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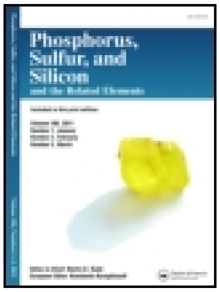

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Introduction of a Novel Reaction of Triacetylmethane: One-Pot Synthesis of Dialkyl-2-(3,1-hydroxyethylidene-2,4-pentanedione-3-yl)-3-(triphenylphosphoranylidene)-butanedioate

Ahmad Shaabani [a], Ayoob Bazgir [a], Mohammad Bagher Teimouri [a] & Hamid Reza Bijanzadeh [b]

[a] Department of Chemistry, Shahid Beheshti University, Tehran, Iran
[b] Department of Chemistry, Tarbiat Modarres University, Tehran, Iran
Published online: 27 Oct 2010.

To cite this article: Ahmad Shaabani, Ayoob Bazgir, Mohammad Bagher Teimouri & Hamid Reza Bijanzadeh (2002) Introduction of a Novel Reaction of Triacetylmethane: One-Pot Synthesis of Dialkyl-2-(3,1-hydroxyethylidene-2,4-pentanedione-3-yl)-3-(triphenylphosphoranylidene)-butanedioate, Phosphorus, Sulfur, and Silicon and the Related Elements, 177:4, 833-839, DOI: 10.1080/10426500210676

To link to this article: http://dx.doi.org/10.1080/10426500210676

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Phosphorus, Sulfur and Silicon, 2002, Vol. 177:833–839

1042-6507/02 $12.00 + .00

INTRODUCTION OF A NOVEL REACTION OF TRIACETYLMETHANE: ONE-POT SYNTHESIS OF DIALKYL-2-(3,1-HYDROXYETHYLIDENE-2,4-PENTANEDIONE-3-YL)-3-(TRIPHENYLPHOSPHORANYLIDENE)-BUTANEDIOATE

Ahmad Shaabani,[a] *Ayoob Bazgir,*[a] *Mohammad Bagher Teimouri,*[a] *and Hamid Reza Bijanzadeh*[b]
Department of Chemistry, Shahid Beheshti University, Tehran, Iran[a] *and Department of Chemistry, Tarbiat Modarres University, Tehran, Iran*[b]

(Received March 5, 2001; accepted October 11, 2001)

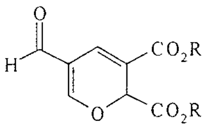
Protonation of reactive 1:1 intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylate by 3-(1-hydroxyethylidene)-2,4-pentanedione leads to vinyl phosphonium salts, which undergo Michael addition with the conjugate base of CH-acid to produce the title compounds in high yield.

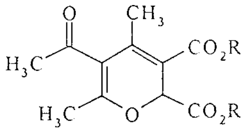
Keywords: Acetylenic esters; dynamic NMR; triacetylmethane; triphenylphosphine

We have recently described[1] the synthesis of dialkyl-formyl-2H-pyran-2,3-dicarboxylate (**1**) from the reaction of triformylmethane with dialkyl acetylenedicarboxylates and triphenylphosphine. With the purpose of preparation of 2H-pyran ring with highly functionalized groups such as (**2**), we performed the reaction of 3-(1-hydroxyethylidene)-2,4-pentanedione (**3**) with triphenylphosphine and dialkyl acetylenedicarboxylates (**4**). This reaction did not afford the corresponding 4,6-dimethyl-2H-pyran-2,3-dicarboxylates (**2**), but as an unusual behavior of compound (**3**) yielded compounds **6a–c** which were as two rotamers 6-*s-cis* and 6-*s-trans* in an about 1:2 ratio in high yields.

