ORGANIC AND BIOLOGICAL CHEMISTRY

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Spin–Spin Coupling Constants between Non-bonded C^{13} and Proton. IV.[1,2] The CH_3CH_2–C^{13} Group

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Spin–spin coupling constants between C^{13} and protons separated by three bonds have been measured from proton n.m.r. at 60 Mc. For the CH_3CH_2–C^{13} group $J_{C^{13}\text{-}C\text{-}C\text{-}H}$ has values between 4–6.5 c.p.s. which do not vary linearly with the degree of sp-hybridization of the C^{13}-atomic orbitals. The following points are emphasized: (1) Calculations, based on the assumption that the Fermi contact term is the dominant term and using the experimental value of 7.2 c.p.s. for $J_{H\text{-}C\text{-}C\text{-}H}$, predict the following for the CH_3CH_2–C^{13} group: For sp^3-hybridized C^{13} $J_{C^{13}\text{-}C\text{-}C\text{-}H}$ should be about 2.2 c.p.s., and for sp^2-hybridized C^{13} it should be about 3.0 c.p.s., values which are in disagreement with the experimental ones. The constancy of the corresponding $J_{H\text{-}C\text{-}C\text{-}H}$, about 7.2 c.p.s., discounts the possibility that the variations are due to conformational effects. (2) In practically all compounds possessing the CH_3CH_2–C^{13} group and having the C^{13} sp^3-hybridized $J_{C^{13}\text{-}C\text{-}C\text{-}H}$ is found to be larger than $J_{C^{13}\text{-}C\text{-}H}$.

Introduction

Studies on the magnitude of $J_{C^{13}H}$ as a function of the hybridization of C^{13} atomic orbitals, the number of bonds separating the two nuclei and molecular conformations, are valuable since they can provide useful information regarding the mechanism of coupling between C^{13} and proton. One can summarize the available information pertinent to the above problem as:

1. $J_{C^{13}\text{-}H}$: The magnitude of $J_{C^{13}\text{-}H}$ (C^{13} and proton directly bonded to each other) has been shown by the early measurements of Lauterbur[3] to be quite large, in the order of 120–250 c.p.s. The fact that a linear correlation exists between $J_{C^{13}\text{-}H}$ and the degree of sp-hybridization of C^{13}-atomic orbitals,[4] coupled with calculations, had led to the conclusion that the Fermi contact term is the dominant term in the coupling.

2. $J_{C^{13}\text{-}C\text{-}H}$: The magnitude of $J_{C^{13}\text{-}C\text{-}H}$, when the C^{13}–C–H angle is tetrahedral, varies between 4–10 c.p.s. Again a linear correlation is found between the magnitude of $J_{C^{13}\text{-}C\text{-}H}$ and the degree of sp-hybridization of C^{13}-atomic orbitals, suggesting that the Fermi contact term is the dominant one.[5] The fact that calculations, based on the assumption that the Fermi contact term is the sole contributor to the coupling, lead to good agreement between calculated and experimental values, supports the above suggestion further.

3. $J_{C^{13}\text{-}C\text{-}C\text{-}H}$: The finding[6] that a crude linearity exists between $J_{C^{13}\text{-}C\text{-}C\text{-}H}$ and the corresponding $J_{H\text{-}C\text{-}C\text{-}H}$ in compounds having the isopropyl group bonded to C^{13} suggested the following possibilities: (a) The same factors contribute to both $J_{H\text{-}C\text{-}C\text{-}H}$ and $J_{C^{13}\text{-}C\text{-}C\text{-}H}$; since the Fermi contact term has been shown[7] to be the dominant term in $J_{H\text{-}C\text{-}C\text{-}H}$ it would follow that the same is true in $J_{C^{13}\text{-}C\text{-}C\text{-}H}$. (b) The correlation was fortuitous. (c) Conformational effects could be responsible. The finding that $J_{C^{13}\text{-}C\text{-}C\text{-}H}$ is almost constant when the symmetrical *t*-butyl group is bonded to C^{13}, made possibility (c) more attractive.

In order to gain better understanding of the factors affecting $J_{C^{13}\text{-}C\text{-}C\text{-}H}$ and to evaluate the importance of the Fermi contact term, compounds possessing the ethyl group bonded to C^{13} were chosen for our studies. The choice of such compounds was suggested by the fact that the ethyl group shows a constant $J_{H\text{-}C\text{-}C\text{-}H}$ (about 7.2 c.p.s.), thus minimizing comformational effects. This paper presents the results[8] of our investigations on $J_{C^{13}\text{-}C\text{-}C\text{-}H}$.

