron density follows the trend predicted by Barfield and Grant<sup>23</sup> but only, of course, if  $J_{gem}$  is assumed to have a negative sign. If this slight trend is of any significance, it indicates the relatively small hyperconjugative interaction between geminal protons and a substituent containing  $\pi$  electrons separated by a carbon-carbon bond.

**Chemical Shifts.**—The correlation of the internal chemical shifts,  $\delta_{CH_2} - \delta_{CH}$ , with the electronegativity of the substituent has been demonstrated by Dailey and Shoolery<sup>25</sup> for 19 different ethyl compounds. Most of these compounds were re-examined by Cavanaugh and Dailey<sup>12</sup> in dilute carbon tetrachloride solution to correct the anomalous dilution effects of the benzene solutions employed in the first investigation. On the basis of this new work, Cavanaugh and Dailey set up the equation given above defining electronegativity in terms of the internal chemical shift.

In the present work we can distinguish two separate chemical shifts for the protons on the carbon adjacent to the carbon atom bearing the substituent. In Fig. 4 these internal chemical shifts (Table I) are plotted against the electronegativities (as defined by Cavanaugh and Dailey) of the substituents. We have fitted these data to the equation

$$\delta_{internal} = E(88.5 - 21.8 \cos \phi) + 38.8 \cos \phi - 157.5$$

(23) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **83**, 4726 (1961); M. Barfield and D. M. Grant, *J. Chem. Phys.*, **36**, 2054 (1962).

(24) H. S. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959).

(25) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

(17) R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956).

(18) At the suggestion of A. A. Bothner-By, private communication.

(19) R. R. Fraser, R. U. Lemieux and J. D. Stevens, *J. Am. Chem. Soc.*, **83**, 3901 (1961).

(20) F. Kaplan and J. D. Roberts, *ibid.*, **83**, 4666 (1961).

(21) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **83**, 231 (1961).

(22) J. A. Elvidge and L. M. Jackman, *Proc. Chem. Soc.*, 89 (1959).

where  $\delta_{\text{Internal}}$  is the internal chemical shift,  $\delta_X - \delta_B$  or  $\delta_X - \delta_A$  in c.p.s. at 60 Mc. between the X proton and the adjacent proton in question,  $E$  is the electronegativity of the substituent and  $\phi$  is the dihedral angle between the X proton and the proton in question on the adjacent carbon atom. The two solid lines are calculated for  $\phi = 0^\circ$  and  $\phi = 120^\circ$  corresponding to the dihedral angles between the protons in the bicyclic chloro compounds. The internal chemical shift for the corresponding ethyl derivatives, being a rotational average over all possible orientations of the methylene protons with respect to the methyl protons, can be calculated from the chemical shifts at  $120^\circ$  and  $0^\circ$  for any given compound by

$$\delta_{\text{Int. av.}} = \frac{1}{3}[2\delta_{\text{Int}}(\phi = 120^\circ) + \delta_{\text{Int}}(\phi = 0^\circ)]$$

The values for this average chemical shift are represented by the dashed line and are found to correspond to the internal chemical shift for the individual ethyl derivatives (the square points) as determined by Cavanaugh and Dailey. In view of the highly anisotropic environment of the protons on the bicyclic chloro compounds, it is surprising that any single relationship can be found between these chemical shifts and those of the corresponding ethyl derivatives; therefore the relationship observed above may be purely fortuitous. It is known, for instance, that a proton lying in the plane of a double bond is shielded and a proton located above the plane of a double bond is deshielded with respect to an unperturbed proton.<sup>26</sup> This phenomenon has been employed by Fraser<sup>27</sup> to establish the configuration of carboxylic acid derivatives of bicyclo-[2.2.1]-hept-2-enes. As in the bicyclic chloro compounds the *endo* protons in Fraser's compounds are usually found at higher fields than the *exo* protons since the *endo* proton lies above the plane of the double bond and the *exo* proton is in a position approximately in the plane of the double bond.

In the series of bicyclic chloro compounds there are undoubtedly both paramagnetic and diamagnetic contributions to the shieldings of the three protons arising from the presence of the anisotropic double bond, and the bridge and bridgehead chlorine atoms. However, these shielding contributions should remain essentially constant through the series of compounds. The observed differences in internal chemical shifts are therefore functions of the substituent and presumably (as calculated above) also functions of the dihedral angles

(26) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 129.

(27) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

between the protons. However, internal chemical shifts for only two angles have been obtained, therefore the angular dependence of this internal chemical shift is not well established. It is clear, however, despite fairly wide variations of some of the points that the differences in internal chemical shifts are dependent on the electronegativity<sup>28</sup> of the substituent.

