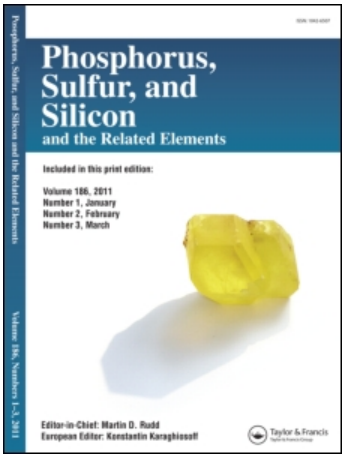

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An Efficient Synthesis of Stable Phosphorus Ylides Derived from Hydantoin and 5,5-dialkylhydantoins

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AN EFFICIENT SYNTHESIS OF STABLE PHOSPHORUS YLIDES DERIVED FROM HYDANTOIN AND 5,5-DIALKYLHYDANTOINS

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Stable crystalline phosphorus ylides are obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong NH-acids, such as hydantoin and 5,5-dialkylhydantoins. These stable ylides exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon-carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group.

Keywords: Acetylenic ester; dynamic NMR; restricted rotation; triphenylphosphine

INTRODUCTION

Phosphorus ylides are reactive systems, which take part in many reactions of value in organic synthesis.[1–11] These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and an alkyl halide.[1–5] Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins among other methods.[1,2] We wish to describe here an efficient synthetic route to hydantoin-containing stable phosphorus ylides. The hydantoin moiety has important medicinal[12,13] as well as agrochemical[14,15] activities; a large number of hydantoins have been synthesized for various

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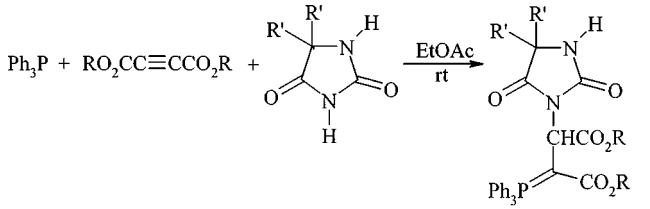
biological applications.[15] Thus, reaction of triphenylphosphine with dialkyl acetylenedicarboxylates **1** in the presence of strong NH-acids **2** leads to the corresponding stable heterocyclic phosphorus ylides **3** in excellent yields (Scheme 1).



1	R
a	Me
b	Et
c	tBu

2	2R'
a	2H
b	2Me
c	2Et
d	$(CH_2)_5$

3	R	2R'	%Yield
a	tBu	2H	89
b	Me	2Me	95
c	tBu	2Me	98
d	Me	2Et	86
e	Et	2Et	82
f	tBu	2Et	94
g	Me	$(CH_2)_5$	94
h	Et	$(CH_2)_5$	93
i	tBu	$(CH_2)_5$	91

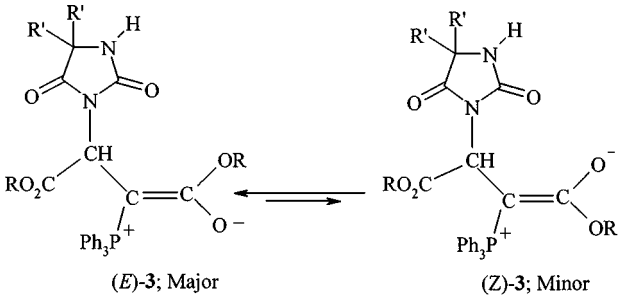
SCHEME 1

RESULTS AND DISCUSSION

The reaction of hydantoin and 5,5-dialkylhydantoins with dialkyl acetylenedicarboxylates **1** in the presence of triphenylphosphine proceeded at room temperature in ethyl acetate, and was finished within a few hours. ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **3**. Any product other than **3** could not be detected by NMR spectroscopy. The structures of compounds **3a–i** were deducted from their elemental analyses and IR, ^{1}H-, ^{13}C-, and ^{31}P NMR spectra. The mass spectra of these stable ylides displayed molecular ion peaks at appropriate *m/z* values. Any initial fragmentation involves loss from or complete loss of the side chains and scission of the heterocyclic ring system.