Results

Table I summarizes the experimentally determined spin–spin coupling constants, each value representing the average of about twelve measurements. The excess C^{13}-content in the compounds examined varied from 30 to 60%. In the case of the 2,4-dinitrophenylhydrazone and semicarbazone of diethyl ketone, $J_{C^{13}\text{-}C\text{-}C\text{-}H}$ could not be determined with good accuracy (only ±0.4 c.p.s.) due to the non-equivalence of the methyl groups. The spectrum of the unlabeled compounds shows the methyl protons as two triplets chemically shifted by 0.04τ unit, due to the magnetic anisotropy of the phenyl and carbonyl groups.

All coupling constants were calculated on the basis of first-order splitting. For compounds having the C^{13} sp^2 hybridized $\delta_{AB}/J_{AB} > 10$, the spectra show good first-order splitting, and evaluation of coupling constants is simple and accurate. A typical example is the spectrum of diethyl ketone-*carbonyl*-C^{13} (Fig. 1A). For compounds having the C^{13} sp^3 hybridized δ_{AB}/J_{AB} is about 4–6, the spectra are more complex, and $J_{C^{13}\text{-}C\text{-}H}$ and $J_{C^{13}\text{-}C\text{-}C\text{-}H}$ were evaluated from the satellites of the third line of the quartet (increasing field) and the middle line of the triplet, respectively. Typical examples are shown in Fig. 1B-G.

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(1) Acknowledgment is made to the donors of Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research.

(2) Presented at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(3) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957); see also *J. Am. Chem. Soc.*, **83**, 1838, 1846 (1961).

(4) (a) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959); (b) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).

(5) G. J. Karabatsos, J. D. Graham and F. Vane, *J. Phys. Chem.*, **65**, 1657 (1961).

(6) G. J. Karabatsos, *J. Am. Chem. Soc.*, **83**, 1230 (1961).

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

(8) For a preliminary report see G. J. Karabatsos, J. D. Graham and F. Vane, *J. Am. Chem. Soc.*, **83**, 2778 (1961).

TABLE I

SPIN–SPIN COUPLING CONSTANTS (C.P.S.) BETWEEN C^{13} AND PROTON

Compound	$J_{C^{13}-H}$	$J_{C^{13}-C-H}$	$J_{C^{13}-C-C-H}$	$J_{C^{13}-O-C-H}$	$J_{C^{13}-O-C-C-H}$	$J_{H-C-C-H}$ (ethyl)
$CH_3CH_2\overset{13}{C}D_2OH$		∽4	6.4 ± 0.2			7.3 ± 0.3
$(CH_3CH_2)_2\overset{13}{C}DOH$		4.0 ± 0.1	5.3 ± .2			7.3 ± .3
$(CH_3CH_2)_3\overset{13}{C}OH$		3.8 ± .2	4.5 ± .2			7.5 ± .3
$CH_3\overset{\alpha}{C}H_2\overset{13}{C}(OH)(\overset{\beta}{C}H_3)_2$		(α)4.0 ± .1 (β)4.1 ± .1	4.0 ± .2			7.3 ± .3
$CH_3\overset{\alpha}{C}H_2\overset{13}{C}(Cl)(\overset{\beta}{C}H_3)_2$		(α)3.7 ± .2 (β)3.9 ± .1	5.7 ± .1			7.5 ± .3
$C^{13}H_3\text{—}\overset{\overset{\alpha CH_3}{\vert}}{C}(OH)\overset{\beta}{C}H_2CH_3$	129 ± 3		(α)3.2 ± .2 (β)3.0 ± .2			
$\overset{13}{C}H_3\overset{\overset{\alpha CH_3}{\vert}}{C}(Cl)\overset{\beta}{C}H_2CH_3$	132 ± 3		(α)4.2 ± .2 (β)3.2 ± .2			
$CH_3\underset{13}{C}OOCH_2CH_3$		6.0 ± .1		3.1 ± 0.1	0	
$(CH_3CH_2)_2\overset{13}{C}{=}O$		5.7 ± .1	4.7 ± .1			7.5 ± .1
$CH_3CH_2\overset{13}{C}O_2H$		6.4 ± .2	5.5 ± .2			7.4 ± .1
$CH_3CH_2\overset{13}{C}O_2CH_3$		6.5 ± .3	5.3 ± .1	4.0 ± 0.05		7.4 ± .1
$(CH_3CH_2)_2\overset{13}{C}{=}NNH\phi(NO_2)_2$		6.5 ± .3	4.8 ± .4			7.2 ± .2
$(CH_3CH_2)_2\overset{13}{C}{=}NNHCONH_2$		4.0 ± .4	4.0 ± .3			7.5 ± .2
$\overset{13}{C}H_3C\equiv CH^a$	131.4		3.6			
$CH_3C\equiv \overset{13}{C}H^a$	247.6		4.8			
$\overset{\alpha}{C}H_3\overset{13}{C}\equiv \overset{\beta}{C}H^a$		(α)10.6 (β)50.8				
$\overset{13}{C}H_3COH^b$		26.6				

