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THREE AND FOUR BOND PHOSPHORUS-PROTON COUPLINGS IN ISOMERIC TOLYLPHOSPHONATES AND TOLYLPHOSPHINE OXIDES[1]

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Abstract—The preparation and PMR spectra of the isomeric dimethyl tolylphosphonates and tolyldiphenylphosphine oxides are reported. In the *ortho*-isomers, a four bond coupling (1–1·7 c/s) of the methyl protons with the phosphorus atom was observed; no evidence for a similar five or six bond coupling in the *meta*- and *para*-isomers was obtained. The aromatic proton resonances of dimethyl *para*-tolylphosphonate were analyzed as an ABX system; the proton *ortho* to phosphorus in the corresponding *ortho*-isomer had the peak multiplicity of the A portion of an ABCX spectrum.

LONG-RANGE spin-spin couplings between aromatic and side-chain protons have been observed in a variety of benzenoid and heteroaromatic compounds.[4] This interaction is generally restricted to the four-bond coupling between benzylic and *ortho* protons[4] and is an apparently general phenomenon in methylbenzene systems.[5–8] The magnitudes of these coupling constants are generally small, but readily observable in a number of cases. For example, a four-bond coupling of this type with a magnitude of 0·62 c/s has been observed in mesitylene.[5,8] In some cases, five- and six-bond couplings of similar type have been detected, e.g., couplings of the methyl protons with the *ortho*- (0·63 c/s), *meta*- (0·36 c/s) and *para*- (0·63 c/s) protons have been reported for the isomeric tetrachlorotoluenes.[8] A similar situation apparently prevails in fluorinated compounds; relative to the H^1–H^1 couplings, an enhancement of the magnitude of the F^{19}–H^1 coupling constant is observed. Thus, F^{19}–H^1 coupling constants of 2·5 and 1·5 c/s have been assigned tentatively for interactions involving the *ortho*- and *para*- positions in pentafluorotoluene.[9] Related five-bond F^{19}–H^1 couplings have been reported recently in a variety of *ortho*-fluorinated aromatics possessing an $-X-CH_3$ side-chain, e.g., pentafluoroanisole ($J_{HF} = 1{\cdot}1$ c/s).[10]

In the studies published to date of the PMR spectra of organophosphorus compounds, a number of coupling constant-structure relationships have been observed for

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[1] Phosphonic Acids and Esters XII. For Part XI, see R. B. LaCount and C. E. Griffin, *Tetrahedron Letters* 3071 (1965).

[2] U.S. Public Health Service Predoctoral Fellow, 1962–1965.

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

[4] S. Sternhell, *Rev. Pure Appl. Chem.* **14,** 15 (1964).

[5] R. A. Hoffman, *Mol. Phys.* **1,** 326 (1958).

[6] G. V. D. Tiers, F. A. Bovey and B. L. Shapiro, *J. Chem. Phys.* **37,** 1564 (1962).

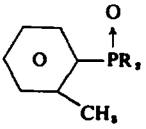
[7] H. Rottendorf and S. Sternhell, *Tetrahedron Letters* 1289 (1963).

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

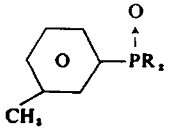
[9] A. G. Massey, E. W. Randall and D. Shaw, *Chem. & Ind.* 1244 (1963).

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

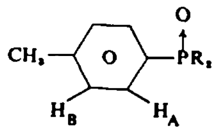
P^{31}–H^1 couplings which parallel those observed for H^1–H^1 couplings.[11–13] The magnitudes of P^{31}–H^1 coupling constants are generally larger than the analogous H^1–H^1 coupling constants. In the light of these findings, it might be anticipated that P^{31}–H^1 interactions comparable to those described above might be observed in phosphorus substituted methylbenzenes. Since the demonstration of such interactions might be of significant value in the determination of structure of organophosphorus compounds, the PMR spectra of a series of isomeric dimethyl tolylphosphonates (I, II and III) and tolyldiphenylphosphine oxides (IV, V and VI) have been examined.



