can be related to the substituents interaction with the π system by induction and resonance.[3] Recently this technique has been applied to various phosphorus-containing substituents.[4,5] These studies have included tri- and tetrasubstituted phosphorus compounds. Two pentasubstituted compounds, *m*- and *p*-fluorophenyltetrafluorophosphoranes, were also investigated.

The reaction of trisubstituted phosphorus compounds with diethyl peroxide provides a general route to phosphoranes.[6] This method has now been used to prepare tris-*p*-fluorophenyldiethoxyphosphorane (1) and tris-*m*-fluorophenyldiethoxyphosphorane (2). The quantities

$$\int_{\mathrm{H}}^{m\text{-X}}, \int_{\mathrm{H}}^{p\text{-X}}, \text{ and } \int_{m\text{-X}}^{p\text{-X}}$$

have been determined by recording the ^{19}F nmr spectra of 1 and 2 with fluorobenzene as an external standard. Using these data, σ_I, the inductive parameter, and σ_R, the resonance parameter, have been calculated. The values are +0.147 and +0.059, respectively. Positive values indicate that the substituent, $P(OC_2H_5)_2(C_6H_4F)_2$, is electron withdrawing both by induction and resonance. The magnitude of the parameters is so small that it is clear that the substituent has little effect on the π system. By comparison the substituent, $P(C_6H_4F)_2$ has σ_I +0.26 and σ_R −0.01 and $P(O)(C_6H_4F)_2$ has σ_I +0.45 and σ_R +0.12.[5] These values indicate that both substituents withdraw electrons by induction and the latter has some resonance interaction, although it is not strong. The σ_I value found for PF_4 (0.45) indicates that it is an inductive electron-withdrawing group and is of similar strength to PF_2 (0.39) and PCl_2 (0.44). Interestingly, the σ_R (0.35) for PF_4 was the largest observed in an extensive study of phosphorus-containing substituents. The difference between the pπ–dπ interactions in the two pentasubstituted phosphorus compounds is certainly remarkable and other systems should be studied.

Experimental Section

Preparation of 1 and 2.—The phosphines were prepared from the appropriate Grignard reagent and phosphorus trichloride. Their properties agreed well with those reported in the literature.[5] Tris-*p*-fluorophenylphosphine, 0.195 g (0.000616 mol), in 0.2 ml of methylene chloride in a cooled nmr tube was treated with 0.07 ml of diethyl peroxide. The course of the reaction was followed by ^{31}P and ^{1}H nmr spectroscopy.[7] The +9.2 absorption of the phosphine diminished and new absorptions appeared at +55 (1) and −26 (corresponding to oxide); the ratio was 6:1. Crystallization of 1 occurred and solvent was added to give a homogeneous solution. The ^{1}H nmr spectrum showed a characteristic apparent quintet for the methylene hydrogens of the ethoxy group at 2.58 ($J_{PH} = J_{HH} = 7$ Hz). The methyl protons were found at 0.77 ($J_{HH} = 7$ Hz). The ^{19}F nmr spectrum (94.1 MHz) showed an absorption at −2.18 ppm relative to fluorobenzene as external standard.

Tris-*m*-fluorophenylphosphine, 0.181 g (0.000572 mol), in 0.3 ml of methylene chloride was allowed to react with 0.07 ml of diethyl peroxide. Once again the phosphine absorption, +5, disappeared and that of 2, +55, and its corresponding oxide, +25, formed in a ratio of 5:1. The ^{1}H nmr spectrum had an apparent quintet at 2.63 ($J_{PH} = J_{HH} = 7$ Hz) and a triplet at 0.80 ($J_{HH} = 7$ Hz). The ^{19}F absorption was found at −0.44 ppm relative to external fluorobenzene.

Comparative Nmr Measurements.—In this study fluorobenzene was used as an external standard rather than as an internal standard. The change in means of measuring the chemical shifts does not have an appreciable effect on σ_I and σ_R. It was found, for example, that σ_I for *m*-fluorotriphenylphosphine, *ca.* 1.06 *M* in methylene chloride with fluorobenzene as external standard, was +0.27 (lit.[5] +0.26) and σ_R −0.01 (lit.[5] −0.01).