[a] Values taken from J. N. Shoolery, *J. Mol. Spec.*, **63**, 110 (1960). [b] Paul Lauterbur, private communication.

Discussion

Since the main purpose of this work was to assess the contribution of the Fermi contact term—already found to be the dominant term in both $J_{C^{13}-H}$ and $J_{C^{13}-C-H}$— in $J_{C^{13}-C-C-H}$, we wish to show the predicted magnitude and trend of $J_{C^{13}-C-C-H}$ on the assumption that the Fermi contact term is the sole contributor to the coupling. The calculations are analogous to those reported previously.[5]

For two protons, H and H′, the contribution of the Fermi contact term to the electron-coupled nuclear spin–spin interaction constant is given by eq. 1.

$$J_{HH'} = \text{const.}\left(\frac{1}{\Delta E}\right)\gamma_H\gamma_{H'}\phi_H(0)\phi_{H'}(0) \sum_{j,1} c_jc_1\left[\frac{1}{2^{n-ij1}}\right][1 + 2f_{j1}(P_{HH'})] \tag{1}$$

For one proton and a C^{13} eq. 1 becomes 2

$$J_{C^{13}H} = \text{const.}\left(\frac{1}{\Delta E'}\right)\gamma_H\gamma_{C^{13}}\phi_H(0)\phi_{C^{13}}(0) \sum_{j,1} c_jc_1\left[\frac{1}{2^{n-ij1}}\right][1+ 2f_{j1}(P_{HC^{13}})] \tag{2}$$

If $\Delta E'$ (mean excitation energy of C^{13}–C–C–H group), $\gamma_{C^{13}}$ (magnetogyric ratio of C^{13}) and $\phi_{C^{13}}(0)$ (electron density at C^{13} nucleus) were expressed in terms of ΔE, γ_H and $\phi_H(0)$, with the assumption that c_j and c_1, the coefficients in the ground state wave function, do not change[9] by replacing a proton with C^{13}, calculation of $J_{C^{13}H}$ in terms of J_{HH} becomes feasible. Assuming $\Delta E' = \Delta E \times A$, $\gamma_{C^{13}} = \gamma_H \times B$ and $\phi_{C^{13}}(0) = \phi_H(0) \times C$, eq. 2 becomes 3

$$J_{C^{13}H} = J_{HH} \times \frac{1}{A} \times B \times C \tag{3}$$

B can be calculated from the magnetogyric ratios of C^{13} and proton, and it is 0.2514. Evaluation of A can be achieved from the ratio of the mean excitation energies, $\Delta E_{C^{13}-C-C-H}$ and $\Delta E_{H-C-C-H}$; a value of 0.9 appears reasonable.[10] One can evaluate C as:

From wave function 4 the electron density at C^{13} nucleus, $\phi_{C^{13}}(0)$ is $a^2\psi^2_{2s}(0)$. Evaluation of

$$\Psi = a\Psi_{2s} + b\psi_{2p} \tag{4}$$

$\psi^2_{2s}(0)$ can be approximated by utilization of a 2s hydrogen-like wave function, as

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[9] A similar assumption has been made in the case of F^{19}, M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[10] Since exact values for excitation energies to triplet states are not available, the mean excitation energy can be approximated from bond energies. See A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947), M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959).

