J. Iran. Chem. Soc., Vol. 6, No. 4, December 2009, pp. 705-709.

JOURNAL OF THE
Iranian
Chemical Society

An Efficient Synthesis of Dialkyl 2-(Diphenoxyphosphoryl)-3-(alkylthio)succinates from Alkylthiols, Triphenyl Phosphite and Dialkyl Acetylenedicarboxylates

I. Yavari*, R. Hajinasiri, S.Z. Sayyed-Alangi and N. Iravani
Chemistry Department, Science and Research Branch, Islamic Azad University, Tehran, Iran

(Received 6 June 2008, Accepted 18 September 2008)

An efficient synthesis of dialkyl 2-(diphenoxyphosphoryl)-3-(alkylthio)succinates, as a mixture of two diastereomers, in 78-90% yields, is described *via* reaction between alkylthiols, dialkyl acetylenedicarboxylates, and triphenyl phosphite. The structures of products were deduced from their high-field ^{1}H, ^{13}C, and ^{31}P NMR spectra, and IR spectral data. Since these hosphonate esters possess two stereogenic centers, two diastereomers with *gauche* HCCH arrangements are possible. Observation of $^{3}J_{HH}$ = 3.5-4.6 Hz for the vicinal methine protons confirmed the dominance of the *gauche* arrangement. A mechanism is proposed for the formation of products.

Keywords: Alkylthiols, Triphenyl phosphite, Acetylenic esters, Alkylthiosuccinates, Alkylphosphonates

INTRODUCTION

The rich chemistry that stems from the addition of nucleophiles to activated acetylenic compounds has evoked considerable interest. Trivalent phosphorous nucleophiles are known to form zwitterions with activated acetylene compounds such as dialkyl acetylenedicarboxylates [1-4]. In recent years, work in our laboratory and in other laboratories has shown that these types of zwitterions can be trapped by a variety of electrophiles and proton donors, for the synthesis of organophosphorous compounds [1-12]. Hence, it was of interest to investigate the reactivity of these zwitterions toward alkyl sulfides.

In this paper, we report the results of our studies involving the reactions of zwitterions derived from triphenyl phosphite **1** and dialkyl acetylenedicarboxylates **2** in the presence of alkylthiols **3**, which constitute a synthesis of dialkyl 2-(diphenoxyphosphoryl)-3-(alkylthio)succinates **4**, as a mixture of two diastereoisomers, in 78-90% yields (Scheme 1).

*Corresponding author. E-mail: yavarisa@modares.ac.ir

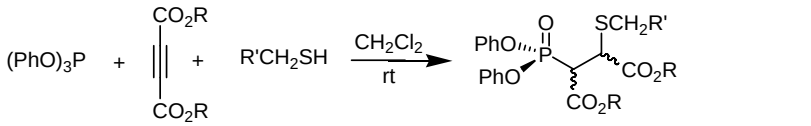
EXPERIMENTAL

Chemicals and Apparatus

Compounds **1-3** were obtained from Fluka and were used without further purification. M.p.: Electrothermal-9100 apparatus. IR Spectra: Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra: Bruker DRX-300 AVANCE instrument; in $CDCl_3$ at 300 and 75 MHz, respectively; δ in ppm, J in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer, in m/z. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer. The results agreed favorably with the calculated values.

General Procedure for the Prepration of Compounds 4

To a stirred solution of 2 mmol of **2** and 2 mmol of **3** in 10 ml of CH_2Cl_2 was added 0.61 g of triphenyl phosphite (2 mmol) at romm temperature. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; hexane/AcOEt 3:1) to afford the adducts as mixtures of two diastereoisomers.



