6 form the characteristic pattern[25] of an $AB_2$ system with A at +2.76 and B at +3.03 $\tau$, with $J/\delta$ = 0.65. The proton at carbon 8 was seen at +5.73 $\tau$. The methylene hydrogens were seen as a pair of doublets with $\tau$ = +6.80, 6.95, 7.83 and 7.98. The peak areas were consistent with the interpretation given.

**2-Nitro-4,5,9,10-tetrahydropyrene (II).**—Nine milliliters of 6 N nitric acid was added in one portion to a solution of 20 mg. of I in 15 ml. of acetic acid. After 1 minute the solution was poured onto excess ice and water. After the ice had melted the precipitate was collected and washed with water. Crystallization of this material from ethanol gave yellow needles, m.p. 110–111°, wt. 205 mg. (88%).

*Anal.* Calcd. for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.21; N, 5.58; Found: C, 76.52, 76.50; H, 5.24, 5.37; N, 5.59.

**2-Amino-4,5,9,10-tetrahydropyrene (III).**—Hydrogenation of nitro compound II was carried out at room temperature in methanol with a palladium-on-charcoal catalyst. The theoretical amount of hydrogen was taken up, the solution was filtered, the solvent was removed under vacuum, and the residue was crystallized from ethanol. The product was obtained as colorless needles, m.p. 165–166.5°, yield 84%.

*Anal.* Calcd. for $C_{16}H_{15}N$: C, 86.88; H, 6.83. Found: C, 86.72; H, 6.81.

The infrared spectrum in chloroform showed the strong bands characteristic of a nitro group at 6.60 and 7.50 $\mu$. The n.m.r. spectrum[24] in carbon tetrachloride showed peaks at +2.11, 2.91 and 6.60$\tau$. The first of these was assigned to protons 1 and 3; the second to protons 6, 7 and 8; and the third, which showed no splitting, was assigned to the methylene protons. The band areas were consistent with this assignment.

The acetyl derivative, prepared by allowing III to stand for several hours with excess acetic anhydride and pyridine, was obtained as a white powder from ethanol, m.p. 201–201.5°.

*Anal.* Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51. Found: C, 81.51; H, 6.31.

**4,5,9,10-Tetrahydropyrene (IV).**—Nitro compound II, 250 mg., was reduced in ethanol solution with palladium-on-carbon. The solution was acidified with hydrochloric acid, filtered and evaporated to dryness at 40° to give the amine hydrochloride. The hydrochloride was added to a solution of 1 ml. of water in 6 ml. of acetic acid, and the suspension was stirred at 50°. Hydrochloric acid (0.5 ml.) was added and some of the hydrochloride remained undissolved. After dropwise addition of a solution of 0.37 g. of sodium

nitrite in 2 ml. of water, a clear yellow solution resulted. After 5 min., 6 ml. of hypophosphorus acid was added to the solution. The reaction mixture was allowed to stand for 18 hours at room temperature. Brownish-yellow plates resulted, which were recrystallized (charcoal) once from ethanol and melted at 133–136°. A second recrystallization brought the m.p. up to 137–138°. The mixture melting point with an authentic sample[26] showed no depression, and the two samples had identical ultraviolet spectra.

**Perhydro[2.2]metacyclophane (VI).**—Compound I, 100 mg., was hydrogenated using 500 mg. of platinum oxide in 20 ml. of acetic acid. Six moles of hydrogen was taken up in 24 hours. Ether was added to the solution to dissolve the crystals which had separated, the solution was filtered, and the solvent was evaporated. The residue, recrystallized from ethanol, yielded needles, wt. 97 mg. (91%), m.p. 174.0–174.3°.

*Anal.* Calcd. for $C_{16}H_{28}$: C, 87.27; H, 12.72. Found: C, 87.30; H, 12.69.

**Hexahydro[2.2]metacyclophane (V).**—Compound I, 350 mg., was hydrogenated with 500 mg. of platinum oxide in 30 ml. of acetic acid. The reaction was stopped after 3 moles of hydrogen had been taken up. Ether was added to the solution to dissolve the solid which had precipitated, the catalyst was removed by filtering the solution, and the solvent was evaporated. The residual white solid was dissolved in pentane and chromatographed with pentane on a column of 12 g. of neutral alumina of activity I.[27] The first 30 ml. of eluate contained 110 mg. of VI. The next 40 ml. of eluate contained no solid, while the following 30 ml. yielded 40 mg. of V. The column was then washed with pentane–ether, and 180 mg. of I was obtained. Crystallization of V from ethanol yielded needles, m.p. 121–121.5°. The mixture melting point of V with I was depressed.

*Anal.* Calcd. for $C_{16}H_{22}$: C, 89.72; H, 10.27. Found: C, 89.86; H, 10.04.

