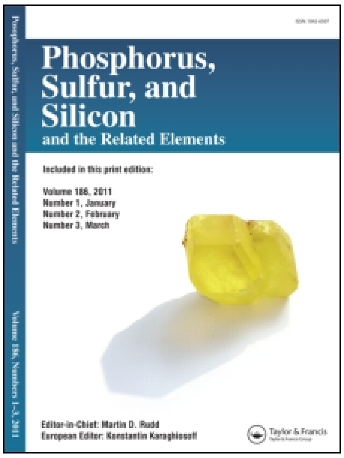

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UNUSUAL DOWNFIELD DEUTERIUM ISOTOPE SHIFT EFFECT ON THE ^{31}P CHEMICAL SHIFTS OF DIALKYL BENZYLPHOSPHONATES

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SHORT COMMUNICATION

UNUSUAL DOWNFIELD DEUTERIUM ISOTOPE SHIFT EFFECT ON THE ^{31}P CHEMICAL SHIFTS OF DIALKYL BENZYLPHOSPHONATES

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A surprising linear *downfield* effect on the ^{31}P chemical shift of a benzylphosphonate of deuterium substitution on the benzyl carbon has been noted. Its potential usefulness in mechanistic studies is suggested.

Key Words Benzylphosphonate ^{31}P NMR P–^{2}H coupling constant Isotope shift

Shielding effects of deuterium substitution chemical shifts have been widely reported.[1,2] However, deshielding isotopic substitution phenomena are much more rare, especially in ^{31}P NMR.[2] More specifically, to our knowledge the only example of such a phenomenon resulting from deuterium β to phosphorus is that reported[3] for glucose-6-phosphate on the replacement by deuterium of the acidic hydrogens of the phosphate group ($\Delta\delta = -0.12$ ppm at pH = 3). A likely explanation[2] in this case is the effect of isotopic substitution on the equilibrium constant for ionization of the phosphate group, which would in itself cause a downfield chemical shift.

We report here the unambiguous, linear *downfield* effect on the ^{31}P chemical shift of successively replacing the benzyl hydrogens of dialkyl benzylphosphonate. The isotope shift and $^{2}J_{HP}$ values for the benzyl hydrogens are recorded in Table I. Typical ^{31}P NMR spectra taken at 121.4 MHz are shown in Figure 1 in which the isotope shift and multiplets resulting from phosphorus deuterium couplings are clearly evident. Examples of the normal *upfield* shift effect of deuterium substitution are the *one-bond* secondary isotope effect seen for $(CH_3O)_2P(O)D$ ($\Delta\delta = +0.33$ ppm[4]) and the non-linear effect of successive deuterium substitution for the series PH_3/PH_2D ($\Delta\delta = +0.804$), PH_2D/PHD_2 ($\Delta\delta = +0.845$), PHD_2/PD_3 ($\Delta\delta = +0.888$).[5]

The data of the Table show the *two-bond* secondary isotope effect on δ ^{31}P to be linear, i.e. 0.041–0.043 ppm (5.0–5.2 Hz at 121.4 MHz) per deuterium. The observed $^{2}J_{PD}$ on dueterium substitution is lower in each case than the predicted coupling based on $^{2}J_{PH} \cdot \gamma_D/\gamma_H$. This constitutes a negative primary isotope effect on coupling as also was observed for $^{1}J_{PH}$ of tetracovalent phosphorus compounds, e.g. $(CH_3O)_2P(O)H$ vs. $(CH_3O)_2P(O)D$, and stands in contrast to the

TABLE I

Deuterium isotope effects on the ^{31}P chemical shifts and coupling constants

No.	Compounds	Isotope Shifts $\Delta\delta$ ppm (Hz)	$^2J_{PH}$[a]	$^2J_{PD}$[b]	$^2J^*_{PD}$[c]
1	$(CH_3O)_2(PhCH_2)P{=}O$		21.7		
1D	$(CH_3O)_2(PhCHD)P{=}O$	0.041 (5.0)	21.6	3.1	3.3
$1D_2$	$(CH_3O)_2(PhCD_2)P{=}O$	0.083 (10.1)		3.0	3.3
2	$(EtO)_2(PhCH_2)P{=}O$		21.6		
2D	$(EtO)_2(PhCHD)P{=}O$	0.043 (5.2)	21.6	2.9	3.3
$2D_2$	$(EtO)_2(PhCD_2)P{=}O$	0.085 (10.3)		2.8	3.3

[a] From 300 MHz ^1H NMR.

[b] From 121.4 MHz $^{31}P\{^1H\}$ NMR.