1	2	R	3	R'
	a	Me	a	2-Furyl
	b	Et	b	$HSCH_2CH_2$
			c	MeO_2CCH_2

4	R	R'	Yield/ %
a	Me	2-Furyl	85
b	Me	$HSCH_2CH_2$	88
c	Me	MeO_2CCH_2	90
d	Et	2-Furyl	84
e	Et	$HSCH_2CH_2$	78
f	Et	MeO_2CCH_2	82

Scheme 1

Dimethyl 2-(diphenoxyphosphoryl)-3-[(2-furylmethyl) sulfanyl]succinate (4a). Yellow oil; yield: 0.83 g (85%). IR (KBr): $\bar{\nu}$ = 1738 (C=O), 1246 (P=O), 2953 (CH) cm^{-1}. EI-MS: 490 (2, M^+), 459 (5), 351 (35), 236 (38), 233 (38), 105 (100), 93 (85), 77 (86). Anal. Calc. for $C_{23}H_{23}O_8PS$ (490.46): C 56.33, H 4.73%; found: C 56.63, H 5.03%. NMR data for the major isomer (64%); ^{1}H NMR: 3.71 (s, MeO), 3.72 (s, MeO), 3.90 (AB quartet, $\Delta\nu_{AB}$ = 7 Hz, J_{AB} = 15.1, SCH_2), 4.02 (dd, $^3J_{HH}$ = 4.0, $^2J_{HP}$ = 17.1, CH), 5.01 (dd, $^3J_{HH}$ = 4.0, $^3J_{HP}$ = 9.2, CH), 6.23-6.24 (m, 2CH), 7.13-7.20 (m, 11CH). ^{13}C NMR: 29.7 (CH_2), 44.6 (d, $^2J_{CP}$ = 2.3, CH), 48.5 (d, CH, $^1J_{CP}$ = 127.4), 53.3 (MeO), 53.4 (MeO), 109.1 (CH), 110.9 (CH), 120.8 (d, $^3J_{CP}$ = 4.9, 4CH of $2C_6H_5$), 125.8 (s, 2CH of $2C_6H_5$), 130.1 (s, 4CH of $2C_6H_5$), 142.8 (CH), 150.1 (C), 150.5 (s, $2C_{ipso}$ of $2C_6H_5$), 166.6 (d, $^2J_{CP}$ = 5.5, C=O), 170.5 (d, $^3J_{CP}$ = 4.4, C=O). ^{13}P NMR: 11.45 [P(O)$(OC_6H_5)_2$]. NMR data for the minor isomer (36%); ^{1}H NMR: 3.70 (s, MeO), 3.75 (s, MeO), 3.84 (AB quartet, $\Delta\nu_{AB}$ = 9 Hz, J_{AB} = 15.8, SCH_2), 4.22 (dd, $^3J_{HH}$ = 4.2, $^2J_{HP}$ = 16.9 Hz, CH), 5.04 (dd, $^3J_{HH}$ = 4.2, $^3J_{HP}$ = 8.9, CH), 6.29-6.35 (m, 2CH), 7.24-7.32 (m, 11CH). ^{13}C NMR: 29.3 (CH_2), 44.3 (d, $^2J_{CP}$ = 2.1, CH), 48.3 (d, $^1J_{CP}$ = 137.6, CH), 53.4 (MeO), 53.6 (MeO), 109.1 (CH), 110.9 (CH), 120.9 (d, $^3J_{CP}$ = 4.9, 4CH of $2C_6H_5$), 125.9 (s, 2CH of $2C_6H_5$), 130.2 (s, 4CH of $2C_6H_5$), 142.9 (CH), 150.1 (C), 150.5 (s, $2C_{ipso}$ of $2C_6H_5$), 167.9 (d, $^2J_{CP}$ = 5.2, C=O), 171.8 (d, $^3J_{CP}$ = 18.8, C=O). ^{13}P NMR: 11.84 [P(O)$(OC_6H_5)_2$].

