Long-Range ^{31}P–^{1}H Spin–Spin Couplings in Benzyl and Tolyl Phosphorus Compounds[1]

C. E. Griffin and M. Gordon[2]

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213. *Received April 5, 1967*

Abstract: Examination of the spectra of a series of tolyl- and benzylphosphonium salts, phosphonates, and phosphine oxides shows the existence of two types of long-range ^{31}P–^{1}H spin–spin couplings. Four-bond allylic couplings (1–2.5 Hz) are observed in both series of compounds; the magnitude of $^{4}J_{PH}$ depends upon the position of attachment (sp^2 or sp^3 carbon) of phosphorus to the allylic triad. Both five- and seven-bond homoallylic couplings are observed in the benzylphosphorus systems. The magnitudes of $^{7}J_{PH}$ (2.3–2.6 Hz) are greater than those of $^{5}J_{PH}$ (1.1–1.7 Hz). Neither six-bond couplings in the benzyl series nor five- and six-bond couplings in the tolyl analogs are observed. Both inductive hyperconjugation and overlap hyperconjugation coupling mechanisms are considered for the homoallylic interactions; on the basis of certain consistent patterns of J_{PH} behavior and the study of model compounds, the latter mechanism is favored.

Investigations of the proton magnetic resonance spectra of a variety of types of organophosphorus compounds have shown that allylic (H—C—C═C—P or H—C═C—C—P,[3-5] H—C—C≡C—P or H—C≡C—C—P,[6,7] H—C═C—O—P[8]) and homoallylic (H—C—C═C—C—P,[3] H—C—C═C—O—P[9]) ^{31}P–^{1}H couplings are readily observable and show certain general patterns of behavior. Homoallylic systems are symmetric with respect to the double bond, and only a stereochemical dependence is observed for $^{5}J_{PH}$ in these systems.[3,9] However, the allylic systems are unsymmetrical in that the phosphorus atom may be bonded to either sp^2- (sp) or sp^3-hybridized carbon, and it has been shown that the magnitude of $^{4}J_{PH}$ is dependent upon structure in this respect.[6,10] Thus, in propynyl [$CH_3C{\equiv}CP(O)(OR)_2$] and propargyl [$HC{\equiv}CCH_2P(O)(OR)_2$] phosphonates, $^{4}J_{PH}$ of 4.6 and 6.7 Hz, respectively, are observed.[6] Four-bond allylic (H—C—C═C—P) couplings are also observed in *o*-tolyl(diphenyl)phosphine oxide (**1**) and dimethyl *o*-tolylphosphonate (**4**);[4] in these cases, a portion of the benzene ring provides the necessary allylic π electrons. Similar four-bond ^{1}H–^{1}H couplings between side-chain and ring protons in benzenoid and heteroaromatic systems are commonly observed[11] and corresponding ^{19}F–^{1}H couplings between side-chain protons and ring fluorines have been reported.[12,13] Less commonly, five-, six-, and seven-bond couplings of these types have been observed.[11-15]

The demonstrations of the dependence of the magnitude of the allylic $^{4}J_{PH}$ on structure in the propynyl and propargyl phosphonates and the existence of ^{1}H–^{1}H and ^{19}F–^{1}H couplings over more than four bonds in substituted aromatics indicated that a more extensive study of allylic and longer range ^{31}P–^{1}H couplings in isomeric tolyl ($CH_3C_6H_4P$) and methylbenzyl ($CH_3C_6H_4CH_2P$) phosphorus systems might be fruitful. On the basis of these previous studies, a structural dependence for $^{4}J_{PH}$ in analogous tolyl and benzyl compounds, as well as longer range couplings, might be anticipated.

Accordingly, the spectra of a number of substituted phenyl and benzyl phosphine oxides, phosphonates, phosphonium salts, and phosphates have been examined; the observed four- to seven-bond coupling constants are listed in Table I. Four-bond allylic couplings of 1 and 1.7 Hz were previously reported for the H—C—C═C—P systems of the *o*-tolylphosphorus derivatives **1** and **4**.[4] The isomeric allylic system (H—C═C—C—P) of the benzyl phosphorus structures **11–13**, **15**, and **18–20** exhibits a $^{4}J_{PH}$ of somewhat larger magnitude (2.2–2.5 Hz);[16] the coupling in this instance is between phosphorus and the *ortho* proton. As in the case of the propynyl and propargyl systems,[6] the larger coupling is exhibited by the allylic system in which phosphorus is bonded to sp^3-hybridized carbon.