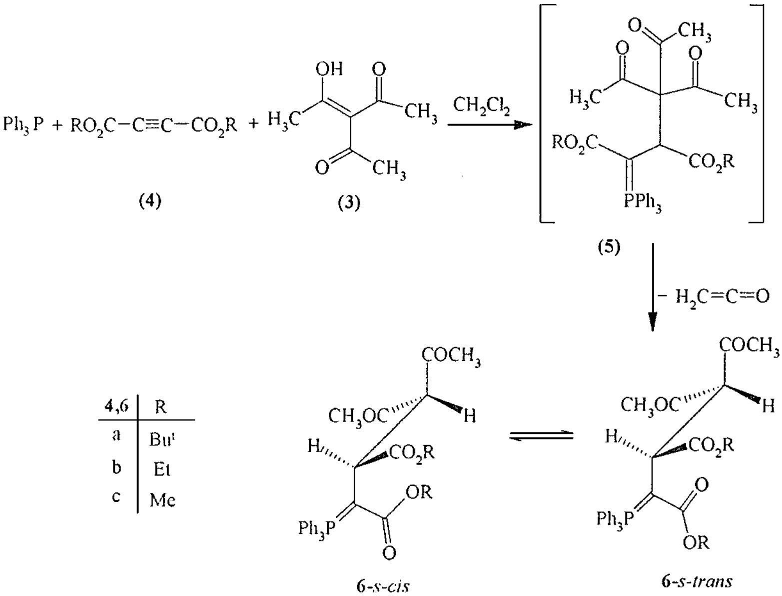
We gratefully acknowledge financial support from the Research Council of Shahid Beheshti University.

Address correspondence to A. Shaabani, Department of Chemistry, Shahid Beheshti University, PO Box 19396-4716, Tehran, Iran. E-mail: a-shaabani@cc-sbu.ac.ir


(1)


(2)

On the basis of the well established chemistry of trivalent phosphorus nucleophiles[2–6] it is reasonable to assume that compound (**5**) results from the initial addition of triphenylphosphine to the acetylenic ester and a concomitant protonation of the 1:1 adduct by compound (**3**). Then, the positively charged ion is attacked by the enolate anion of the CH acid to form compound (**5**).[7–11] Compound (**5**) is converted to the compounds **6a–c** probably by extraction of ketene following deprotonation by triphenylphosphine.



4,6	R
a	Bu^t
b	Et
c	Me

SCHEME 1

All the compounds are stable solid powders whose structure is fully supported by elemental analyses and IR, high-field ^{1}H, ^{13}C, and ^{31}P NMR and mass spectrometry data. The mass spectra of these compounds displayed molecular ion peaks at m/z of 504, 532, and 588 respectively. Initial fragmentation involved the loss of ester moieties. The ^{1}H NMR spectra of compounds **6a**, **6b**, and **6c** showed the *s-trans* rotamer is the major (about 68%) and *s-cis* rotamer is the minor (about 32%).

The ^{1}H NMR spectra of **6a** exhibited two sets of sharp lines at δ 1.41 and 0.96 for *s-trans* rotamer and δ 1.39 and 1.49 for *s-cis* rotamer arising from *tert*-butyl protons. The shift at 0.96 of the *tert*-butyl group of the *s-trans* rotamer is shielded because of anisotropy of phenyl groups of triphenylphosphine. The ^{1}H NMR spectra of rotamers **6a** displayed signals for CH protons of $CHCO_2R$ which appears as two sets of doublet or doublet at δ 3.17 and 3.12 ($^3J_{PH}$ 17.40 Hz and $^3J_{HH}$ 10.50 Hz) for *s-trans* and *s-cis* rotamers, along with a characteristic two sets of doublet of CH(CO) moiety at δ 5.53 and 5.12 ($^3J_{HH}$ 10.50 Hz, $^3J_{HH}$ 10.90 Hz) for *s-trans* and *s-cis* rotamers, respectively (Table I). The acetyl groups are diastereotopic and show two separate signals in ^{1}H and ^{13}C NMR spectra for each of the rotamers.

The ^{1}H NMR spectra of **6b** and **6c** are similar to those of **6a** except for the ester groups, which exhibit characteristic signals with appropriate chemical shifts.

