

Downfield ^{31}P Three Bonds Deuterium Isotope Shift in Dialkyl Phosphonate

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While the isotope shielding effects on chemical shifts in NMR spectroscopy have been widely observed,^{1,2} the downfield isotope shifts is rarely reported, especially in ^{31}P NMR.^{2,3} With this known shielding effect, the resonance of the molecule enriched with isotope is frequently assigned to the high field peak without suspicion.⁴ Recently, through the introduction of the new generation in high-field superconducting magnet, the measurement of isotope effects transmitted through several bonds can be now greatly facilitated and new experimental information becomes of a potential use for spectral assignments, structure determinations, and related investigations.^{4,6} Additional experimental results bearing on these parameters are, therefore, of interest.

The intrinsic shielding isotope effect is fitted well on the one-bond, $^1\Delta\text{P}(\text{D})$, phosphorus chemical shifts.⁷ The two-bond, $^2\Delta\text{P}(\text{D})$, effect showed, however, unusual downfield phenomenon. More specifically, the only unambiguous example of such a phenomenon is that reported for dialkyl benzylphosphonate on the replacement by deuterium of the ben-

Table 1. Deuterium Isotope Effects of the ^{31}P Chemical Shifts and Coupling Constants

No.	Compounds	Isotope shifts ppm(Hz)	$^2J_{\text{PH}}^{\text{a}}$	$^3J_{\text{PH}}^{\text{a}}$	$^2J_{\text{PD}}^{\text{b}}$	$^3J_{\text{PD}}^{\text{b}}$	$^*J_{\text{PD}}^{\text{b}}$
1	$(\text{EtO})_2(\text{PhCH}_2\text{CH}_2)\text{P}=\text{O}$		17.8	10.1			
2	$(\text{EtO})_2(\text{PhCH}_2\text{CD}_2)\text{P}=\text{O}$	0.0988(12.0)		10.1	2.5		2.7
3	$(\text{EtO})_2(\text{PhCD}_2\text{CH}_2)\text{P}=\text{O}$	0.0448(5.4)	17.8			1.3	1.6

^aFrom 300.13 MHz ^1H NMR. ^bFrom 121.49 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR.

$$^*J_{\text{PD}} = \frac{\gamma_{\text{D}}}{\gamma_{\text{H}}} J_{\text{PH}}$$

zylic hydrogen.⁸ In this communication we now report what appears to be the first instance of the three-bond, $^3\Delta\text{P}(\text{D})$, deuterium effect of a ^{31}P chemical shift.

The compounds studied were synthesized from the corresponding chlorides and trialkyl phosphite by the Arbuzov rearrangement.⁹ The α,α -dideuterated chloride was made from the thionyl chloride and the corresponding alcohol which was prepared from the phenylacetic acid by the LiAlD_4 reduction. The β,β -dideuterated alcohol was made from the LiAlH_4 reduction of α,α -dideuterated phenylacetic acid which was prepared by the deuterium exchange of phenylacetic acid in deuterium oxide solution in the presence of sodium methoxide.¹⁰

The proton-decoupled ^{31}P NMR spectra obtained on a Bruker AM-300 spectrometer at 121.49 MHz are shown in the Figure 1. Each α - and β -dideuterated phosphonate gave the quintet absorptions, respectively, expected from the deuterium coupling. Added undeuterated phosphonate produced an upfield singlet. The observed J_{PD} on deuterium substitution is smaller in each case than the calculated constants based on $J_{\text{PH}} \cdot \gamma_{\text{D}}/\gamma_{\text{H}}$ (see Table 1).

This negative primary isotope effect on the spin-spin coupling constants is consistent with those for other phosphorus compounds.^{7,8,11} Regarding the isotope effect, the most important finding is the downfield shifts of three-bond deuterium effect on a ^{31}P chemical shift. The downfield two-bond shift observed here is in good agreement with our previous results.⁸ Even without detailed experimental results, this unusual behavior of two-bond shift could be rationalized by the bigger isotope effect of hyperconjugation than that of through bond.

This hyperconjugation effect was observed in ^{13}C NMR of carbocations, acetone, and toluene.^{2,12} The majority three-bond ^{13}C NMR shifts reported were high field shifts except for a few observations made for cyclohydrocarbons and hydroxy groups where hydrogen bonding is involved.^{2,13} The three-bond ^{31}P down field shift observed in this experiment is, therefore, very unusual. In our opinion it seems clear that this effect should be of interest to theoretical chemist and will enhance the range of application on the phosphorus che-