Examination of model compounds incorporating the analogous five-bond systems $H{-}C{-}\dot{C}\overset{\cdot}{-}\dot{C}\overset{\cdot}{-}\dot{C}{-}P$ and $H{-}\dot{C}\overset{\cdot}{-}\dot{C}\overset{\cdot}{-}\dot{C}{-}C{-}P$ failed to show any evidence for long-range coupling. Thus, the methyl resonances

---

[1] Presented in part at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Symposium on Theoretical and Empirical Aspects of Chemical Shifts and Coupling Constants, Pittsburgh, Pa., March 1, 1965.

[2] National Science Foundation Cooperative Graduate Fellow, 1961–1964.

[3] D. J. Martin, M. Gordon, and C. E. Griffin, *Tetrahedron*, **23**, 1831 (1967).

[4] C. E. Griffin, R. B. Davison, and M. Gordon, *ibid.*, **22**, 561 (1966).

[5] F. A. Cotton and R. A. Schunn, *J. Am. Chem. Soc.*, **85**, 2392 (1963); A. Meisters and J. M. Swan, *Australian J. Chem.*, **18**, 155 (1965); J. R. Little and P. F. Hartman, *J. Am. Chem. Soc.*, **88**, 96 (1966).

[6] M. Gordon and C. E. Griffin, *J. Org. Chem.*, **31**, 333 (1966).

[7] M. P. Simonnin, *J. Organometal. Chem.* (Amsterdam), **5**, 155 (1966); G. M. Bogolyubov and A. A. Petrov, *J. Gen. Chem. USSR*, **35**, 705, 944 (1965); C. Charrier, W. Chodkiewicz, and P. Cadiot, *Bull. Soc. Chim. France*, 1002 (1966).

[8] A. R. Stiles, C. A. Reilly, G. R. Pollard, C. T. Tiesman, L. F. Ward, D. D. Phillips, S. B. Soloway, and R. R. Whetstone, *J. Org. Chem.*, **26**, 3960 (1961).

[9] W. G. Bentrude and E. R. Witt, *J. Am. Chem. Soc.*, **85**, 2522 (1963).

[10] A stereochemical dependence has also been observed in these systems.[8]

[11] For a review of long-range ^{1}H–^{1}H couplings, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[12] A. G. Massey, E. W. Randall, and D. Shaw, *Chem. Ind.* (London), 1244 (1963).

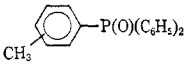
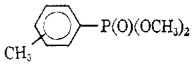
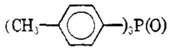
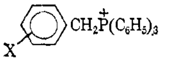
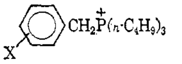
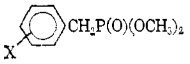
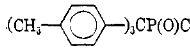
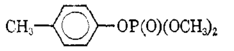
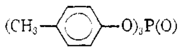
[13] J. Burdon, *Tetrahedron*, **21**, 1101 (1965).

[14] H. Rottendorf and S. Sternhell, *Australian J. Chem.*, **17**, 1315 (1964).

[15] P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *J. Am. Chem. Soc.*, **88**, 2459 (1966).

[16] An analogous coupling (1.0 Hz) in two examples of H—C═C—O—P systems (*p*-sulfonylphenyl phosphate and methyl phosphonate) has been reported recently: J. Herweh, *J. Org. Chem.*, **31**, 2422 (1966).

Table I. Long-Range ^{31}P–^{1}H Couplings in Tolyl and Benzyl Phosphorus Compounds

Compound	Coupling constants[a]				Solvent[b]
	$^4J_{PH}$	$^5J_{PH}$	$^6J_{PH}$	$^7J_{PH}$	
					
1, *ortho*	1.0(CH$_3$)[c]				CDCl$_3$
2, *meta*		–(CH$_3$)			CDCl$_3$
3, *para*			–(CH$_3$)		CDCl$_3$
					
4, *ortho*	1.7(CH$_3$)[c]				CCl$_4$
5, *meta*		–(CH$_3$)			CCl$_4$
6, *para*			–(CH$_3$)		CCl$_4$
7, 			–(CH$_3$)		CDCl$_3$
					