Dimethyl 2-(diphenoxyphosphoryl)-3-[(3-sulfanyl-propyl)sulfanyl]succinate (4b). Yellow oil; yield: 0.85 g (88%). IR (KBr): $\bar{\nu}$ = 1737 (C=O), 1246 (P=O), 2952 (CH) cm^{-1}. EI-MS: 484 (2, M^+), 318 (10), 285 (80), 223 (58), 140 (46), 94 (40), 77 (100). Anal. Calc. for $C_{21}H_{25}O_7PS_2$ (484.52): C 52.06, H 5.20%; found: C 52.39, H 5.51%. NMR data for the major isomer (62%); ^{1}H NMR: 1.25-1.26 (m, SH), 1.86-1.89 (m, CH_2), 2.52-2.54 (m, CH_2), 2.83-2.86 (m, CH_2), 3.71 (s, MeO), 3.78 (s, MeO), 4.08 (dd, $^3J_{HH}$ = 4.1, $^2J_{HP}$ = 16.6, CH), 4.92 (dd, $^3J_{HH}$ = 4.1, $^3J_{HP}$ = 9.0, CH), 7.10-7.21 (m, 5CH), 7.28-7.32 (m, 5CH). ^{13}C NMR: 29.7 (CH_2), 31.5 (CH_2), 33.0 (CH_2), 45.1 (d, $^2J_{CP}$ = 2.4, CH), 48.7 (d, $^1J_{CP}$ = 127.6, CH), 53.3 (MeO), 53.5 (MeO), 120.9 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 126.0 (s, 2CH of $2C_6H_5$), 130.2 (s, 4CH of $2C_6H_5$), 150.5 (s, $2C_{ipso}$ of $2C_6H_5$), 166.7 (d, $^2J_{CP}$ = 5.3, C=O), 170.7 (d, $^3J_{CP}$ = 4.0, C=O). ^{13}P NMR: 11.46 [P(O)$(OC_6H_5)_2$]. NMR data for the minor isomer (38%); ^{1}H NMR: 1.25-1.27 (m, SH), 1.86-1.88 (m, CH_2), 2.52-2.60 (m, CH_2), 2.83-2.85 (m, CH_2), 3.75 (s, MeO), 3.82 (s, MeO), 4.19 (dd, $^3J_{HH}$ = 4.2, $^2J_{HP}$ = 16.6 Hz, CH), 5.02 (dd, $^3J_{HH}$ = 4.2, $^3J_{HP}$ = 8.7, CH), 7.28-7.32 (m, 10CH). ^{13}C NMR: 31.0 (CH_2), 32.1 (CH_2), 32.7 (CH_2), 44.5 (d, $^2J_{CP}$ = 2.0, CH), 48.6 (CH, d, $^1J_{CP}$ = 137.0, CH), 53.4 (MeO), 53.6 (MeO), 120.7 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 126.0 (s, 2CH of $2C_6H_5$), 130.2 (s, 4CH of $2C_6H_5$), 150.5 (s, $2C_{ipso}$ of $2C_6H_5$), 167.91 (d, $^2J_{CP}$ = 5.1, C=O), 171.6 (d, $^3J_{CP}$ = 20.3, C=O). ^{13}P NMR: 11.95 [P(O)$(OC_6H_5)_2$].

Dimethyl 2-(diphenoxyphosphoryl)-3-[(3-methoxy-3-oxopropyl)sulfanyl]succinate (4c). Colorless oil; yield: 0.89 g (90%). IR (KBr): $\bar{\nu}$ = 1738 (C=O), 1252 (P=O), 2953 (CH) cm^{-1}. EI-MS: 496 (2, M^+), 485 (32), 318 (16), 285 (68), 223 (44), 140 (42), 105 (100), 94 (43), 77 (70). Anal. Calc. for $C_{22}H_{25}O_9PS$ (496.46): C 53.22, H 5.08%; found: C 53.52, H 5.38%. NMR data for the major isomer (60%); ^{1}H NMR: 2.57-2.64 (m, CH_2), 2.92-3.08 (m, CH_2), 3.67 (s, MeO), 3.74 (s, MeO), 3.80 (s, MeO), 4.05 (dd, $^3J_{HH}$ = 3.9, $^2J_{HP}$ = 16.8, CH), 5.11 (dd, $^3J_{HH}$ = 3.9, $^3J_{HP}$ = 9.0, CH), 7.13-7.20 (m, 10CH). ^{13}C NMR: 28.2 (CH_2), 34.4 (CH_2), 45.4 (d, $^2J_{CP}$ = 2.6, CH), 48.6 (d, $^1J_{CP}$ = 127.7, CH), 52.2 (MeO), 53.3 (MeO), 53.5 (MeO),