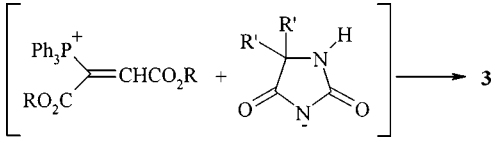
^{1}H-, ^{13}C-, and ^{31}P NMR spectra of ylides **3b**, **3d**, **3e**, **3g**, and **3h** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in (*E*)-**3** and (*Z*)-**3** geometrical isomers (Scheme 2) is slow on the NMR timescale at ambient temperature. Selected ^{1}H-, ^{13}C-, and ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds

3b, **3d**, **3e**, **3g**, and **3h** are shown in Table I. Only one geometrical isomer was observed for di-*tert*-butyl derivatives of **3**, presumably, because of the bulky *tert*-butyl groups.



SCHEME 2

On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[1–5] it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the N—H acid to form phosphoranes **3** (see Scheme 3).

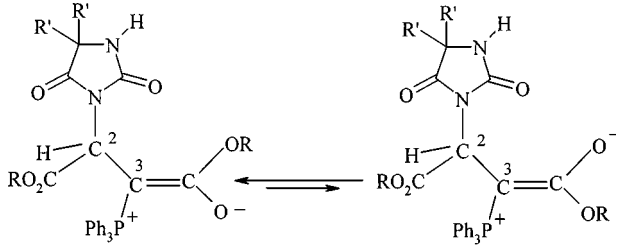


SCHEME 3

The methoxy region of the ^{1}H NMR spectrum of **3b** in $CDCl_3$ at ambient temperature (25°C) exhibits two sharp singlets for the CO_2CH_3 groups of (*E*) and (*Z*) isomers and two fairly broad singlets for the OCH_3 groups. Near 10°C the broad lines become sharper. The ^{1}H NMR of **3b** in 1,2-dichlorobenzene at 10°C is similar to that measured in $CDCl_3$ (see Table II). Increasing the temperature results in coalescence of the OCH_3 resonances. At 125°C, a relatively broad singlet was observed for the OCH_3 group, while the CO_2CH_3 protons appear as a sharp single resonance.

Although, an extensive line-shape analysis in relation to the dynamic ^{1}H NMR effect observed for **3b** was not undertaken, the variable temperature spectra allowed to calculate[16] the free energy of barrier (if not the enthalpy and entropy of activation) for the dynamic NMR process

TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-2, OR, CO_2R, C-2, and C-3 in the Major (M) and Minor (m) Diastereoisomers of Compounds **3a–i**



(*E*)-**3**; Major (*Z*)-**3**; Minor

		^{1}H NMR spectroscopic data			^{13}C NMR data		
Compound	Isomer (%)	H-2 ($^{3}J_{PH}$)	OR	CO_2R	C-2 ($^{2}J_{PC}$)	C-3 ($^{1}J_{PC}$)	^{31}P NMR
3a	M	4.16 (18.7)	0.92	1.51	55.3 (17)	39.9 (128)	23.52
3b	M (52)	4.53 (15.8)	3.08	3.72	54.7 (17)	37.2 (131)	23.48
3b	m (48)	4.56 (17.2)	3.65	3.67	55.5 (16)	39.1 (138)	23.81
3c	M	4.44 (17.2)	0.99	1.59	56.5 (18)	36.3 (123)	22.65
3d	M (53)	4.54 (16.5)	3.10	3.65	54.1 (17)	36.5 (131)	22.65
3d	m (47)	4.61 (17.5)	3.56	3.72	54.8 (17)	38.5 (139)	23.19
3e	M (56)	4.52 (19.8)	3.59[a]	4.00[a]	54.9 (17)	39.9 (131)	22.75
3e	m (44)	4.55 (17.1)	3.77[a]	4.12[a]	55.4 (17)	38.6 (140)	23.04
3f	M	4.37 (17.6)	0.92	1.51	56.1 (18)	36.4 (132)	22.38
3g	M (51)	4.56 (15.7)	3.11	3.71	54.3 (17)	36.7 (131)	22.84
3g	m (49)	4.59 (17.1)	3.58	3.7	55.2 (17)	38.6 (135)	22.55
3h	M (53)	4.57 (16.1)	3.63[a]	4.01[a]	54.4 (17)	38.0 (125)	22.67
3h	m (47)	4.58 (17.5)	3.78[a]	4.26[a]	55.2 (17)	38.1 (125)	22.73
3i	M	4.37 (17.2)	0.94	1.53	56.1 (17)	35.9 (132)	22.02