[c] $^2J^*_{PD} = \frac{\gamma_D}{\gamma_H} \cdot {}^2J_{PH}$.

positive primary isotope effects found for tricovalent phosphorus, e.g. PH_3 vs. PH_2D.[5] On the other hand comparison of compound 1 vs. 1D or 2 vs. 2D reveals no effect of deuterium substitution on directly measured $^2J_{PH}$. Such secondary isotopic coupling effects may be beyond the precision of the measured couplings (±0.16 Hz).

The downfield ^{31}P shift effects reported here should be useful in mechanistic studies utilizing deuterium label. Indeed, we have found the combination of

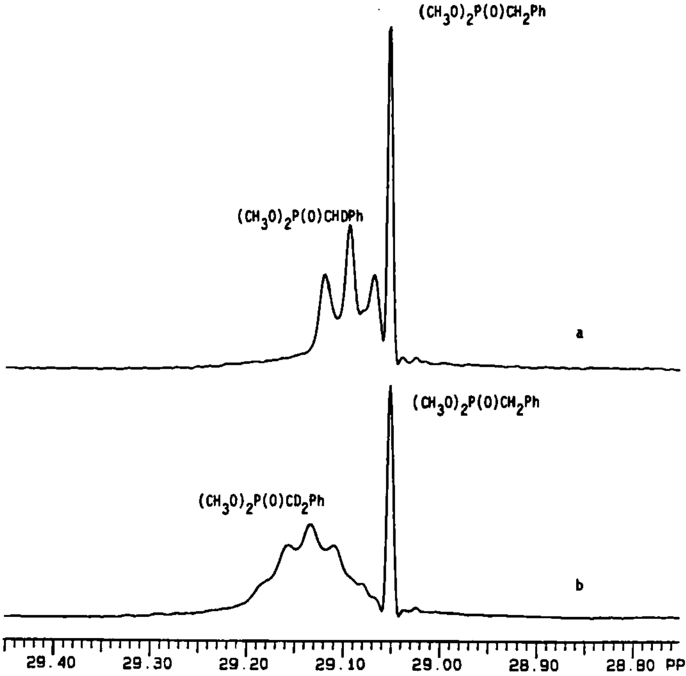
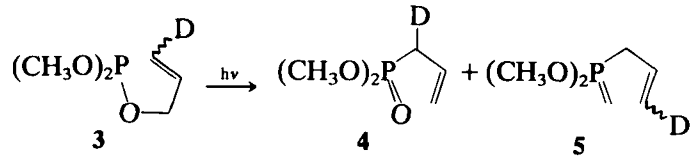


FIGURE 1 The $^{31}P\{^1H\}$ NMR spectrum (at 121.4 MHz) of (a) a mixture of 1 + 1D and (b) of 1 + $1D_2$. For illustrative purpose, resolution enhancement was carried out on the spectra using Lorentz-Gauss multiplication of the FID prior to Fourier transformation.

deuterium splittings and ^{31}P chemical shift differences diagnostic of the regiochemistry of the photorearrangement:



Allyl phosphite **3** rearranges regiospecifically to **4** when **3** is irradiated in benzene through quartz, a condition of presumed triplet sensitization. However, irradiation in cyclohexane yields both **4** and **5**. Under the sensitized conditions, the downfield, triplet splitting of the ^{31}P resonance by deuterium expected of **4** was noted. The mixture of **4** and **5** from direct irradiation of **3** displayed a large enhancement of the most upfield triplet peak as a result of overlap with the ^{31}P singlet of **5** ($\Delta\delta = 0.024$ ppm for **4** vs. **5**, 2.9 Hz at 121.4 MHz). More precise measurements of the **4**/**5** ratio were obtained from ^{2}H NMR spectra.[6]

The ^{31}P isotope shift approach thus appears to be quite complementary to ^{2}H NMR spectroscopy and especially valuable where ^{2}H NMR probes are not available. The unusual downfield direction of the two-bond secondary deuterium isotopes chemical shift should be of considerable interest to investigators concerned with the theory of chemical shift effects.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 98 spectrometer. Boiling points are uncorrected. NMR spectra were recorded on Varian XL-300 spectrometers at 121.4 (^{31}P) 75.4 (^{13}C) and 46.1 (^{2}H) MHz. Chemical shifts were reported relative to internal TMS for ^{1}H and ^{13}C NMR and 85% H_3PO_4 as external standard for ^{31}P NMR spectra. Positive shifts are downfield of standard. The computer digital resolutions of ^{1}H and ^{31}P spectra were 0.20 and 0.16 Hz, respectively.

