Selective *C*-acylation of CH-active dicarbonyl compounds with ketenylidenetriphenylphosphorane: syntheses and structures of 3-phosphoranylideneacyltetronic acids, 3-phosphoranylideneacyl-4-oxocoumarins, and 4-phosphoranylideneacylpyrazol-5-ones

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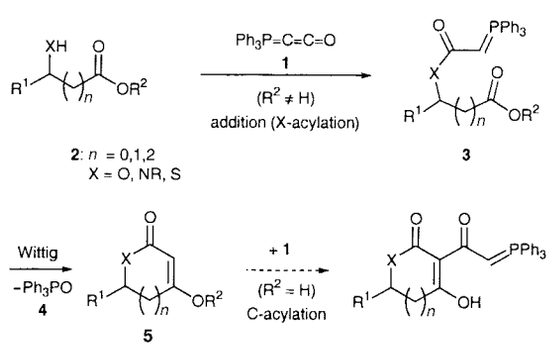
Selective *C*- over *O*-/*N*-acylation of acyclic, carbocyclic and heterocyclic carbonyl compounds bearing active α-CH groups is described. β-Ketoesters give the corresponding α-acylylidic derivatives in good yields. Likewise, tetronic acids and 4-hydroxycoumarins furnish the respective 3-acylylidic derivatives, and pyrazol-5-ones exclusively yield the corresponding 4-acylylidic compounds despite the possibility of tautomerism. X-Ray single crystal structure and NMR analyses of the product tricarbonyl ylides are presented and structure–reactivity interdependencies are discussed. As a rule, compounds with wide-spread conjugation of the π-system like **9/13** do not readily undergo Wittig olefination. Acylylides **11** with separated β-keto moieties react normally.

Introduction

We have recently described the use of ketenylidenetriphenylphosphorane **1** as a 1,2-dipolar C_2-building block for the synthesis of various heterocycles such as tetronates,† coumarins, benzoxepinones and their *N*- and *S*-analogues, from carboxylic esters **2** bearing OH, NHR or SH groups by an addition–Wittig olefination sequence.[1] These and other reactions with similarly functionalized carboxylic acid derivatives,[2] start with an addition of the acidic group XH (X = O, NR, S) across the C=C bond of **1** leading to formally *X*-acylated new phosphorus compounds **3**, which then can undergo follow-up chemistry like *intra*molecular olefination of the ester group to give heterocycles **5** (Scheme 1).



Scheme 1

A significant number of the naturally occurring or biologically relevant tetronates,[3] tetramates,[4] and coumarins[5] feature 3-acyl residues.[6] The simplest approach to these systems clearly is the direct acylation of the heterocyclic parent compounds. Several methods were published for tetronates and tetramates. However, most of them have serious drawbacks beside the mandatory protection of the 4-hydroxy group. Lithiation/acylation has been accomplished but is limited to C5-disubstituted derivatives,[7] Lewis acid catalyzed Friedel–Crafts acylation is too harsh for sensitive compounds,[8] and Ley's Pd-catalyzed acylation of 3-stannyltetronates, though high-yielding and versatile, requires additional *O*-(de)alkylation and 3-bromination/metalation steps.[9] We therefore took a closer look at the reactivity of **1** towards different types of carbonyl systems with active α-CH groups and as a result now report a new method for the mild and regioselective *C*-acylylidation of unprotected tetronic acids, 4-hydroxycoumarins, pyrazol-5-ones and various β-ketoesters,[10] together with the structures and reactivities of the respective products.

Results and discussion

Syntheses

α-Ketoesters **6** followed the normal scheme of reaction with **1** yielding the corresponding 5-alkylidenetetronates **7** in moderate yields *via* a sequence of *O*-acylylidation of the enol tautomer of **6** and a subsequent *intra*molecular Wittig olefination. *n*-Alkyl substituted α-ketoesters gave a single isomer of **7** which we tentatively assigned the *Z*-configuration based on a comparison of the ^{1}H NMR chemical shift data with those of similar tetronates.[7a] α-Disubstituted derivatives gave rise to mixtures of *Z*- and *E*-isomers (Scheme 2). 5-Ylidenetetronates are of interest due to their physiological properties (anti-inflammatory, antipyretic, analgesic, sedative, *etc*.) and to the fact that the naturally occurring derivatives[11] like fadyenolide and piperolide are produced by higher plants (*Piper*) rather than by fungi or algae like other tetronates.

In contrast, β-ketoesters were exclusively *C*-acylated by **1**. The acyclic derivatives **8**, for instance, gave the corresponding

† The IUPAC name for tetronic acid is furan-2,4(3*H*,5*H*)-dione.

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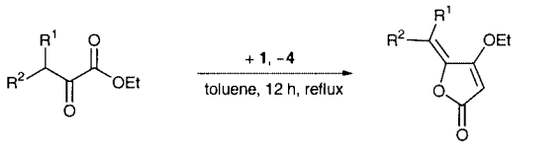
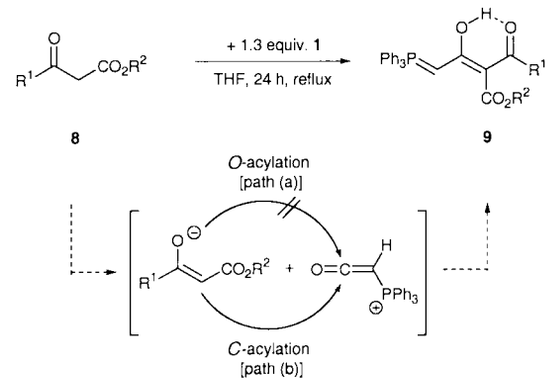


	R^1	R^2	(%)	*E*/*Z*
a	H	Pr^i	25	0/1
b	H	Me	45	0/1
c	Me	Et	35	1/1

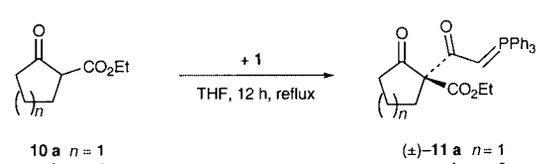
Scheme 2

[(*E*)-3-alkoxycarbonyl-2-hydroxy-4-oxoalk-2-enylidene]triphenylphosphoranes **9** in good to excellent yields (Table 1). The reaction is thought to begin with the generation of a ketenylphosphonium salt by protonation of **1** followed by an orbital-controlled C–C bond formation between the β-carbon atom of the relatively soft enolate anion and the carbonyl carbon atom of the cation [path (b) in Scheme 3]. This second step must take



Scheme 3

place rapidly, as **1** is known to "dimerize" swiftly upon treatment with acids that have a weakly nucleophilic conjugate base by reaction with the initially formed ketenylphosphonium cation. A final keto–enol tautomerization then leads to the most stable structure with a six-membered hydrogen-bridged ring system (*vide infra*). Formation of 4-alkoxypyren-2-ones by a domino *O*-acylation–*intra*-Wittig olefination [path (a)] was not observed in any case. The bias for *C*-alkylation is pronounced even in cases of considerable sterical hindrance. Derivatives with a tertiary α-carbon atom such as ethyl cyclopentanone-2-carboxylate **10a** or ethyl cyclohexanone-2-carboxylate **10b**, readily reacted with **1** to furnish the corresponding acylylides **11** bearing a quaternary α-carbon atom (Scheme 4).

