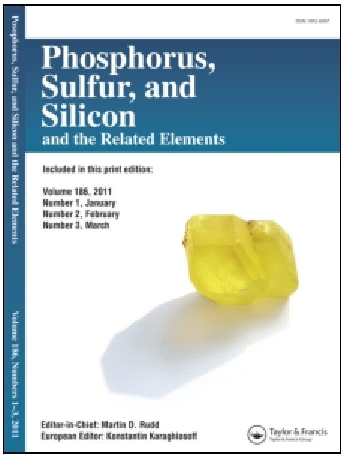

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Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 2,3di-hydroxybenzaldehyde and 2-hydroxy-4-methoxybenzaldehyde. These stable ylides exist in a solution as a mixture of two geometrical isomers as a result of the restricted rotation around the carbon-carbon partial double bond resulting from the conjugation of the ylide moiety with the adjacent carbonyl group.

Keywords Acetylenic ester; geometrical isomers; hydroxy-benzaldehyde; stable phosphorus ylides; triphenylphosphine

INTRODUCTION

The development of simple synthetic routes for widely-used organic compounds from readily available reagents is one of the major tasks in organic chemistry.[1] Phosphorus ylides are reactive systems, which take part in many valuable reactions of organic synthesis.[2–12] These are most often prepared by treatment of a phosphonium salt with a base.

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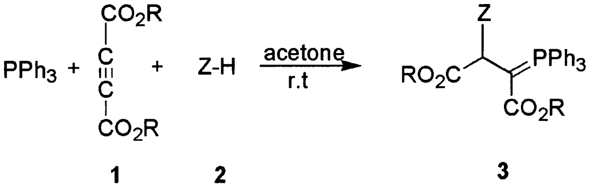
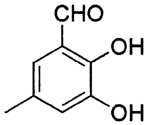
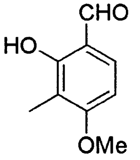
Most of the phosphonium salts are usually made from the phosphine and an alkyl halide,[3–7] and they are also obtained by the Michael addition of phosphorus ncleophiles to activated olefins.[2,3] Here we whish to describe an efficient synthetic route of stable phosphorus ylides **3** using triphenylphosphine, dialkyl acetylenedicarboxylates, 2,3di-hydroxybenzaldehyde, and 2-hydroxy-4-methoxybenzaldehyde (see Scheme 1).

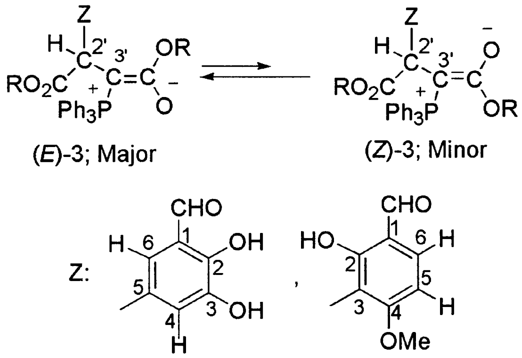


3	Z	R	%Yield
a		Me	85
b		Et	83
c		Bu^t	88
d		Me	89

SCHEME 1

RESULTS AND DISCUSSION

The reactions of 2,3di-hydroxybenzaldehyde and 2-hydroxy-4- methoxybenzaldehyde with dialkyl acetylenedicarboxylates **1** in the presence of triphenylphosphine were carried out in acetone solvent at r.t. and were finished within a few hours. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **3**. Any products other than **3** could not be detected by NMR spectroscopy. The structures of compounds **3a–d** were deduced from their IR,^{1}H,^{13}C, and ^{31}P NMR spectra. The mass spectra of them displayed molecular ion peaks at appropriate m/z values. Any initial fragmentations involve the missing parts or complete loss of the side chains and scission of the hydroxybenzaldehyde ring system. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **3a**, **3b**, and **3d** are consistent with the presence of two isomers. The ylides moiety of these compounds are strongly conjugated with the

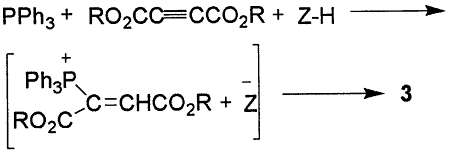


SCHEME 2

adjacent carbonyl group and rotation around the partial double bond in (*E*)-**3** and (*Z*)-**3** geometrical isomers is slow on the NMR time scale at ambient temperature (see Scheme 2). Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **3a–d** are shown in Table I.

As can be seen, only one geometrical isomer was observed for the di-tert-butyl derivative of **3** presumably because of the bulky tert-butyl groups.

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[2–6] it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acid to form phosphoranes **3** (see Scheme 3).



SCHEME 3

Briefly, we have prepared novel phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 2,3di-hydroxybenzaldehyde and 2-hydroxy-4-methoxybenzaldehyde. The present method carries the advantage that not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modifications.