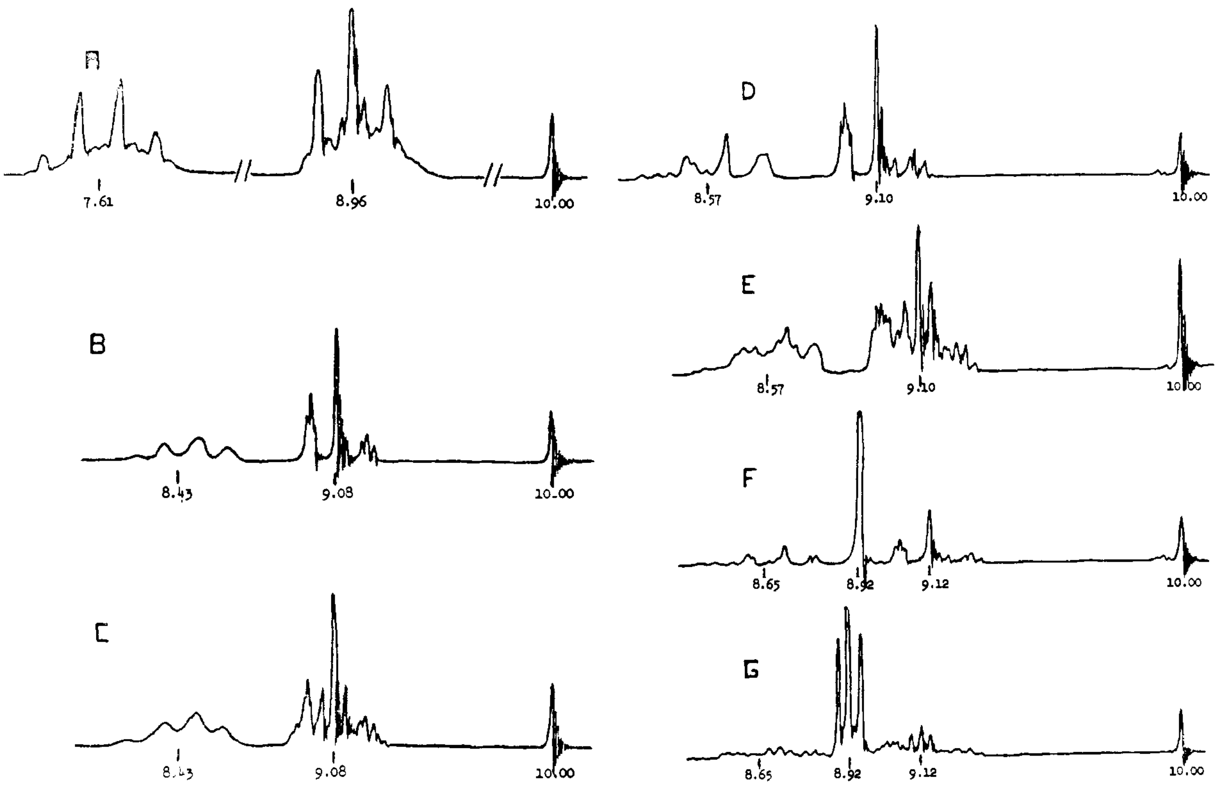

Fig. 1.—60 Mc. proton n.m.r. spectra in τ units, TMS taken as 10.00 τ: A, diethyl ketone-carbonyl-C^{13}, ~20% excess C^{13} (no solvent); τ-values taken from G. V. D. Tiers, "Tables of τ-Values for a Variety of Organic Compounds"; B, 1-propanol-1,1-d_2 (20% solution, CCl_4); C, 1-propanol-1,1-d_2-1-C^{13}, ~40% excess C^{13} (20% solution, CCl_4); D, 3-pentanol-3-*d* (20% solution, CCl_4); E, 3-pentanol-3-*d*-3-C^{13}, ~45% excess C^{13} (20% solution, CCl_4); F, *t*-amyl alcohol (20% solution, CCl_4); G, *t*-amyl alcohol-2-C^{13}, ~55% excess C^{13} (20% solution, CCl_4).

$$\psi_{2s}(0) = \frac{1}{2\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \qquad (5)$$

$$\psi^2_{2s}(0) = \frac{1}{8\pi}\left(\frac{Z}{a_0}\right)^3 = \frac{Z^3}{8} \times \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 \qquad (6)$$

Since $\phi_H(0) = \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3$, the value of $\phi_{C^{13}}(0)$ is given by eq. 7

$$\phi_{C^{13}}(0) = \frac{a^2Z^3}{8}\phi_H(0) \qquad (7)$$

Thus, C assumes the value $a^2Z^3/8$, where Z is the effective atomic number for carbon, taken as 3.25. The numerical value of a^2 depends on the hybridization of C^{13}. For sp^3, $a^2 = 1/4$; for sp^2, $a^2 = 1/3$; for sp, $a^2 = 1/2$.