**1,2-Bis-(3-methylphenyl)-ethane.**—Fifteen grams of α-bromo-m-xylene in 25 ml. of ether was added dropwise to 6 g. of magnesium in 10 ml. of ether. The reaction mixture was then diluted with water and the aqueous phase was extracted with ether. The ether extracts were combined and dried and the ether was evaporated. The product was distilled, b.p. 110–114° (0.1 mm.). A center cut was redistilled for analysis, $n^{25}D$ 1.5546.

*Anal.* Calcd. for $C_{16}H_{18}$: C, 91.42; H, 8.56. Found: C, 91.09; H, 8.45.

(25) J. A. Pople, W. G. Schneider and H. G. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, p. 123.

(26) E. D. Bergmann and Z. Pelchowicz, *Bull. Res. Council Israel*, **3**, 91 (1953). We are indebted to Dr. Bergmann for furnishing us with the authentic material.

(27) H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

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# The Nuclear Magnetic Resonance Spectra of Monosubstituted Acetylenes

BY MAURICE M. KREEVOY, HUGH B. CHARMAN AND DANIEL R. VINARD

N.m.r. and infrared spectroscopic methods were used to obtain a formation constant of 0.1–0.2 for the hydrogen bonded complex of phenylacetylene with pyridine. This hydrogen bonding results in a downfield shift of about one p.p.m. in the resonance line of the acetylenic proton of phenylacetylene and other monosubstituted acetylenes in pyridine solution. Monosubstituted acetylenes show long-range spin–spin coupling constants of 2–3 c. sec.$^{-1}$ if the substituents are saturated. Spin–spin coupling is undetectable in vinylacetylene and propynal, however. This is interpreted in terms of two mechanisms for transmission of coupling. The data also support the hypothesis that the Baker–Nathan effect and inductive effects are approximately independent.

The nuclear magnetic resonance (n.m.r.) spectra of monosubstituted acetylenes are interesting both for theoretical and practical reasons. They give some new insight into the electronic structure of such compounds and the nature of their solutions. They provide an additional tool for the identification of this structural element in molecules of unknown structure. In the present paper salient features of the n.m.r. spectra of a number of monosubstituted acetylenes are described and interpreted. To aid in the interpretation, n.m.r. spectra and also infrared spectra were obtained for a series of pyridine–carbon tetrachloride–phenylacetylene mixtures, and a formation constant was evaluated for the hydrogen bonded complex of phenylacetylene and pyridine. Esti-

mates of the carbon–nitrogen distance in the hydrogen-bonded species were made from both types of spectroscopic data and they are in good agreement. Evidence is presented supporting the separability of inductive and Baker–Nathan effects.

## Results

Table I gives $\tau$-values[1] for the acetylenic proton in a number of monosubstituted acetylenes, $RC\equiv CH$. The solvent is carbon tetrachloride, and tetramethylsilane was used as an internal reference. Most of the acetylenic protons gave rise to closely spaced doublets or triplets due to long range spin–spin coupling. Measurements were made to the central line of a triplet or to the center of a doublet. The reproducibility of the listed $\tau$-values is about 0.02 p.p.m. unless otherwise specified.

When pyridine is used as a solvent instead of carbon tetrachloride, the major part of each spectrum remains essentially unchanged, but the multiplet due to the acetylenic proton undergoes a shift toward lower field, $\Delta\tau$, which in most cases is very close to 1.0 p.p.m. These shifts are also given in Table I.

### Table I

Values, Solvent Shifts and Long-range Spin-Spin Couplings in Monosubstituted Acetylenes, $RC\equiv CH$

| R | $\tau$-CCl₄, p.p.m. | $\Delta\tau$, p.p.m. | $J$, c./sec. |
|---|---|---|---|
| H | 8.20 | | >0.5 |
| $n$-C₃H₇ | 8.21 | | 2.7 |
| $n$-C₄H₉ | 8.27 | | 2.4 |
| $n$-C₅H₁₁ | 8.25 | 0.95[a] | 2.1 |
| ClCH₂ | 7.60[b] | | 2.7[c] |
| BrCH₂ | 7.67[b] | | 2.7[c] |
| ICH₂ | 7.81[c] | | 2.8[c] |
| HOCH₂ | 7.67[b] | 0.85 | 2.7[b] |
| HOC(CH₃)₂ | 7.72 | 0.92 | >0.5 |
| CH₃OCH₂ | 7.63 | 0.92 | 2.5 |
| CH₃OC(CH₃)₂ | 7.67 | 0.92 | >0.5 |
| C₆H₅OCH₂ | 7.99 | 1.39 | 2.35 |
| (C₂H₅)₂OCH | 7.61 | 1.21 | 1.61 |
| O=CH | 8.11 | | >0.5 |
| C₆H₅ | 7.07[b] | 1.04 | > .5 |
| CH₂=CH | 7.08 | | > .5 |
| HOCH₂CH₂ | 8.08[d] | | 2.4 |

[a] Measured in 10% aqueous pyridine rather than pure pyridine. [b] Private communication from G. V. D. Tiers. [c] Taken from ref. 2: measured in tetramethylsilane as a solvent. [d] Measured on the pure liquid.