TABLE I **Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (*J* in Hz) for H-2′, H-4, H-5, H-6, OR, CO$_2$R, C-2′, and C-3′, in the Major (M)and Minor (m) Diastereoisomers of Compounds 3a–d**

		^{1}H NMR spectroscopy data					^{13}C NMR data		
Compound	Isomer (%)	H-2′ ($^{3}J_{PH}$)	H-4(5)	H-6	OR	CO$_2$R	C-2′($^{2}J_{PC}$)	C-3′($^{1}J_{PC}$)	^{31}PNMR
3a	M (61)	3.66 (21.4)	6.42 (5)	7.20 (s)	3.11	3.73	60.17 (17.1)	44.11 (125.3)	23.38
3a	m (39)	3.57 (21.1)	6.80 (s)	7.26 (s)	3.54	3.67	60.33 (17.8)	44.37 (135.9)	23.74
3b	M (57)	3.88 (18.5)	6.73 (s)	7.06 (s)	3.68	4.18	59.24 (16.2)	43.25 (125.5)	23.19
3b	m (43)	3.74 (18.3)	6.85 (s)	7.19 (s)	4.11	4.25	59.46 (16.5)	43.73 (136.2)	23.68
3c	M	3.40 (17.9)	6.91 (s)	7.23 (s)	0.95	1.5	60.04 (18.1)	44.53 (123.4)	22.92
3d	M (51)	4.25 (17.9)	6.43 (d)	7.63 (s)	3.09	3.41	60.32 (15.2)	44.19 (124.8)	24.21
3d	m (49)	4.19 (17.6)	6.27 (d)	7.58 (s)	3.05	3.14	59.84 (15.6)	43.87 (132.3)	24.51

2,3 Di-hydroxybenzaldehyde- and 2-hydroxy-4-methoxybenzaldehyde-containing phosphorus ylides **3a–d** may be considered as potentially useful synthetic intermediates. It seems that the procedure described here may be employed as an acceptable method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. Also, the^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained from a BRUKER DRX-500 AVANCE instrument with $CDCl_3$ as an solvent at 500.1, 125.8, and 202.4 MHz, respectively. In addition, the mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates, triphenlphosphine, 2,3di-hydroxybenzaldehyde, and 2-hydroxy-4-methoxybenzaldehyde were purchased from Fluka (Buchs, Switzerland) and used without further purifications.

Preparation of Dimethyl 2-(2,3Di-hydroxybenzaldehyde-5-yl)-3-(triphenylphosphoranylidene)-butanedioate (3a): General Procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g or 1 mmol) and 2,3di-hydroxybenzaldehyde (0.14 g or 1 mmol) in 10 mL of acetone as solvent, a mixture of dimethyl acetylenedicarboxylate (0.23 g or 1 mmol) in 4 mL of acetone at -5°C over 10 min was added dropwise. After approximately 10 h stirring at r.t., the product was filtered and recrystallized from acetone.

Colorless crystals. m.p. 142-144°C, yield 0.46 g, 85%. IR (KBr) (ν_{max}, cm^{-1}) 1732 and 1625 (C=O). MS (m/z, %): 542 (M, 3), 483 (M-CO_2Me, 2), 407 (M-PPh_3,6), 262 (PPh_3, 87), 183 (PPh_2, 100), 108 (PPh, 50).

Diethyl 2-(2,3Di-hydroxybenzaldehyde-5-yl)-3-(triphenylphosphoranylidene)-butanedioate (3b)

Colorless crystals. m.p. 125–127°C, yield 0.47 g, 83%. IR (KBr) ($\nu_{max,}$ cm^{-1}): 1731 and 1620 (C=O). MS (m/z, %): 462 (M-PPh, 9), 417 (M-PPh and OEt, 2), 387 (M-PPh_2, 2), 308 (M-PPh_3, 3), 262 (PPh_3, 50), 183 (PPh_2, 96), 108 (PPh, 33).

Di-tert-buthyl 2-(2,3Di-hydroxybenzaldehyde-5-yl)-3-(triphenylphosphoranylidene)-butanedioate (3c)

Colorless crystals. m.p. 151–153°C, yield 0.53 g, 95%. IR (KBr) (ν_{max}, cm^{-1}) 1736 and 1629 (C=O). MS (m/z, %): 556 (M^+, 17), 489 (M-heterocycle, 10), 455 ($M-CO_2CMe_3$, 38), 262 (PPh_2, 21), 183 (PPh_2, 14), 108 (PPh, 13), 77 (Ph, 6), 67 (heterocyclic, 3), 57 (CMe_3, 47).

Dimethyl 2-(2-Hydroxy-4-methoxybenzaldehyde-3-yl)-3-(triphenylphosphoranylidene)-butanedioate (3d)

White powder, m.p. 143–145°C, yield 0.49 g, 89%. IR (KBr) (υ_{max}, cm^{-1}): 1725, 1620 (C=O). MS (m/z, %): 405 ($M-C_8H_7O_3$, 100); 374 ($M-C_8H_7O_3$ and OCH_3, 1); 294 (M-PPh3, 5); 262 (PPh_3, 23); 183 (PPh_2, 64); 108 (PPh, 18).

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