[a]The methylene group of the OR moiety.

TABLE II Selected Proton Chemical Shifts (at 500.1 MHz, in ppm, Me_4Si) and Activation Parameters (kJ mol^{-1}) for **3b** and **3g** in 1,2-dichlorobenzene

Compound	Temp (°C)	Resonance (P—C—CO_2CH_3)		$\Delta\nu$ (Hz)	k (s^{-1})	T_c (K)	$\Delta G^{\neq}$
3b	10	3.14	3.59	225	500	362	70.5 ± 2
	125	3.36					
3g	10	3.17	3.60	215	477	358	69.7 ± 2
	120	3.39					

in this ylide (see Table II). The experimental data available are not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, even though the errors in $\Delta G^{\neq}$ are not large.[17] A similar dynamic ^{1}H NMR effect was observed for compound **3g**. From coalescence of the methoxy proton resonances, the first-order rate constant for dynamic NMR in **3g** is 477 s^{-1} at 358 K. The calculated free-energy of activation for the dynamic process in **3g** is 69.7 ± 2 kJ mol^{-1}, which is slightly lower than for compound **3b** (see Table II).

In summary, we have prepared novel hydantoin-containing phosphorus ylides via one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong NH-acids such as hydantoin and 5,5-dialkylhydantoins. The present method, carries the advantage that, not only is the reaction performed under neutral conditions, but the substances can be mixed without any activation or modification. Hydantoin-containing phosphorus ylides **3a–i** may be considered as potentially useful synthetic intermediates. The procedure described here may be an acceptable method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured on a Shimadzu IR 460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a BRUKER DRX-500 AVANCE instrument with $CDCl_3$ as solvent at 500.1, 125.8, and 202.4 MHz respectively. The mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates **1a–c**, were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Hydanthoins **2a–d** were prepared according to a published procedure.[18]

Preparation of Di-*tert*-buthyl 2-(2,5-dioxo-imidazolidin-1-yl)-3-(triphenylphosphanylidene)-succinate 3a

General Procedure

To a magnetically stirred solution of 0.52 g triphenylphosphine (2 mmol) and 0.20 g hydantoin (2 mmol) in 10 mL of ethyl acetate was added, dropwise, a mixture of 0.28 g dimethyl acetylenedicarboxylate (2 mmol) in 3 mL of ethyl acetate at −5°C over 10 min. After 8 h

stirring at room temperature, the product was filtered off and recrystallized from ethyl acetate. Colorless crystals, m.p. 197–199°C, yield 1.05 g, 89%. IR (KBr) (ν_{max}, cm^{-1}): 3170 (N–H), 1758 and 1690 (C=O), 1627 (C=C). Analyses: Calc. for $C_{33}H_{37}N_2O_6P$ (588): C, 67.33; H, 6.34; N, 4.76%. Found C, 67.21; H, 6.40; N, 4.61%.