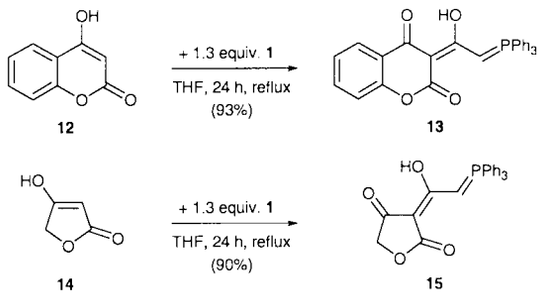


Scheme 4

Table 1 Tricarbonyl substituted phosphorus ylides **9**, **11** from β-keto-esters and **1**

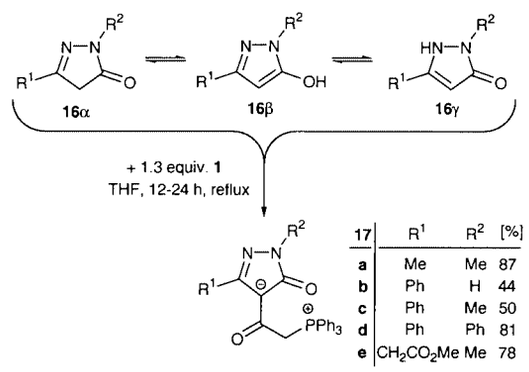
Compound	R^1	R^2	*n*	Yield (%)
9a	Me	Me		95
9b	Me	Et		90
9c	Et	Me		80
9d	Ph	Et		90
11a			1	67
11b			2	68

4-Hydroxycoumarin **12** and tetronic acid **14** both contain a fully enolized formal 1,3-dicarbonyl moiety and thus readily reacted with **1** upon heating in THF to produce the corresponding 3-(triphenylphosphoranylideneoxoethyl) derivatives **13** and **15**, respectively, in excellent yields (Scheme 5).



Scheme 5

To investigate the preference of **1** for *C*-acylation of compounds with more than one alternative heteroatomic acidic group, we reacted it with 1,3-disubstituted pyrazol-5-ones **16** which can exist as three possible tautomers, the CH (α), OH (β) and NH (γ) forms (Scheme 6).[12] The only isolable and well-



17	R^1	R^2	[%]
a	Me	Me	87
b	Ph	H	44
c	Ph	Me	50
d	Ph	Ph	81
e	CH_2CO_2Me	Me	78

Scheme 6

defined products formed under standard conditions (12–24 h, THF, heating) in moderate to good yields, were the *C*4-acylated derivatives **17**, although compounds **16** are reported to be present as an equilibrium mixture of all three tautomers (*ca.* α : β : γ = 6 : 3 : 1) in ethereal solvents.[13] Such a regioselectivity has not yet been reported for comparable *C*4-alkylations/acylations.

4-Acylpyrazol-5-ones are the focus of research as potential antifungal agrochemicals[14] and because of their metal-extracting properties.[15] They are also known to show extensive solid-state tautomerism by participation of the 4-acyl substituent.[16]

Structures and properties

All new pyrazolones and the tetronic acid described above, are highly polar due to their formal β-tricarbonyl moieties and precipitated directly from the boiling THF reaction solutions. For the greater part, differences in their solubilities and polarities originate from differences in the degree of enolization which can be drawn from NMR spectra and X-ray single crystal structure analyses. In some cases, however, solubilities differ significantly for derivatives with similar structures (bond lengths, conformations) of the central tricarbonylylidic moiety but bearing different peripheral substituents. This is evident from pyrazolones **17a** and **17e** which are quite soluble in chloroform, whereas derivatives **17b–d** all featuring a 3-phenyl residue, are much more polar, dissolving well only in pyridine or CF_3CO_2H. It is also worth noting, that different tautomers can be predominant in solution and in the solid state, and that it is not necessarily the major tautomer that crystallizes first from

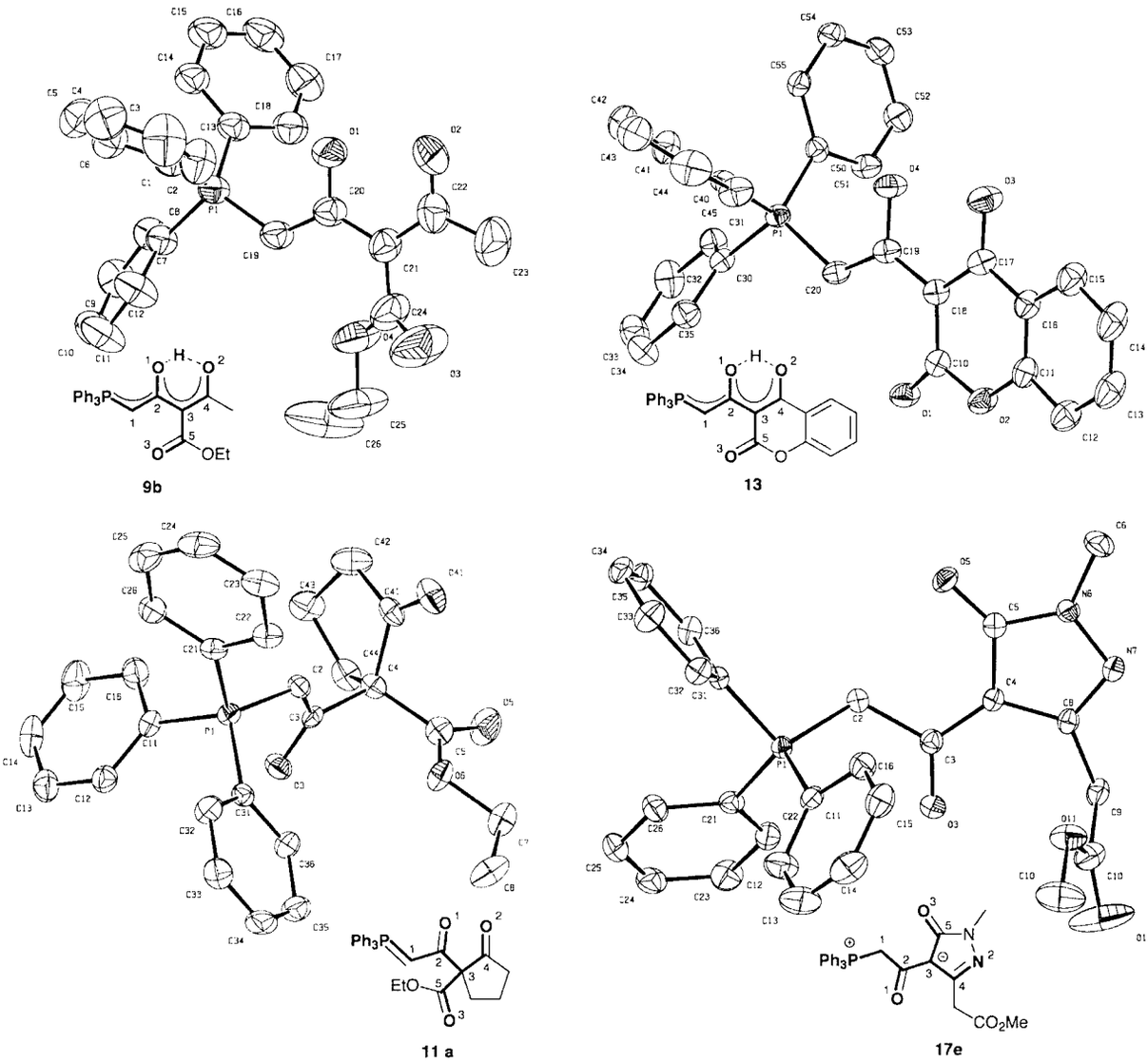


Fig. 1 Molecular structures of selected β-tricarbonyl phosphorus ylides with formula drawings indicating the numbering scheme used in Table 2.

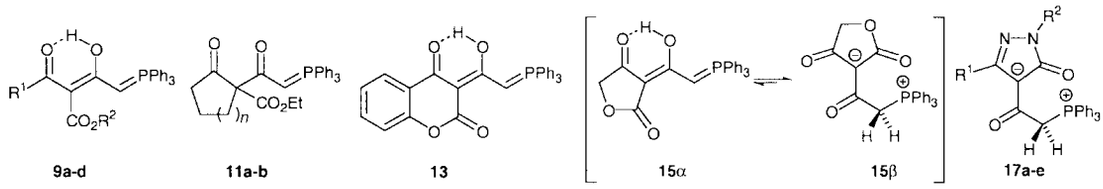
Table 2 Characteristic bond lengths [Å] of the β-tricarbonyl ylides shown in Fig. 1 and of **17c**

Compound	P–C(1)	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(3)–C(5)	C(2)–O(1)	C(4)–O/N(2)	C(5)–O(3)
9b	1.719(3)	1.378(6)	1.462(5)	1.401(6)	1.448(5)	1.322(3)	1.286(4)	1.235(6)
11a	1.722(6)	1.389(7)	1.560(7)	1.529(5)	1.521(9)	1.247(9)	1.207(3)	1.193(1)
13	1.735(0)	1.370(2)	1.448(1)	1.409(2)	1.443(6)	1.334(1)	1.272(9)	1.210(6)
17c	1.788(2)	1.529(4)	1.409(4)	1.445(6)	1.447(5)	1.241(7)	1.322(2)	1.255(4)
17e	1.798(6)	1.530(7)	1.413(2)	1.426(2)	1.446(3)	1.241(9)	1.314(3)	1.254(6)

a saturated solution. In addition, both the major solid-state tautomer and the major tautomer in solution depend on the respective solvent. Fig. 1 depicts the molecular structures of different tricarbonyl-substituted phosphorus "ylides" as obtained from X-ray single crystal analyses, and Table 2 compares the most significant bond lengths within their β-tricarbonylylidic core. Supporting NMR spectra were recorded in the same solvent ($CDCl_3$) as the respective crystals were grown in ($CHCl_3$–pentane), except for compounds **11a** (grown in benzene–hexane) and **17c** (grown in pyridine–pentane). Comparison of these data, with those of related acyl derivatives, allow an estimation of the actual influence of the ylidic substituent on the electronic and geometrical structures.

