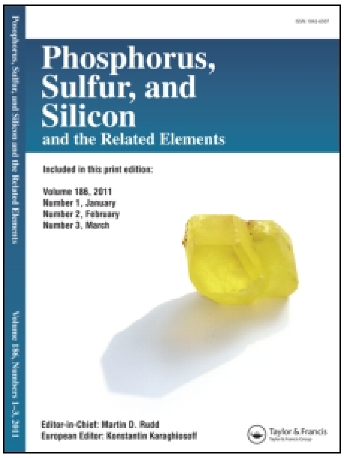

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SYNTHESIS AND TWO-DIMENSIONAL NMR ANALYSIS OF ETHYL ALLYL-*t*-BUTYLPHOSPHINATE

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SYNTHESIS AND TWO-DIMENSIONAL NMR ANALYSIS OF ETHYL ALLYL-*t*-BUTYLPHOSPHINATE

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The synthesis of ethyl allyl-*t*-butylphosphinate via the Michaelis–Arbuzov reaction between diethyl *t*-butylphosphinite and allylbromide is reported. The title compound gives rise to a highly symmetrical and complex ^{1}H NMR spectrum. Two-dimensional homonuclear NMR experiments were used to resolve the diastereotopic proton chemical shifts and their short- and long-range coupling constants, J_{PH} and J_{HH}. These results, along with the computer simulation of the ^{1}H NMR spectrum, are presented herein.

INTRODUCTION

Although numerous accounts have been written about chemical shifts and coupling constants for metal-phosphine complexes,[1–8] fewer reports have appeared on the NMR data of the free ligands or their precursors.[9–12] Two of the precursors used in phosphine ligand syntheses are phosphinites, $P(OR)_2R'$, and phosphinates, $P(O)(OR)RR'$, and the magnitudes of phosphorus-hydrogen, J_{PH}, and hydrogen–hydrogen, J_{HH}, coupling constants in such compounds provide valuable information about the structure and bonding within the molecule.

This paper reports the synthesis of ethyl allyl-*t*-butylphosphinate, *t*-$BuP(O)(OET)(CH_2CHCH_2)$, and the application of two-dimensional homonuclear NMR spectroscopy to determine its P–H and H–H coupling constants. To our knowledge, this is the first detailed proton NMR analysis of an allyl phosphinate.

RESULTS AND DISCUSSION

The diethyl tertiarybutylphosphinite, *t*-$BuP(OEt)_2$, used in this study was prepared according to a literature method (Equation 1).[13–15]

$$t\text{-BuPCl}_2 + 2\text{EtOH} + 2\text{Et}_3\text{N} \rightarrow \underset{\delta(^{31}\text{P}) = 186}{\underset{\mathbf{1}}{t\text{-BuP(OEt)}_2}} + 2\text{Et}_3\text{N}\cdot\text{HCl} \qquad (1)$$

While Stelzer *et al.* have shown that diisopropyl methylphosphinite reacts with primary alkyl halides to yield the desired Michaelis–Arbuzov product,[16–19] little work has been reported with diethyl *t*-butylphosphinite, *t*-$BuP(OEt)_2$. Perhaps the small number of studies with diethyl *t*-butylphosphinite can be attributed to a

1970 publication,[15] which the present authors have proven to be incorrect. Crofts *et al.*[15] reported that under Michaelis–Arbuzov conditions diethyl *t*-butylphosphinite was unreactive toward ethyl and methyl iodide. This surprising lack of reactivity was ascribed to the bulkiness of the *t*-butyl group. However, in 1983 Weisheit *et al.*[20] reported that the reaction between two equivalents of diethyl *t*-butylphosphinite and 1,2-dibromoethane produced ethyl 2-bromoethyl-*t*-butylphosphinate, $t\text{-BuP(O)(OEt)-CH}_2\text{CH}_2\text{Br}$. Lack of formation of 1,2-bis(ethyl *t*-butylphosphinato)ethane, $[t\text{-BuP(O)(OEt)CH}_2]_2$, was attributed to the volatility of the monophosphinate during the course of the reaction.[20]

The discrepancy between the two reports[15,20] on diethyl *t*-butylphosphinite can be rationalized by close examination of the experimental section of Reference 15. In order to remove trace amounts of triethylamine hydrochloride from the ether solution, the solution was washed with water. Since phosphinites are readily converted into their corresponding phosphinates by high temperature or acid-catalysis, the water may have caused isomerization of the phosphinite to the phosphinate (Equation 2).[21] Infrared stretching frequencies reported by Crofts *et al.*[15] at 1210 and 1160 cm⁻¹ are consistent with isomerization to $t\text{-BuP(O)(OEt)(Et)}$. The infrared spectrum obtained in this work did not contain these two absorptions. Therefore, it can be inferred that diethyl-*t*-butylphosphinite was not prepared by Crofts *et al.*[15] This conclusion makes the non-reactivity of the phosphinate understandable.