The check whether the above conclusions regarding the nature of compound **6** are reasonable, we measured the phosphorus-31 NMR spectra of **6a–c**. Two single ^{31}P signal was observed at about 23 and 24 ppm (downfield from 85% H_3PO_4) for *s-cis* and *s-trans* isomer of these compounds, respectively. These shifts are similar to those observed for stable phosphorus ylides [$(Ph)_3P{=}C$].[12,13]

The variable temperature NMR spectra of compound **6a** is studied in $CDCl_3$. The ^{1}H NMR spectrum of **6a** displays two isomers, which are appreciably broadened by increasing temperature. At about 60°C in $CDCl_3$ the four *tert*-butyl signals coalesced and appeared as two fairly broad bands. Also, the resonance of vicinal CH protons of $CHCO_2R$ and CH(CO) which appears as two sets of doublet of doublet and two sets of doublet for two *s-cis* and *s-trans* isomers have coalesced at 55°C. By decreasing temperature, the two isomers are populated again in the ratio about 2:1 at room temperature.

From the coalescence of the *tert*-butyl protons and using the expression

$$k = \pi \Delta\nu/\sqrt{2}$$

we calculate the first order rate constant (k) for C—C bond rotation of P=C—C=O in **6a** is 100.8 s^{-1} at 60°C. Application of the absolute rate theory[14] with a transmission coefficient of 1 gives ΔG of 69.1 $kJmol^{-1}$ (Scheme 2).

EXPERIMENTAL

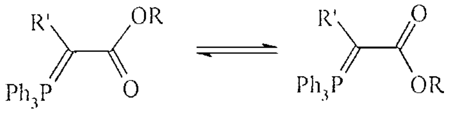
All melting points are uncorrected. Elemental analysis was performed using a Heraeus CHN—O rapid analyzer. Mass spectra were recorded on