Phosphonates (1, 1D, 1D$_2$, 2, 2D, 2D$_2$). All the phosphonates were prepared by the following general procedure.[7] The reaction scale ranged from 0.005 to 0.1 moles and yields were from 30 to 70%. An equimolar mixture of alkyl chloride and trialkyl phosphite was placed in a 25 mL round bottom flask. This mixture was refluxed for 17 h under Argon atmosphere. The product was fractionally distilled under reduced pressure. 1: 56%; b.p. 85–87°C (0.1 mm Hg); ^{1}H NMR ($CDCl_3$) δ 7.2–7.3 (5 H, aromatic), 3.16 (d, 2 H, CH_2, $J_{PH} = 21.7$ Hz), 3.65 (d, 6 H, CH_3O, $J_{PH} = 11.3$ Hz); ^{31}P NMR ($CDCl_3$) δ 29.05. 1D; 30%; b.p. 91–93°C (0.12 mm Hg); ^{1}H NMR ($CDCl_3$) δ 7.2–7.3 (5 H, aromatic), 3.14 (d, CHD, $J_{PH} = 21.6$ Hz), 3.65 and 3.64 (d, 3 H CH_3O, $J_{PH} = 10.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 32.49 (dt, CHD, $J_{PC} = 137.7$ Hz, $J_{C-D} = 19.6$ Hz). 1D$_2$: 43%; b.p. 92–94°C (0.12 mm Hg); ^{1}H NMR ($CDCl_3$) δ 7.2–7.3 (5 H, aromatic), 3.64 (d, 3 H, CH_3, $J_{PH} = 11.07$ Hz); ^{13}C NMR ($CDCl_3$) δ 32.24 (dq, CD_2, $J_{P-C} = 137.4$ Hz, $J_{C-D} = 19.2$ Hz). 2: 71%; b.p. 91–92°C (0.1 mm Hg); ^{1}H NMR ($CDCl_3$) δ 7.2–7.3 (5 H, aromatic), 3.15 (d, 2 H, CH_2, $J_{PH} = 21.6$ Hz), 4.00 (m, 4 H, CH_2O), 1.23 (t, 6 H, CH_3); ^{31}P NMR ($CDCl_3$) δ 26.66. 2D: 60%; b.p. 94–96°C (0.12 mm Hg); ^{1}H NMR ($CDCl_3$) δ 7.2–7.3 (5 H, aromatic), 3.13 (d, 1 H, CHD, $J_{PH} = 21.6$ Hz), 3.95–4.05 (m, 4 H, CH_2O), 1.19–1.25 (m, 6 H, CH_3). 2D$_2$: 56%; b.p. 95–97°C (0.12 mm Hg); ^{1}H NMR ($CDCl_3$) δ 7.2–7.3 (5 H, aromatic), 3.99 (m, 4 H, CH_2O), 1.23 (t, 6 H, CH_3).

α-D-Benzyl Alcohol and α-D-Benzyl Chloride. The alcohol was prepared from benzaldehyde and $LiAlD_4$ by the literature procedure.[8] IR (neat) 3300 cm^{-1} (vs, OH stretch), 2160, 2120 (w, CD stretch). This crude alcohol was used to prepare the α-D-benzyl chloride without further purification. The alcohol (10.8 g, 0.10 mol) and pyridine (7.9 g. 0.10 mol) were dissolved in 150 ml of ether. To this solution, which was cooled with an ice-bath, 11.9 g (0.10 mol) of thionyl chloride was added dropwise. The reaction mixture was stirred for 3 h. $CaCl_2$ was added followed by stirring for another 30 min and

filtration. The product was fractionally distilled under reduced pressure. Yield 24%; b.p. 86–87°C (27 mm Hg); IR (neat) 2200 cm^{-1} (w, CD stretch); ^{1}H NMR ($CDCl_3$) δ 7.42 (aromatic), 4.62 (CHD).

α,α-D_2-Benzyl Alcohol and α,α-D_2-Benzyl Chloride. This alcohol was prepared from ethyl benzoate and $LiAlD_4$ by the literature procedure.[8] IR (neat) 3300 cm^{-1} (vs, OH stretch), 2180, 2120, 2080 cm^{-1} (m, CD stretch). Crude alcohol was used without purification to prepare α,α-D_2-benzyl chloride according to the above procedure for α-D-benzyl chloride. Yield 34%; b.p. 88–89°C (27 mm Hg); IR (neat) 2160 cm^{-1} (w, CD stretch); ^{1}H NMR ($CDCl_3$) δ 7.36 (aromatic).

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