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Vinyltriphenylphosphonium Salt Mediated One-pot Synthesis of Functionalized 3-(Triphenylphosphoranylidene)butyrolactones

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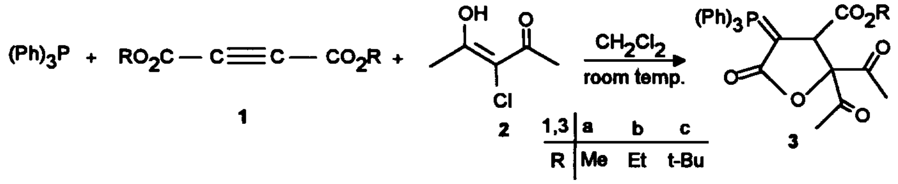
Abstract: *3-Chloropentane-2,4-dione exists, in solution, almost exclusively as enol tautomer, which undergoes a complex reaction with dialkyl acetylenedicarboxylates and triphenylphosphine to produce alkyl 5,5-diacetyl-2-oxo-3-(triphenylphosphoranylidene)tetrahydrofuran-4-carboxylates in moderate to fairly high yields.* © 1997 Published by Elsevier Science Ltd.

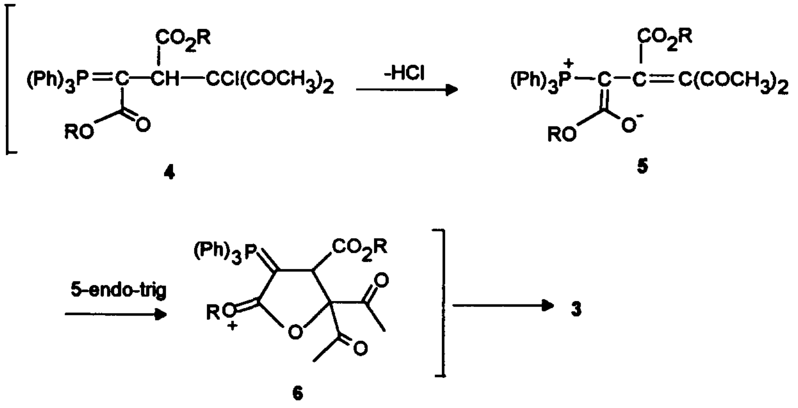
In recent years there has been increasing interest in the synthesis of organophosphorus compounds, i.e. those bearing a carbon atom bound directly to a phosphorus atom.[1-10] This interest has resulted from the recognition of the value of such compounds for a variety of interesting industerial and chemical synthetic uses. As a result a large number of methods have appeared describing novel syntheses of organophosphorus compounds. The successful attack by nucleophilic trivalent phosphorus on a carbon atom is facilitated when the latter is part of, or conjugated with, a carbonyl group, or when it is part of an unsaturated bond otherwise activated.[1-11] The reaction between trivalent phosphorus nucleophiles and α,β-unsaturated carbonyl compounds in the presence of a proton source has been studied using alcohols or phenol as reaction adjuncts.[12] The work reported here was undertaken in order to determine the possibility of trapping the reactive 1:1 intermediate formed in the initial reaction between triphenylphosphine and dialkyl acetylenedicarboxylates (**1**) by a carbon acid such as 3-chloropentane-2,4-dione (**2**). Compound **2** is a comercially available multifunctional system, which is apparently completely enolized in liquid phase, as indicated by ^{1}H and ^{13}C NMR spectroscopy.



1,3	a	b	c
R	Me	Et	t-Bu

This three-component reaction produces the hitherto unknown 3-(triphenylphosphoranylidene)butyrolactones **3a-c** in 46-85% yields. All the compounds are stable crystalline solids whose structure is fully supported by elemental analyses and IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. The mass spectra of compounds displayed molecular ion peaks at *m/z* 488, 503, and 530 for **3a**, **3b**, and **3c**, respectively. Initial fragmentations involved loss from or complete loss of the side chains.