8, X = *o*-CH$_3$		1.1(CH$_3$)			CDCl$_3$
		1.3(CH$_3$)[d]			CDCl$_3$
9, X = *m*-CH$_3$			–(CH$_3$)		CDCl$_3$
			0.5(CH$_3$)[d]		CDCl$_3$
10, X = *p*-CH$_3$				2.5(CH$_3$)	CDCl$_3$
				2.6(CH$_3$)[d]	CDCl$_3$
11, X = *p*-NO$_2$	2.3(*o*-H)				CF$_3$COOH
12, X = *p*-COOCH$_3$	2.3(*o*-H)	–(*m*-H)			CDCl$_3$
13, X = *p*-CH$_3$O	2.5(*o*-H)	–(*m*-H)			CDCl$_3$
					
14, X = *o*-CH$_3$		1.4(CH$_3$)			CDCl$_3$
15, X = *p*-CH$_3$	2.2(*o*-H)	–(*m*-H)		2.3(CH$_3$)	CDCl$_3$
					
16, X = *o*-CH$_3$		1.7(CH$_3$)			CCl$_4$
17, X = *m*-CH$_3$			–(CH$_3$)		CCl$_4$
18, X = *p*-CH$_3$	2.3(*o*-H)	–(*m*-H)		2.3(CH$_3$)	CCl$_4$
19, X = *p*-Br	2.3(*o*-H)	–(*m*-H)			CCl$_4$
20, X = *p*-CH$_3$O	2.4(*o*-H)	–(*m*-H)			CCl$_4$
21, 				2.6(CH$_3$)	CDCl$_3$
22, 				0.6(CH$_3$)	CCl$_4$
23, 				0.9(CH$_3$)	CCl$_4$

[a] Proton involved in coupling indicated in parentheses. [b] No solvent dependencies were observed for long-range J_{PH}. [c] Data taken from ref 4. [d] Data taken from ref 17.

of the *m*-tolyl derivatives **2** and **5** were sharp singlets[4] and the *meta* protons of *para*-substituted benzyl derivatives **11–13**, **15**, and **18–20** showed only the doublet structure expected from the aromatic AB system. However, five-bond homoallylic (H—C—C=C—C—P) couplings are observed in *o*-methylbenzylphosphorus structures (**8**, **14**, and **16**); the nuclear methyl signals in these compounds appear as sharp well-resolved doublets.[17] The magnitudes (1.1–1.7 Hz) of these coupling constants are comparable to those reported by Bentrude and Witt[9] in a $(CH_3)_2C{=}C{-}O{-}P$ system ($^5J_{PH}$ = 1.5, 3.0 Hz), but significantly smaller than have been reported for $(CH_3)_2C{=}CCH_2P$ systems ($^5J_{PH}$ = 4.1–5.8 Hz).[3]

No six-bond (H—C—C=C—C=C—P) interactions were observed in the *p*-tolyl derivatives **3**, **6**, and **7**. Examination of the spectra of the analogous six-bond systems ($\text{H—C—}\dot{\text{C}}\overset{\cdot}{\text{—}}\dot{\text{C}}\overset{\cdot}{\text{—}}\dot{\text{C}}\text{—C—P}$) of the *m*-methylbenzyl derivatives **9** and **17** also showed the absence of detectable long-range couplings. The ring methyl resonances of these compounds were broadened, however, and a $^6J_{PH}$ of 0.5 Hz has been reported by Scott for **9**.[17] It is probable that this value represents an upper limit for coupling in these systems.

---

(17) Since the completion of this study, the observation of five-, six-, and seven-bond couplings in the isomeric methylbenzylphosphonium salts **8–10** has been reported [K. Khaleeluddin and J. M. W. Scott, *Chem. Ind.* (London), 1034 (1966)]. These data are cited in Table I.

Seven-bond homoallylic (H—C—C═C—C═C—C—P) ^{31}P–^{1}H spin–spin interactions were observed in all four *p*-methylbenzyl derivatives (**10**, **15**, **18**, **21**) examined in this study. The methyl protons gave rise to sharp, well-resolved doublets with $^{7}J_{\mathrm{PH}} = 2.3$–2.6 Hz. It should be noted for the two homoallylic systems (*e.g.*, **8** and **10**) that $^{7}J > {}^{5}J$; the reasons for this effect are not apparent, but the lack of attenuation of short-range ^{31}P–^{1}H coupling constants with distance is well established.[18] The substitution of an oxygen atom for the methylene group of this homoallylic system produces an attenuation of the magnitude of $^{7}J_{\mathrm{PH}}$, but the coupling (0.6–0.9 Hz) is readily observable in the *p*-tolyl phosphates **22** and **23**.