When the carbon atom alpha to the triple bond bears one or more hydrogen atoms, there is usually observable spin–spin coupling between these and the acetylenic hydrogen. The various coupling constants, $J$, in cycles sec.$^{-1}$, are given in Table I. Cases where no splitting was observed are listed as less than 0.5 c. sec.$^{-1}$. This is a conservative estimate, as considerably smaller splittings than this have been observed with the present equipment under favorable conditions. The $J$-values were obtained either in pyridine or in carbon tetrachloride as conditions warranted. In a number of cases, it was confirmed that the $J$-values were solvent independent. The uncertainty in the listed $J$-values is thought to be 0.1–0.2 c. sec.$^{-1}$.
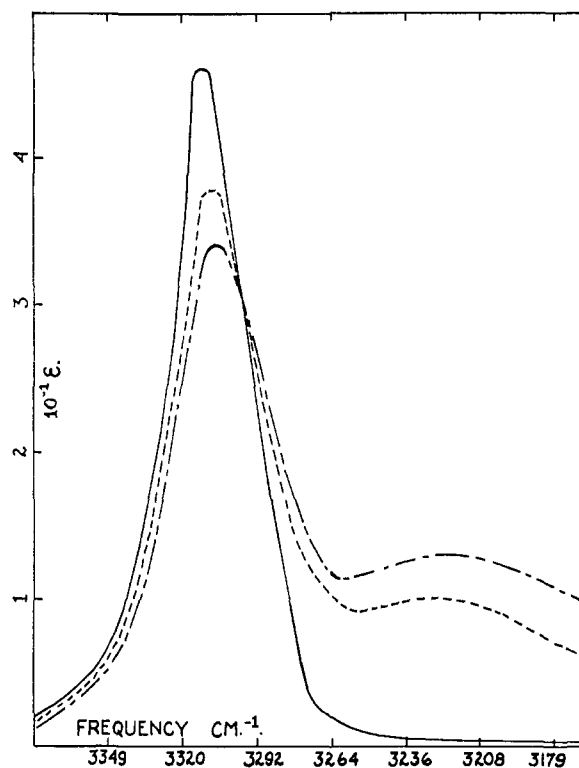
(1) G. V. D. Tiers, J. Phys. Chem., **62**, 1151 (1958).



Fig. 1.—The carbon–hydrogen stretching frequency in phenylacetylene: ———, 0.0285 $M$ phenylacetylene in carbon tetrachloride; ------, 0.0285 $M$ phenylacetylene, 1.49 $M$ pyridine; — — —, 0.285 $M$ phenylacetylene, 2.49 $M$ pyridine, in a 0.13-cm. cell.

To find the cause of the pyridine shift, infrared spectra of pyridine–phenylacetylene–carbon tetrachloride mixtures were obtained in the region between 3000 and 3500 cm.$^{-1}$. Several examples of these spectra are shown in Fig. 1. They show the typical pattern of hydrogen bonded and non-hydrogen bonded stretching frequencies at 3311 and 3229 cm.$^{-1}$, respectively,[2] with an isosbestic point at 3296 cm.$^{-1}$ and the peak positions remain fairly constant.

The molar extinction coefficient at the peak in pure carbon tetrachloride was 44, which is somewhat lower than that previous reported[3,4] and the shoulders on the low frequency side of the peak were not observed. Both of these discrepancies are probably due to the poorer resolution of the present spectrophotometer as compared to the instruments previously used.[3,4] The agreement between the present peak position (3311 cm.$^{-1}$) and that previously reported (3314 cm.$^{-1}$) is satisfactory. The present spectrophotometer is capable of reproducing the peak position of sharp peaks with an average precision of about $\pm 1$ cm.$^{-1}$ in this region.

Five spectra were obtained in a 1-cm. cell on carbon tetrachloride solutions 0.0285 $M$ in phenylacetylene, with pyridine concentrations ranging

(2) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Chap. 3.

(3) J. C. D. Brand, G. Eglinton and J. F. Mormon, J. Chem. Soc., **2526** (1960).

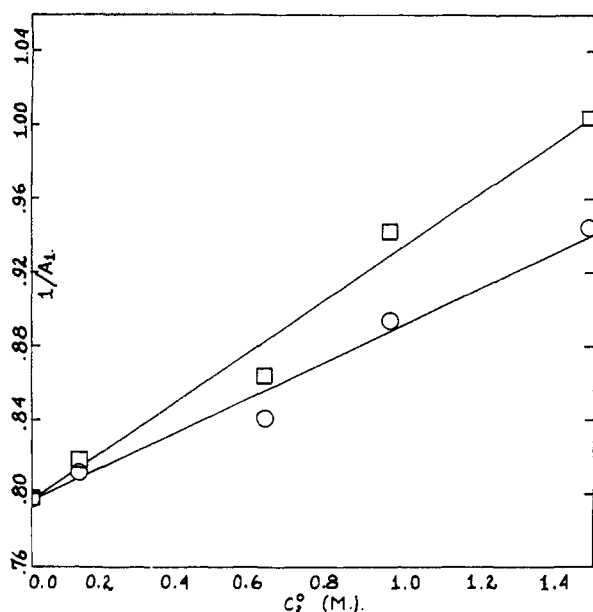(4) R. West and C. S. Kraihanzel, J. Am. Chem. Soc., **83**, 765 (1961).