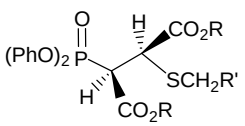
120.7 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 126.1 (s, 2CH of $2C_6H_5$), 130.1 (s, 4CH of $2C_6H_5$), 150.5 (s, $2C_{ipso}$ of $2C_6H_5$), 166.6 (d, $^2J_{CP}$ = 5.4, C=O), 170.7 (d, $^3J_{CP}$ = 4.4, C=O). ^{13}P NMR: 11.41 [P(O)$(OC_6H_5)_2$]. NMR data for the minor isomer (40%); ^{1}H NMR: 2.57-2.62 (m, CH_2), 2.92-3.07 (m, CH_2), 3.63 (s, MeO), 3.70 (s, MeO), 3.77 (s, MeO), 4.14 (dd, $^3J_{HH}$ = 4.2, $^2J_{HP}$ = 16.4 Hz, CH), 5.03 (dd, $^3J_{HH}$ = 4.2, $^3J_{HP}$ = 8.8, CH), 7.28-7.34 (m, 10CH). ^{13}C NMR: 27.7 (CH_2), 34.2 (CH_2), 44.8 (d, $^2J_{CP}$ = 2.2, CH), 48.4 (d, $^1J_{CP}$ = 137.4, CH), 52.2 (MeO), 53.4 (MeO), 53.6 (MeO), 120.7 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 126.0 (s, 2CH of $2C_6H_5$), 130.2 (s, 4CH of $2C_6H_5$), 150.2 (s, $2C_{ipso}$ of $2C_6H_5$), 167.9 (d, $^2J_{CP}$ = 5.1, C=O), 171.5 (d, $^3J_{CP}$ = 20.0, C=O). ^{13}P NMR: 11.91 [P(O)$(OC_6H_5)_2$].

Diethyl 2-(diphenoxyphosphoryl)-3-[(2-furylmethyl) sulfanylsuccinate (4d). Yellow oil; yield: 0.87 g (84%). IR (KBr): $\bar{\nu}$ = 1732 (C=O), 1250 (P=O), 2982 (CH) cm^{-1}. EI-MS: 518 (2, M^+), 485 (10), 318 (10), 285 (65), 223 (34), 140 (62), 105 (87), 94 (43), 77 (100). Anal. Calc. for $C_{25}H_{27}O_8PS$ (518.51): C 57.91, H 5.25%; found: C 58.21, H 5.53%. NMR data for the major isomer (64%); 1.20 (t, $^3J_{HH}$ = 7.2, Me), 1.26 (t, $^3J_{HH}$ = 7.2, Me), 3.90 (AB quartet, $\Delta\nu_{AB}$ = 9 Hz, J_{AB} = 14.6, SCH_2), 3.88 (dd, $^3J_{HH}$ = 3.9, $^2J_{HP}$ = 16.1, CH), 4.94 (dd, $^3J_{HH}$ = 3.9, $^3J_{HP}$ = 8.7, CH), 6.29-6.31 (m, 2CH), 7.11-7.20 (m, 11CH). ^{13}C NMR: 14.3 (Me), 14.5 (Me), 29.7 (CH_2), 44.8 (CH, d, $^2J_{CP}$ = 2.43), 48.5 (d, $^1J_{CP}$ = 127.7, CH), 62.4 (OCH_2), 62.7 (OCH_2), 109.1 (CH), 110.9 (CH), 121.0 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 125.9 (s, 2CH of $2C_6H_5$), 130.2 (s, 4CH of $2C_6H_5$), 142.8 (CH), 149.4 (C), 150.6 (s, $2C_{ipso}$ of $2C_6H_5$), 166.1 (d, $^2J_{CP}$ = 5.3, C=O), 170.1 (d, $^3J_{CP}$ = 4.4, C=O). ^{13}P NMR: 11.43 [P(O)$(OC_6H_5)_2$]. NMR data for the minor isomer (36%); ^{1}H NMR: 1.22 (t, $^3J_{HH}$ = 7.2, Me), 1.27 (t, $^3J_{HH}$ = 7.2, Me), 3.84 (AB quartet, $\Delta\nu_{AB}$ = 9 Hz, J_{AB} = 13.7, SCH_2), 4.18 (dd, $^3J_{HH}$ = 3.9, $^2J_{HP}$ = 16.0 Hz, CH), 4.92 (dd, $^3J_{HH}$ = 3.9, $^3J_{HP}$ = 8.4, CH), 6.29-6.31 (m, 2CH), 7.27-7.36 (m, 11CH). ^{13}C NMR: 14.2 (Me), 14.3 (Me), 29.3 (CH_2), 44.4 (d, $^2J_{CP}$ = 2.3, CH), 48.5 (d, $^1J_{CP}$ = 137.2, CH), 62.4 (OCH_2), 62.7 (OCH_2), 109.2 (CH), 110.8 (CH), 120.3 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 125.9 (s, 2CH of $2C_6H_5$), 130.4 (s, 4CH of $2C_6H_5$), 142.8 (CH), 150.6 (s, $2C_{ipso}$ of $2C_6H_5$), 167.3 (d, $^2J_{CP}$ = 5.2, C=O), 170.8 (d, $^3J_{CP}$ = 19.3, C=O). ^{13}P NMR: 11.86 [P(O)$(OC_6H_5)_2$].