No seven-bond interactions have been observed in *p*-anisylphosphorus systems (H—C—O—C═C—C═C—P). In these cases (phosphine, phosphine oxide, phosphine sulfide, phosphonate, phosphonium cation), the methoxyl signal is a sharp singlet.[19,20] This finding is consistent with the observations outlined above, namely a change in the position of attachment of phosphorus in an allylic system from sp^{3}- to sp^{2}-hybridized carbon, and the substitution of oxygen in such a system produces an attenuation of long-range coupling constants. It has also been found that there is no observable coupling between phosphorus and methoxyl protons in *o*- and *m*-anisylphosphonates.[19] The absence of any observable $^{5}J_{\mathrm{PH}}$ or $^{6}J_{\mathrm{PH}}$ is also predictable on the basis cited above. However, the corresponding $^{5}J_{\mathrm{FH}}$ has been observed in *o*-fluoroanisole[13] and *o*-ethyl and *t*-butyl fluorobenzenes[15] and a six-bond ^{19}F–^{1}H coupling has been observed in pentafluorotoluene.[12]

The results cited above for long-range ^{31}P–^{1}H couplings are self-consistent for the aromatic systems and are analogous to the behavior observed in olefinic and acetylenic phosphorus derivatives, confirming the expectations on which this study was based. It might be pointed out that there is essentially no dependence of the magnitudes of the homoallylic J_{PH} on the nature of substitution at phosphorus. For example, the observed $^{7}J_{\mathrm{PH}}$ for phosphonium salts **10** and **15**, phosphonate **18**, and phosphonic dichloride **21** are essentially identical (2.3–2.6 Hz) within the limits of experimental error. This behavior is in sharp contrast to that of geminal and vicinal ^{31}P–^{1}H coupling constants which show a marked dependence on the nature of substitution at phosphorus,[18,21–23] *e.g.*, $^{2}J_{\mathrm{PH}}$ of 13.1, 17.0, and 16.4 Hz are observed for $[\mathrm{CH_3P(C_6H_5)_3}]^{+}$,[22] $\mathrm{CH_3P(O)(OCH_3)_2}$,[23] and $\mathrm{CH_3P(O)Cl_2}$.[21] This insensitivity to substitution is not general, however, for long-range ^{31}P–^{1}H couplings; it has been reported that four- and six-bond couplings in acetylenic phosphorus systems reflect the oxidation state of the phosphorus atom.[7]

The mechanisms involved in long-range spin–spin interactions in proton–proton systems have been reviewed briefly by Sternhell.[11] It is apparent that these effects are transmitted by π electrons, as compared to short-range couplings which involve σ electrons. "Ground-state hyperconjugation" or "σ–π configuration interaction" have been the terms used to describe, among others, allylic and homoallylic couplings. Karplus[24] has used hyperfine splitting constants obtained from radical fragments in a valence bond treatment to predict the signs and magnitudes of these coupling constants. Hyperconjugation, involving delocalization of the electrons forming the carbon–hydrogen bond, is a reasonable mechanism for putting π character into an otherwise sigmoid bond. This argument is valid for the involvement of the terminal methyl groups in the examples cited in this study. In these cases, the methyls are bonded to π systems and "classical" hyperconjugation can put π character into the terminal carbon–carbon bond. This mechanism could also be invoked to put π-electron density into sp^{3} carbon–phosphorus bonds.[25]

Recently, Khaleeluddin and Scott[17,26] have interpreted the long-range couplings in the methylbenzylphosphonium salts **8**–**10** on the basis of an inductive-hyperconjugation model. These investigators indicated that the positive charge induced on the methylene group by the electropositive phosphorus atom could be distributed around the ring and that the methyl groups could then interact with the "positive holes" by hyperconjugation, the interaction decreasing in the order *para* > *ortho* > *meta*, as is observed. This discussion, while providing a mechanism for putting π character into the methyl groups, gives no indication of the mechanism involved in placing the phosphorus atom in the π system. Two inconsistencies can be seen in their argument. If the inductive-hyperconjugation model is important in the methylbenzylphosphorus compounds, it should be even more important in the tolylphosphorus derivatives, in which the phosphorus atom is attached directly to the π system, and parallel behavior should be observed in the long-rang coupling constants of the two systems. Secondly, this model would indicate that the magnitude of the coupling constant should reflect the inductive strength[27] of the phosphorus substituent. The data of Table I are inconsistent with both of these expectations.