Fig. 2.—Plot of the reciprocal of the optical density ($1/A_1$) at 3311 cm.$^{-1}$ vs. pyridine concentration at 0.0285 $M$ phenylacetylene in carbon tetrachloride: O are points uncorrected for the absorption of the complex; □ are corrected points. The equilibrium constants are obtained from the slopes of the lines and the known absorption in the absence of pyridine which is $C_1^0\epsilon_1$.

up to 1.5 $M$. Optical densities taken from these are more reliable than those obtained at higher concentrations and shorter path length because the path length is more reliably known. If a 1:1 complex is formed and if this complex does not contribute to the optical density at 3311 cm.$^{-1}$ ($A_1$), that optical density should be given by eq. 1,[5] where $K$ is the equilibrium constant, $\epsilon_1$ is the molar extinction coefficient of phenylacetylene at 3311 cm.$^{-1}$, $C_1^0$ is the initial concentration of phenylacetylene and $C_2^0$ is the initial concentration

$$\frac{1}{A_1} = \frac{1}{C_1^0\epsilon_1} C_2^0 \qquad (1)$$

of pyridine. As predicted by eq. 1, a plot of $1/A$ vs. $C_2^0$ (shown in Fig. 2) is linear within the experimental uncertainty. From it a value of 0.08 is obtained for $K$. A somewhat more accurate value of $K$ can be obtained by noting that the broad peak for the hydrogen bonded complex almost certainly contributes somewhat to the optical density at 3311 cm.$^{-1}$. Corrections for these contributions can be made by assuming that the 3229 cm.$^{-1}$ peak is symmetrical, and subtracting from the optical density at 3311 cm.$^{-1}$ that at 3147 cm.$^{-1}$. The resulting curve (shown in Fig. 2) is also linear and gives 0.11 for $K$. Since the non-hydrogen bonded phenylacetylene does not contribute appreciably to the optical density at 3229 cm.$^{-1}$ ($A_2$), it should be governed by eq. 2, in which $\epsilon_2$ is the molar extinction coefficient of the complex at 3229 cm.$^{-1}$.[5] Figure 3 shows a plot of $1/A_2$ vs. $1/C_2^0$. As required, it is linear. From its inter-

(5) Equation 2 is essentially the Benesi and Hildebrand equation (H. A. Benesi and J. A. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949)), and eq. 1 was derived in similar fashion.
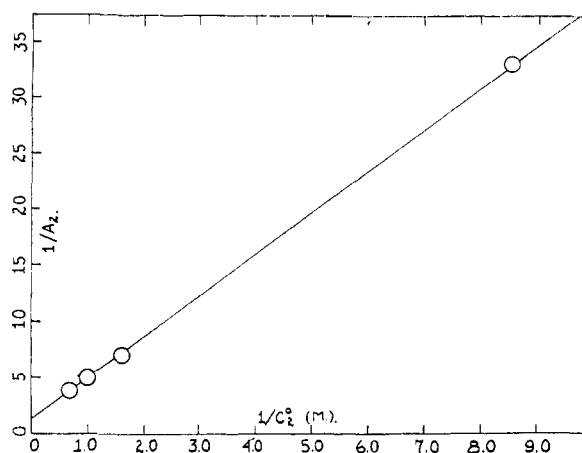
Fig. 3.—A plot of $1/A_2$ vs. $1/C_2^0$. The intercept is $1/C_1^0\epsilon_2$ and the slope is $1/C_1^0\epsilon_2 K$. The phenylacetylene concentration is 0.0285.

cept, $\epsilon_2$ is 27.0, and from its slope the equilibrium constant is 0.21. Considering the approximations involved (i.e., that up to 12% by volume of pyridine does not alter the molar extinction coefficients,

$$\frac{1}{A_2} = \frac{1}{C_1^0\epsilon_2} + \frac{1}{C_2^0} \times \frac{1}{C_1^0\epsilon_2 K} \qquad (2)$$

and that the solutions are ideal), and the experimental uncertainties, the two constants are considered to be in acceptable agreement.