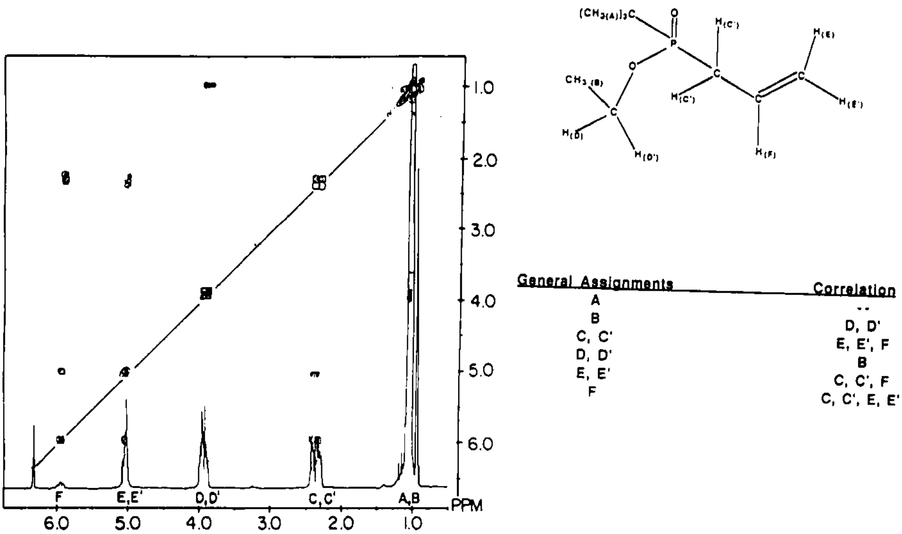
$$\text{R'P(OR)}_2 \xrightarrow{\Delta\ \text{or}\ \text{H}^+} \text{R'P(O)(OR)R} \qquad (2)$$

After diethyl *t*-butylphosphinite, $t\text{-BuP(OEt)}_2$, was purified via vacuum distillation, it was treated with allyl bromide according to Equation (3). After purification of ethyl allyl-*t*-butylphosphinate, **2**, via vacuum distillation (82°C/0.1 torr), the phosphorus-31 NMR spectrum showed only one singlet at 55.3 ppm. The proton NMR spectrum, however, yielded four highly symmetrical and complex patterns centered at 2.36, 3.90, 5.02, and 5.90 ppm (Figure 1). In order to analyze this ^{1}H-NMR spectrum two-dimensional NMR spectroscopy was employed.

$$t\text{-BuP(OEt)}_2 + \text{CH}_2\text{CHCH}_2\text{Br} \xrightarrow[15\ \text{hrs.}]{\text{reflux}} \underset{\mathbf{2}}{t\text{-BuP(O)(OEt)(CH}_2\text{CHCH}_2)} \qquad (3)$$

$\delta(^{31}\text{P})$: 55.3
$\nu(\text{POH})$: 1040 cm^{-1}
$\nu(\text{PO})$: 1240 cm^{-1}

The proton resonances for compound **2** were analyzed by two-dimensional correlated spectroscopy, COSY. In general, a COSY spectrum plots the one-dimensional spectrum at a 45° angle to the two chemical shift axes. The signals located off the diagonal, *J*-cross peaks, arise from coupling between nuclei. Therefore, off-diagonal signals correlate nuclei that share coupling. The COSY spectrum and correlation assignments for compound **2** are shown in Figure 2. Information obtained from this spectrum are: (1) that the sample does not contain a mixture of organic compounds; and, (2) long-range (*i.e.* four-bond)



General Assignments	Correlation
A	--
B	D, D'
C, C'	E, E', F
D, D'	B
E, E'	C, C', F
F	C, C', E, E'

FIGURE 1 Expansion of the ^{1}H NMR spectrum of ethyl allyl-*t*-butylphosphinate, *t*-BuP(O)(OEt)(CH_2CHCH_2).