The bond lengths of the open-chained **9b** and the coumarin derivative **13** are quite similar. The cores of the molecules are very close to planar and π-delocalization spreads over atoms C1, C2, C3, C4, O1 and O2 with the respective bond lengths ranging between typical values for single and double bonds. However, marked differences between C2–C3 and C3–C4 [**9b**: 1.462(5)/1.401(6)], in combination with the successful location and refinement of the tautomeric hydrogen atom in **9b**, reveal a distinct asymmetry of this six-membered pseudo-chelate system. The ylide functions participate in these conjugated π-systems (short bonds C1–C2) of **9b** and **13** which consequently show a very low reactivity in Wittig reactions, even towards activated aldehydes. They are best represented by the formula drawings in Fig. 1. Compound **11a**, however, has a structure typical of acylylides. No conjugation is possible between the three carbonyl groups due to the tertiary carbon atom C3 separating them and as a result, all bonds are of either typical single or double bond lengths. As a consequence, ylides **11** olefinate reactive aldehydes like ethyl glyoxylate **18**, to give the corresponding diketodiesters **19** in acceptable yields (Scheme 7).

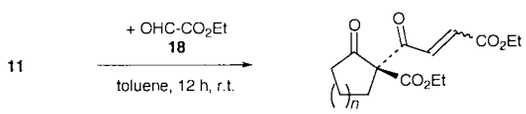
Table 3 Characteristic NMR data of compounds **9**, **11**, **13**, **15** and **17**



9a-d **11a-b** **13** **15α** **15β** **17a-e**

	^{13}C-NMR α-CH δ(ppm)	$^{1}J_{PC}$/ Hz	^{13}C-NMR α-CH_2 δ(ppm)	$^{1}J_{PC}$/Hz	^{13}C-NMR PPh^{ipso} δ(ppm)	$^{1}J_{PC}$/ Hz	^{13}C-NMR $P^{+}Ph^{ipso}$ δ(ppm)	$^{1}J_{PC}$/Hz	^{31}P-NMR Ph_3P=CH δ(ppm)	^{31}P-NMR Ph_3P^{+}–CH_2 δ(ppm)
9a	52.8	97.4	—	—	125.7	91.9	—	—	17.3	—
9b	52.4	104.8	—	—	125.9	91.9	—	—	17.3	—
9c	52.6	102.2	—	—	126.0	91.5	—	—	17.4	—
9d	52.6	114.0	—	—	127.2	62.6	—	—	17.0[b]	—
11a	52.3	108.5	—	—	126.4	90.0	—	—	16.3	—
11b	53.0	109.7	—	—	127.0	91.1	—	—	17.2	—
13	60.1	104.8	—	—	124.5	91.5	—	—	16.8[b]	—
15α	56.5[b]	—[a]	—	—	122.5[b]	92.8[b]	—	—	16.9 16.9[b]	—
15β	—	—	[35.6[b] + 36.0[b]]	[58.5[b] + 54.8[b]]	—	—	[118.3[b] + 118.5[b]]	[89.8[b] + 89.3[b]]	—	24.0 [23.7[b] + 24.1[b]]
17a	—	—	32.7	51.5	—	—	119.8	88.5	—	24.9
17b	—	—	36.4[c]	55.4	—	—	118.3[c]	88.6	—	23.4[c]
17c	—	—	36.0[c]	57.0	—	—	117.7[c]	88.3	—	23.4[c]
17d	—	—	30.4[c]	36.8	—	—	119.0[c]	88.6	—	23.4[c]
17e	—	—	32.6	50.4	—	—	119.6	87.0	—	23.8

[a] In the range of 100–110 Hz. [b] At −58 °C. [c] In $CDCl_3$–CF_3CO_2D.



(±)-**19**	*n*	(%)	*E*/*Z*
a	1	66	7/1
b	2	74	6/1

Scheme 7

In the case of pyrazolones **17c** and **17e**, thorough NMR and X-ray crystallographic investigations of similar 4-cinnamoyl-1,3-dimethylpyrazol-5-ones by Steel and Guard[16c] allow a direct comparison and a pin-pointing of the actual influence of the 4-acylylidic residue on the electron distribution and structure. Whereas Steel could separate and identify an NH and an OH tautomer of his 4-cinnamoyl derivatives, all C–O and C–N bond lengths as well as NMR data of **17**, strongly suggest them to be CH tautomers. As the P–C1 and the C1–C2 bonds (**17e**: 1.798(6) and 1.530(7) Å, respectively) are unusually long, the depicted 1,4-betaine structure, *i.e.* a formal zwitterionic phosphonium salt, is the most appropriate structural description. As **17e** is sufficiently soluble in $CDCl_3$ supporting NMR spectra were recorded. They showed a doublet at 5.26 ppm with a $^{2}J_{PH}$ = 14.3 Hz for the methylene group in the ^{1}H NMR and a resonance at 23.84 ppm (typical "phosphonium salt" region, *ca*. 10 ppm downfield from normal acylylides) in the ^{31}P NMR. Surprisingly, the negative charge of the betaine is mostly localized at carbon atom C3, as can be seen from the double bond character of the adjoining carbonyl and imino moieties. Semiempirical (MOPAC) single-point calculations for the X-ray geometry also suggest a localization of electron density at C3. Compound **17c**, whose X-ray structure is quite similar to that of **17e**, with regards to the pyrazolone core, is insoluble in $CDCl_3$ and it was necessary to add triflic acid to record its NMR spectrum. This demonstrates that polarity and solubility are not only a matter of tautomeric and isomeric equilibria but also of the nature of substituents.

The 3-acylylidenetetronic acid **15** could not be obtained in a form suitable for X-ray single crystal structure analysis, but was sufficiently soluble in $CDCl_3$ to allow NMR characterization (^{1}H, ^{13}C, ^{31}P at 30 °C and at −58 °C). The NMR spectra of **15** showed the presence of two species at 30 °C, an ylide (^{31}P: 16.9 ppm) reminiscent of the open-chained tricarbonyl ylides **9** and the coumarin **13**, and a phosphonium-betaine type compound (^{31}P: 24.0 ppm) similar to the pyrazolones **17**. At −58 °C two different tautomers of the phosphonium isomer (^{31}P: 23.7, 24.1 ppm) of hitherto unknown structure could be observed in all three sorts of NMR spectra whereas the ylidic form remained almost unchanged and did not split into different tautomers. In other words, the tetronic acid derivative **15** is of a borderline nature regarding its isomeric and tautomeric preferences, capable of adopting structural features typical of both the compounds **9**/**13** and of **17**. Table 3 provides an overview of the most significant resonance peaks for all compound classes discussed in this paper.