Major isomer (*E*)-**3a**, ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.92 and 1.51 (18 H, 2 s, C*Me*$_3$), 4.16 (1 H, d, $^2J_{HH}$ = 18.7 Hz, HC–*H*), 4.41 (1 H, d, $^3J_{PH}$ = 17.2 Hz, CH), 4.61 (1 H, d, $^2J_{HH}$ = 18.7 Hz, HC–*H*), 7.5–7.6 (15 H, m, 3 C_6H_5), 8.17 (1 H, s, NH). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 28.2 and 28.3 (2 C*Me*$_3$), 39.9 (d,$^1J_{PC}$ = 128 Hz, P–C), 49.7 (CH_2), 55.3 (d, $^2J_{PC}$ = 17 Hz, CH), 77.5 and 81.1 (2 *CMe*$_3$), 127.1 (d, $^1J_{PC}$ = 92 Hz, P–C_{ipso}), 128.8 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.2 (d, $^4J_{PC}$ = 3 Hz, C_{para}), 133.6 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 155.9 (N–CO–N), 168.8 (d, $^3J_{PC}$ = 12 Hz, C=O), 170.5 (d, $^2J_{PC}$ = 12 Hz, P–C=*C*), 172.4 (N–C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$), δ 23.52 (Ph_3P^+–C).

Dimethyl 2-(4,4-dimethyl-2,5-dioxo-imidazolidin-1-yl)-3-(triphenylphosphanylidene)-succinate 3b

Colorless crystals, m.p. 188–190°C, yield 1.01 g, 95%. IR (KBr) (ν_{max}, cm^{-1}): 3270 (N–H), 1734, 1705, 1632 (C=O), 1605 (C=C). Analyses: Calc. for $C_{29}H_{29}N_2O_6P$ (532.52): C, 65.40; H, 5.49; N, 5.26%. Found C, 65.48; H, 5.54; N, 5.48%. MS (*m/z*, %): 532 (M, 3); 473 (M–CO_2Me, 30); 405 (M-heterocycle, 10); 262 (PPh_3, 95).

Major isomer (*E*)-**3b** (52%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.24 and 1.32 (6 H, 2 s, 2 CH_3), 3.08 and 3.72 (6 H, 2 s, 2 OCH_3), 4.53 (1 H, d, $^3J_{PH}$ = 15.8 Hz, CH), 6.04 (1 H, s, NH) 7.4–7.7 (15 H, m, 3 C_6H_5) ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 25.2 and 25.4 (2 CH_3), 37.2 (d, $^1J_{PC}$ = 131 Hz, P–C), 49.4 and 50.8 (2 OCH_3), 54.7 (d, $^2J_{PC}$ = 17 Hz, CH), 58.0 (*C*Me$_2$), 126.7 (d, $^1J_{PC}$ = 91 Hz, P–C), 129.2 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.4 (d, $^4J_{PC}$ = 2 Hz, C_{para}), 134 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 156.6 (N–CO–N), 169.4 (d, $^3J_{PC}$ = 13 Hz, C=O), 171.7 (d, $^2J_{PC}$ = 14 Hz, P–C=*C*), 176.8 (N–C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.48 (Ph_3P^+–C).

Minor isomer (*Z*)-**3b** (48%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.23 and 1.30 (6 H, 2 s, 2 CH_3), 3.55 and 3.67 (6 H, 2 s, 2 OCH_3), 4.56 (1 H, d, $^3J_{PH}$ = 17.2 Hz, CH), 5.97 (1 H, s, NH), 7.4–7.7 (15 H, m, 3 C_6H_5).: ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 25.2 and 25.4 (2 CH_3), 39.1 (d, $^1J_{PC}$ = 138 Hz, P–C), 52.8 and 53.1 (2 OCH_3), 55.5 (d, $^2J_{PC}$ = 16 Hz, CH), 58.1 (*C*Me$_2$), 127.4 (d, $^1J_{PC}$ = 90 Hz, P–C), 129.2 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.5 (d, $^4J_{PC}$ = 2 Hz, C_{para}), 134.0 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 156.6 (N–CO–N), 169.4 (d, $^3J_{PC}$ = 13 Hz, C=O), 171.6 (d, $^2J_{PC}$ = 14 Hz, P–C=*C*), 177.0 (N–C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.81 (Ph_3P^+–C).