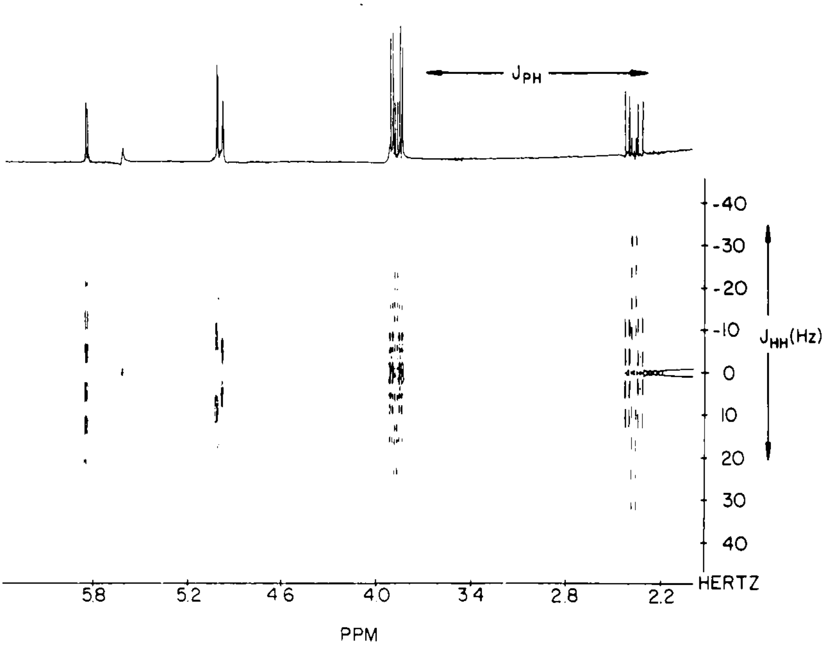


FIGURE 2 The 500 MHz COSY 2D-^{1}H NMR spectrum of compound **2**.

proton–proton coupling is being observed. However, this experiment does not provide any information concerning the magnitude of the coupling constants.

The complexity of the ^{1}H-coupled spectrum is due to both phosphorus–proton, J_{PH}, and proton–proton, J_{HH}, coupling. Since the protons in question are diastereotopic, they may be indistinguishable without the use of a chiral shift reagent. Selective homonuclear decoupling would be difficult, if not impossible, owing to the similarity of the proton chemical shifts (i.e., D, D′), as well as the inherent line-width of the spectra. Therefore, a homonuclear J-resolved 2-D NMR experiment was used to determine the magnitude of J_{PH} and J_{HH}. Fourier transformations with respect to t_2 give an axis with chemical shift values $\pm J_{PH}$. Transformations with respect to t_1 yield an axis with J_{HH} coupling only. Therefore, this technique simplified analysis of the proton chemical shifts by completely separating both the hetero- and homonuclear couplings.[22–24]

The J-resolved two-dimensional NMR spectrum from 2.0 ppm to 6.4 ppm for compound **2** is presented in Figure 3. If no other NMR-active nuclei were present, seven singlets corresponding to the proton chemical shifts would appear along the x-axis. However, owing to P–H coupling, the x-axis gives rise to seven

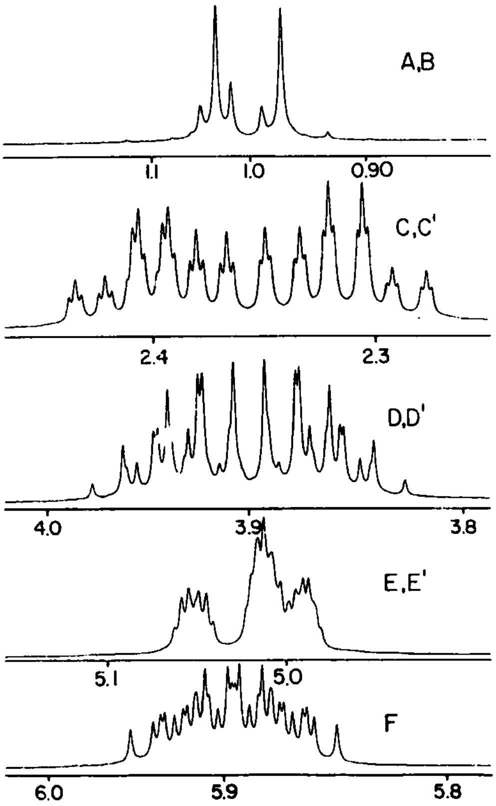


FIGURE 3 The 500 MHz J-resolved 2D ^{1}H-NMR spectrum of compound **2** from 2.0 to 6.4 ppm.