The observation of long-range coupling in tris-*p*-tolylmethylphosphonic dichloride (**21**) provides evidence against the importance of hyperconjugation as a mechanism for putting π character into the phosphorus–carbon bond. In this case, the methylene group of the *p*-methylbenzyl system has been replaced by a function (diarylmethylene) incapable of hyperconjugative interaction.

An alternative model for coupling behavior in these systems is suggested by their geometry. Examination of Fisher–Hirshfelder–Taylor models of the benzylphosphorus compounds indicates that the phosphorus atom lies over the inner circumference of the aromatic ring and, thus, over the π orbital.[28] The same rela-

---

(18) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, 20, 449 (1964).

(19) M. Gordon, Ph.D. Thesis, University of Pittsburgh, 1965.

(20) C. E. Griffin, *Tetrahedron*, 20, 2399 (1964).

(21) J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, **22**, 565 (1966).

(22) C. E. Griffin and M. Gordon, *J. Organometal. Chem.* (Amsterdam), **3**, 414 (1965).

(23) G. Mavel and G. Martin, *J. Chim. Phys.*, **59**, 762 (1962).

(24) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(25) A hyperconjugative interaction of this type [$\mathrm{R_3PCHR_2}^{+} \longleftrightarrow \mathrm{R_3P{=}CR_2\ H^{+}}$] has recently been advanced as an explanation for certain anomalies in the ^{31}P chemical shifts of phosphonium salts [S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, 70, 581 (1966)].

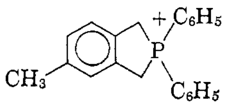
(26) K. Khaleeluddin and J. M. W. Scott, *Chem. Commun.*, 511 (1966).

(27) D. J. Martin and C. E. Griffin, *J. Org. Chem.*, **30**, 4034 (1965).

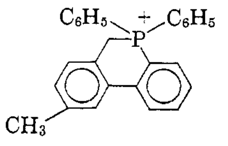
(28) Evidence derived from studies of phosphorus hyperfine coupling constants in nitroaromatic anion radicals also suggests that the pre-

tionship is observed in the allylphosphorus systems and in the aryloxyphosphorus systems. Such a geometric relationship is obviously not possible when the phosphorus atom is directly bonded to the π system. In the benzyl compounds, the phosphorus could be placed in the π system by the formation of a bent σ bond involving the aromatic π system or the π orbital of C_1 of the ring and an empty d orbital of phosphorus.[30] A similar overlap mechanism involving the filled p orbitals of fluorine and the aromatic π system has been postulated by Sheppard to explain the observed chemical and spectral behavior of substituted benzotrifluorides.[31] The differences in long-range J_{PH} behavior in the benzyl and tolyl systems observed in this study are consistent with a mechanism involving an interaction of this type. The overlap mechanism does not, however, explain why the magnitude of $^{7}J_{\mathrm{PH}}$ is greater than that of $^{5}J_{\mathrm{PH}}$ in the *p*- and *o*-methylbenzyl phosphorus compounds.

One necessary consequence of such a mechanism would be a dependence of the long-range J_{PH} on the angle between the carbon–phosphorus bond and the plane of the π-electron system, with J_{PH} reaching a minimum at an angle of 0°. A similar angular dependency has been suggested by Gulick and Geske[29] for phosphorus hyperfine coupling constants (a_{P}) in nitroaromatic anion radicals and Allen and Bond[32] have reported that "large" values of a_{P} in semiquinone phosphate radicals are only observed when bulky groups *ortho* or di-*ortho* to the phosphate group are present. As a test of the postulated angular dependency, the spectra of two *p*-methylbenzylphosphonium salts, **24** and **25**, were examined. In these salts, the inclusion of the phosphorus atom in a cyclic system should result in a constraint of that atom to the approximate plane of the aromatic system.[33] Values of $^{6}J_{\mathrm{PH}}$ of 0.9 and 0.4 Hz were observed for **24** and **25**, respectively; in the analogous noncyclic salts (**10** and **15**), $^{7}J_{\mathrm{PH}}$ = 2.3–2.6 Hz. This decrease in $^{7}J_{\mathrm{PH}}$ is clearly consistent with the proposed angular dependency.