I, $R = OCH_3$
IV, $R = C_6H_5$



II, $R = OCH_3$
V, $R = C_6H_5$



III, $R = OCH_3$
VI, $R = C_6H_5$

The PMR parameters for compounds I–VI are presented in Table 1. The ring methyl signal in the *ortho*-isomers is split cleanly into a doublet by coupling with the phosphorus with $J_{PH} = 1{\cdot}7$ c/s for I and 1 c/s for IV. These couplings are assigned as P^{31}–H^1 rather than H^1–H^1 interactions because of their magnitudes (the maximum values observed for the comparable $^4J_{HH}$ are less than 0·7 c/s) and the lack of comparable splitting in the *meta*- and *para*-isomers. Each of the peaks of the methyl doublets observed for I and IV are relatively broad indicating that a coupling of small magnitude may exist with the proton *ortho* to the methyl group. For the *meta*- (II and V) and the *para*- (III and VI) isomers, only singlets are observed, indicating the lack of appreciable five- and six-bond P^{31}–H^1 couplings. The singlets observed for these compounds are, however, relatively broad (2·5 c/s at half peak height) which probably indicates the existence of either long-range P^{31}–H^1 couplings of small magnitude or four-bond H^1–H^1 couplings to the protons *ortho* to the methyl group.[14] Three other *para*-tolylphosphorus compounds (tris-*p*-tolylphosphine, tris-*p*-tolylphosphine oxide,[12] and tetrakis-*p*-tolylphosphonium chloride) examined in this laboratory also show a similar lack of a six-bond P^{31}–H^1 coupling.

A progressive shielding of the methyl group is observed in both series of compounds, shielding increasing from the *ortho* to *para* isomers. This progression (0·45 ppm for the series I–III) is most probably a reflection of the attenuation with distance of the inductive effect of the phosphono substituent.[11,12] Alternatively, the deshielding of the *ortho*-methyls in I and IV may arise from dispersion effects produced by the proximity of the large phosphono group.

The PMR spectrum of dimethyl p-tolylphosphonate (III) showed, in addition to the ring methyl singlet and ester methyl doublet, an eight line pattern for the aromatic protons which was interpreted as an ABX system ($X = P$).[12] The downfield signal, for the protons (H_A) *ortho* to the phosphono group, appears as a sharp doublet of doublets,

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

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

[13] C. E. Griffin and M. Gordon, *J. Organometal. Chem.* **3**, 414 (1965).

[14] For evidence relevant to the latter point, see the following discussion of the aromatic proton spectra of III.

TABLE 1. PMR SPECTRA OF ISOMERIC TOLYLPHOSPHONATES AND PHOSPHINE OXIDES

Proton	Mult.[a]	τ (ppm)[b]	J_{PH} (c/s)
	Dimethyl o-*tolylphosphonate* (I)[c]		
CH_3–C	2	7·50	1·7[d]
CH_3–O	2	6·36	11·0
Aromatic	c	2·80, 2·20	
	Dimethyl m-*tolylphosphonate* (II)[c]		
CH_3–C	1	7·64	
CH_3–O	2	6·37	11
Aromatic	c	2·70, 2·42	
	Dimethyl p-*tolylphosphonate* (III)[c]		
CH_3–C	1	7·95	
CH_3–O	2	6·36	11
H_B	2 × 2	2·82	4·2[e]
H_A	2 × 2	2·42	12·9[e]
	o-*Tolyldiphenylphosphine oxide* (IV)[f]		
CH_3	2	7·55	1
Aromatic	c	3·08–2·17	
	m-*Tolyldiphenylphosphine oxide* (V)[f]		
CH_3	1	7·64	
Aromatic	c	2·70–2·12	
	p-*Tolyldiphenylphosphine oxide* (VI)[f]		
CH_3	1	7·70	
Aromatic	c	2·92–2·15	

[a] Multiplicity of observed peaks indicated by numbers (c = complex).

[b] Chemical shifts are given as the centres of the observed multiplets or as ranges where no sub-structure is observable for the multiplet.

[c] Spectrum determined in carbon tetrachloride.

[d] The same coupling constant was observed in the spectrum of neat 1.

[e] J_{AB} = 8·3 c/s.

[f] Spectrum determined in $CDCl_3$.

J_{PH_A} = 12·9 c/s, J_{AB} = 8·3 c/s; the upfield signal (H_B) is again a doublet of doublets, J_{PH_B} = 4·2 c/s. The magnitudes of both P^{31}–H^1 coupling constants are larger than those observed in the analogous ABX system of tris-*p*-tolylphosphine oxide for which J_{PH_A} = 11·3 c/s and J_{PH_B} = 3·1 c/s.[12] This enhancement in the magnitude of the P^{31}-H^1 coupling constants on going from the phosphine oxide to the corresponding phosphonate appears to be general for all *para*-substituted arylphosphorus systems. The upfield four line portion (H_B) of the spectrum of III apppears to be further split by the ring methyl protons, each line appearing as a poorly resolved quartet with separations of 0·7 c/s. Thus, it is most probable that the broadness of the ring methyl signals for the *meta*- (II and V) and *para*- (III and V)isomers is due to H^1-H^1 couplings, rather than any long-range P^{31}-H^1 couplings.