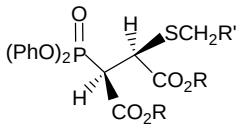
Diethyl 2-(diphenoxyphosphoryl)-3-[(3-sulfanylpropyl) sulfanyl]succinate (4e). Yellow oil; yield: 0.80 g (78%), IR (KBr): $\bar{\nu}$ = 1735 (C=O), 1246 (P=O), 2982 (CH) cm^{-1}. EI-MS: 512 (2, M^+), 485 (23), 318 (19), 285 (64), 223 (24), 140 (53), 105 (100), 94 (24), 77 (63). Anal. Calc. for $C_{23}H_{29}O_7PS_2$ (512.57): C 53.90, H 5.70%; found: C 54.20, H 6.01%. NMR data for the major isomer (62%); ^{1}H NMR: 1.17-1.29 (m, CH_2, 2Me), 1.88-1.96 (m, SH), 2.78-2.86 (m, $2CH_2$), 3.83 (dd, $^3J_{HH}$ = 4.1, $^2J_{HP}$ = 15.5, CH), 4.71 (dd, $^3J_{HH}$ = 4.1, $^3J_{HP}$ = 8.2, CH), 4.07-4.19 (m, $2OCH_2$), 7.13-7.17 (m, 10CH). ^{13}C NMR: 14.3 (Me), 14.5 (Me), 28.3 (CH_2), 28.5 (CH_2), 31.9 (CH_2), 45.3 (d, $^2J_{CP}$ = 2.5, CH), 48.7 (d, $^1J_{CP}$ = 127.6, CH), 62.1 (OCH_2), 62.6 (OCH_2), 120.7 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 125.1 (s, 2CH of $2C_6H_5$), 130.0 (s, 4CH of $2C_6H_5$), 150.6 (s, $2C_{ipso}$ of $2C_6H_5$), 166.7 (d, $^2J_{CP}$ = 5.3, C=O), 170.7 (d, $^3J_{CP}$ = 3.8, C=O). ^{13}P NMR: 11.48 [P(O)$(OC_6H_5)_2$]. NMR data for the minor isomer (38%); ^{1}H NMR: 1.17-1.29 (m, CH_2, 2Me), 1.86-1.96 (m, SH), 2.78-2.86 (m, $2CH_2$), 4.20 (dd, $^3J_{HH}$ = 4.0, $^2J_{HP}$ = 16.5 Hz, CH), 4.81 (dd, $^3J_{HH}$ = 4.0, $^3J_{HP}$ = 8.4, CH), 3.78-3.87 (m, $2OCH_2$), 7.27-7.30 (m, 10CH). ^{13}C NMR: 14.3 (Me), 14.4 (Me), 28.2 (CH_2), 28.4 (CH_2), 31.3 (CH_2), 45.3 (d, $^2J_{CP}$ = 2.5, CH), 48.8 (d, $^1J_{CP}$ = 135.9, CH), 62.3 (CH_2), 62.8 (OCH_2), 120.4 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 125.6 (s, 2CH of $2C_6H_5$), 130.1 (s, 4CH of $2C_6H_5$), 150.0 (s, $2C_{ipso}$ of $2C_6H_5$), 167.9 (d, $^2J_{CP}$ = 5.2, C=O), 171.6 (d, $^3J_{CP}$ = 20.3, C=O). ^{13}P NMR: 11.95 [P(O)$(OC_6H_5)_2$].