Di-*tert*-buthyl 2-(4,4-dimethyl-2,5-dioxo-imidazolidin-1-yl)-3-(triphenylphosphanylidene)-succinate 3c

Colorless crystals, m.p. 132–135°C, yield, 1.21 g, 98%. IR (KBr) (ν_{max}, cm^{-1}): 3245 (N–H), 1772, 1737, 1716 (C=O), 1607 (C=C). Analyses: Calc. For $C_{35}H_{41}N_2O_6P$ (616.68): C, 68.16; H, 6.70; N, 4.54%. Found C, 68.76; H, 7.05; N, 4.49%.

Major isomer (*E*)-**3c**, ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.99 and 1.59 (18 H, 2 s, 2 CMe_3), 1.37 and 1.43 (6 H, 2 s, 2 CMe_2), 4.44 (1 H, d, $^3J_{PH}$ = 17.2 Hz, CH), 5.68 (1 H, s, NH), 7.5–7.8 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 25.5 and 25.8 (2 C*M*e$_2$), 28.6 and 28.8 (2 *C*Me$_3$), 36.3 (d, $^1J_{PC}$ = 131 Hz, P–C), 56.5 (d, $^2J_{PC}$ = 18 Hz, CH), 57.9 (*C*Me$_2$), 77.2 and 81.1 (2 *C*Me$_3$), 128.3 (d, $^1J_{PC}$ = 91 Hz, P–C), 128.9 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.2 (d, $^4J_{PC}$ = 2 Hz, C_{para}), 134.1 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 156.7 (N–CO–N), 168.1 (d, $^3J_{PC}$ = 12 Hz, C=O), 169.8 (d, $^2J_{PC}$ = 14 Hz, P–C=*C*), 176.3 (N–C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.01 (Ph_3P^+–C).

Dimethyl 2-(4,4-diethyl-2,5-dioxo-imidazolidin-1-yl)-3-(triphenylphosphanylidene)-succinate 3d

Colorless crystals, m.p. 198–201°C, yield 0.96, 86%, IR (KBr) (ν_{max}, cm^{-1}): 3240 (N–H), 1765, 1743 and 1708 (C=O), 1618 (C=C), Analyses: Calc. for $C_{31}H_{33}N_2O_6P$ (560.58): C, 66.42; H, 5.93; N, 5.00%. Found C, 66.20; H, 6.13; N, 5.01%. MS (*m/z*, %): 560 (M, 2); 501 (M–CO_2Me, 20); 405 (M-heterocycle, 10); 262 (PPh_3, 95); 108 (PPh, 35).

Major isomer (*E*)-**3d** (53%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.64 and 0.85 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_3), 1.50 (2 H, ABX_3 system, CH_2), 1.75 (2 H, ABX_3 system, CH_2), 3.10 and 3.65 (6 H, 2 s, 2 OCH_3), 4.54 (1 H, d, $^3J_{PH}$ = 16.5 Hz, CH), 5.85 (1 H, s, NH), 7.4–7.7 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.1 and 7.2 (2 CH_3), 29.1 and 29.4 (2 CH_2), 36.5 (d, $^1J_{PC}$ = 131 Hz, P–C), 48.5 and 51.8 (2 OCH_3), 54.1 (d, $^2J_{PC}$ = 17. Hz, CH), 64.8 (*C*Et$_2$) 125.9 (d, $^1J_{PC}$ = 86 Hz, P–C), 128.7 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 131.5 (C_{para}), 133.1 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 156.8 (N–CO–N), 168.6 (d, $^3J_{PC}$ = 12 Hz, C=O), 170.8 (d, $^2J_{PC}$ = 14 Hz, P–C=*C*), 174.7 (N–C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.65 (Ph_3P^+–C).