Conclusion

A general method was found for the regioselective introduction of the –COCH=PPh_3 group into the active methylene position of various acyclic, carbocyclic and heterocyclic β-dicarbonyl or β-iminocarbonyl compounds by a C–C bond formation. This group is a strong electron donor and most tricarbonyl-functionalized phosphorus species, derived from β-dicarbonyl compounds, tend to form chelate structures with a pronounced conjugation of the π-system, geometrical reasons permitting. Open-chained [(*E*)-2-hydroxy-3-alkoxycarbonyl-4-oxoalk-2-enylidene]triphenylphosphoranes **9** and 3-acylylidic coumarins **13** always feature an ylide functional group (Ph_3P=CH–), but only derivatives with decoupled carbonyl groups such as **11** show normal ylide reactivity in Wittig olefinations. The 4-acylylidic derivatives of pyrazol-5-ones are also formed regioselectively as a single CH tautomer, but with an unexpected phosphonium-betaine structure (Ph_3P^{+}–CH_2–CO–C^{-}). In these cases, the ylide function does not act as an electron donor but as a base, strong enough to abstract a proton from C4 and so generate a localized anion at this point. In terms of structure and tautomerism, 3-phosphoranylideneacyltetronic acid **15** lies somewhere between the pyrazolones **17** and the systems **9** and **13**, as it exists as a mixture of ylidic and phosphonium-betaine forms. That latter isomer shows a clear preference for a

certain tautomer only at room temperature, whereas at lower temperature several different tautomers appear to co-exist.

The high *C*-selectivity and the exclusive formation of certain tautomers in most of the acylation reactions described in this paper, should give rise to fruitful preparative applications, and a lot of functional group conversions are already known for stabilized phosphorus ylides.[17] Even normal Wittig reactivity could be initiated by anionic activation (*i.e.* by removal of the chelated hydrogen atom with bases), by alkylation with Meerwein salts, or by metalation which has been successfully demonstrated for the similar (3-ethoxycarbonyl-2-oxopropylidene)triphenylphosphorane.[18] Work currently in progress includes applications of consecutive *O*-/*C*-acylylidations of HX-functionalized carboxylic acid derivatives with ylide **1** to natural product synthesis.

Experimental

Melting points were recorded using a Gallenkamp or a Wagner & Munz apparatus and are uncorrected. IR spectra were recorded on a Bruker FT-IR Vektor 22 and a Perkin-Elmer Model 983G instrument coupled to a Perkin-Elmer 3700 Data Station as potassium bromide (KBr) disks, or films (film). Nuclear magnetic resonance (NMR) spectra were recorded under conditions as indicated using Bruker DPX 300 and DRX 500 and JEOL GX400 NMR spectrometers. Chemical shifts are given in parts per million (δ) downfield from tetramethylsilane as internal standard, and coupling constants (J) are given in Hz. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, *qua* = quaternary atom. Mass spectra were recorded using a Double Focusing Triple Sector VG Auto Spec, a Varian MAT 311A (EI), and a Micromass Zabspec (FAB). Microanalyses were obtained using a Perkin-Elmer 2400 CHN and a Heraeus CHN Mikromonar elemental analyzer. X-Ray single crystal structure analyses were carried out with Siemens P3, Siemens P4, and Nonius Mach 3 diffractometers. Analytical TLC was carried out on Merck Kieselgel 60254 plates. Flash chromatography was effected using Merck Kieselgel 60 (230–400 mesh).

Ylide **1**[19] and the pyrazolones **16**[20] were prepared by the literature methods, all other starting compounds were purchased from Aldrich and used as such without further purification.

General experimental procedure for the reaction of 1 with α-ketoesters 6 or with β-dicarbonyl compounds 8, 10, and 12

A solution of **1** (3.9 g, 13.0 mmol) and 10 mmol of the respective α-ketoester **6** in toluene (50 mL) or of the respective β-oxo compound **8/10/12** in THF (50 mL) was heated under reflux for 12 hours with exclusion of air and moisture. The solvent was then removed under reduced pressure and the resulting residue was purified by column chromatography (silica gel; ethyl acetate).

4-Ethoxy-5-[(*Z*)-isobutylidene]furan-2(5*H*)-one 7a. Yellow, viscous oil (0.43 g, 2.5 mmol, 25%) from ethyl α-oxo-γ-methylvalerate (1.58 g), R_f 0.40 (diethyl ether–pentane 1 : 1, v/v) (Found: C, 65.91; H, 7.78. $C_{10}H_{14}O_3$ requires C, 65.91; H, 7.74%); ν_{max}(film)/cm^{-1} 1780 s, 1740 s and 1640 s; δ_H (400 MHz; $CDCl_3$) 1.09 (6 H, d, *J* 6.59, CH*Me*$_2$), 1.45 (3 H, t, *J* 7.08, CH$_2$C*H*$_3$), 2.92–2.94 (1 H, m, C*H*Me$_2$), 4.11 (2 H, q, *J* 7.08, C*H*$_2$CH$_3$), 5.14 (1 H, s, 3-H) and 5.32 (1 H, d, *J* 9.99, =CH); δ_C (100.5 MHz; $CDCl_3$) 14.09, 22.47 (Me), 25.78 (CH), 68.22 (CH_2), 88.79, 117.41 (CH), 142.52 and 169.12 (C-*qua*); *m*/*z* (EI) 182 (M^+, 10%), 153 ($M^+ - C_2H_5$, 20%), 126 (80%) and 69 (100%).

4-Ethoxy-5-[(*Z*)-ethylidene]furan-2(5*H*)-one 7b. Colorless, viscous oil (0.70 g, 4.5 mmol, 45%) from ethyl methylpyruvate (1.30 g), R_f 0.40 (diethyl ether–pentane 1 : 1, v/v) (Found: C, 62.51; H, 6.60. $C_8H_{10}O_3$ requires C, 62.33; H, 6.54%); ν_{max}(film)/cm^{-1} 1770 s, 1610 s and 1200; δ_H (400 MHz; $CDCl_3$) 1.44 (3 H, t, *J* 7.08, CH$_2$C*H*$_3$), 1.89 (3 H, d, *J* 7.33, CHC*H*$_3$), 4.11 (2 H, q, *J* 7.08, C*H*$_2$CH$_3$), 5.14 (1 H, s, 3-H) and 5.50 (1 H, q, *J* 7.33, C*H*CH$_3$); δ_C (100.5 MHz; $CDCl_3$) 11.09, 14.09 (Me), 68.18 (CH_2), 88.76, 105.64 (CH), 144.68, 168.78 and 169.05 (C-*qua*); *m*/*z* (EI) 154 (M^+, 100%), 141 ($M^+ - CH_3$, 40%), 127 (25%) and 56 (50%).

4-Ethoxy-5-(butan-2-ylidene)furan-2(5*H*)-one 7c. Mixture of isomers (*E* : *Z* = 5 : 4) as a yellow, viscous oil (0.62 g, 3.5 mmol, 35%) from ethyl α-oxo-β-methylvalerate (1.58 g), R_f 0.3 (diethyl ether–pentane 1 : 1, v/v) (Found: C, 65.88; H, 7.66. $C_{10}H_{14}O_3$ requires C, 65.91; H, 7.74%); ν_{max}(film)/cm^{-1} 1750 s, 1600 s and 1190; δ_H (400 MHz; $CDCl_3$) *major isomer*: 1.05–1.10 (3 H, m, CH$_2$C*H*$_3$), 1.45–1.52 (3 H, m, OCH$_2$C*H*$_3$), 1.96 (3 H, s, CH$_3$), 2.48 (2 H, q, *J* 7.15, C*H*$_2$CH$_3$), 4.11 (2 H, q, *J* 7.08, OC*H*$_2$CH$_3$) and 5.19 (1 H, s, 3-H); *minor isomer*: 1.05–1.10 (3 H, m, CH$_2$C*H*$_3$), 1.45–1.52 (3 H, m, OCH$_2$C*H*$_3$), 2.05 (3 H, s, CH$_3$), 2.35 (2 H, q, *J* 7.70, C*H*$_2$CH$_3$), 4.11 (2 H, q, *J* 7.08, OC*H*$_2$CH$_3$) and 5.20 (1 H, s, 3-H); δ_C (100.5 MHz; $CDCl_3$) *mixture*: 11.87, 12.82, 14.10, 15.25, 17.30 (Me), 24.53, 26.61, 68.23 (CH_2), 89.71 (CH), 128.34, 128.75, 138.37, 138.73, 168.71, 169.87 and 170.20 (C-*qua*); *m*/*z* (EI) 182 (M^+, 60%), 167 ($M^+ - CH_3$, 10%), 154 (20%) and 69 (100%).