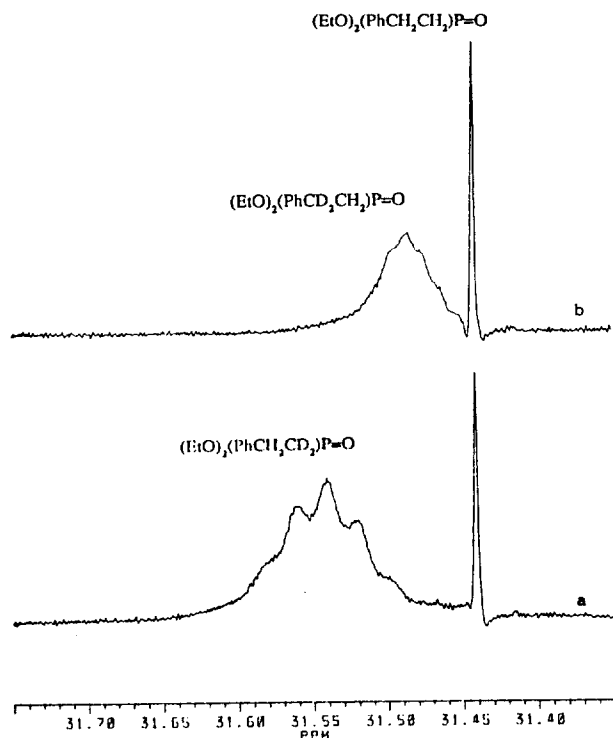


Figure 1. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (at 121.49 MHz) of (a) a mixture of 1 + 2 and (b) of 1 + 3. The computer digital resolution was 0.14 Hz. Resolution enhancement was carried out on the spectra using Lorentz-Gauss multiplication of the FID prior to the Fourier transformation.

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Synthetic Studies on the Sesquiterpenoids in Nature: ar-Turmerone, α -Curcumene, Nuciferal

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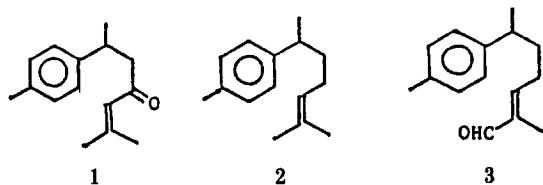
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ar-Turmerone(1), α -curcumene(2), and nuciferal(3) are structurally related aromatic sesquiterpenic compounds in nature. The ketonic sesquiterpene 1 was obtained as the chief component of the essential oil of turmeric^{1,2}, and the sesquiterpenic hydrocarbon 2 was first detected as a constituent of the essential oil from the rhizomes of *Curcuma aromatica* Salisb by Simonsen *et al.*³ The aldehydic sesquiterpene 3 was separated as a constituent of the volatile oil from the wood *Torreya Nucifera*⁴, and the structure bears a resemblance to that of sinenals⁵ which has to do with the orange flavors.

In previous papers, a number of syntheses of 1⁶⁻¹³, 2¹⁴⁻¹⁶, and 3¹⁷⁻²³ have been reported independently. In the present work, we have been interested in convenient syntheses of these three terpenoids in a synthetic procedure; the synthesis of 1, the conversion of 1 into 2, and then into 3 successively.



The α,β -unsaturated ketone 1 was synthesized by modifying the Garcia-Maldonado's procedure⁸, as shown in Scheme 1: A freshly prepared *n*-butyllithium, obtained by the reaction of lithium shavings (2.3 g, 320 mmol) with *n*-butyl bromide (22 g, 160 mmol) in anhydrous ether (85 ml) under nitrogen, was added at 0 °C to a solution of diisopropyl-

amine (12 g, 120 mmol) in tetrahydrofuran (120 ml) to give lithium diisopropylamide(LDA). To this solution, cooled to -78 °C, was added dropwise with stirring a solution of mesityl oxide (4, 10.8g, 110 mmol) in tetrahydrofuran (30 ml) to give a kinetically controlled enolate ion 5, followed by the addition of a solution of *p*-tolualdehyde (6, 12.0g, 100 mmol). The hydrolytic work-up and chromatography afforded a ketonic alcohol 7 in 75% yield, which showed IR(neat) bands at 3450 (OH), 1680(C = O), 1620(C = C), 1515(arom. C = C), 1450, and 820 cm⁻¹, and ¹H-NMR(CDCl₃) signals at δ 7.2(s, 4H_{arom}), 6.05(m, 1H, vinylic), 5.1(m, 1H, ArCH), 3.7(d, 1H, OH), 2.8(d, 2H, O = CCH₂), 2.3(s, 3H, ArCH₃), 2.15(s, 3H, *cis* allylic CH₃), 1.85(s, 3H *trans* allylic CH₃).

The dehydration of the ketonic alcohol 7 was carried out by refluxing it with *p*-toluenesulfonic acid in benzene in a flask fitted with a Dean-Stark trap for 2 hr, to give 85% yield of a dienone 8, yellow needles (m.p. 77-78 °C), which showed IR(KBr) bands at 1680(w), 1655(w), 1640(C = O), 1600(arom. C = C), 1510, 810 cm⁻¹, and ¹H-NMR(CDCl₃) signals at δ 7.5 (d, 1H, CH = C-C = O, J = 16 Hz), 7.3(m, 4H_{arom}), 6.7(d, 1H, CH-C = O, J = 16 Hz), 6.3(m, 1H, Me₂C = CH), 2.3(s, 3H, ArCH₃), 2.2(s, 2H, *cis* CH₃), 1.9(s, 3H, *trans* CH₃).

The Michael addition of methyl group to the dienone 8 was accomplished by the reaction of lithium cyanodimethyl cuprate(9)²⁴ with 8, to give a regioselective conjugate addition product ar-turmerone(1). When lithium dimethylcuprate^{25,26} was used instead of Me₂Cu(CN)Li₂(9), not only longer reaction time was needed (10 min. to 2 hr), but also the yield was reduced (70% to 50%). Thus, a freshly prepared methyl-lithium, obtained from lithium shavings (1.25g, 180 mmol)