### Experimental

The proton magnetic resonance spectra were obtained with a Varian Associates DP-60 high-resolution n.m.r. spectrometer operating at a frequency of 60 Mc./sec. The line positions were obtained by the side band technique with graphical interpolation and are the average of about ten measurements. Chemical shifts are considered accurate to  $\pm 1$  c.p.s. and coupling constants to  $\pm 0.2$  c.p.s. Each sample was run as a ten per cent solution in carbon disulfide containing tetramethylsilane as an internal reference. The samples were sublimed at 0.4 mm. at  $120^\circ$  and had the melting points given in Table III. Despite the fairly wide melting point ranges observed, the samples were homogeneous as far as could be ascertained from the n.m.r. spectra with no extraneous lines appearing in any of the spectra.

TABLE III

DIELS-ALDER ADDUCTS OF HEXACHLOROCYCLOPENTADIENE AND MONOSUBSTITUTED ETHYLENES

I R =	M.p. found, °C.	M.p. reported, °C.	Ref.
CN <sup>a</sup>	143-145.5	143	c
COOH <sup>a</sup>	178-180	181-182.5	d
C <sub>6</sub> H <sub>5</sub> <sup>a</sup>	72-73	73-76	e
Cl <sup>a,b</sup>	130-142.5	125-136	f
OH <sup>b</sup>	156-157	155	g
OAc <sup>a,b</sup>	42-42.5	44	h

<sup>a</sup> Sample from Hooker Electrochemical Co., Niagara Falls, N. Y.; <sup>b</sup> Sample from Monsanto Chemical Co., St. Louis, Mo.; <sup>c</sup> E. A. Prill, *J. Am. Chem. Soc.*, **69**, 62 (1947); <sup>d</sup> S. B. Soloway, J. G. Morales and J. Van Overbeek, U. S. Patent 2,758,918, C.A., **50**, 17307b (1956); <sup>e</sup> S. H. Herzfeld, R. E. Lidov and H. Bluestone, U. S. Patent, 2,606,910, C.A., **47**, 8775b (1953); <sup>f</sup> H. Bluestone, U. S. Patent 2,676,132 C.A., **48**, 8474b (1954); <sup>g</sup> E. K. Fields, *J. Am. Chem. Soc.*, **78**, 5821 (1956).

**Acknowledgment.**—The author is grateful to Dr. Paul E. Hoch of the Hooker Electrochemical Co., Niagara Falls, N. Y., and to Dr. Victor Mark of the Monsanto Chemical Co., St. Louis, Mo., for the compounds used in this work. He is also grateful to Dr. G. E. Bates of Mount Holyoke College for a helpful discussion. For considerable help with the n.m.r. spectrometer, the author would like to thank Dr. Thomas Stengle of the University of Massachusetts.

(28) It has been pointed out by Dr. Norman Sheppard (private communication) that the apparent electronegativities derived from chemical shift data on the ethyl compounds probably include not inconsiderable contributions from magnetic anisotropies within them, therefore the linear correlations observed between the internal chemical shifts in these cyclic compounds and Cavanaugh and Dailey's internal shifts may well reflect a parallelism in magnetic anisotropies as well as "true" electronegativities.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED, MURRAY HILL, NEW JERSEY]

## Kinetic Study of the H<sub>2</sub>POOH-D<sub>2</sub>O Exchange by Nuclear Magnetic Resonance

BY A. FRATIELLO AND E. W. ANDERSON

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The exchange with D<sub>2</sub>O of the phosphorus bonded hydrogens of hypophosphorous acid has been studied using a nuclear magnetic resonance technique. Intensity measurements were used to follow concentration changes during the exchange. The rate law for the exchange, which is acid catalyzed, was found to be: rate =  $k_1[\text{H}_3\text{PO}_2]^2 + k_2[\text{H}_3\text{PO}_2][\text{H}^+ + \text{D}^+]$ . The rate constants for the reaction are compared to those determined for the tritium exchange and an isotope effect is discussed.

### Introduction

Several studies have been made on the exchange of phosphorus bonded hydrogens. Luz and Silver<sup>1,2</sup> and

Hammond<sup>3</sup> made nuclear magnetic resonance investigations of the exchange of several dialkyl phosphonates with D<sub>2</sub>O, and Martin<sup>4</sup> has studied deuterium exchange

(1) Z. Luz and B. Silver, *J. Am. Chem. Soc.*, **83**, 4518 (1961).

(2) Z. Luz and B. Silver, *ibid.*, **84**, 1095 (1962).

(3) P. R. Hammond, *J. Chem. Soc.*, (London), 1365 (1962).

(4) R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1574 (1959).