Diethyl 2-(diphenoxyphosphoryl)-3-[(3-methoxy-3-oxo-propyl)sulfanyl]succinate (4f). Yellow oil; yield: 0.86 g (82%). IR (KBr): $\bar{\nu}$ = 1736 (C=O), 1249 (P=O), 2983 (CH) cm^{-1}. EI-MS: 524 (2, M^+), 469 (31), 351 (24), 236 (42), 233 (35), 105 (100), 93 (58), 77 (73). Anal. Calc. for $C_{24}H_{29}O_9PS$ (524.52): C 54.96, H 5.57%; found: C 55.26, H 5.87%. NMR data for the major isomer (64%); ^{1}H NMR: 1.23 (t, $^3J_{HH}$ = 7.2, Me), 1.28 (t, $^3J_{HH}$ = 7.2, Me), 2.64-2.70 (m, CH_2), 2.98-3.10 (m, CH_2), 3.68 (s, MeO), 3.97 (dd, $^3J_{HH}$ = 3.7, $^2J_{HP}$ = 16.4, CH), 4.87 (dd, $^3J_{HH}$ = 3.7, $^3J_{HP}$ = 9.0, CH), 4.11-4.31 (m, $2OCH_2$), 7.14-7.21 (m, 10CH). ^{13}C NMR: 14.3 (Me), 14.4 (Me), 28.2 (CH_2), 34.5 (CH_2), 45.6 (d, $^2J_{CP}$ = 2.6, CH), 48.7 (d, $^1J_{CP}$ = 137.4, CH), 52.2 (MeO), 62.4 (OCH_2), 62.9 (OCH_2), 120.8 (d, $^3J_{CP}$ = 4.8, 4CH of $2C_6H_5$), 125.0 (s, 2CH of $2C_6H_5$), 130.1 (s, 4CH of $2C_6H_5$), 150.6 (s, $2C_{ipso}$ of $2C_6H_5$), 166.2 (d, $^2J_{CP}$ = 5.3, C=O), 170.3 (d, $^3J_{CP}$ = 4.5, C=O), 172.3 (C=O). ^{13}P NMR: 11.43 [P(O)$(OC_6H_5)_2$]. NMR data for the minor isomer (36%); ^{1}H NMR: = 1.24 (t, $^3J_{HH}$ = 7.2, Me), 1.27 (t, $^3J_{HH}$ = 7.2, Me), 2.64-2.70 (m, CH_2), 2.98-3.10 (m, CH_2), 3.62 (s, MeO), 4.03 (dd, $^3J_{HH}$ = 3.88, $^2J_{HP}$ = 16.0 Hz, CH), 5.00 (dd, $^3J_{HH}$ =

3.88, $^3J_{HP}$ = 8.5, CH), 3.83-4.11 (m, 2OCH_2), 7.27-7.30 (m, 10 CH). ^{13}C NMR: 14.2 (Me), 14.5 (Me), 27.7 (CH_2), 34.3 (CH_2), 45.6 (d, $^2J_{CP}$ = 2.6, CH), 48.7 (d, $^1J_{CP}$ = 137.4, CH), 52.2 (MeO), 62.0 (OCH_2), 62.7 (OCH_2), 120.6 (d, $^3J_{CP}$ = 4.8, 4CH of 2C_6H_5), 124.8 (s, 2CH of 2C_6H_5), 130.2 (s, 4CH of 2C_6H_5), 150.3 (s, 2C_{ipso} of 2C_6H_5), 167.2 (d, $^2J_{CP}$ = 5.2, C=O), 171.0 (d, $^3J_{CP}$ = 20.1, C=O), 172.4 (C=O). ^{13}P NMR: 11.91 [P(O)(OC_6H_5)$_2$].