Compound **3** apparently results[13] from the initial addition of the phosphine to the acetylenic ester and the concomitant protonation of the 1:1 adduct, then attack by the enolate anion to form the intermediate **4**, which is then converted to the butyrolactone **3** presumably by elimination of HCl and ring closure.[14]



The ^{1}H NMR spectrum of **3a** exhibited three single sharp lines readily recognizeable as arising from the methyl (δ 2.35 and 2.50) and methoxy (δ 3.21) protons, along with a doublet ($^{3}J_{PH}$ = 2.1 Hz) at δ 4.16 for the methine proton. A fairly complex multiplet was observed for the aromatic fragments at δ 7.4-7.8. The ^{13}C NMR spectra of **3a** displayed eleven distinct resonances in agreement with the lactone structure. Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra of **3a**, it helps in assignment of the signals by long-range couplings with ^{1}H and ^{13}C nuclei (see Table 1).The ^{1}H and ^{13}C NMR spectra of **3b** and **3c** are similar to those of **3a**, except for the ester groups, which exhibited characteristic resonances with appropriate chemical shifts (see Table 1).

Functionalized butyrolactones **3a-c** may be considered as potentially useful synthetic intermediates[15,16] because they possess carbon atoms with different oxidation states. The procedure described here mey be an acceptable method for the preparation of butyrolactones with variable functionalities.

Table 1 Proton and carbon-13 NMR data for compounds **2** and **3a-c**

Compound	$^1H/^{13}C$	δ (ppm) ($CDCl_3$-Me_4Si)
2	^1H	2.40 (6 H, s, 2 CH_3), 15.40 (1 H, s, O-H....O=C)
	^{13}C	23.66 (2 CH_3), 108.07 (C-Cl), 188.82 (2 C=O)
3a	^1H	2.35 and 2.50 (6 H, 2 s, 2 CH_3C=O), 3.21 (3 H, s, CH_3O), 4.16 (1 H, d, $^3J_{PH}$ 2.1 Hz, CH), 7.4-7.8 (15 H, m, 3 C_6H_5)
	^{13}C	26.31 and 28.02 (2 $^{13}CH_3CO$), 36.32 (d, $^1J_{PC}$ 138.0 Hz, P=C), 51.43 (OCH_3), 52.75 (d, $^2J_{PC}$ 13.8 Hz, CH), 94.66 (d, $^3J_{PC}$ 12.0 Hz, $^{13}CAc_2$), 124.20 (d, $^1J_{PC}$ 93.9 Hz, *ipso*-C), 128.61 (d, $^3J_{PC}$ 12.9 Hz, *meta*-C), 132.89 (d, $^4J_{PH}$ 2.8 Hz, *para*-C), 133.52 (d, $^2J_{PC}$ 10.1 Hz, *ortho*-C), 171.31 (d, $^2J_{PC}$ 20.2 Hz, P=C-^{13}C=O), 173.84 (C=O ester), 202.14 and 205.11 (2 C=O of 2 Ac).
3b	^1H	0.90 (3 H, t, $^3J_{HH}$ 8.0 Hz, CH_3), 2.32 and 2.48 (6 H, 2 s, 2 CH_3C=O), 3.66 (2 H, q of AB system, J_{AB} -10.8 Hz, $^3J_{HH}$ 8.0 Hz, CH_2), 4.15 (1 H, d, $^3J_{PH}$ 2.1 Hz, CH), 7.3-7.9 (15 H, m, 3 C_6H_5)
	^{13}C	13.64 ($^{13}CH_3$-CH_2), 26.27 and 28.10 (2 $^{13}CH_3C$=O), 36.26 (d, $^1J_{PC}$ 139.0 Hz, P=C), 52.81 ($^2J_{PC}$ 12.9 Hz, CH), 60.67 (CH_2), 94.81 (d, $^3J_{PC}$ 12.0 Hz, $^{13}CAc_2$), 124.40 (d, $^1J_{PC}$ 93.9 Hz, *ipso*-C), 129.11 (d, $^3J_{PC}$ 12.0 Hz, *mata*-C), 132.99 (d, $^4J_{PC}$ 2.7 Hz, *para*-C), 133.50 (d, $^2J_{PC}$ 10.1 Hz, *ortho*-C), 171.33 (d, $^2J_{PC}$ 21.0 Hz, P=C-^{13}C=O), 173.31 (C=O ester), 202.10 and 204.78 (2 C=O of 2 Ac)
3c	^1H	1.10 (9 H, s, CMe_3), 2.30 and 2.45 (6 H, 2 s, 2 CH_3C=O), 4.07 (1 H, d, $^3J_{PH}$ 2.2 Hz, CH), 7.3-7.8 (15 H, m, 3 C_6H_5)
	^{13}C	26.35 and 28.38 (2 $^{13}CH_3C$=O), 27.61 (3 CH_3 of CMe_3), 36.56 (d, $^1J_{PC}$ 137.1 Hz, P=C), 53.62 (d, $^2J_{PC}$ 12.9 Hz, CH), 81.36 ($^{13}CMe_3$), 95.41 (d, $^3J_{PC}$ 11.1 Hz, $^{13}CAc_2$), 124.38 (d, $^1J_{PC}$ 93.0 Hz, *ipso*-C), 129.12 (d, $^3J_{PC}$ 12.9 Hz, *meta*-C), 132.93 (d, $^4J_{PC}$ 2.8 Hz, *para*-C), 133.62 (d, $^2J_{PC}$ 10.1 Hz, *ortho*-C), 171.85 (d, $^2J_{PC}$ 20.2 Hz, P=C-^{13}C=O), 172.53 (C=O ester), 202.55 and 204.38 (2 C=O of 2 Ac)