On the basis of the above calculations eq. 3 can be written as

1. $J_{C^{13}H} = J_{HH} \times 0.3036$ (for sp^3-hybridized C^{13}) (8)
2. $J_{C^{13}H} = J_{HH} \times 0.4046$ (for sp^2-hybridized C^{13}) (9)
3. $J_{C^{13}H} = J_{HH} \times 0.6069$ (for sp-hybridized C^{13}) (10)

Prediction of the values of $J_{C^{13}\text{-C-C-H}}$ now can be achieved by use of eqs. 8, 9 and 10, provided that the corresponding values of $J_{\text{H-C-C-H}}$ are known. Calculations on the magnitude of $J_{\text{H-C-C-H}}$ as a function of the dihedral angle have been done by Karplus.[11] Because of lack of data as to the exact values of the dihedral angles of our compounds we have utilized the experimental values of $J_{\text{H-C-C-H}}$ (Table I). According to these values one should expect, for sp^3-hybridized C^{13}, $J_{C^{13}\text{-C-C-H}}$ to be in the vicinity of 2.2 c.p.s. and, for sp^2-hybridized C^{13}, in the vicinity of about 3.0 c.p.s. Actually, the experimental values are much higher than the predicted ones. Moreover, no correlation exists between the magnitude of these values and the extent of sp-hybridization of the C^{13}-atomic orbitals; the values for propanol (6.4 c.p.s.) and *t*-amyl chloride (5.7 c.p.s.), where the C^{13} is sp^3-hybridized, are higher than any value where the C^{13} is sp^2-hybridized. The same trend was observed[6] with neopentyl alcohol-1-C^{13} (4.8 c.p.s.) and trimethyl acetic acid-*carbonyl*-C^{13} (4.2 c.p.s.). These findings suggest that the Fermi contact term may not be the dominant term in $J_{C^{13}\text{-C-C-H}}$.

The possibility that the Fermi contact term might be the dominant term, and the experimentally observed variations in $J_{C^{13}\text{-C-C-H}}$ might be due to differences in relative populations of rotational isomers (variations in the magnitude of dihedral angle affect the coupling) was considered. Such a possibility seems unreasonable since $J_{\text{H-C-C-H}}$ of the ethyl group (Table I) is practically constant. Changes in dihedral angle should affect both $J_{\text{H-C-C-H}}$ and $J_{C^{13}\text{-C-C-H}}$.

The possibility that the variations may be due to differences in the electronegativity and nature of the groups attached to C^{13} was considered also.[12] No rational correlation can be made. It is hoped that experiments with various cyclopropane com-

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(11) M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960).

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

pounds and other rigid systems, where the dihedral angle is known, will furnish further information on the problem.

It was pointed out previously[6] that, within the same compound, $J_{C^{13}-C-C-H}$ is occasionally larger in magnitude than $J_{C^{13}-C-H}$. Table I shows that such anomalous spin–spin couplings seem to be the rule rather than the exception in compounds where the C^{13} is sp^3-hybridized.[13]

We wish to point out that changes in the hybridization of the carbon atoms through which the coupling is transmitted result to unusually large coupling (last two cases in Table I).

Experimental

Preparation of C^{13}-Labeled Compounds.—All labeled compounds were synthesized according to well established preparative methods. Three compounds, diethyl ketone-*carbonyl*-C^{13} (Isotopes Specialties Co., Calif.), methyl propionate-*carbonyl*-C^{13} (Isotopes Specialties Co., Calif.) and methyl iodide-C^{13} (Isomet Corporation, N. J.) served as starting materials.

a. **Propionic acid-1-C^{13}** was prepared by saponification of methyl propionate-*carbonyl*-C^{13}, acidification, extraction with ether, evaporation of ether and collection through a Beckman Megachrom.

b. **3-Deuterio-3-pentanol-3-C^{13}** was prepared by reduction of diethyl ketone-*carbonyl*-C^{13} with lithium aluminum deuteride. Purification of product was achieved by collection through Megachrom.

c. **1,1-Dideuterio-1-propanol-1-C^{13}** was prepared by reduction of methyl propionate-*carbonyl*-C^{13} with lithium aluminum deuteride. Product purification was achieved by use of Megachrom.