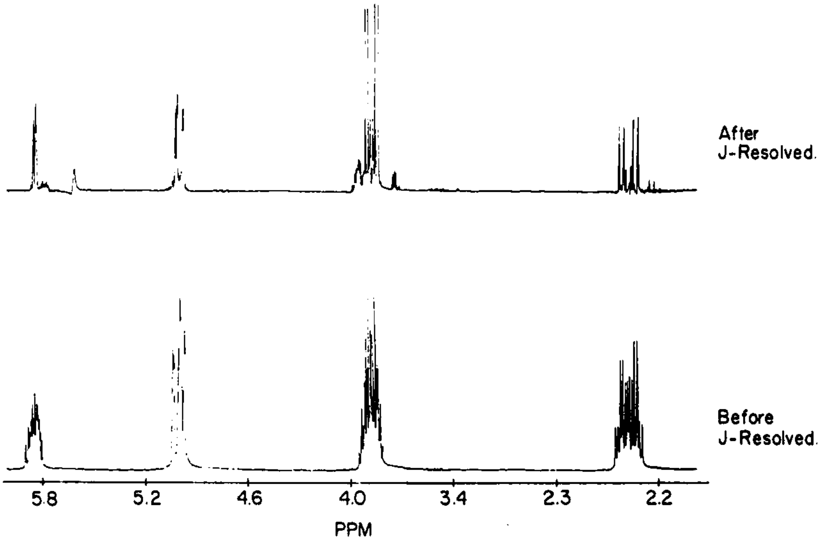


FIGURE 4 A comparison of the ^{1}H-NMR spectra before and after J-resolved 2D ^{1}H-NMR.

sets of doublets; one doublet for each proton C and C′, D and D′, E and E′, and F. The proton–proton splitting patterns and the coupling constants, J_{HH}, can be determined from the *y*-axis. A comparison of the ^{1}H-NMR spectra before and after the *J*-resolved two-dimensional NMR experiment is presented in Figure 4.

In order to calculate more exact values for the proton chemical shifts and coupling constants, J_{PH} and J_{HH}, each proton region was expanded. From these expansions the $^1H\{^{31}P\}$-spectrum can be calculated. The decoupled spectrum would be expected to show two doublets at 2.45 and 2.37 ppm for ^1H_C and $^1H_{C'}$, respectively. The resonances for ^1H_D and $^1H_{D'}$ would appear as a doublet of quartets at 3.98 and 3.92 ppm. Protons E and E′ would give rise to a doublet of doublets at 5.08 and 5.05 ppm, respectively. Proton F would yield a doublet of doublets of triplets centered at 5.95 ppm. Once all the coupling constants and chemical shifts had been measured from the *J*-resolved 2D-NMR spectrum, the ^{1}H-NMR spectrum was simulated with the Bruker PANIC program. In order to simulate compound **2**, it was separated into an allyl- and an ethoxy-section. Justification for the separation comes from the COSY spectrum, which indicates that none of the ethoxy- and allylprotons were coupled. Final chemical shift and coupling constant values are summarized in Table I. Two spectral comparisons are represented by Figures 5 and 6.

In conclusion, this investigation demonstrated the ability of *t*-BuP(OEt)$_2$ to undergo the Michaelis–Arbuzov rearrangement and of two-dimensional NMR spectroscopy in resolving the proton chemical shifts, proton–proton and phosphorus–proton coupling constants for diastereotropic protons. With the exception of one geminal proton–proton coupling constant ($^2J_{EE'} = -1.7$ Hz), all geminal ($^2J_{HH}$), vicinal ($^3J_{HH}$) and long-range ($^4J_{HH}$) coupling constants were consistent with the expected magnitudes and signs.