Minor isomer (*Z*)-**3d** (47%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.66 and 0.85 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_3), 1.50 (2 H, ABX_3 system, CH_2), 1.75 (2 H, ABX_3 system, CH_2), 3.56 and 3.72 (6 H, 2 s, 2 OCH_3) 4.61 (1 H, d, $^3J_{PH}$ = 17.5 Hz, CH), 5.95 (1 H, s, NH), 7.4–7.7 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.2 and 7.3 (2 CH_3), 29.3 and 29.6 (2 CH_2), 38.5 (d, $^1J_{PC}$ = 139 Hz, P–C), 49.8 and 52.1 (2 OCH_3), 54.8

(d, $^2J_{PC}$ = 17 Hz, CH), 64.8 (*C*Et$_2$), 126.7 (d, $^1J_{PC}$ = 87 Hz, P–C), 128.7 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 131.6 (C_{para}), 133.2 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 156.9 (N–CO–N), 168.6 (d, $^3J_{PC}$ = 12 Hz, C=O), 170.8 (d, $^2J_{PC}$ = 14 Hz, P–C=*C*), 174.9 (N–C=O), ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.19 (Ph_3P^+–C).

Diethyl 2-(4,4-diethyl-2,5-dioxo-imidazolidin-1-yl)-3-(triphenylphosphanylidene)-succinate 3e

Colorless crystals, m.p. 183–184°C, yield 0.96 g, 82%. IR (KBr) (ν_{max}, cm^{-1}): 3230 (N–H), 1766, 1738 and 1705 (C=O), 1620 (C=C): Analyses: Calc. for $C_{33}H_{37}N_2O_6P$ (588.63) C, 67.33; H, 6.34; N, 4.76%. Found C, 67.19; H, 6.44; N, 4.64%. MS (*m/z*, %): 588 (M, 1); 515 (M–CO_2Et, 16); 433 (M-heterocycle, 8); 262 (PPh_3, 95); 108 (PPh, 28).

Major isomer (*E*)-**3e** (56%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.42 and 0.67 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_2CH_3), 0.90 and 1.1 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 OCH_2CH_3), 1.52 (2 H, ABX_3 system, CH_2), 1.76 (2 H, ABX_3 system, CH_2), 3.59 and 4.00 (4 H, 2 ABX_3 system, 2 OCH_2CH_3), 4.52 (1 H, d, $^3J_{PH}$ = 19.8 Hz, CH), 5.44 (1 H, s, NH), 7.4–7.7 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.7 and 7.8 (2 CH_2CH_3), 13.9 and 14.1 (2 OCH_2CH_3), 29.6 and 30.0 (2 CH_2CH_3), 39.9 (d, $^1J_{PC}$ = 131 Hz, P–C), 54.9 (d, $^2J_{PC}$ = 17 Hz, CH), 58.6 and 65.4 (2 OCH_2), 63.0 (*C*Et$_2$), 126.6 (d, $^1J_{PC}$ = 91 Hz, P–C), 128.5 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.1 (C_{para}), 133.7 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 157.5 (N–CO–N), 168.6 (d, $^3J_{PC}$ = 13 Hz, C=O), 170.8 (d, $^2J_{PC}$ = 15 Hz, P–C=*C*), 175.2 (N–C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 22.75 (Ph_3P^+–C).

Minor isomer (*Z*)-**3e** (44%), ^{1}H NMR (500.1 MHz, $CDCl_3$), δ 0.67 and 0.87 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_2CH_3), 0.92 and 1.26 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 OCH_2CH_3), 1.55 (2 H, ABX_3 system, CH_2), 1.85 (2 H, ABX_3 system, CH_2), 3.77 and 4.12 (4 H, 2 ABX_3 system, 2 OCH_2CH_3), 4.55 (1 H, d, $^3J_{PH}$ = 17.1 Hz, CH), 5.41 (1 H, s, NH), 7.4–7.7 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.7 and 7.8 (2 CH_2CH_3), 14.1 and 14.7 (2 OCH_2CH_3), 29.8 and 30.1 (2 CH_2CH_3), 38.6 (d, $^1J_{PC}$ = 140 Hz, P–C), 55.4 (d, $^2J_{PC}$ = 17 Hz, CH), 57.5 and 61.3 (2 OCH_2), 63.0 (*C*Et$_2$), 127.1 (d, $^1J_{PC}$ = 87 Hz, P–C), 128.7 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.0 (C_{para}), 133.7 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 157.7 (N–CO–N), 168.6 (d, $^3J_{PC}$ = 13 Hz, C=O), 171.1 (d, $^2J_{PC}$ = 14 Hz, P–C=*C*), 175.1 (N–C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$); δ 23.04 (Ph_3P^+–C).