Registry No.—1, 27531-53-9; 2, 27570-95-2.

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[3] (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963); (b) R. W. Taft, E. Price, J. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

[4] J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *ibid.*, **90**, 5236 (1968).

[5] A. W. Johnson and H. L. Jones, *ibid.*, **90**, 5232 (1968).

[6] (a) D. B. Denney and D. H. Jones, *ibid.*, **91**, 5821 (1969); (b) D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *ibid.*, **91**, 5243 (1969).

[7] All ^{31}P spectra are reported in parts per million relative to 85% phosphoric acid.

Long-Range Effects in the Proton Nuclear Magnetic Resonance Spectra of Allenes

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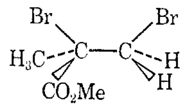
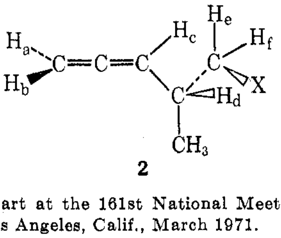
It is well known that the pmr spectrum of an acyclic compound containing both a methylene group and a neighboring asymmetrically (or pseudoasymmetrically) substituted atom can be considerably more complex than would be expected on the basis of simple spin–spin coupling rules. Thus the methylene protons in methyl 2,3-dibromo-2-methylpropionate (1) give rise to an AB



1

pattern, rather than a singlet, because the time-averaged magnetic environments of the two protons differ, and no rotational processes can occur to bring about exchange between these two environments.[2] In this case the methylene protons are said to be diastereotopically related, and as such are, in theory, distinguishable by nmr.

In connection with our study of homoallenic participation,[3] we had occasion to synthesize 2-methyl-3,4-pentadien-1-ol (2a), the derived acetate 2b, and tosylate 2c. The pmr spectra of these compounds[4] are



2

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[1] Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.

[2] K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966. It is important to realize that this effect can be observed whether or not the compound has been optically resolved.

[3] (a) T. L. Jacobs and R. Macomber, *J. Amer. Chem. Soc.*, **91**, 4824 (1969). (b) The solvolytic properties of **2c** have been investigated and are reported separetely, along with synthetic details: R. S. Macomber, *ibid.*, **92**, 7101 (1970).

[4] Spectra were recorded using a Varian A-60 instrument, with samples 15% in carbon tetrachloride containing 1% TMS.

TABLE I

NMR PARAMETERS FOR SIMULATED SPECTRUM OF **2a**[a]

ω_a	ω_b	ω_c	ω_d	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	J_{cd}
281.57	281.57	307.90	134.79	0.0	6.57	3.19	6.57	3.19	6.06

[a] Frequencies in hertz downfield from TMS; coupling constants (absolute values) in hertz.

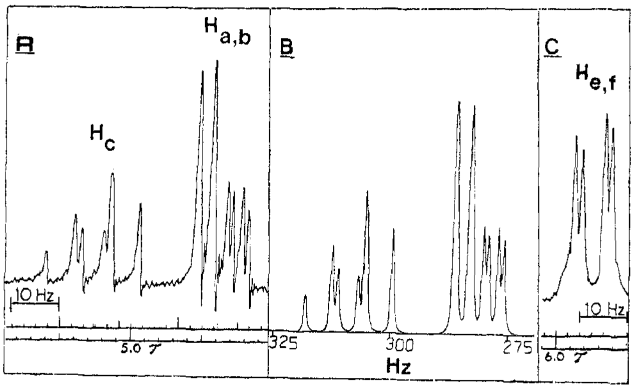

Figure 1.—A, 60-MHz pmr spectrum of the allenic protons in **2a**; B, computer-simulated spectrum of protons in A; C, 60-MHz pmr spectrum of the methylene protons in **2c**.

particularly interesting with respect to long-range proton–proton coupling and the effects of a remote asymmetric center. See Figure 1.