[(*E*)-2-Hydroxy-3-methoxycarbonyl-4-oxopent-2-enylidene]-triphenylphosphorane 9a. White solid (4.00 g, 9.5 mmol, 95%) from methyl acetoacetate (1.16 g), R_f 0.86 (ethyl acetate), mp 105 °C (Found: C, 71.83; H, 5.41. $C_{25}H_{23}O_4P$ requires C, 71.76; H, 5.54; P, 7.40%); ν_{max}(KBr)/cm^{-1} 1680 s, 1553 s and 1436 s; δ_H (400 MHz; $CDCl_3$) 2.30 (3 H, s, 5-H), 3.73 (3 H, s, OCH$_3$), 5.07 (1 H, s, 1-H), 7.44–7.68 (15 H, m, ArH) and 18.28 (1 H, s, OH); δ_C (100.5 MHz; $CDCl_3$) 27.96 (C-5), 50.30 (OCH$_3$), 52.85 (d, $^1J_{PC}$ 97.4, C-1), 98.81 (C-3), 125.75 (d, $^1J_{PC}$ 91.9, C-*ipso*), 128.92 (d, $^3J_{PC}$ 12.8, C-*meta*), 132.37 (C-*para*), 133.09 (d, $^2J_{PC}$ 9.2, C-*ortho*), 170.08 and 181.94 and 192.35 (C-2, C-4, *C*O$_2$Me); δ_P (161.7 MHz; $CDCl_3$) 17.33; *m*/*z* (EI) 418 (M^+, 3%), 385 ($M^+ - OCH_3$, 4%), 301 (100%), 262 (PPh_3^+, 59%), 199 (31%), 183 (70%), 165 (61%), 152 (36%), 116 (80%) and 69 ($CO_2CH_3^+$, 66%).

[(*E*)-3-Ethoxycarbonyl-2-hydroxy-4-oxopent-2-enylidene-triphenyl]phosphorane 9b. White solid (3.83 g, 8.9 mmol, 89%) from ethyl acetoacetate (1.30 g), R_f 0.73 (ethyl acetate), mp 133 °C (from $CHCl_3$–pentane) (Found: C, 72.24; H, 5.86. $C_{26}H_{25}O_4P$ requires C, 72.21; H, 5.83; P, 7.16%); ν_{max}(KBr)/cm^{-1} 1678 s, 1566 s and 1437 s; δ_H (400 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7.05, OCH$_2$C*H*$_3$), 2.32 (3 H, s, 5-H), 4.21 (2 H, q, *J* 7.05, OC*H*$_2$CH$_3$), 5.06 (1 H, s, 1-H), 7.43–7.68 (15 H, m, ArH) and 18.31 (1 H, s, OH); δ_C (100.5 MHz; $CDCl_3$) 14.47 (CH$_2$*C*H$_3$), 27.97 (C-5), 52.41 (d, $^1J_{PC}$ 104.8, C-1), 59.17 (CH_2), 99.09 (d, $^3J_{PC}$ 7.4, C-3), 125.9 (d, $^1J_{PC}$ 91.9, C-*ipso*), 128.97 (d, $^3J_{PC}$ 13.9, C-*meta*), 132.43 (d, $^4J_{PC}$ 3.7, C-*para*), 133.13 (d, $^2J_{PC}$ 9.2, C-*ortho*), 169.69 and 182.13 and 192.08 (C-2, C-4, *C*O$_2$Et); δ_P (161.7 MHz; $CDCl_3$) 17.29; *m*/*z* (EI) 432 (M^+, 4%), 385 ($M^+ - C_2H_5O$, 14%), 301 ($M^+ - C_6H_9O$, 100%) and 262 (PPh_3^+, 56%).

X-Ray crystal structure analysis of compound 9b.‡ $C_{26}H_{25}O_4P$, M = 432.4. Triclinic, a = 10.047(2), b = 13.614(2), c = 18.555(2) Å, α = 97.040(8)°, β = 104.117(9)°, γ = 106.888(8)°, V = 2303.3(6) Å^3, space group $P\bar{1}$, Z = 4. μ(Mo-Kα) = 0.148 mm^{-1}. 8050 unique reflections measured giving 5866 with $I > 2\sigma(I)$. Final R_1 = 0.0576, wR_2 = 0.0501.

[(*E*)-2-Hydroxy-3-methoxycarbonyl-4-oxohex-2-enylidene-triphenyl]phosphorane 9c. White solid (3.42 g, 7.9 mmol, 79%)

‡ CCDC reference number 207/425. See http://www.rsc.org/suppdata/p1/b0/b001541p/ for crystallographic files in .cif format.

from methyl propanoylacetate (1.30 g), R_f 0.70 (ethyl acetate), mp 108 °C (Found: C, 72.11; H, 5.77. $C_{26}H_{25}O_4P$ requires C, 72.21; H, 5.83; P, 7.16%); ν_{max}(KBr)/cm^{-1} 1682 s, 1549 s and 1437 s; δ_H (400 MHz; $CDCl_3$) 1.12 (3 H, t, *J* 7.32, 6-H), 2.63 (2 H, q, *J* 7.32, 5-H), 3.73 (3 H, s, OCH_3), 4.97 (1 H, s, 1-H), 7.43–7.67 (15 H, m, ArH) and 18.37 (1 H, s, OH); δ_C (100.5 MHz; $CDCl_3$) 10.83 (C-6), 32.60 (C-5), 50.37 (OCH_3), 52.58 (d, $^1J_{PC}$ 102.2, C-1), 97.08 (C-3), 125.98 (d, $^1J_{CP}$ 91.5, C-*ipso*), 128.89 (d, $^3J_{CP}$ 12.2, C-*meta*), 132.35 (C-*para*), 133.11 (d, $^2J_{CP}$ 10.7, C-*ortho*), 170.24 and 182.19 and 195.48 (C-2, C-4, *C*O_2Me); δ_P (161.7 MHz; $CDCl_3$) 17.37; *m*/*z* (FAB) 433 (MH^+, 81%), 401 ($M^+ - OCH_3$, 44%), 303 (Ph_3P=CH–CHO^+, 100%) and 262 (PPh_3^+, 38%).

[(*E*)-3-Ethoxycarbonyl-2-hydroxy-4-oxo-4-phenylbut-2-enylidene]triphenylphosphorane 9d. Yellow solid (4.46 g, 9.0 mmol, 90%) from ethyl benzoylacetate (1.92 g), R_f 0.66 (ethyl acetate), mp 151 °C (decomp.) (Found: C, 75.34; H, 5.56. $C_{31}H_{27}O_4P$ requires C, 75.29; H, 5.50; P, 6.26%); ν_{max}(KBr)/cm^{-1} 1681 s, 1589 s and 1437 s; δ_H (400 MHz; $CDCl_3$) 0.66 (3 H, t, *J* 7.03, CH_3), 3.78 (2 H, q, *J* 7.03, CH_2), 5.03 (1 H, d, $^2J_{PH}$ 21.0, 1-H), 7.28–7.79 (20 H, m, ArH) and 17.69 (1 H, s, OH); δ_C (100.5 MHz; $CDCl_3$) 13.26 (CH_3), 52.59 (d, $^1J_{PC}$ 114.0, C-1), 59.18 (CH_2), 98.75 (C-3), 127.21 (d, $^1J_{CP}$ 62.5, P–C-*ipso*), 128.60 (Ph-*meta*), 128.87 (Ph-*ortho*), 129.08 (d, $^3J_{PC}$ 11.1, P–C-*meta*), 132.60 (P–C-*para*), 133.11 (Ph-*para*), 133.26 (d, $^2J_{PC}$ 11.0, P–C-*ortho*), 136.66 (Ph-*ipso*), 170.42 and 181.09 and 188.09 (C-2, C-4, *C*O_2Et); δ_P (161.7 MHz; $CDCl_3$; –58 °C) 17.04; *m*/*z* (FAB) 495 (MH^+, 100%), 449 ($M^+ - OC_2H_5$, 42%), 303 (Ph_3P=CH–CHO^+, 82%) and 262 (PPh_3^+, 41%).