d. **3-Ethyl-3-pentanol-3-C^{13}** was prepared from ethyl magnesium bromide and diethyl ketone-*carbonyl*-C^{13}.

e. **Ethyl acetate-carbonyl-C^{13}** was given to us by Dr. R. L. Schwendeman.

f. **C^{13}-Labeled *t*-Amyl Alcohols and *t*-Amyl Chlorides.**—The preparation of these compounds will be reported elsewhere.

g. **2,4-Dinitrophenylhydrazone and semicarbazone** of diethyl ketone-*carbonyl*-C^{13} were prepared by conventional methods and recrystallized from absolute ethanol.

Measurements.—All spectra were taken with a model V4300-2 Varian Associates high resolution n.m.r. spectrometer at 60 Mc. Solutions of about 20% of the labeled compounds in carbon tetrachloride were used with the following exceptions: Diethyl ketone, methyl propionate and the *t*-amyl chlorides were examined as neat liquids. The spectra of 2,4-dinitrophenylhydrazone and the semicarbazone of diethyl ketone were taken in nitrobenzene and chloroform. In all cases thin-walled Wilmad Glass Co. tubes were used. Spin–spin coupling constants were measured using the standard side band technique,[14] a frequency counter being employed.

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[13] We have been informed (P. T. Narasimhan, private communication) that $J_{C_{13}—C-H}$ is negative while $J_{C_{13}-C-C-H}$ is positive.

[14] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KAN.]

Addition of Weak Acids to Vinylmetallocenes

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The addition of absolute acetic acid and of hydrogen azide to vinylferrocene has been shown to proceed in accordance with Markownikoff's rule. These addition reactions, which occur even at room temperature, demonstrate an unusual reactivity of the vinyl group. Vinylruthenocene and vinylosmocene have been prepared and these compounds also add absolute acetic acid readily. The rates of addition of acetic acid to the three vinylmetallocenes have been measured and fall in the relative order 4.62:1.19:1.00 for vinylosmocene:vinylruthenocene:vinylferrocene. These results indicate that the α-metallocenyl transition carbonium ions possess unusual stability relative to ordinary carbonium ions derivable from 1-alkenes in addition reactions.

In a preliminary communication[1] from this Laboratory it was reported that hydrogen azide and also acetic acid readily add across the double bond of vinylferrocene. This extraordinary reactivity of the vinyl group was so striking that we decided to extend the investigation to vinylruthenocene and vinylosmocene and to determine the rates of addition of absolute acetic acid to the three vinylmetallocenes.

The uncatalyzed addition of weak acids to olefins does not generally occur readily, and there is little information on the subject in the literature. Fort and Girard[2] have shown that anhydrous formic acid adds to alkenes, such as 1-octene, at 80°, according to Markownikoff's rule. These investigators have provided evidence that the mechanism of addition is analogous to that of the addition of strong acids to olefins.[3] Specifically, a π-complex between the proton of the acid and the olefin is first formed, and this rearranges to a carbonium ion, which then adds the formate ion. Chablay[4] has found that *t*-amyl acetate may be obtained in 4% yield by treatment of trimethylethylene with absolute acetic acid at 125° for 200 days.

In our preliminary paper[1] we reported that vinylferrocene, prepared by the method of Arimoto and Haven,[5] undergoes reaction with a solution of hydrogen azide and absolute acetic acid in benzene to give a mixture of α-ferrocenylethyl azide, a relatively small quantity of a second, unidentified azide, α-ferrocenylethyl acetate and acetylferrocene. α-Ferrocenylethyl azide was characterized by its conversion to the known α-ferrocenylethylamine[6] under conditions of catalytic hydrogenation, by preparation of the same azide from α-ferrocenylethyl alcohol by reaction with hydrogen azide under the same conditions as used in the addition of the acid to vinylferrocene, and by the presence of an

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[1] G. R. Buell, W. E. McEwen and J. Kleinberg, *Tetrahedron Letters*, No. **5**, 16 (1959).

[2] A. W. Fort and C. A. Girard, *Petroleum Research Fund Report*, 42 (1958); 27 (1959).

[3] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 5372 (1952).

[4] A. Chablay, *Compt. rend.*, **250**, 2722 (1960).

[5] F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955).

[6] P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson and G. M. Whitman, *ibid.*, **79**, 3416 (1957).