N.m.r. spectra were obtained for a series of solutions containing 0.95 $M$ phenylacetylene, ~1% tetramethylsilane, and various molarities of pyridine in carbon tetrachloride. Equation 3 governs the $\tau$-values for the acetylenic proton if the following assumptions are made: (1) all of the phenyl-acetylene is present either as simple molecules or as a 1:1 complex with pyridine; (2) the $\tau$-value for each species is unaffected by the solvent variations involved; (3) the complexed and uncomplexed phenylacetylene exchanged very rapidly.[6,7] In eq. 3, $\tau$ pertains to the mixture, $\tau_1$ to the non-hydrogen bonded phenylacetylene, and $\tau_3$

$$\tau = (\tau_1 C_1 + \tau_3 C_3)/C_1^0 \qquad (3)$$

and $C_3$ to the hydrogen-bonded phenylacetylene. If ideal solutions are assumed and 0.16 is taken for the equilibrium constant (the average of the two values previously determined), the concentrations can be calculated. Since $\tau_1$ is known from measurements in pure carbon tetrachloride, eq. 3 can be rearranged to give $\tau_3$, which should be a constant. Table II shows the results obtained. The values are constant within the experimental uncertainty through 20% pyridine by volume, but drop thereafter. Averaging $\tau_3$, as obtained from the 10–20% pyridine experiments, a value of 6.13 is obtained. The calculated $\tau$ in 89% pyridine is 6.48 p.p.m., so that, of the observed 1.04 p.p.m. solvent shift the ideal solution approximations account for 0.59 p.p.m., somewhat over half. The remaining 0.45 p.p.m. must be attributed to solvent effects on $K$, on $\tau_1$ or on $\tau_3$.

(6) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1958, Chap. 4.

(7) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21** 1688 (1953).

TABLE II

THE CONSTANCY OF $\tau_3$

| Pyridine, % | 5 | 10 | 15 | 20 | 30 | 89 |
|---|---|---|---|---|---|---|
| $\tau_3$ | $6^a$ | 6.0 | 6.2 | 6.2 | 5.9 | 5.5 |

$^a$ This value is less precise than the others because of the low concentration of complex involved.

It should be noted that the constancy of $\tau_3$, while required by the foregoing treatment, does not provide a critical check of the value of $K$ because any value below about one would provide fairly constant $\tau_3$ values up to 20% pyridine. On the other hand *no* value of $K$ for simple one-to-one complexing in ideal solutions can reproduce the changes in $\tau$ through the whole range of pyridine concentrations.

## Discussion

The $\tau$ values pertaining to carbon tetrachloride are in good general agreement with those previously reported for acetylenic hydrogens.[8–13] The values are very similar to those frequently obtained for methine and methylene protons, with the result that the acetylenic functional group is hard to identify. If there are hydrogen atoms alpha to the triple bond, the difference in chemical shift between these and the acetylenic hydrogen is often not too large with respect to the coupling constant so that the spectrum is hard to analyze.[9,10,12]

All these difficulties disappear if the n.m.r. spectrum is also obtained in pyridine, because this solvent removes the spectrum of the acetylenic proton from the immediate neighborhood of that of the methylene or methine protons. The occurrence and magnitude of the shift seem to be good diagnostic indications of the presence of a monosubstituted acetylene and the coupling constant can readily be obtained from the spectra in pyridine. These coupling constants have been shown to be very nearly solvent independent.[8,9]

While the present work was in progress unambiguous evidence for hydrogen bonding between acetylenes and electron-donating substances has appeared from a number of sources.[3,4,14,15] The present results are in agreement with this conclusion. It seems quite certain that this hydrogen bonding is the origin of the major part of the observed downfield solvent shifts in pyridine.

If it is assumed that the ring current[16] in pyridine is responsible for $\Delta\tau$ and is similar to that in benzene, the distance from the acetylenic proton to the center of the pyridine ring can be estimated from $(\tau_3 - \tau_1)$ using Fig. 1 of Johnson and Bovey.[17]

Such a shift should accompany complexing to an aromatic system even though the hydrogen bond involves the lone pair on nitrogen rather than the $\pi$-electrons. A value of 3.6 Å. is obtained, which leads to a nitrogen-hydrogen distance of 2.2 Å. and a nitrogen–carbon distance $(R)$ of 3.3 Å. provided the complex is linear. The latter distance should also be roughly correlated with the frequency shift $(\Delta\nu)$ in the carbon–hydrogen stretching frequency that accompanies the formation of the hydrogen bond.[18] No previous studies of carbon–hydrogen–nitrogen bonds seem to be available, but the nitrogen–hydrogen–nitrogen bonds seem to be of about comparable stability and the carbon atom would be replaced with one of similar size and electronegativity. Using the linear relation between $R$ and $\Delta\nu$ defined by Pimentel and Sederholm for nitrogen–hydrogen bonds, the observed $\Delta\nu$ of 92 cm.$^{-1}$ gives an $R$ of 3.3 Å. The agreement between this value and that obtained from $(\tau_3 - \tau_1)$ provides support for the approximations and the complexing constant used.