(±)-2-Ethoxycarbonyl-2-[2′-(triphenylphosphoranylidene)-1′-oxoethyl]cyclopentan-1-one 11a. White solid (3.07 g, 6.7 mmol, 67%) from (±)-ethyl 2-oxocyclopentane-1-carboxylate (1.56 g), R_f 0.64 (ethyl acetate), mp 122 °C (from benzene–pentane) (Found: C, 73.31; H, 5.01. $C_{28}H_{27}O_4P$ requires C, 73.35; H, 4.95; P, 6.76%); ν_{max}(KBr)/cm^{-1} 1736 s, 1715 s, 1551 s and 1438 s; δ_H (400 MHz; $CDCl_3$) 1.26 (3 H, t, *J* 7.08, CH_3), 1.84–1.88 (2 H, m, 4-H), 2.24–2.48 (3 H, m, 5-H, 3-H), 2.83–2.88 (1 H, m, 3-H′), 3.93 (1 H, d, $^2J_{PH}$ 24.17, C-2′), 4.22 (2 H, q, *J* 7.08, CH_3CH_2) and 7.42–7.65 (15 H, m, ArH); δ_C (100.5 MHz; $CDCl_3$) 14.17 (CH_2CH_3), 19.71, 32.72, 38.40 (C-3, C-4, C-5), 52.35 (d, $^1J_{PC}$ 108.5, C-2′), 61.20 (CH_2CH_3), 72.58 (d, $^3J_{PC}$ 12.9, C-2), 126.44 (d, $^1J_{PC}$ 90.0, C-*ipso*), 128.85 (d, $^3J_{PC}$ 12.9, C-*meta*), 132.16 (C-*para*), 133.10 (d, $^2J_{PC}$ 9.2, C-*ortho*), 169.98 (CO_2), 180.83 (d, $^2J_{PC}$ 3.7, C-1′) and 212.86 (C-1); δ_P (161.7 MHz; $CDCl_3$) 16.28; *m*/*z* (EI) 458 (M^+, 3%), 385 ($M^+ - CO_2C_2H_5$, 5%), 301 (385 − $C_5H_8O^+$, 32%), 128 (30%) and 73 ($CO_2C_2H_5^+$, 40%).

X-Ray crystal structure analysis of compound 11a.‡ $C_{28}H_{27}O_4P$; *M* = 485.5. Monoclinic, *a* = 25.351(3), *b* = 12.9583(12), *c* = 16.409(2) Å, *α* = 90°, *β* = 103.679(8)°, *γ* = 90°, *V* = 5237.6(10) Å^3, space group *C*2/*c* (no. 15), *Z* = 4. *μ*(Mo-K*α*) = 0.1 mm^{-1}. 4618 unique reflections measured giving 2810 with $I > 2\sigma(I)$. Final $R_1 = 0.0611$, $wR_2 = 0.1310$.

(±)-2-Ethoxycarbonyl-2-[2′-(triphenylphosphoranylidene)-1′-oxoethyl]cyclohexan-2-one 11b. White solid (3.21 g, 6.8 mmol, 68%) from (±)-ethyl 2-oxocyclohexanecarboxylate (1.70 g), R_f 0.65 (ethyl acetate), mp 112 °C (Found: C, 73.76; H, 6.17. $C_{29}H_{29}O_4P$ requires C, 73.71; H, 6.19; P, 6.50%); ν_{max}(KBr)/cm^{-1} 1723 s, 1699 s, 1538 s and 1436 s; δ_H (300 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.1, CH_2CH_3), 1.46–2.15 (4 H, m, 4-H, 5-H), 1.22–2.28, 2.42–2.48, 2.62–2.67, 2.78–2.89 (each 1 H, each m, 3-H, 6-H), 3.66 (1 H, d, $^2J_{PH}$ 23.48, 2′-H), 4.25 (2 H, q, *J* 7.1, CH_2CH_3) and 7.34–7.80 (15 H, m, ArH); δ_C (75.4 MHz; $CDCl_3$) 14.55 (CH_3), 22.54 (C-3), 27.57 (C-4), 53.02 (d, $^2J_{PC}$ 109.7, C-2′), 61.40 (CH_2CH_3), 73.51 (d, $^3J_{PC}$ 12.9, C-2), 127.04 (d, $^1J_{PC}$ 91.1, C-*ipso*), 129.23 (d, $^3J_{PC}$ 12.4, C-*meta*), 132.54 (d, $^4J_{PC}$ 2.6, C-*para*), 133.49 (d, $^2J_{PC}$ 10.25, C-*ortho*), 171.62 (CO_2), 184.17 (C-1′) and 208.49 (C-1); δ_P (121.4 MHz; $CDCl_3$) 17.22; *m*/*z* (FAB) 473 (MH^+, 14%) and 303 (100%).

4-Hydroxy-3-[2′-(triphenylphosphoranylidene)-1′-oxoethyl]-coumarin 13. White solid (4.31 g, 9.3 mmol, 93%) from 4-hydroxycoumarin (1.62 g), R_f 0.74 (ethyl acetate), mp 218 °C (from $CHCl_3$–pentane; decomp.) (Found: C, 74.94; H, 4.48. $C_{29}H_{21}O_4P$ requires C, 74.99; H, 4.56; P, 6.67%); ν_{max}(KBr)/cm^{-1} 1694 s, 1610 s, 1487 s and 1438 s; δ_H (400 MHz; $CDCl_3$) 6.09 (1 H, d, $^2J_{PH}$ 21.97, PCH), 7.17–8.02 (19 H, m, 5-H, 6-H, 7-H, 8-H, PPh_3) and 17.39 (1 H, s, OH); δ_C (100.5 MHz; $CDCl_3$) 60.12 (d, $^1J_{PC}$ 104.8, C-2′), 95.04 (d, $^3J_{PC}$ 11.4, C-3), 116.34 (C-8), 123.08 (C-6), 124.54 (d, $^1J_{PC}$ 91.5, P–C-*ipso*), 125.24 (C-5), 129.23 (d, $^3J_{PC}$ 12.7, P–C-*meta*), 132.69 (C-7), 132.59 (d, $^4J_{PC}$ 3.6, P–C-*para*), 133.24 (d, $^2J_{PC}$ 11.0, P–C-*ortho*), 133.57 (C-10), 153.47 (C-9), 162.82 (C-2), 178.82 (d, $^4J_{PC}$ 7.8, C-4) and 179.74 (d, $^2J_{PC}$ 7.8, C-1′); δ_P (161.7 MHz; $CDCl_3$; −58 °C) 16.80; *m*/*z* (FAB) 465 (MH^+, 100%), 303 (Ph_3P=CH–CHO^+, 20%) and 262 (PPh_3^+, 35%).

X-Ray crystal structure analysis of compound 13.‡ $C_{29}H_{21}O_4P$, *M* = 464.4. Monoclinic, *a* = 8.938(2), *b* = 22.265(5), *c* = 1.629(2) Å, *α* = 90°, *β* = 95.56(3)°, *γ* = 90°, *V* = 2303.3(6) Å^3, space group *P*2(1)/*c*, *Z* = 4. *μ*(Mo-K*α*) = 0.15 mm^{-1}. 4043 unique reflections measured giving 2776 with $I > 2\sigma(I)$. Final $R_1 = 0.0857$, $wR_2 = 0.1303$.

General experimental procedure for the reaction of 1 with 4-hydroxyfuran-2(5*H*)-one 14 or with the pyrazolones 16

A solution of **1** (3.9 g, 13 mmol) and of tetronic acid **14** (1.00 g, 10 mmol) or of the respective pyrazolone **16** (10 mmol) in THF (50 mL) was heated under reflux for 12 to 24 hours with exclusion of air and moisture. Upon cooling of the reaction mixture the solid products precipitated quantitatively. They were collected on a Büchner funnel, washed several times with THF and finally dried on an oil pump.

