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New One-pot Synthesis of tetra-Alkoxycarbonylallylidenetriphenylphosphoranes

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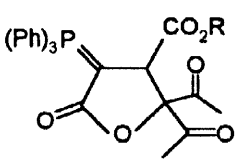
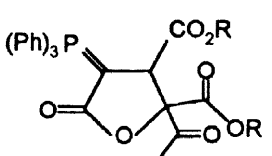
Abstract: Dimethyl chloromalonate or diethyl bromomalonate undergo a complex reaction with dialkyl acetylenedicarboxylates and triphenylphosphine to produce tetra-alkoxycarbonylallylidene-triphenylphosphoranes in moderate yields.

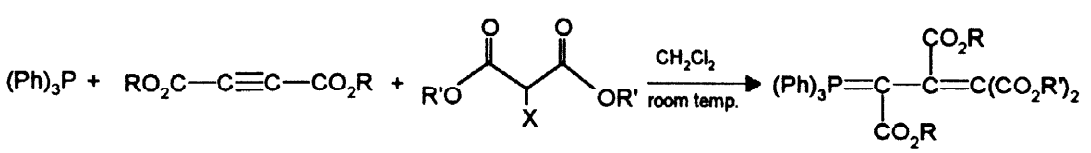
We have recently described[1] the synthesis of 5,5-diacetyl-2-oxo-3-(triphenylphosphoranylidene)-tetrahydrofuran-4-carboxylates (**1**) from the reaction of 3-chloropentane-2,4-dione with dialkyl acetylenedicarboxylates and triphenylphosphine. With the purpose of preparation of butyrolactones having two alkoxycarbonyl groups at C-5, such as **2**, we performed the reaction of dimethyl chloromalonate (**4a**) or diethyl bromomalonate (**4b**) with triphenylphosphine and dialkyl acetylenedicarboxylates (**3**). This reaction did not afford the corresponding butyrolactone **2**, but yielded compounds **5a-c** in moderate yields.



1



2



3	R
a	Me
b	Et

4	X	R'
a	Cl	Me
b	Br	Et

5	R	R'	% yield
a	Me	Me	40
b	Me	Et	51
c	Et	Et	38

Scheme 1

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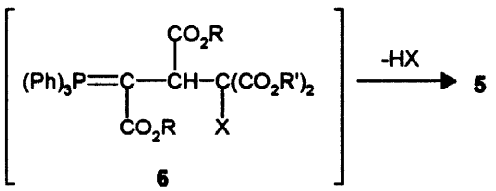
PII: S0040-4039(97)10725-0

On the basis of the well established chemistry of trivalent phosphorus nucleophiles[2-7] it is reasonable to assume that compound **5** results[8] from the initial addition of triphenylphosphine to the acetylenic ester and a concomitant protonation of the 1:1 adduct by dialkyl halomalonate (**4**). Then, the positively charged ion is attacked by the enolate anion of the CH-acid to form intermediate **6**, which is then converted to the allylidenephosphorane **5** presumably by elimination of HX.[9]



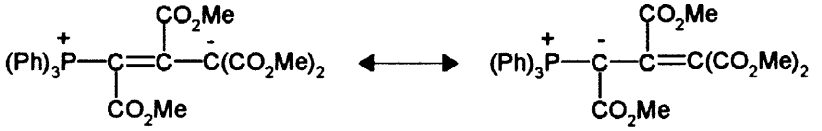
The structures of compounds **5a-c** were deduced from their elemental analyses and their ^1H and ^{13}C NMR spectra. The nature of these compounds as dehydrohalogenated 1:1:1 adducts was apparent from the mass spectra which displayed molecular ion peaks at m/z = 534, 562, and 590, respectively.

The most noteworthy feature of the ^1H NMR spectrum of **5a** in $CDCl_3$ at room temprature (25 °C) is the methoxy region which exhibits two sharp (δ = 3.17 and 3.38 ppm) and one broad (δ = 3.65 ppm) component. Each sharp component has one half the area of the broad component, and thus must belong to a methoxy group. The aromatic protons appear as a multiplet at δ = 7.2-8.0 ppm. Near 50 °C the broad line of the high field methoxy resonance becomes sharper. Decreasing the temprature below room temperature results in the splitting of the broad resonance into a doublet with an intensity ratio of 1:1 (coalescence temprature, -8 ± 1 °C). No further dynamic NMR effect was observed down to -80 °C.