24



25

Although the proposed coupling mechanism is not completely satisfactory, it is felt that the observed results are best explained by such an overlap mechanism coupled with terminal group hyperconjugation.

Experimental Section

Determination of Spectra. Pmr spectra were determined on a Varian Associates Model A-60 spectrometer at 27 or 37° (probe temperature) on 5–10% solutions; no concentrational or temperature dependencies were observed for J_{PH} in these ranges. Chemical shifts are reported on the τ scale from internal tetramethylsilane; these values are the average of at least two spectral determinations and are accurate to at least ±0.015 ppm. The coupling constants were obtained from 50-Hz sweep-width spectra and are the average of at least three runs; the values are accurate to ±0.15 Hz or better. The origin of the reported $^{4-7}J_{\mathrm{PH}}$ for a number of model compounds (**1**, **4**, **8**, **10**, **13**, **15**, **18**, and **21–23**) were confirmed by double-resonance experiments. Irradiation at the resonance frequency (24.3 MHz) of phosphorus with an NMR Specialties Model SD-60 heteronuclear spin decoupler resulted in collapse of all nuclear methyl doublets to singlets.

Preparation of Model Compounds. With the exception of those compounds listed below, the preparation and pmr spectra of the compounds listed in Table I have been described previously.[4,22] Samples of compounds **24** and **25** were provided through the courtesy of Dr. P. Barrington.

Preparation of Benzylphosphonates. The dimethyl benzylphosphonates were prepared by Arbuzov reactions between the appropriate benzyl bromides and excess trimethyl phosphite. The reactants were warmed under nitrogen at 80° until the distillation of methyl bromide ceased. The excess trimethyl phosphite and most of the dimethyl methylphosphonate were removed by distillation to 100° at reduced pressure (water pump); the residue was distilled under vacuum to give some dimethyl methylphosphonate and the desired dimethyl benzylphosphonate, which was obtained as a clear colorless liquid. **Dimethyl *o*-methylbenzylphosphonate (16)** showed the following physical properties: bp 95° (0.2 mm); infrared spectrum: 3058w, 3030w, 2950m, 2849w, 1497w, 1464w, 1412w, 1258s, 1183w, 1059s, 1035s, 869m, and 858w cm^{-1}; pmr spectrum (in τ values): doublet, 7.60 (J_{PH} = 1.7 Hz, (CH_3–C); doublet, 6.90 (J_{PH} = 22.5 Hz, CH_2; doublet, 6.38 (CH_3–O); complex multiplet, 2.72 (aromatic). **Dimethyl *m*-methylbenzylphosphonate (17)** showed bp 104° (0.3 mm); infrared spectrum: 3012w, 2950m, 2907w, 2849w, 1610w, 1490w, 1458m, 1408w, 1255s, 1217w, 1183m, 1062s, 1034s, 919w, 905w, 882w, and 852m cm^{-1}; pmr spectrum (in τ values): singlet, 7.72 (CH_3–C); doublet, 7.02 (J_{PH} = 21.6 Hz, CH_2; doublet, 6.50 (CH_3–O); complex multiplet, 3.03 (aromatic). **Dimethyl *p*-methylbenzylphosphonate (18)** showed bp 111° (0.2 mm), 120° (0.5 mm); infrared spectrum: 2985w, 2950m, 2907w, 2849w, 1511w, 1447w, 1404w, 1255s, 1182m, 1062s, and 860 cm^{-1}; pmr spectrum (in τ values): doublet, 7.53 (J_{PH} = 2.3 Hz, CH_3–C); doublet, 7.03 (J_{PH} = 21.5 Hz, CH_2); doublet, 6.45 (J_{PH} = 10.6 Hz, CH_3–O); broad singlet, 2.95 (aromatic). **Dimethyl *p*-bromobenzylphosphonate (19)** showed bp 146.5–147.5° (0.6 mm), solidifies on standing; infrared spectrum: 2994w, 2959m, 2915vw, 2849w, 1490m, 1408w, 1276m(sh), 1255s, 1181m, 1062s, 1034s, 1014s, and 872s cm^{-1}; pmr spectrum (in τ values): doublet, 7.02 (J_{PH} = 21.8 Hz, CH_2); doublet, 6.41 (J_{PH} = 10.7 Hz, CH_3); doublet of doublets, 2.90 [J_{AB} = 8.6 Hz, J_{AB} = 2.3 Hz (H_{A})]; doublet, 2.60 [J_{AB} = 8.6 Hz (H_{B})].[34] **Dimethyl *p*-methoxybenzylphosphonate (20)** showed bp 175–176° (3.3 mm); infrared spectrum: 2994w, 2933m, 2899w, 2825w, 1613m, 1508m, 1462m, 1443w(sh), 1406w, 1321w, 1300m, 1250s, 1178m, 1127w, 1059s, 1034w, and 860s cm^{-1}; pmr spectrum (in τ values): doublet, 7.03 (J_{PH} = 21.8 Hz, CH_2); doublet, 6.46 (J_{PH} = 10.8 Hz, CH_3–O–P); singlet, 6.27 (CH_3–O–C); doublet, 3.27 [J_{AB} = 8.9 Hz (H_{B})]; doublet of doublets, 2.87 [J_{AB} = 8.9 Hz, J_{PH} = 2.4 (H_{A})].