4-Hydroxy-3-[2′-(triphenylphosphoranylidene)-1′-oxoethyl]-furan-2(5*H*)-one 15. White solid (3.63 g, 9.0 mmol, 90%) from 4-hydroxyfuran-2(5*H*)-one **14**, mp >200 °C (decomp.) (Found: C, 71.67; H, 4.81. $C_{24}H_{19}O_4P$ requires C, 71.64; H, 4.76; P, 7.70%); ν_{max}(KBr)/cm^{-1} 1736 s, 1657 s, 1638 s and 1468 s; δ_C (100.5 MHz; $CDCl_3$, −58 °C) *isomer 15a*: 56.46 (Ph_3P=*C*H), 69.46 (C-5), 89.52 (d, $^3J_{PC}$ 12.9, C-3), 122.50 (d, $^1J_{PC}$ 92.8, C-*ipso*), 171.55 and 177.27 and 194.35 (C-1′, C-2, C-4); δ_C (100.5 MHz; $CDCl_3$; −58 °C) *isomer 15β*: 35.16 and 35.61 (each d, $^1J_{PC}$ 54.8, 58.5, Ph_3P^+-*C*H_2), 69.46 and 70.32 (C-5), 96.88 and 96.93 (each d, $^3J_{PC}$ 19.8, 19.9, C-3), 118.34 and 118.53 (each d, $^1J_{PC}$ 89.0, 89.3, C-*ipso*), 173.77 and 174.09 (both C-2 or C-4), 179.44 and 179.52 (each d, $^2J_{PC}$ 24.0, 23.6, C-1′), 195.42 and 195.65 (both C-4 or C-2); further phenyl signals of *15a* and *15β* (not assignable): 129.3, 129.6, 129.8, 130.1, 131.7, 132.7, 132.8, 133.3, 133.4, 133.5, 133.6, 134.4 and 135.2; δ_P (121.4 MHz; $CDCl_3$; 30 °C) 16.86 (*15a*) and 24.0 (*15β*); δ_P (121.4 MHz; $CDCl_3$; −58 °C) 16.92 (*15a*), 23.72 and 24.09 (*15β*); *m*/*z* (EI) 402 (M^+, 50%), 301 (100%), 277 (36%), 262 (Ph_3P^+, 22%) and 183 (66%).

1,3-Dimethyl-4-[2′-(triphenylphosphoranylidene)-1′-oxoethyl]pyrazol-5-one 17a. White solid (3.60 g, 8.7 mmol, 87%) from 1,3-dimethylpyrazol-5-one (1.12 g), mp >202 °C (decomp.) (Found: C, 72.52; H, 5.64; N, 6.68. $C_{25}H_{23}N_2O_2P$ requires C, 72.45; H, 5.59; N, 6.76; P, 7.47%); ν_{max}(KBr)/cm^{-1} 1605 s, 1579 s, 1515 s and 1438 s; δ_H (400 MHz; $CDCl_3$) 2.20 (3 H, s, 3-CH_3), 3.33 (3 H, s, 1-CH_3), 5.39 (2 H, d, $^2J_{PH}$ 13.74, 2′-H) and 7.42–7.76 (15 H, m, Ph); δ_C (100.5 MHz; $CDCl_3$) 16.13 (3-CH_3), 30.86 (1-CH_3), 32.66 (d, $^1J_{PC}$ 51.5, C-2′), 103.90 (d, $^3J_{PC}$ 4.6, C-4), 119.83 (d, $^1J_{PC}$ 88.5, C-*ipso*), 129.68 (d, $^3J_{PC}$ 13.7, C-*meta*), 134.24 (C-*para*), 134.69 (d, $^2J_{PC}$ 9.2, C-*ortho*),

147.90 (C-5), 166.42 (C-3) and 177.12 (d, $^2J_{PC}$ 6.1, C-1′); δ_P (121.4 MHz; $CDCl_3$) 24.86; *m/z* (EI) 414 (M^+, 36%), 301 (80%), 275 (91%), 262 (Ph_3P^+, 25%), 199 (38%), 183 (100%), 165 (40%) and 152 (43%).

4-[2′-(Triphenylphosphoranylidene)-1′-oxoethyl]-3-phenylpyrazol-5-one 17b. White solid (2.03 g, 4.4 mmol, 44%) from 3-phenylpyrazol-5-one (1.60 g), mp >202 °C (decomp.) (Found: C, 75.38; H, 5.09; N, 6.02. $C_{29}H_{23}N_2O_2P$ requires C, 75.31; H, 5.01; N, 6.06; P, 6.70%); ν_{max}(KBr)/cm^{-1} 1610 s, 1587 s, 1484 s and 1436 s; δ_C (75.4 MHz; $CDCl_3$–F_3CCO_2H) 36.36 (d, $^1J_{PC}$ 55.4, C-2′), 103.04 (C-4), 118.30 (d, $^1J_{PC}$ 88.6, P–C-*ipso*), 128.74, 129.15, 129.49 (Ph-CH), 130.22 (d, $^3J_{PC}$ 13.0, P–C-*meta*), 130.32 (Ph-*ipso*), 133.65 (d, $^2J_{PC}$ 10.4, P–C-*ortho*), 135.14 (P–C-*para*), 150.30 (C-5), 162.05 (C-3) and 181.52 (C-1′); δ_P (121.4 MHz; $CDCl_3$–F_3CCO_2H) 23.38; *m/z* (FAB) 463 (MH^+, 100%), 275 (24) and 183 (11).

1-Methyl-4-[2′-(triphenylphosphoranylidene)-1′-oxoethyl]-3-phenylpyrazol-5-one 17c. White solid (2.40 g, 5.0 mmol, 50%) from 1-methyl-3-phenylpyrazol-5-one (1.74 g), mp >225 °C (from pyridine–pentane; decomp.) (Found: C, 76.68; H, 5.23; N, 5.94. $C_{30}H_{25}N_2O_2P$ requires C, 76.62; H, 5.29; N, 5.88; P, 6.50%); ν_{max}(KBr)/cm^{-1} 1611 s, 1568 s, 1467 s and 1436 s; δ_C (100.5 MHz; $CDCl_3$–F_3CCO_2H) 31.15 (1-CH_3), 35.97 (d, $^1J_{PC}$ 57.0, C-2′), 104.31 (d, $^3J_{PC}$ 3.7, C-4), 117.72 (d, $^1J_{PC}$ 88.3, P–C-*ipso*), 126.60, 128.74, 128.80 (Ph-CH), 130.37 (d, $^3J_{PC}$ 14.7, P–C-*meta*), 131.44 (P–C-*para*), 133.54 (d, $^2J_{PC}$ 11.0, P–C-*ortho*), 135.44 (Ph-*ipso*), 149.75 (C-5), 160.82 (C-3) and 183.71 (d, $^2J_{PC}$ 7.4, C-1′); δ_P (121.4 MHz; $CDCl_3$–F_3CCO_2H) 23.36; *m/z* (FAB) 477 (MH^+, 100%), 303 ($Ph_3P{=}CH{-}CHO^+$, 29) and 275 (39).

4-[2′-(Triphenylphosphoranylidene)-1′-oxoethyl]-1,3-diphenylpyrazol-5-one 17d. White solid (4.36 g, 8.1 mmol, 81%) from 1,3-diphenylpyrazol-5-one (2.36 g), mp >240 °C (decomp.) (Found: C, 77.94; H, 5.11; N, 5.24. $C_{35}H_{27}N_2O_2P$ requires C, 78.05; H, 5.05; N, 5.20; P, 5.75%); ν_{max}(KBr)/cm^{-1} 1621 s, 1597 s, 1478 s and 1438 s; δ_C (75.4 MHz; $CDCl_3$–F_3CCO_2H) 30.40 (d, $^1J_{CP}$ 36.8, C-2′), 104.45 (C-4), 118.97 (d, $^1J_{PC}$ 88.6, P–C-*ipso*), 123.19, 127.62, 128.46, 129.36, 129.54, 130.09 (Ph-CH), 130.54 (d, $^3J_{PC}$ 12.9, P–C-*meta*), 131.20 (Ph–C-*ipso*), 134.61 (d, $^2J_{PC}$ 10.5, P–C-*ortho*), 135.92 (d, $^4J_{PC}$ 2.5, P–C-*para*), 136.61 (Ph–C-*ipso*), 151.80 (C-5), 161.80 (C-3) and 182.40 (C-1′); δ_P (121.4 MHz; $CDCl_3$–F_3CCO_2H) 23.36; *m/z* (FAB) 539 (MH^+, 100%) and 275 (31).