From the coalescence of the high field methoxy proton resonances and using the expression

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

we calculate that the first order rate constant (k) for C=C bond rotation in **5a** is 16 s^{-1} at -8 °C. Application of the absolute rate theory[10] with a transmission coefficient of 1 gives $\Delta G^{\neq}$ of 58.5 ± 1 kJ mol^{-1}. These spectral changes can be most easily interpreted in terms of C=C bond rotation in **5a**. Significant contribution of structures **5a'** and **5a''** to the resonance hybrid of **5a** with delocalisation into the carbomethoxy groups appears to be a plausible factor in reduction of the free-energy barrier for the C=C bond rotation in **5a**.



5a' **5a''**

The ^{13}C NMR spectrum of **5a** displayed fifteen distinct resonances at -30 °C in agreement with the phosphorane structure (see Table 1). Although the presence of the ^{31}P nucleus complicates both the ^1H and ^{13}C NMR spectra of **5a**, it helps in assignment of the signals by long-range coupling with ^1H and ^{13}C nuclei. The ^1H and ^{13}C NMR

Table 1 Proton and Carbon-13 NMR data for compounds **5a-c**

Compound	$^{1}H/^{13}C$	δ (ppm) ($CDCl_3$-Me_4Si)	Temp. (°C)
5a	^{1}H	3.17 (3 H, s, OCH_3), 3.38 (3 H, s, OCH_3), 3.65 (6H, s, 2 OCH_3), 7.2-8.0 (15 H, m, 3 C_6H_5)	+ 25
	^{1}H	3.15 (3 H, s, OCH_3), 3.35 (3 H, s, OCH_3), 3.60 (3 H, s, OCH_3), 3.68 (3 H, s, OCH_3), 7.2-8.0 (15 H, m, 3 C_6H_5)	- 80
	^{13}C	50.53 and 51.80 (2 OCH_3), 52.49 and 52.63 (2 OCH_3), 58.23 (d, $^{1}J_{PC}$ 128.7, P=C), 119.52 (d, $^{3}J_{PC}$ 9.1, P=C-C=^{13}C), 124.79 (d,$^{1}J_{PC}$ 91.6, ipso-C), 128.68 (d, $^{3}J_{PC}$ 12.7, meta-C), 132.22 (d, $^{4}J_{PC}$ 2.1, para-C), 133.63 (d, $^{2}J_{PC}$ 10.0, ortho-C), 147.33 (d, $^{2}J_{PC}$ 12.7, P=C-^{13}C), 167.20 (C=O), 167.99 (d, $^{2}J_{PC}$ 12.9, C=O), 168,05(C=O), 170.82 (d, $^{3}J_{PC}$ 3.0, C=O)	-30
5b	^{1}H	1.22 (6 H, t, $^{3}J_{HH}$ 8.0 Hz, 2 CH_3), 3.20 (3 H, s, OCH_3), 3.45 (3 H, s, OCH_3), 4.10 (4 H, q, $^{3}J_{HH}$ 8.0 Hz, 2 OCH_2), 7.3-8.1 (15 H, m, 3 C_6H_5)	+25
	^{1}H	1.17 (3 H, t, $^{3}J_{HH}$ 7.2, CH_3), 1.24 (3 H, t, $^{3}J_{HH}$ 7.2, CH_3), 3.25 (3 H, s, OCH_3), 3.35 (3 H, s, OCH_3), 4.05 (2 H, q, $^{3}J_{HH}$ 7.2 Hz, OCH_2), 4.13 (2 H, q, $^{3}J_{HH}$ 7.2 Hz, OCH_2), 7.3-8.1 (15 H, m, 3 C_6H_5)	- 40
	^{13}C	12.56 (CH_3), 13.80 (CH_3), 49.80, 51.67 (2 OCH_3), 55.48 (d, $^{1}J_{PC}$ 129.6 Hz, P=C), 59.86 and 60.39 (2 OCH_2), 122.21 (d, $^{3}J_{PC}$ 9.2 Hz, P=C-C=^{13}C), 125.32 (d, $^{1}J_{PC}$ 91.5, ipso-C), 128.25 (d, $^{3}J_{PC}$ 11.8 Hz, meta-C), 131.77 (d, $^{4}J_{PC}$ 2.0 Hz, para-C), 133.74 (d, $^{2}J_{PC}$ 10.0 Hz, ortho-C), 145.41 (d, $^{2}J_{PC}$ 12.7, P=C-^{13}C), 166.34 and 167.46 (2 $^{13}CO_2Et$), 168.10 (d, $^{2}J_{PC}$ 13.2, $^{13}CO_2CH_3$), 170.11 (d, $^{3}J_{PC}$ 3.2, $^{13}CO_2CH_3$)	- 30
5c	^{1}H	0.85 (3 H, t, $^{3}J_{HH}$ 7.2 Hz, CH_3), 1.03 (3 H, t, $^{3}J_{HH}$ 7.2 Hz, CH_3), 1.18 (6 H, t, $^{3}J_{HH}$ 7.2 Hz, 2 CH_3), 3.55 (2 H, q, $^{3}J_{HH}$ 7.2, OCH_2), 3.82 (2 H, q, $^{3}J_{HH}$ 7.2 Hz, OCH_2), 4.07 (4 H, q, $^{3}J_{HH}$ 7.2 Hz, OCH_2), 7.3-8.0 (15 H, m, 3 C_6H_5)	+25
	^{13}C	13.40 and 13.72 (2 CH_3), 14.05 (2 CH_3), 55.38 (d, $^{2}J_{PC}$ 128.7, P=C), 58.88 (OCH_2), 60.55 (2 OCH_2), 61.33 (OCH_2), 122.11 (d, $^{3}J_{PC}$ 9.0 Hz, P=C-C=^{13}C), 125.91 (d, $^{2}J_{PC}$ 88.2, ipso-C), 128.72 (d, $^{3}J_{PC}$ 12.8 Hz, meta-C), 131.95 (d, $^{4}J_{PC}$ 2.2 HZ, para-C), 134.23 (d, $^{2}J_{PC}$ 10.0 Hz, ortho-C), 146.18 (d, $^{2}J_{PC}$ 13.0 Hz, P=C-^{13}C=C), 167.10 (2 C=O), 167.69 (d, $^{2}J_{PC}$ 12.7 Hz, C=O), 170.13 (d, $^{3}J_{PC}$ 3.6 Hz, C=O)	+ 25