On the other hand, downfield shifts usually accompany hydrogen bond formation even in the absence of a ring current.[19,20] Much stronger hydrogen bonds are usually involved. Huggins[21] found downfield shifts in chloroform proton resonance of about 1 p.p.m. accompanying the formation of hydrogen bonds to acetone and triethylamine but the equilibrium constants are about 2 moles l.$^{-1}$, about ten times those observed in the present case. If an approximately linear solution exists between $(\tau_3 - \tau_1)$ and $K$, the former should be only about $-0.1$ p.p.m., in the present case, in the absence of a ring current effect. On the other hand, Schneider[20] has suggested a correlation between infrared frequency shifts and n.m.r. shifts which would seem to account for the observed n.m.r. shift without considering the ring current at all. Ring current effects accompany the hydrogen bonding of chloroform to aromatic systems.[20] In those cases the anomalous shift is toward high field because the hydrogen bonding is to the $\pi$-electrons, while in the present case the anomalous shift is toward low field because the hydrogen bonding involves the non-bonding $\sigma$-electrons of the pyridine nitrogen atom, which are in the plane of the ring.

The rather large spin–spin coupling constants between acetylenic protons and protons on the carbon adjacent to the other end of the triple bond has been observed and commented on before.[8,13] The absence of such coupling in compounds such as vinylacetylene does not seem to have been previously noted. The following explanation is offered. In compounds such as methylacetylene, only one coupling mechanism is available. The sign of the resulting coupling constant is negative.[22] In vinylacetylene and propynal, however, a second type of coupling is made available.

(8) E. B. Whipple, J. H. Goldstein, L. Mandell, G. S. Reddy and G. R. McClure, *J. Am. Chem. Soc.*, **81**, 1321 (1959).

(9) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *ibid.*, **81**, 4761 (1959).

(10) W. R. Vaughn and R. C. Taylor, *J. Chem. Phys.*, **31**, 1425 (1959).

(11) J. V. Hatton and R. E. Richards, *Trans. Faraday Soc.*, **56**, 315 (1960).

(12) N. Braillon and R. Romanet, *Arch. Sci. (Geneva)*, **12**, Fasc. spec., 234 (1959).

(13) G. V. D. Tiers, private communication.

(14) S. Murahashi, B. Ryutani and K. Hatadee, *Bull. Chem. Soc., Japan* **32**, 1001 (1959).

(15) E. V. Shuvalova, *Opt. i Spektrosko.*, **6**, 696 (1959).

(16) (a) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956); (b) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

(17) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(18) (a) Reference 3, p. 85; (b) C. G. Pimentel and C. H. Sederholm, *J. Chem. Phys.*, **24**, 639 (1956).

(19) Reference 3, pp. 143–156.

(20) W. G. Schneider, "Hydrogen Bonding," ed. by D. Hadži, Permagon Press, New York, N. Y., 1959, p. 55.

(21) C. M. Huggins, *J. Chem. Phys.*, **23**, 1244 (1955).

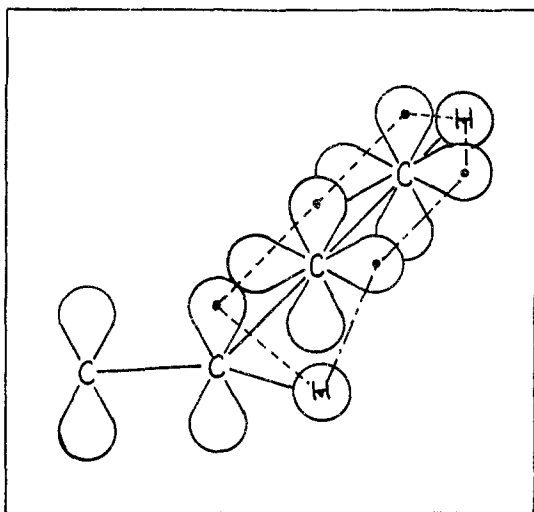(22) M. Karplus, *ibid.*, **33**, 1842 (1960).

Fig. 4.—Long-range spin–spin coupling in vinylacetylene of types one, —·—·—, and two, ----.

It presumably proceeds from the vinyl proton by Fermi contact to the hydrogen 1s-electron, to the vinyl carbon 2p π-orbital, thence down the conjugated system to the acetylenic hydrogen 1s-orbital and by Fermi contact to the acetylenic proton. This type of coupling must give rise to positive coupling constants. The first type of coupling, which gives rise to a negative coupling constant, is thought to proceed from the vinyl hydrogen 1s-electron directly into the nearest 2p-orbital,[23] and thence to the acetylenic proton. The two types of coupling are shown schematically in Fig. 4. Valence-bond theory suggests that spin couplings through π-electron systems in alternant hydrocarbons are positive for protons separated by an odd number of carbon–carbon bonds but negative for even numbers,[24] which would give the present coupling constants the proper sign. When observed independently in suitable molecules the magnitudes of the two types of coupling constants are such that they might well approximately cancel.