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13. The typical process for the preparation of methyl 5,5-diacetyl-2-oxo-3-(triphenylphosphoranylidene)tetrahydrofuran-4-carboxylate (**3a**) is described as an example. To a magnetically stirred solution of triphenylphosphine (0.524 g, 2 mmol) and 3-chloropentane-2,4-dione (**1**) (0.269 g, 2 mmol) in CH_2Cl_2 (10 ml) was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (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 temperature and stirred for 24 h. The solvent was removed under reduced pressure and the orange precipitate was filtered. Recrystallization from chloroform: diethyl ether mixture yielded **7a** as orange solid (0.83 g, 85%), m.p. 247-250 °C (decomp.). IR (KBr) (ν_{max}, cm^{-1}): 1730, 1688 and 1649 (C=O); 1298, 1208 and 1181 (C-O); MS (*m/z*, %): 488 (M^+, 4); 429 (M^+ - CO_2Me, 6); 343 (M^+ - CO_2Me - 2 COMe, 6); 183 (M^+ - $P\phi_3$ - COMe, 100). (Found: C, 67.7; H, 5.0. $C_{28}H_{25}O_6P$ requires C, 68.84; H, 5.16%). Selected data for **3b**: m.p. 132-135 °C, yield 0.62 g (62%). IR (KBr) (ν_{max}, cm^{-1}): 1724 and 1684 (C=O); 1294 and 1194 (C-O); MS (*m/z*, %): 503 (MH^+, 100); 459 (M^+ - COMe, 43); 429 (M^+ - CO_2Et, 65); 343 (M^+ - CO_2Et - 2 COMe, 14); 183 (M^+ - $P\phi_3$ - CO_2Me, 90). (Found: C, 68.5; H, 5.4. $C_{29}H_{27}O_6P$ requires C, 69.31; H, 5.42%). Selected data for **3c**: m.p. 154-157 °C, yield 0.49 g (46%). IR (KBr) (ν_{max}, cm^{-1}): 1796, 1765, 1728 and 1688 (C=O); 1298, 1252 and 1196 (C-O); MS (*m/z*, %): 530 (M^+, 48); 475 (M^+ - CH_2= CMe_2, 6); 429 (M^+ - CO_2CMe_3, 78); 387 (M^+ - CO_2Bu^t - COMe, 28); 183 (M^+ - $P\phi_3$ - 2 COMe, 14); 57 (CMe_3^+, 100). (Found: C, 69.2; H, 5.8. $C_{31}H_{31}O_6P$ requires C, 70.18; H, 5.89%).
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