(2*R*,3*R*)-**4** or (2*S**,3*S**)-**4**



(2*R*,3*S*)-**4** or (2*S**,3*R**)-**4**

Scheme 2

RESULTS AND DISCUSSION

The reaction between triphenyl phosphite (**1**), dialkyl acetylenedicarboxylates **2**, and alkylthiols **3** proceeds smoothly in CH_2Cl_2 at room temperature to produce dialkyl 2-(diphenoxyphosphoryl)-3-(alkylthio) succinates **4**, as a mixture of two diastereoisomers, in 78-90% yields (Scheme 1).

The structures of compounds **4a-4f** were deduced from their elemental analyses and high-field ^{1}H, ^{13}C and ^{31}P NMR spectra and IR spectral data. The mass spectra of these compounds exhibited molecular ion peaks at the appropriate *m/z* values. The ^{1}H NMR spectrum of **4a** in $CDCl_3$ showed two singlets at δ = 3.71 and 3.72 ppm for the methoxy protons, together with an AB quartet for SCH_2 group, and two double doublets at δ = 4.30 ($^2J_{PH}$ = 25.3, $^3J_{HH}$ = 4.0 Hz) and 5.21 (dd, $^3J_{HP}$ = 7.8, $^3J_{HH}$ = 4.0) for the methane protons.

Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra of **4a-4f**, it helps in the assignment of the signals by long-range coupling with ^{1}H and ^{13}C nuclei (see Experimental section). Observation of $^3J_{HH}$ = 3.5-4.6 Hz for the vicinal methine protons in **4a-4f** confirms the dominance of the *gauche* arrangement. Since compound **4** possesses two stereogenic centers, two diastereomers with *gauche* HCCH arrangements are possible (Scheme 2).

The three-bond carbon-phosphorus coupling constant, $^3J_{CP}$, depends on conformation, as expected, transoid couplings being larger than cisoid ones. The Karplus relation can be derived from the data for organophosphorus compounds with tetra- and penta-valent phosphorus [13,14]. The observation of $^3J_{CP}$ = 3.8-4.5 Hz for the *C*O_2Me group is in agreement with the (2*R*,3*R*) or (2*S**,3*S**) diastereoisomer as the major isomer (60-64%). Since, the minor diastereoisomer shows $^3J_{CP}$ = 18.8-20.3 Hz for the *C*O_2Me group, its configuration is (2*R*,3*S*) or (2*S**,3*R**).

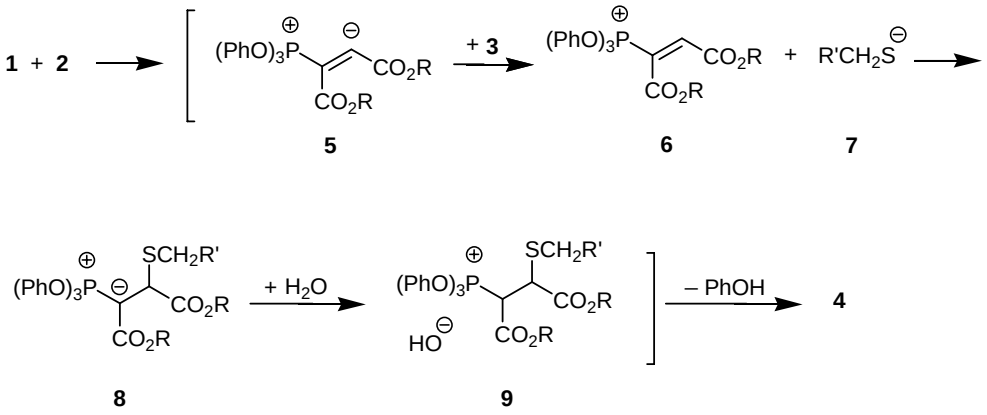
Characteristic ester carbonyl resonances for the major diastereoisomer of **4a** appeared at δ = 166.6 (d, $^2J_{PC}$ = 5.5 Hz) and 170.5 (d, $^3J_{PC}$ = 4.4 Hz), whereas the carbon atom of the P-CH moiety appeared at δ = 48.5 (d, $^1J_{PC}$ = 127.4 Hz). The presence of three electronegative oxo substituents on the phosphorus atom increases the $^1J_{CP}$ value. Finally, the ^{31}P shifts of 11.41-11.95 ppm are in accord with the presence of C-P(O)(OC_6H_5)$_2$ groups in both diastereoisomers of **4**.