spectra of **5b** and **5c** are similar to those of **5a**, except for the ester groups, which exhibited characteristic resonances with appropriate chemical shifts (see Table 1).

Functionalized phosphorus ylides **5a-c** may be considered as potentially useful synthetic intermediates[2-5] because they possess carbon atoms with different oxidation states. The procedure described here may be an acceptable method for the preparation of phosphoranes with variable functionalities.

References and Notes

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8. The typical process for the preparation of tetra-methoxycarbonylallylidenetriphenylphosphorane (**5a**) is described as an example. To a magnetically stirred solution of triphenylphosphine (0.524 g, 2 mmol) and dimethyl chloromalonate (0.33 g, 2 mmol) in CH_2Cl_2 (6 ml) was added, dropwise, a mixture of dimethylacetylenedicarboxylate (0.284 g, 2 mmol) in CH_2Cl_2 (2 ml) at -10 °C over 10 min. The reaction mixture was then allowed to warm up to room temprature and stirred for 24 h. The solvent was removed under reduced pressure and the viscous residue was purified by silica gel (Merck silica gel 60, 230-400 mesh) column chromatography using ether-ethyl acetate-hexane (2:1:1) as eluent. The solvent was removed under reduced pressure and the product (0.45 g, yellow oil, 42%) was obtained. Recrystallization from ether-pentane yielded **5a** as a yellow solid (0.43 g, 40%), m. p. 174-175 °C. IR (KBr) (ν_{max}, cm^{-1}): 1713 and 1644 (C=O); MS (*m/z*, %): 534 (M^++1, 4); 475 (M^+- CO_2Me, 11); 262 ($P\phi_3$, 100). (Found: C, 64.6; H, 5.1. $C_{29}H_{27}O_8P$ requires C, 65.16; H, 5.06%). Selected data for **5b**: m.p. 165-166 °C, yield 0.57 g (51%). IR (KBr) (ν_{max}, cm^{-1}): 1728, 1715, 1696 and 1620 (C=O); MS (*m/z*, %): 563 (M^++1, 73); 534 (M^+- CH_2=CH_2, 87); 490 (M^+- CO_2Et, 100); 262 ($P\phi_3$, 100). (Found: C, 66.0; H, 5.5. $C_{31}H_{31}O_8P$ requires C, 66.18; H, 5.55%). Selected data for **5c**: m. p. 142 °C, yield 0.45 g (38%). IR (KBr) (ν_{max}, cm^{-1}): 1721, 1713, 1705, and 1611 (C=O); MS (*m/z*, %): 591 (M^++1, 8); 563 (M^+- CH_2=CH_2, 51); 262 ($P\phi_3$, 100). (Found: C, 66.7; H, 6.2. $C_{33}H_{35}O_8P$ requires C, 67.11; H, 5.97%).
9. We have used triethylamine to mop-up the HX. However, this complicates the work-up process and increases the yield hardly at all.
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