Tris *p*-tolylmethylphosphonic dichloride (21) was prepared by the general procedure of Boyd and Chignell.[35] Tri-*p*-tolylcarbinol (0.60 g, 2.0 mmoles) was added to a warm solution of phosphorus trichloride (2 ml) in 25 ml of anhydrous benzene. The solution turned yellow immediately, then colorless, and a gas was then evolved. When the evolution of gas ceased, the solvent was removed under reduced pressure to give **21** as a colorless solid, 0.76 g (95%),

---

ferred orientation of the $CH_2P(O)(OR)_2$ group in benzyl phosphonates places the phosphorus atom out of the plane of the aromatic ring.[29]

(29) W. M. Gulick, Jr., and D. H. Geske, *J. Am. Chem. Soc.*, **88**, 2928 (1966).

(30) In the most favorable conformation as shown by Fisher–Hirshfelder–Taylor models, the distance between the phosphorus atom and C_1 as measured using Dreiding models for the bond distances is 2.7 A. This value is significantly smaller than the sum of the van der Waals radius of phosphorus (1.9 A) and the half-thickness of an aromatic ring (1.85 A) [L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260].

(31) W. A. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965).

(32) B. Allen and A. Bond, *J. Phys. Chem.*, **68**, 2439 (1964).

(33) The essential coplanarity of these ring systems is indicated by the observation that the methylene resonances of both **24** and **25** are the expected simple doublets (AX spectrum) resulting solely from coupling with phosphorus. Any significant deviation of the phosphorus atom from coplanarity would be expected to lead to methylene nonequivalence and the observation of an ABX spectrum. This observation is not, however, unequivocal evidence for coplanarity; the AX spectrum could result from a rapid inversion at phosphorus. The occurrence of a rapid inversion would not, however, affect the conclusions drawn from the spectra of **24** and **25** since an average coplanar configuration would be the result of this phenomenon.

(34) H_{A} refers to the aromatic proton *ortho* to the methylene group; H_{B} is *meta* to the methylene group.

(35) D. R. Boyd and G. Chignell, *J. Chem. Soc.*, **123**, 813 (1923).

mp 166–169°; pmr spectrum (in τ values): doublet, 7.65 (J_{PH} = 2.6 Hz, CH_3); complex multiplet, 2.78 (aromatic).

Tri-*p*-tolyl phosphate (23) was a commercial product (Eastman White Label) and was used without further purification; pmr spectrum (in τ values): doublet, 7.70 (J_{PH} = 0.9 Hz, CH_3); singlet, 2.93 (aromatic).

Dimethyl *p*-tolyl phosphate (22) was prepared using the method of Kenner and Williams[36] and obtained as a clear, colorless liquid, bp 121–121.5° (0.9 mm) [lit.[37] bp 114° (0.5 mm), 172.2° (20 mm)]; infrared spectrum: 2994w, 2950m, 2924w, 2857w, 1613w, 1502m, 1451w, 1294s, 1280s, 1220s, 1208m(sh), 1186m, 1167w, 1068s, 1046s, 1020w, 955s, 932m(sh), and 855s cm^{-1}; pmr spectrum (in τ values): doublet, 7.73 (J_{PH} = 0.6 Hz, CH_3–C); doublet, 6.30 (CH_3–O); broad singlet, 3.02 (aromatic).