Owing to the asymmetric atom (C_2) in **2**, the methylene protons (H_e and H_f) are diastereotopic, giving rise to two doublets instead of one. The close similarity in chemical shift precludes observation of coupling between H_e and H_f. The two doublets are best resolved in the spectrum of **2c** ($\Delta\delta$ = 1.6 Hz; $|J_{de}| = |J_{df}|$ = 6.5 Hz) shown in Figure 1C.

More interesting, however, were the absorptions due to the allenic protons. All three compounds gave spectra in which the allenic regions were virtually superimposable, except for small differences in chemical shift. A typical spectrum is shown in Figure 1A.[5] The patterns, however, were considerably more complex than would have been anticipated from consideration of the spectra of 2,2-dimethyl-3,4-pentadienol[6] and 3,4-pentadienol,[2] which display typical A_2B and A_2BX_2 patterns, respectively.

The rigid geometry of the allenic system and the presence of the asymmetric atom render H_a and H_b diastereotopic.[5] One possible explanation for the added spectral complexity, then, could be that H_a and H_b were observably magnetically distinct. Such a long-range effect of an asymmetric center is not without precedent. It has been shown[7] that compounds of generic structure **3** give rise to diastereomers where the H* proton resonances are distinguishable.

$$R{-}O{-}CH^*{=}C{=}CHCH(R')OR''$$

3

An alternative explanation for the added complexity is the importance of second-order effects in what can be regarded as an A_2BX system (H_a *not* distinguishable from H_b), where X (H_d) is coupled to both terminal allenic protons with a coupling constant of ~3 Hz.[8] In either of these cases coupling between H_a and H_b should *not* be observable owing to the identity (or close similarity) in chemical shift, although the magnitude of such geminal coupling ranges from 13–15 Hz.[9] Also, it should be realized that the symmetry of the system places H_c on a plane which bisects the asymmetric atom; thus the resonance for H_c must be independent of the configuration about C_2.

That the second explanation in fact accounts for the added complexity was first suggested by decoupling experiments. Both field-swept and frequency-swept decoupling of the complex pattern attributed to H_d caused the collapse of the resonances due to H_a and H_b to a slanting doublet, indicating that coupling between the terminal protons and H_d *was* important. Similarly the multiplet due to H_c collapsed to a slanting triplet, and the methyl and methylene absorptions (not shown in the figures) collapsed to broad singlets.

Final confirmation that the second explanation accounts fully for the observed spectrum was obtained from a computer-simulated spectrum[10] (Figure 1B) using values shown in Table I.

Thus we see no reason to invoke magnetic distinguishability between diastereotopic protons H_a and H_b to explain our observations. The chemical shifts of H_a and H_b can differ no more than 1 Hz. It is interesting to note that H_d has the distinction of being coupled to all eight other protons shown in **2**!

Registry No.—**2a**, 26674-94-2; **2c**, 26674-95-3.

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[5] No absolute selection between H_a and H_b is intended.

[6] R. S. Bly, A. R. Ballentine, and S. U. Knock, *J. Amer. Chem. Soc.*, **89**, 6993 (1967). We wish to thank Professor Bly for copies of the spectra of 2,2-dimethyl-3,4-pentadienol and derivatives.

[7] M. L. Martin, R. Mantione, and G. J. Martin, *Tetrahedron Lett.*, 4809 (1967).

[8] Typical coupling constants are for $H_3CC\mathbf{H}{=}C\mathbf{H}Cl$ J = −5.8 Hz; $\mathbf{H}_3CCH{=}C{=}C\mathbf{H}_2$ J = 3.0 Hz: J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I., Pergamon Press, London, 1967.

[9] M. L. Martin and G. J. Martin, *J. Mol. Spectrosc.*, **34**, 53 (1970).

[10] The program was LAOCOON III (used in the iterative mode) and NMRPLT, a plotting routine.

Reactions of Enamines. XI. The Reaction of Enamines with Cyanoacetic Acid[1]

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In previous papers in this series,[1,2] it was shown that enamines react with trichloroacetic acid (**1**, R = $-CCl_3$)

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[1] Part X: G. H. Alt, *J. Org. Chem.*, **33**, 2858 (1968).

[2] G. H. Alt and A. J. Speziale, *ibid.*, **31**, 1340 (1966).