TABLE I ^{1}H, ^{13}C, and ^{31}P NMR Data for Compounds **6a–c**

Compound	^{1}H/^{13}C/^{31}P	δ(ppm) (CDCl$_3$—Me$_4$Si)
6a		*s-trans* rotamer (68%)
	^{1}H	0.95 and 1.40(18H, 2s, 2CMe$_3$), 2.10 and 2.34(6H, 2s, 2MeC=O), 3.17(1H, dd, $^3J_{HP}$ 17.4 Hz and $^3J_{HH}$ 10.5 Hz, CH—C=P), 5.52(1H, d, $^3J_{HH}$ 10.5 Hz), 7.45–7.68(m, Ph$_3$P).
	^{13}C	28.15 and 28.30(2C$\underline{\text{Me}}_3$), 30.20 and 33.34(2$\underline{\text{Me}}$—C=O), 38.64(d, $^1J_{PC}$ 124.19 Hz, P=C), 45.20(d, $^2J_{PC}$ 13.7 Hz, P=C—$\underline{\text{C}}$), 66.34(d, $^3J_{PC}$ 4.4 Hz, P=C—C—$\underline{\text{C}}$), 76.97 and 77.26(2 $\underline{\text{C}}$Me$_3$), 128.14(d, $^3J_{PC}$ 12 Hz, *meta*-C), 131.76(bs, *para*-C), 134.11(d, $^2J_{PC}$ 7.8 Hz, *ortho*-C), 168.87(d, $^2J_{PC}$ 13.1 Hz, P=C—$\underline{\text{C}}$=O), 173.84(d, $^3J_{PC}$ 4.5 Hz, P=C—C—$\underline{\text{C}}$=O), 201.87 and 205.03(2Me$\underline{\text{C}}$=O).
	^{31}P	22.99(1s, Ph$_3$P=C).
		s-cis rotamer (32%)
	^{1}H	1.39 and 1.48(18H, 2s, 2CMe$_3$), 2.04 and 2.21(6H, 2s, 2MeC=O), 3.12(1H, dd, $^3J_{HP}$ 17.8 Hz and $^3J_{HH}$ 10.9 Hz, CH—C=P), 5.11 (1H, d, $^3J_{HH}$ 10.9 Hz), 7.45–7.68(m, Ph$_3$P).
	^{13}C	28.15 and 28.95(2C$\underline{\text{Me}}_3$), 29.46 and 32.74(2$\underline{\text{Me}}$—C=O), 40.47(d, $^1J_{PC}$ 131.84 Hz, P=C), 44.53(d, $^2J_{PC}$ 13.3 Hz, P=C—$\underline{\text{C}}$), 68.42(d, $^3J_{PC}$ 4.8 Hz, P=C—C—$\underline{\text{C}}$), 80.24 and 80.27(2$\underline{\text{C}}$Me$_3$), 128.30(d, $^3J_{PC}$ 12.25 Hz, *meta*-C), 131.76(bs, *para*-C), 134.11(d, $^2J_{PC}$ 7.8 Hz, *ortho*-C), 170.57(d, $^2J_{PC}$ 19.3Hz, P=C—$\underline{\text{C}}$=O), 173.48(d, $^3J_{PC}$ 3.8 Hz, P=C—C—$\underline{\text{C}}$=O), 202.40 and 204.46 (2Me$\underline{\text{C}}$=O).
	^{31}P	24.16(1s, Ph$_3$P=C).
6b		*s-trans* rotamer (65%)
	^{1}H	0.43 and 1.16(6H, 2t, $^3J_{HH}$ 7.1 Hz, 2$\underline{\text{Me}}$—CH$_2$), 2.16 and 2.28 (6H, 2s, 2MeC=O), 3.34(1H, bm, CH—C=P), 3.52–4.12(4H, m, 2ABX$_3$, 2CH$_2$), 5.51(1H, bs, C$\underline{\text{H}}$—CH—C=P), 7.46–7.68(m, PPh$_3$).
	^{13}C	13.91 and 14.07(2O—CH$_2$—$\underline{\text{Me}}$), 30.49 and 32.82(2$\underline{\text{Me}}$C=O), 39.07(d, $^1J_{PC}$ 123.9 Hz, C=P), 44.42(d, $^2J_{PC}$ 13.4 Hz, P=C—C), 57.44 and 60.73(2CH$_2$—O), 66.56(bs, P=C—C—$\underline{\text{C}}$), 126.50(d, $^1J_{PC}$ 85.0 Hz, *ipso*—C), 128.33(d, $^3J_{PC}$ 12.25 Hz, *meta*-C), 131.91(*para*-C), 134.01(d, $^2J_{PC}$ 9.25 Hz, *ortho*-C), 169.29(d, $^2J_{PC}$ 13.5 Hz, P=C—$\underline{\text{C}}$=O), 174.59(d, $^3J_{PC}$ 3.75 Hz, P=C—C—$\underline{\text{C}}$=O), 201.98 and 203.95 (2s, 2Me—$\underline{\text{C}}$=O).
	^{31}P	23.67(1s, Ph$_3$P=C).
		s-cis rotamer (35%)
	^{1}H	1.21 and 1.25(6H, 2t, $^3J_{HH}$ 6.9 Hz, 2$\underline{\text{Me}}$—CH$_2$) 2.09 and 2.19(6H, 2s, 2MeC=O), 3.34(1H, bm, CH—C=P), 3.52–4.12(4H, m, 2ABX$_3$, 2CH$_2$), 5.12(1H, d, $^3J_{HH}$ 9.8 Hz, $\underline{\text{CH}}$—CH—C=P), 7.46–7.68(m, PPh$_3$).
	^{13}C	14.17 and 15.23(2O—CH$_2$—$\underline{\text{Me}}$), 29.83 and 30.49(2 $\underline{\text{Me}}$C=O), 39.07(d, $^1J_{PC}$ 123.9 Hz, C=P), 43.64(d, $^2J_{PC}$ 13.1 Hz, P=C—C), 58.12 and 60.73(2CH$_2$—O), 68.30(bs, P=C—C—$\underline{\text{C}}$),