Long-range spin coupling of the first type has been attributed to hyperconjugation,[8,9,25] but this attribution seems to rest principally on analogy. Most of the effects attributable to hyperconjugation seem to be explained by α-hydrogen bonding[23] or a combination of the two.[26] A recent, successful, theoretical treatment of these coupling constants[22] utilizes essentially the α-hydrogen bonding model. In any event, it seems likely that coupling of the first type is identifiable with the Baker–Nathan effect on reactivity. If such an identification is permissible, the present J-values and those previously reported[8,13] provide very strong support for the approximate separability of inductive and Baker–Nathan effects and for the approximate independence of the latter from inductive effects.[27]

(23) This type of 1,3-interaction has been called α-hydrogen bonding (M. M. Kreevoy and H. Eyring, J. Am. Chem. Soc., 79, 5121 (1957)).

(24) H. M. McConnell, J. Chem. Phys., 30, 126 (1959).

(25) R. A. Hoffman, Mol. Phys., 1, 326 (1958).

(26) M. M. Kreevoy, Tetrahedron, 5, 233 (1959).

(27) (a) M. M. Kreevoy and R. W. Taft, Jr., J. Am. Chem. Soc., 77, 5590 (1955); (b) R. W. Taft, Jr., and M. M. Kreevoy, ibid., 79, 4011 (1957).

Table I and previous work show that an extremely wide variation in the electronegativity of the groups accompanying the hydrogen atom on the carbon adjacent to the triple bond produces at most a twofold variation in J. The variations that are observed seem to be more closely related to the number of attached groups than to their electronegativity.[11]

## Experimental[28]

Phenylacetylene was purchased from Chemical Intermediates and Research, Inc., in a stated purity of 99%. It was distilled through a spinning-band column and the first and last portions rejected. The central 60% was used. It had b.p. 75° (80 mm.) and $n^{25}$D 1.5463, and did not discolor in pyridine, as did undistilled samples. Campbell and Campbell[29] give a b.p. of 73–74° (80 mm.) and $n^{29}$D 1.5465–1.5484.

2-Methyl-2-methoxy-3-butyne.—Dimethyl sulfate (25 g.) was added at 40° to 2-methyl-3-butyne-2-ol (33 g.) in water (15 ml.) and 50% sodium hydroxide (36 ml.) at such a rate that the temperature remained under 60°. After the addition the mixture was stirred for 2 hours at 50–60°, washed with dilute, aqueous sodium hydroxide, and distilled. The crude product was redistilled through a spiral wire column, b.p. 81°, $n^{20}$D 1.4000; b.p. 78.5° (750 mm.) and $n^{20}$D 1.4003, have been previously reported.[30]

1-Methoxy-2-propyne was prepared by the method of Heilbron, Jones and Lacey.[31] After distillation through a spinning-band column, the center cut had b.p. 60.5° and $n^{23}$D 1.3950; Heilbron, Jones and Lacey[31] report b.p. 63–64° and $n^{19}$D 1.3975.

Propynal was prepared by the oxidation of propargyl alcohol.[32] It was washed four times with 4 N aqueous sodium hydroxide and redistilled immediately before use.

1,1-Diethoxy-2-propyne.—The diethyl acetal of 2-propynal was prepared from ethyl orthoformate (20 ml.) and the aldehyde itself (9 g.) with anhydrous ethanol (80 ml.) as solvent and 1 drop of sulfuric acid as a catalyst. After neutralization, the solvent was stripped off under vacuum and the product distilled. It was finally redistilled through a spinning-band column to give a center cut with b.p. 60° (40 mm.) and $n^{25}$D 1.4098; b.p. 45.7° (18 mm.) and $n^{25}$D 1.4100 have been previously reported.[33]

Vinylacetylene was prepared by the method of Hennion, Price and McKeon,[34] and was used without further purification.

3-Butyn-1-ol.—2-Butyn-1-ol was prepared by the method of Schulte and Reiss[35] and redistilled through a spiral wire column, b.p. 129°. Vapor-phase chromatography showed a slight contamination with water and no other impurities. Schulte and Reiss[35] report b.p. 127–129°.

1-Phenoxy-2-propyne.—Phenol (39 g.) and sodium hydroxide (16 g.) were dissolved in 60 ml. of alcohol, 130 ml. of ether was added, and the mixture allowed to stand overnight. The precipitate which formed was filtered off and the ether solution washed with aqueous sodium hydroxide and with water. After drying, the ether was stripped off under vacuum and the product distilled through a spiral wire column. It had b.p. 60° (8 mm.), $n^{25}$D 1.5312, $n^{9}$D 1.5383; b.p. 98° (23 mm.), $n^{9}$D 1.5397 have been reported.[36]

Other Materials.—Propargyl chloride, bromide and alcohol were gifts of the General Aniline and Film Corporation, and 2-methyl-3-butyn-2-ol was purchased from Chemical Intermediates and Research. All were redistilled

(28) All b.p.'s are uncorrected.

(29) K. N. Campbell and B. K. Campbell, Org. Syntheses, 30, 72 (1950).

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(34) G. F. Hennion, C. C. Price and T. F. McKeon, Jr., Org. Syntheses, 38, 70 (1958).