TABLE I

Final chemical shifts and coupling constants from simulation of the proton spectrum of compound **2**

Chemical Shifts (in Hz)

W(F) = 2974.409
W(E) = 2538.300
W(E′) = 2526.546
W(C) = 1227.233
W(C′) = 1184.817
W(P) = 50000.000

Indirect Coupling Constants (in Hz)

J(F,E) = 17.228
J(F,E′) = 10.106
J(F,C) = 6.957
J(F,C′) = 7.929
J(F,P) = 5.188
J(E,E′) = −1.646
J(E,C) = 1.580
J(E,C′) = 1.415
J(E,P) = 3.889
J(E′,C) = 1.327
J(E′,C′) = 1.174
J(E′,P) = 2.837
J(C,C′) = −14.571
J(C,P) = 13.380
J(C′,P) = 14.748
RMS for error estimation = 0.106

Chemical Shifts (in Hz)

W(P) = 50000.000
W(D′) = 1960.931
W(D) = 1991.777
W(B) = 541.101

Indirect Coupling Constants (in Hz)

J(P,D′) = 7.861
J(P,D) = 8.032
J(P,B) = 0.000
J(D′,D) = −10.272
J(D,B) = 7.069
J(D′,B) = 7.059

RMS for error estimation = 0.044

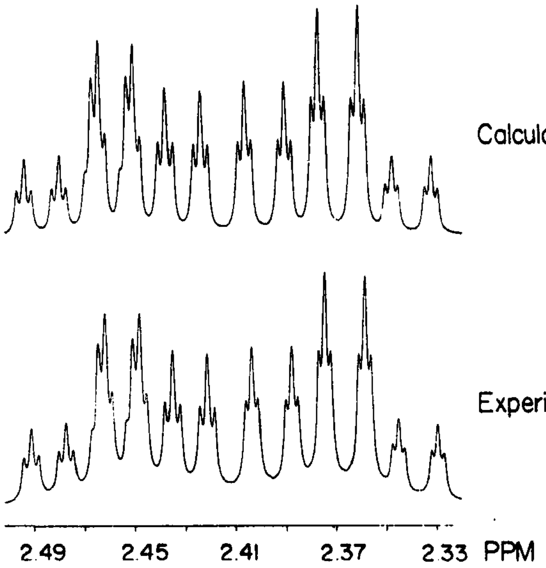


FIGURE 5 Calculated (top) versus experimental (bottom) spectra for protons C and C′.

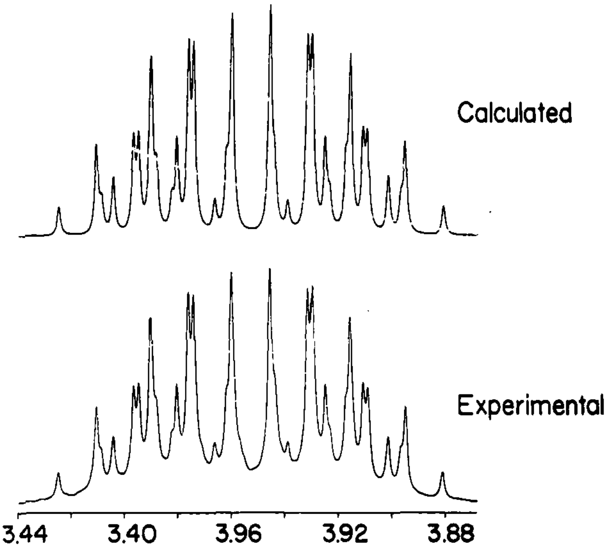


FIGURE 6 Calculated (top) versus experimental (bottom) spectra for protons D and D′.

EXPERIMENTAL

A. General Experimental Procedures. Allyl bromide was purchased from Aldrich Chemical Company and distilled from anhydrous magnesium sulfate under nitrogen before use. Dichlorotertiarybutylphosphine was purchased from Strem Chemical Company and used without further purification. Triethylamine was distilled from phosphorus pentoxide under nitrogen before use.[26] All other chemicals were reagent-grade and used as obtained, unless stated otherwise.

All reactions were performed in a well ventilated fume hood under an atmosphere of high-purity nitrogen or argon using standard techniques for the manipulation of air-sensitive materials.[27] Nitrogen was further purified by passing it through a deoxygenating column (Ridox, obtained from Fisher Scientic Company), followed by a column containing anhydrous calcium sulfate. Solvents were distilled from appropriate drying agents under nitrogen before use.[26]

Infrared spectra were measured on a Perkin–Elmer model 283B grating spectrophotometer from 200 to 4000 cm^{-1}. The samples were examined as Nujol mulls or neat samples pressed between potassium bromide plates, or as solutions with a matched set of demountable potassium bromide infrared cells (approximate path length = 0.2 mm). All infrared spectra were calibrated with a polystyrene film.