The following mechanism may be invoked for the formation of compounds **4**. Conceivably, the starting point of the reaction is the formation of a 1:1 zwitterionic species [1,2] **5** between **1** and **2**, which is protonated by the SH-acidic **3** (Scheme 3). Then, the positively charged ion might be attacked by enolate anion of **3** to produce the ylide **8**. Compound **4** is apparently formed by addition of adventitious water that leads to the hydrolysis of **8**. Hydrolysis of alkyl triphenyl phosphonium salts in water has been reported to yield diphenyl alkylphosphonates [15].

In conclusion, the reaction between acetylenic esters, alkylthiols, and triphenyl phosphite provides a simple one-pot synthesis of stable dialkyl 2-(diphenoxyphosphoryl)-3-(alkylthio)succinates of potential synthetic interest. The present procedure has the advantage that the reaction is performed under neutral conditions, and the starting material can be used without any activation or modification. The procedure described here provides an acceptable method for the preparation of sulfur-containing phosphorylated succinates.

ACKNOWLEDGEMENTS

We are grateful to Kimia Exir Chemical Company for partial support of this work.



Scheme 3

REFERENCES

[1] E. Winterfeldt, D. Schumann, H. Dillinger, J. Chem. Ber. 102 (1994) 1656.

[2] H.J. Dillinger, G. Fengler, D. Schumann, E. Winterfeldt, Tetrahedron 30 (1994) 2553 and 2561.

[3] H. Junjappa, M.K. Saxena, D. Ramaiah, B.B. Lohray, N.P. Rath, M.V. George, J. Org. Chem. 63 (1994) 9801.

[4] V. Nair, C. Rajesh, A.U. Vinod, S. Bindu, A.R. Sreekanth, J.S. Mathen, L. Balagopal, Acc. Chem. Res. 36 (1994) 899.

[5] I. Yavari, M.H. Mosslemin, A.R. Montahaei, J. Chem. Res. (S) (1994) 576.

[6] I. Yavari, A. Alizadeh, H. Mohebbi, Phosphorus, Sulfur and Silicon 178 (1994) 1741.

[7] I. Yavari, M. Anari-Abbasinejad, Z. Hossaini, Org. Biomol. Chem. 1 (1994) 560.

[8] I. Yavari, Z. Hossaini, A. Alizadeh, Monatsh. Chem. 137 (1994) 1083.

[9] A. Ramazani, A.R. Kazemizadeh, E. Ahmadi, N. Noshiranzadeh, A. Souldozi, Curr. Org. Chem. 11 (1994) 59.

[10] I. Yavari, Z. Hossaini, E. Karimi, Monatsh. Chem. 138 (1994) 1267.

[11] I. Yavari, R. Amiri, M. Haghdadi, Croatica Chem. Acta 80 (1994) 25.

[12] I. Yavari, S. Ali-Asgari, K. Porshamsian, M. Bagheri, J. Sulfur Chem. 28 (1994) 477.

[13] M. Karplus, J. Am. Chem. Soc. 88 (1994) 2870.

[14] C.A. Haasnoot, F.A.A.M. de Leeuw, C. Altona, Tetrahedron 36 (1994) 2783.

[15] D. Maffre, P. Dumy, J.-P. Vidal, R. Escale, J.-P. Girard, J. Chem. Res. (S) (1994) 30.