TABLE I ^{1}H, ^{13}C and ^{31}P NMR Data for Compounds **6a–c** *(Continued)*

Compound	^{1}H/^{13}C/^{31}P	δ(ppm) (CDCl$_3$—Me$_4$Si)
		127.30(d, $^{1}J_{PC}$ 85.0 Hz, *ipso*—C), 128.43(d, $^{3}J_{PC}$ 14.6 Hz, *meta*-C), 131.91(*para*-C), 134.01(d, $^{2}J_{PC}$ 9.25 Hz, *ortho*-C), 170.30(d, $^{2}J_{PC}$ 14.6 Hz, P=C—$\underline{C}$=O), 174.82(d, $^{3}J_{PC}$ 4.0 Hz, P=C—C—$\underline{C}$=O), 201.98 and 203.95 (2s, 4Me—$\underline{C}$=O).
	^{31}P	23.86(1s, Ph$_3$P).
6c		*s-trans* rotamer (65%)
	^{1}H	2.17 and 2.27(6H, 2s, 2MeCO), 3.06, and 3.60(6H, 3s, 2OMe), 3.42(1H, bm, 2C$\underline{H}$(COMe)$_2$), 5.49(1H, bs, C$\underline{H}$—C=P), 7.21–7.73(m, P(Ph)$_3$).
	^{13}C	29.81 and 30.46(2$\underline{Me}$CO), 39.36(d, $^{1}J_{PC}$ 123.81 Hz, P=C), 44.26(d, $^{2}J_{PC}$ 13.35 Hz, P=C—$\underline{C}$), 48.75 and 51.70(2OMe), 66.69(bs, P=C—C—$\underline{C}$), 126.33(d, $^{1}J_{PC}$ 83.25Hz, *ipso*-C), 128.42(d, $^{3}J_{PC}$ 12.0H *meta*-C), 131.97(d, $^{4}J_{PC}$ 2.1 Hz, *para*-C), 133.84(d, $^{2}J_{PC}$ 9.1 Hz, *ortho*-C), 169.61(d, $^{2}J_{PC}$ 13.25 Hz, P=C—$\underline{C}$=O), 174.96(d, $^{3}J_{PC}$ 3.75 Hz, P=C—C—$\underline{C}$=O), 201.95 and 203.71(2MeC=O).
	^{31}P	23.81 (s, Ph$_3$P=C).
		s-cis rotamer (35%)
	^{1}H	2.04 and 2.19(6H, 2s, 2MeCO), 3.59 and 3.60(6H, 2s, 2OMe), 3.42(1H, bm, 2C$\underline{H}$(COMe)$_2$), 5.11(1H, bs, C$\underline{H}$—C=P), 7.21–7.73(m, P(Ph)$_3$).
	^{13}C	30.46 and 32.74(2$\underline{Me}$CO), 39.98(d, $^{1}J_{pc}$ 127.87 Hz, P=C), 43.16(d, $^{2}J_{PC}$ 12.99 Hz, P=C—$\underline{C}$), 50.07 and 51.70(3s, 4OMe), 68.01(bs, P=C—C—$\underline{C}$), 127.03(d, $^{1}J_{PC}$ 83.25 Hz, *ipso*-C), 128.52(d, $^{3}J_{PC}$ 11.90 Hz, *meta*-C), 131.97(d, $^{4}J_{pc}$ 2.1 Hz, *para*-C), 133.84(d, $^{2}J_{PC}$ 9.1 Hz, *ortho*-C), 170.68(d, $^{2}J_{PC}$ 15.0 Hz, P=C—$\underline{C}$=O), 175.18(d, $^{3}J_{PC}$ 4.0 Hz, P=C—C—$\underline{C}$=O), 201.95 and 203.89(4MeC=O).
	^{31}P	23.81 (s, Ph$_3$P=C).