Acknowledgment. This study was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant No. AF-AFOSR-470-64. Double-resonance studies were carried out with instrumentation provided by a grant (FR 00292) from the Division of Research Facilities and Resources, National Institutes of Health. We are indebted to Drs. A. A. Bothner-By and H. Dreeskamp for helpful discussions and suggestions.

(36) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955).

(37) H. D. Orloff, C. J. Worrel, and F. X. Markley, *J. Am. Chem. Soc.*, **80**, 727 (1958).

Coupling Constants in the Nuclear Magnetic Resonance Spectra of *endo*- and *exo*-Norbornene Derivatives

F. A. L. Anet, H. H. Lee, and J. L. Sudmeier

Contribution No. 2044 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received April 5, 1967*

Abstract: The synthesis of *endo*- and *exo*-2-carbomethoxybicyclo[2.2.1]hept-5-ene-1,4,5,6,7,7-d_6 is described. The proton magnetic resonance spectra, obtained with deuterium decoupling, of the *endo* and *exo* esters gave accurate chemical shifts and coupling constants for the protons in the two compounds. The claim that *endo–endo* vicinal coupling constants are much smaller than *exo–exo* coupling constants is shown to be incorrect. The relative signs of the geminal and the two vicinal coupling constants in the *exo* ester have been established by means of INDOR spectra.

There has been much interest in the factors that determine the values of vicinal coupling constants in ethanic systems.[1,2] The dependence of such coupling constants on dihedral angles is well established,[1-3] and there is also a dependence on substituents[4] and on distortions from the normal tetrahedral angle.[1,2] Rigid molecules are particularly attractive for study because the dihedral angles are fixed and are often accurately known from other evidence.[3b,4a,5-11]

In the norbornane[4a,5-7] and norbornene[10,11] systems, it has been reported that *cis*-vicinal coupling constants between pairs of *endo* protons are appreciably different from the *cis*-vicinal coupling constants between pairs of *exo* protons, even though the dihedral angle (0°) and the substituents are the same for both cases. In derivatives of norbornane, $J_{endo-endo}$ is 1 to 2 cps smaller than $J_{exo-exo}$. Even larger differences have been quoted for norbornene derivatives (Table I).

Table I. Vicinal Coupling Constants (cps) Reported for Norbornene Derivatives

2-Substituent	$J_{endo-endo}$	$J_{exo-exo}$	Ref
exo-OH	5.6		10
endo-OH		8.0	10
exo-CN	4.5		10
endo-CN		9.1	10
exo-COOMe	4.4		10
endo-COOMe		8.8	10
exo-Cl	5.0		11
endo-Cl		8.2	11
exo-Br	8.0		11
endo-Br		8.2	11
exo-OAc	7.0		11
endo-OAc		8.2	11

The spectra of norbornene derivatives, especially of the *exo* isomers, are often complex. In such cases the use of the partial analysis, including decoupling, can lead to errors. We have therefore decided to examine the nmr spectra of some extensively and specifically deuterated norbornene derivatives, where spectral analysis can be carried out completely and unambiguously.

Results and Discussion

Chemical Shifts. The nmr spectra of *endo*- and *exo*-2-carbomethoxybicyclo[2.2.1]hept-5-ene-1,4,5,6,7,7-d_6, with the exception of the methyl bands, are given in Figures 1 and 2. The proton (H_2) on C_2, which bears

---

(1) M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, **1**, 149 (1965).

(2) A. A. Bothner-By, *ibid.*, **1**, 195 (1965).

(3) (a) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963); (b) G. Conroy, *Advan. Org. Chem.*, **2**, 265 (1960).

(4) (a) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); (b) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1964).

(5) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(6) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 516 (1963); **86**, 1171 (1964).

(7) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

(8) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

(9) E. W. C. Wong, and C. C. Lee, *Can. J. Chem.*, 42, 1245 (1964).

(10) J. Paasivirta, *Suomen Kemistilehti*, **38B**, 130 (1965).

(11) J. C. Davis, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965).