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(36) L. Bert and E. Andor, Compt. rend., 194, 886 (1932).

before use and had appropriate physical properties. Pentyne, hexyne, and heptyne were purchased from Farchan Research Laboratories and were used without further purification. Pyridine was reagent grade, purchased from Merck, stored over solid potassium hydroxide and distilled before use. All solutions in pyridine were made up in an atmosphere of $CO_2$-free nitrogen. Carbon tetrachloride was analytical reagent grade, purchased from Mallinckrodt, and used without further purification. Tetramethylsilane was a gift of Minnesota Mining and Manufacturing Co.

N.m.r. spectra were obtained on Varian model 4300B and 4311 high-resolution spectrometers operating at 40.000 and 56.442 megacycles, respectively. Side-band frequencies accurate to ±0.1 c.p.s. were read from a Hewlett–Packard counter. The $\tau$-values in Table I were obtained by interpolation and are reproducible with a precision of ±0.02 p.p.m. Sweep rates were approximately 3 c.p.s. per sec.

Near infrared spectra of phenylacetylene–pyridine–carbon tetrachloride mixtures were obtained on a Beckman DK-2 spectrophotometer equipped with a quartz prism and a germanium filter to remove stray light of higher frequency. The photometric accuracy of this machine was determined by verifying Beer's law with known solutions. It was found to be about ±0.5% at optical densities around 1.0. The resolution and frequency accuracy were studied by examining the spectrum of ammonia vapor in the region around 3300 cm.$^{-1}$. Frequencies of sharp bands were found to be reproducible with a precision of ±1 cm.$^{-1}$; but the resolution, as judged by the height and shape of the bands, was not good.

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# Isomerization of Aldoximes to Amides under Substantially Neutral Conditions[1]

BY LAMAR FIELD, PATRICIA BARNETT HUGHMARK, SUSAN HOLROYD SHUMAKER AND W. STANLEY MARSHALL

Ten aldoximes were isomerized to amides in good yields, according to the equation $RCH{=}NOH \rightarrow RCONH_2$. Reaction was effected by heating the oxime in a solvent with as little as 0.2 mol. % of nickel acetate tetrahydrate as a catalyst. Generality was demonstrated by applying the reaction to a saturated and to an unsaturated acid-sensitive aliphatic oxime and to aromatic aldoximes; the aromatic oximes could contain electron-donating or -withdrawing substituents, even though certain of these were in the *ortho* position and others lend sensitivity toward acidic catalysts. The reaction was unsatisfactory only with 2,4-dihydroxybenzaldoxime and with 9-anthraldoxime (which gave the nitrile). Isomerization of aldoximes with small amounts of nickel acetate thus affords a promising means of characterizing oily oximes and of converting aldehydes to amides, under substantially neutral conditions. Isomerization can be effected also with certain other compounds of metals and with nickel.

While studying the hydrogenation of aldoximes with Raney nickel as catalyst, Paul found that amides were formed.[2] Using several aldoximes, he was able to show that the form ordinarily available could be isomerized effectively to a single amide, with Raney nickel as catalyst, according to the equation $RCH{=}NOH \rightarrow RCONH_2$. Ketoximes did not react. More recently, he isomerized furfuraldoxime also with a nickel–boron catalyst.[3] Amides result in low yield in hydrogenation of certain oximes with reduced copper at 200° but, since ketoximes react, the isomerization probably differs from that of Paul.[4]

Reactions of this type have not attracted the attention they merit from both the standpoint of their theoretical interest and their promise for synthesis and characterization. Only Caldwell and Jones have capitalized on them, in isomerizing some oily unsaturated oximes to solid amides.[5] Our interest was attracted to such reactions because of the obvious applications of this simple means of isomerizing aldoximes to amides under substantially neutral conditions.

In our hands, reaction of benzaldoxime with Raney nickel in a number of experiments gave no worse than fair results and frequently quite good ones. Nevertheless, the number of variables inherent in the heterogeneous bulk reaction of an oxime and a metal clearly will lead to difficulty in obtaining reproducibly good results; some of these variables are suggested parenthetically in the description in the Experimental of a process based on Paul's. Furthermore, often there is some inconvenience in obtaining Raney nickel of standard activity. In an effort to improve the utility of the isomerization, we sought first to determine the most effective catalyst and next to use the most promising in a homogeneous mixture.

A reasonably reproducible procedure was developed for isomerizing benzaldoxime to benzamide with nickel and then was used for evaluating other possible catalysts. Table I shows that several substances effectively catalyze this isomerization. Other substances tried gave only highly colored oils which did not crystallize in 2–3 months. These included ferric chloride and ferric oxide, cobaltous carbonate, anhydrous cobaltous chloride and cupric chloride, silver oxide, yellow mercuric oxide, and iron powder ("by reduction"); cupric acetate monohydrate gave pale blue solid with an m.p. exceeding 235°.

(1) Based on the M.A. Thesis of Patricia Barnett, June, 1956, the M.S. Thesis of Susan Holroyd, June, 1960, and the A.B. Honors Research of W.S.M. We wish to thank Professors D. E. Pearson and M. M. Jones for helpful suggestions.

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