Fourier mode proton NMR spectra were obtained on either a Bruker HX-90 spectrometer operating at 90.0 MHz, an IBM NR-80 operating at 80.13 MHz or a Bruker AM-500 spectrometer operating at 500.136 MHz. Proton spectra were obtained in deuterated solvents and standardized against internal tetramethylsilane (TMS, $\delta = 0.00$ ppm) or solvent residual proton peaks.

Broad-band, Fourier-mode proton-decoupled phosphorus-31 NMR spectra were collected on either the Bruker HX-90 operating at 36.43 MHz or the Bruker AM-500 spectrometer at 202.42 MHz. Spectra were recorded in nondeuterated solvents and calibrated by use of a coaxial insert tube containing both trimethylphosphate ($\delta = 1.59$ ppm relative to 85% H_3PO_4) and deuterated acetone. During data acquisition, the coaxial insert remained in the sample tube. Spectra were obtained in either the ^{1}H-coupled or broadband-noise ^{1}H-decoupled mode. Phosphorus-31 chemical shifts are reported relative to 85% H_3PO_4, with positive numbers being downfield from the standard.

The two-dimensional NMR experiments were performed by Dr. C. E. Cottrell at The Ohio State University Chemical Instrument Center on the Bruker AM-500 spectrometer. Computer simulations of experimental spectra were performed with the PANIC Program provided by Bruker Instruments, Inc.

TABLE II

Two-dimensional NMR acquisition parameters

	COSY	δ/J resolved
Data size	1024 (F_1) × 2048 (F_2)	256 (F_1) × 8192 (F_2)
Spectral width	1572 Hz (F_1)	47 Hz (F_1)
	3145 Hz (F_2)	3612 Hz (F_2)
Digital resolution	1.54 Hz (F_1)	0.18 Hz (F_1)
	1.54 Hz (F_2)	0.37 Hz (F_2)
Delay	4 sec.	3 sec.
Acquisition time	2.3 hr.	0.9 hr.

B. Detailed NMR Procedures. Two-dimensional COSY and δ/J resolved spectra were obtained by use of the Bruker Aspect 3000 software and the aquisition parameters presented in Table II. Delays given in Table II between $90°-\tau_1-180°-\tau_1$-acquire(τ_2) pulse-cycles were used and four transients were acquired for each value of τ_1 (quadrature detection) to give the total acquistion times. The data were multipled by sine bell (COSY spectrum) or shifted sine bell, $\pi/10$, (δ/J resolved spectrum) window functions before Fourier transformations; the resulting two-dimensional spectra were tilted by 45°. Peak positions are accurate to ±1.5 Hz (COSY) or ±0.4 Hz (δ/J resolved).

C. Syntheses

(1) *Diethyl tertiarybutylphosphinite, t-BuP(OEt)$_2$.* Substitution of dichloro-*t*-butylphosphine (30.00 g, 0.1887 moles) and ethanol (26.0 mL, 0.443 moles) for dichloromethylphosphine and isopropanol, respectively, according to Reference 14 produced the title compound. Yield 18.0 mL, 9.09×10^{-2} moles (48% based on *t*-BuPCl$_2$). Boiling point range, 50–55°C at 1.5 torr. (Literature[15] value: 85°C/torr)

Spectroscopic Data:

$\delta(^{31}P)$: 186.1 ppm (s)
ν(POC): 1101 cm^{-1}
$\nu(CH_2CH_3)$: 1389 cm^{-1}
ν(C-CH$_3$): 1361, 1362 cm^{-1}
ν(P-*t*-Bu): 833 cm^{-1}

(2) *Ethyl allyl-t-butylphosphinate, t-BuP(O)(OEt)(CH$_2$CHCH$_2$).* Diethyl *t*-butylphosphinite (10.0 mL, 5.05×10^{-2} moles) and allylbromide (5.0 mL, 5.6×10^{-2} moles) were mixed together at room temperature. The mixture was then refluxed at 62°C/760 torr for 15 hours. The title compound was obtained after vacuum distillation. Boiling point, 82°C/0.1 torr; yield was 7.3 g (76% based on compound **1**).

ACKNOWLEDGMENT

FT-NMR spectra at 11.75 Tesla (500 MHz) were obtained at the Ohio State University Chemical Instrument Center on a Bruker AM-500 spectrometer, which was funded, in part, by NIH Grant #1 S10 RR01458-01A1.

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