The aromatic portion of the spectrum of dimethyl *ortho*-tolylphosphonate (I) is cleanly separated into a one proton signal (τ = 2·20 ppm) for the proton (H_A) *ortho* to the phosphono group and a three proton signal ($\tau = 2{\cdot}80$ ppm) for the protons *meta* (H_B) and *para* (H_C) to the phosphono group and *ortho* (H_D) to the methyl. The deshielding effect exerted by phosphono substituents relative to electron donor substituents has been conclusively established.[11,12] Furthermore, the signal due to H_A is split into an eight line pattern interpretable as the A portion of an ABCX (X = P) spectrum with $J_{PH} = 14{\cdot}7$ c/s, $J_{AB} = 8{\cdot}0$ c/s and $J_{AC} = 2{\cdot}4$ c/s. The shielding effect of the phosphono group is again evident in the aromatic portion of the spectrum of the *meta*-isomer (II) with two multiplets of equal intensity being observed at $\tau = 2{\cdot}42$ and 2·70 ppm. The lower field signal is presumably due to the protons *ortho* to the phosphono group. However, in this case, the spectrum was not amenable to ready interpretation. For the phosphine oxides (IV–VI), no aromatic proton assignments are possible since the signals due to the mono-substituted phenyl rings obscure any observable features of the spectrum of tolyl aromatic protons.

The preparation of the tolylphosphonates and phosphine oxides was achieved by established procedures. Photolysis of the appropriate iodotoluene in trimethyl phosphite resulted in the formation of I, II and III in acceptable yields. In the original report of the photolytic formation of arylphosphonates,[15] 1:1 molar ratios of trialkyl phosphite to aryl iodide were employed; 6:1 molar ratios were employed in the present study and significantly higher yields of product resulted.[16] The phosphine oxides IV, V and VI were obtained by hydrogen peroxide oxidation of the corresponding phosphines prepared by the reaction of the appropriate tolylmagnesium halide with chlorodiphenylphosphine;[17] the phosphines were not purified prior to oxidation. All of these compounds had satisfactorily analyses and their infrared and PMR spectra were consistent in all respects with their postulated structures. Compounds V and VI had been previously prepared by the alkaline cleavage of the corresponding tolyltriphenylphosphonium halides.[18]

This study provides additional evidence for the parallelism between P^{31}–H^1 and H^1–H^1 coupling phenomena through the demonstration of a four-bond P^{31}–H^1 coupling in tolylphosphorus systems and for the utilization of PMR spectroscopy for the determination of the structures of arylphosphorus compounds. Further studies of other long-range P^{31}–H^1 couplings are in progress.

EXPERIMENTAL[19]

Preparation of dimethyl tolylphosphonates. A solution of 13·1 g (0·06 mole) of the appropriate iodotoluene and 37·2 g (0·30 mole) trimethyl phosphite was placed in a double walled quartz reaction vessel. A condenser fitted with a $CaCl_2$ drying tube was placed on the inner vessel containing the reaction mixture; the reaction mixture was purged with N_2 and stirred continuously with a magnetic stirrer. The reaction temp was maintained at 25° by passing a stream of water through the outer jacket of the reaction vessel. The reaction mixture was irradiated for 31·5 hr with a 450 watt Hanovia quartz lamp used as an external source. The reaction mixture was distilled without prior treatment

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[15] J. B. Plumb and C. E. Griffin, *J. Org. Chem.* **27**, 4711 (1962).

[16] In this reaction, the Arbuzov rearrangement of the trialkyl phosphite to the corresponding dialkyl [redacted]

[17] K. D. Berlin and G. B. Butler, *Chem. Revs.* **60**, 243 (1960).

[18] L. Horner, H. Hoffman, H. G. Wippel and G. Hassel, *Chem. Ber.* **91**, 52 (1958).

[19] IR spectra were determined on a Beckman IR-8 spectrophotometer. Microanalyses were performed by Galbraith Microanalytical Laboratories. M.ps are uncorrected.

to yield a low boiling fraction [48–100° (1 mm)] consisting of unreacted trimethyl phosphite and dimethyl methylphosphonate; the product distilled above this range.

Dimethyl o-*tolylphosphonate* (I). Obtained in 73% yield; b.p. 107–110·5° (1 mm). (Found: C, 53·71, 53·65; H, 6·70, 6·74; P, 15·30, 15·42. Calc. for $C_9H_{13}O_3P$: C, 54·00; H, 6·55; P, 15·47%.)

IR spectrum (film): 2967 m, 2865 w, 1587 m, 1453 m, 1250 vs, 1185 m, 1148 m, 1089 m, 1022 vs, 826 s, 816 s, 758 s, 718 m and 681 m cm^{-1}.

Dimethyl m-*tolylphosphonate* (II). Obtained in 22% yield;[20] b.p. 141° (4 mm). (Found: C, 54·07; H, 6·63; P, 15·61. Calc. for $C_9H_{13}O_3P$: C, 54·00; H, 6·55; P, 15·47%.)

IR spectrum (film): 2967 m, 2857 w, 1603 w, 1582 w, 1453 m, 1258 vs, 1227 m, 1188 m, 1125 s, 1052 vs, 1026 vs, 877 m, 826 s, 769 s and 697 s cm^{-1}.