3-Methoxycarbonylmethyl-1-methyl-4-[2′-(triphenylphosphoranylidene)-1′-oxoethylpyrazol-5-one 17e. White solid (3.50 g, 7.4 mmol, 74%) from 3-methoxycarbonylmethyl-1-methylpyrazol-5-one (1.70 g), mp >212 °C (from $CHCl_3$–pentane; decomp.) (Found: C, 68.71; H, 5.37; N, 5.88. $C_{27}H_{25}N_2O_4P$ requires C, 68.64; H, 5.33; N, 5.93; P, 6.56%); ν_{max}(KBr)/cm^{-1} 1609 s, 1582 s, 1509 s, 1475 s and 1438 s; δ_H (400 MHz; $CDCl_3$) 2.32 (3 H, s, 1-CH_3), 3.52 (3 H, s, OCH_3), 3.64 (2 H, s, 3-CH_2), 5.26 (2 H, d, $^2J_{PH}$ 14.3, 2′-H) and 7.56–7.74 (15 H, m, ArH); δ_C (100.5 MHz; $CDCl_3$) 31.06 (1-CH_3), 32.60 (d, $^1J_{PC}$ 50.4, C-2′), 35.88 (3-CH_2), 51.45 (OCH_3), 103.67 (d, $^3J_{PC}$ 4.6, C-4), 119.59 (d, $^1J_{PC}$ 87.0, C-*ipso*), 129.66 (d, $^3J_{PC}$ 13.7, C-*meta*), 133.91 (d, $^2J_{PC}$ 10.7, C-*ortho*), 134.30 (C-*para*), 143.95 (C-5), 166.08, 171.38 (C-3, *C*O_2Me) and 176.78 (d, $^2J_{PC}$ 6.1, C-1′); δ_P (161.7 MHz; $CDCl_3$) 23.84; *m/z* (FAB) 473 (MH^+, 100%), 440 ($M^+ - OCH_3$, 11%), 413 ($M^+ - CO_2Me$, 6%) and 303 ($Ph_3P - CH_2 - CO^+$, 26%).

X-Ray crystal structure analysis of compound 17e.‡ $C_{27}H_{25}N_2O_4P$, $M = 472.46$. Triclinic, $a = 9.2630(10)$, $b = 11.2170(10)$, $c = 11.8390(10)$ Å, $\alpha = 77.810(10)°$, $\beta = 89.500(10)°$, $\gamma = 82.390(10)°$, $V = 1191.5(2)$ Å^3, space group $P\bar{1}$, $Z = 2$. μ(Mo-Kα) = 0.2 mm^{-1}. 4152 unique reflections measured giving 3176 with $I > 2\sigma(I)$. Final $R_1 = 0.0393$, $wR_2 = 0.0932$.

General experimental procedure for the synthesis of olefins 19

A solution of the ylide **11** (2.5 mmol) and of ethyl glyoxylate **18** (3.75 mmol) in toluene (20 mL) was stirred at room temperature for 12 hours with exclusion of air and moisture. The solvent was then removed on a rotary evaporator and the resulting residue was purified by column chromatography (silica gel; diethyl ether–*n*-pentane, 1 : 1, v/v).

2-Ethoxycarbonyl-2-(3′-ethoxycarbonyl-1′-oxopropenyl)cyclopentan-1-one 19a. Inseparable mixture of *E*- and *Z*-isomers (*E* : *Z* = 7 : 1) as a colorless oil (0.46 g, 1.63 mmol, 66%) from **11a** (1.15 g), R_f 0.44 (diethyl ether–*n*-pentane 1 : 1; v/v) (Found: C, 59.63; H, 6.46. $C_{14}H_{18}O_6$ requires C, 59.57; H, 6.43%); ν_{max}(film)/cm^{-1} 1756 s, 1726 s, 1699 s and 1626 s; δ_H (400 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.08, CH_2CH_3), 1.32 (3 H, t, *J* 7.08, CH_2CH_3), 1.83–2.10 (2 H, m, 4-H), 2.27–2.50 (3 H, m, 5-H, 1 × 3-H), 2.75–2.80 (1 H, m, 1 × 3-H′), 4.21 (2 H, q, *J* 7.08, CH_2CH_3), 4.26 (2 H, q, *J* 7.08, CH_2CH_3), 6.06 (1 H, d, *J* 11.71, 3′-H-*cis*), 6.75 (1 H, d, *J* 15.63, 3′-H-*trans*), 6.86 (1 H, d, *J* 11.71, 2′-H-*cis*) and 7.45 (1 H, d, *J* 15.63, 2′-H-*trans*); *E-isomer*: δ_C (100.5 MHz; $CDCl_3$) 13.94, 14.14 (2 × CH_3), 19.62 (C-4), 30.87 (C-3), 38.53 (C-5), 61.40, 62.59 (2 × CH_2CH_3), 73.29 (C-2), 131.87 (C-3′), 136.27 (C-2′), 165.05, 167.77 (2 × CO_2), 189.59 and 208.00 (C-1, C-1′); *Z-isomer*: δ_C (100.5 MHz, $CDCl_3$) 13.99, 14.17 (2 × CH_3), 19.96 (C-4), 30.63 (C-3), 38.07 (C-5), 61.37, 62.46 (2 × CH_2CH_2), 72.18 (C-2), 125.82 (C-3′), 139.73 (C-2′), 165.83, 167.66 (2 × CO_2), 193.99 and 208.46 (C-1, C-1′); *m/z* (FAB) 283 (MH^+, 100%), 237 ($M^+ - C_2H_5O$, 19%) and 209 (41%).

2-Ethoxycarbonyl-2-(3′-ethoxycarbonyl-1′-oxopropenyl)cyclohexan-1-one 19b. Colorless oil (0.54 g, 1.82 mmol, 74%) from **11b** (1.18 g), separable mixture of isomers (*E* : *Z* = 6 : 1) (Found: C, 60.85; H, 6.72. $C_{15}H_{20}O_6$ requires C, 60.80; H, 6.80%); *mixture*: ν_{max}(KBr)/cm^{-1} 1712 s, 1295 s and 1265 s; *m/z* (FAB) 297 (MH^+, 40%), 251 ($M^+ - C_2H_5O$, 100%) and 205 [$M^+ - (2 \times C_2H_5O)$, 11%].

Pure E-isomer: colorless oil (0.46 g, 1.54 mmol, 62%), R_f 0.83 (diethyl ether–*n*-pentane 1 : 1; v/v); δ_H (500 MHz; $CDCl_3$) 1.29 (3 H, t, *J* 7.11, CH_3), 1.31 (3 H, t, *J* 7.14, CH_3), 1.69–1.99 (4 H, m, 4-H, 5-H), 2.44–2.69 (4 H, m, 3-H, 6-H), 4.25 (2 H, q, *J* 7.14, CH_2CH_3), 4.30 (2 H, q, *J* 7.11, CH_2CH_3), 6.77 (1 H, d, *J* 15.53, 3′-H) and 7.20 (1 H, d, *J* 15.53, 2′-H); δ_C (125.7 MHz; $CDCl_3$) 13.98, 14.12 (2 × CH_3), 21.37 (C-3), 26.76, 32.22 (C-4, C-5), 42.38 (C-6), 61.43, 62.52 (2 × CH_2CH_3), 73.69 (C-2), 131.60 (C-3′), 136.05 (C-2′), 165.07, 167.69 (2 × CO_2), 192.56 and 205.16 (C-1, C-1′).

Pure Z-isomer: colorless oil (0.08 g, 0.28 mmol, 11%), R_f 0.72 (diethyl ether–*n*-pentane 1 : 1; v/v); δ_H (500 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.12, CH_3), 1.30 (3 H, t, *J* 7.15, CH_3), 1.66–1.97 (4 H, m, 4-H, 5-H), 2.33–2.68 (4 H, m, 3-H, 6-H), 4.21 (2 H, q, *J* 7.12, CH_2CH_3), 4.26 (2 H, q, *J* 7.15, CH_2CH_3), 6.10 (1 H, d, *J* 12.13, 3′-H) and 6.65 (1 H, d, *J* 12.13, 2′-H); δ_C (125.7 MHz; $CDCl_3$) 13.92, 13.95 (2 × CH_3), 21.34 (C-3), 26.78, 31.97 (C-4, C-5), 41.31 (C-6), 61.31, 62.34 (2 × CH_2CH_3), 74.24 (C-2), 128.85 (C-3′), 136.84 (C-2′), 165.07, 167.69 (2 × CO_2), 194.35 and 205.16 (C-1, C-1′).

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