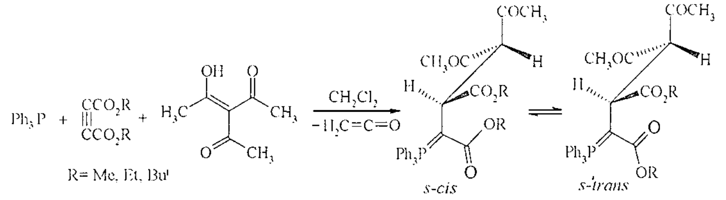


6-*s-cis* 6-*s-trans*

R' =(CH$_3$CO)$_2$CH-CH[CO$_2$C(CH$_3$)$_3$]-

SCHEME 2

Reaction between triphenylphosphine and dialkyl acetylenedicarboxylate and triacetylmethane leads to vinyl phosphonium salts, which undergo Michael addition with the conjugate base of CH-acid to produce the title compounds in high yield.



Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-470 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer at 500, 125.77 and 202.46 MHz respectively.

*The typical procedure for the preparation of ditert-butyl-2-(3,1-hydroxyethylidene-2,4-pentanedione-3-yl)-3-(triphenylphosphoranylidene)-butanedioate (**6a**).* To a magnetically stirred solution of 3-(1-hydroxyethylidene)-2,4-pentanedione (0.28 g, 2 mmol) and triphenylphosphine (0.52 g, 2 mmol) in dichloromethane (10 ml) was added dropwise a mixture of *ditert*-butyl acetylenedicarboxylate (0.45 g, 2 mmol) in dichloromethane (5 ml) at −5°C over 10 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 24 h. The precipitate was filtered and washed with ethyl acetate (10 ml). The product was recrystallized from 1:1 dichloromethane: ethyl acetate to yield **6a** as white powder (0.95 g, 81%). m.p. 144–146°C (decom.); $\nu_{\max}$/cm^{-1} (KBr) 1715 and 1620(C=O) (M/Z, %) 588(M, 2), 487(M CO_2Bu^t, 16), 431(MH—CO_2Bu^t—Bu^t, 22), 371(M—2CO_2Bu^t—Me, 15), 277(Ph_3PO—H, 11), 262(Ph_3P, 97 183($C_{12}H_8P$, 90), 108 (PhP, 46), 57(Bu^t, 100), 43(CHCO, 58). (Found: C, 71.30%; H, 7.03%. $C_{35}H_{41}O_6P$ requires: C, 71.43%; H, 7.02%).

*Selected data for **6b**.* White powders, 0.79 g, yield 74%, m.p. 165–167°C (decom.), $\nu_{\max}$/cm^{-1} (KBr 1724 and 1624(C=O). (M/Z, %): 532(M, 14), 459(M—CO_2Et, 32), 277(Ph_3PO—H, 15), 262(Ph_3P, 96) 183($C_{12}H_8P$, 67), 108(PhP, 40), 43(MeCO, 100). (Found: C, 69.46%; H, 6.20%; $C_{31}H_{33}O_6P$, requires: C 69.90%; H, 6.24%).

*Selected data for **6c**.* White powders, 0.83g, yield 82%, m.p. 183–185°C (decom.), $\nu_{\max}$/cm^{-1} (KBr 1725 and 1622 (C=O); (M/Z, %): 504(M$^+$, 9), 445 (M$^+$—CO_2 Me, 23), 405(M$^+$—$(MeCO)_2CH$, 46), 333(M $(MeCO)_2CH$—$CHCO_2Me$, 15), 277(Ph_3PO—H, 19), 262(Ph_3P, 97), 183($C_{12}H_8P$, 98), 108(Ph—P, 51) 59(CO_2Me, 14), 43(MeCO, 100).

(Found: C, 68.65%; H, 5.70%. $C_{29}H_{29}O_6P$ requires C, 69.03%; H, 5.79%).

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