Dimethyl p-*tolylphosphonate* (III). Obtained in 78·5% yield; b.p. 106·0–106·5° (1 mm). (Found: C, 54·21; H, 6·50; P, 15·69. Calc. for $C_9H_{13}O_3P$: C, 54·00; H, 6·55; P, 15·47%.)

IR spectrum (film): 2959 s, 2857 m, 1608 m, 1456 m, 1404 w, 1250 vs, 1217 w, 1185 s, 1133 s, 1053 vs, 1027 vs, 911 w, 809 s, 796 s, 712 w and 694 s cm^{-1}.

Preparation of tolyldiphenylphosphine oxides. A solution of Grignard reagent was prepared from 126 g (1·0 mole) of the appropriate chlorotoluene and 24·3 g Mg in 250 ml anhydrous tetrahydrofuran by initiation with 4 ml EtBr. The Grignard solution was cooled to 0° in an ice bath and a solution of 220·6 g (1·0 mole) chlorodiphenylphosphine in 100 ml anhydrous tetrahydrofuran was added slowly with stirring. The reaction mixture was allowed to come to room temp and was refluxed for 1·5 hr. After cooling to room temp, the reaction mixture was poured into a mixture of 85 ml conc. HCl and 500 g ice. The organic layer was separated and the aqueous layer was washed with two 200 ml portions ether. The tetrahydrofuran solution and the ethereal extracts were combined, washed with 10% $NaHCO_3$aq and reduced in volume to give the crude phosphine. This material was suspended in 2 vols acetone and 10% H_2O_2 (1 equiv.) was added slowly. The *ortho*-isomer (IV) precipitated from solution during the oxidation reaction and, after cooling overnight, was collected by filtration and washed with water. The *meta*- (V) and *para*- (VI) isomers failed to crystallize from the oxidation reaction medium; in these cases, the crude product obtained by evaporation of solvent was distilled and the material distilling at 260° (2 mm) crystallized. All three phosphine oxides were recrystallized from acetone-Skellysolve B (60–70°) to give samples of analytical purity.

o-*Tolyldiphenylphosphine oxide* (IV). Obtained in 63% yield; m.p. 122–123°. (Found: C, 78·14; H, 5·99; P, 10·78. Calc. for $C_{19}H_{17}OP$: C, 78·07; H, 5·86; P, 10·60%.)

IR spectrum ($CHCl_3$ solution): 3077 m, 2994 s, 1592 m, 1486 w, 1471 w, 1435 m, 1383 w, 1312 w, 1282 w, 1174 s, 1126 s, 1120 s, 1107 s, 1071 m, 1028 w, 998 w, 693 s and 660 m cm^{-1}.

m-*Tolyldiphenylphosphine oxide* (V). Obtained in 61% yield; m.p. 124–125° (lit. m.p. 123–125°[18]). (Found: C, 77·91, 77·83; H, 5·70, 5·71; P, 10·69, 10·77. Calc. for $C_{19}H_{17}OP$: C, 78·07; H, 5·86; P, 10·60%.)

IR spectrum ($CHCl_3$ solution): 3086 w, 2994 s, 1597 w, 1490 w, 1443 m, 1171 s, 1121 s, 1088 w, 1072 w, 1030 w, 999 w, 867 w and 664 s cm^{-1}.

p-*Tolyldiphenylphosphine oxide* (VI). Obtained in 55% yield; m.p. 131·5–132·4° (lit. m.p. 129–130°[18]). (Found: C, 77·79, 77·84; H, 6·03, 6·11; P, 10·87. Calc. for $C_{19}H_{17}OP$: C, 78·07; H, 5·86; P, 10·60%.)

IR spectrum ($CHCl_3$ solution): 3058 w, 2985 s, 1608 m, 1486 w, 1437 m, 1399 w, 1310 w, 1248 w, 1174 s, 1119 s, 1093 m, 1071 w, 1028 w, 1018 w, 999 w, 807 m, 691 s, 661 m and 633 s cm^{-1}.

Determination of PMR spectra. Spectra were determined at 27° or 37° (probe temp) using a Varian Associates Model A-60 spectrometer. The chemical shifts, determined from a 500 c/s sweep width spectrum, are reported on the τ-scale with reference to internal tetramethylsilane (τ = 10·00 ppm). Coupling constant data were obtained from the average of at least 3 runs at a spectrum width of 50 c/s. The estimated probable errors for chemical shift and coupling constant data are 0·015 ppm and 0·15 c/s, respectively, although the average deviations are much smaller.

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. We are indebted to the Stauffer Chemical Company for the provision of generous samples of starting materials.

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[20] The corresponding diethyl ester has been prepared in ca. 70% yield by the same procedure (C. E. Griffin and R. Obrycki, unpublished results).