Di-*tert*-buthyl 2-(4,4-diethyl-2,5-dioxo-imidazolidin-1-yl)-3-(triphenylphosphanylidene)-succinate 3f

Colorless crystals, m.p. 176–178°C, yield 1.21 g, 94%. IR (KBr) (ν_{max}, cm^{-1}): 3238 (N–H), 1731 and 1704 (C=O), 1624 (C=C). Analyses: Calc.

for $C_{37}H_{45}N_2O_6P$ (644.74): C, 68.92; H, 7.04; N, 4.35%. Found C, 68.96; H, 7.35; N, 4.31%. MS (*m/z*, %): 644 (M, 2); 543 (M—CO_2^tBu, 10); 489 (M-heterocycle, 4); 262 (PPh_3, 100); 108 (PPh, 35).

Major isomer (*E*)-**3f**, ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.68 and 0.91 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_2CH_3), 0.92 and 1.51 (18 H, 2 s, 2 CMe_3), 1.58 (2H, ABX_3 system, CH_2), 1.79 (2 H, ABX_3 system, CH_2), 4.37 (1 H, d, $^3J_{PH}$ = 17.6 Hz, CH), 5.44 (1 H, s, NH), 7.4–7.7 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 7.8 and 8.1 (2 CH_3), 25.4 and 28.3 (2 C*Me*$_3$), 29.3 and 30.2 (2 CH_2), 36.4 (d, $^1J_{PC}$ = 132 Hz, P—C), 56.1 (d, $^2J_{PC}$ = 18 Hz, CH), 65.1 (*C*Et_2), 76.9 and 80.6 (2 *C*Me_3), 128.1 (d, $^1J_{PC}$ = 90 Hz, P—C), 128.5 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 131.8 (d, $^4J_{PC}$ = 2 Hz, C_{para}), 133.8 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 157.5 (N—CO—N), 167.5 (d, $^3J_{PC}$ = 12 Hz, C=O), 169.4 (d, $^2J_{PC}$ = 13 Hz, P—C=*C*), 175.0 (N—C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.38 (Ph_3P^+—C).

Dimethyl 2-(2,5-dioxo-1,3-diaza-spiro[4.5]dec-3-yl)-3-(triphenylphosphanylidene)-succinate 3g

Colorless crystals, m.p. 201–203°C, yield 1.08, 94%. IR (KBr) (ν_{max}, cm^{-1}): 3150 (N—H), 1735 and 1700 (C=O), 1585 (C=C). Analyses: Calc. for $C_{32}H_{33}N_2O_6P$ (572.59): C, 67.12; H, 5.81; N, 4.89%. Found C, 66.93; H, 6.04; N, 4.68%. MS (*m/z*, %): 572 (M, 1); 405 (M-heterocycle, 5); 347 (M-heterocycle and CO_2Me, 5); 333 ($MeO_2CC{=}PPh_3$, 2); 262 (PPh_3, 100); 167 (heterocycle, 20); 108 (PPh, 35); 77 (Ph, 75).

Major isomer (*E*)-**3g** (51%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 1.34–1.92 (10 H, m, 5 CH_2), 3.11 and 3.71 (6 H, 2 s, 2 OCH_3), 4.56 (1 H, d, $^3J_{PH}$ = 15.7 Hz, CH), 6.71 (1 H, s, NH), 7.0–7.5 (15 H, m, C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 21.7–33.6 (5 CH_2), 36.7 (d, $^1J_{PC}$ = 131 Hz, P—C), 46.0 and 52.8 (2 OCH_3), 54.3 (d, $^2J_{PC}$ = 17 Hz, P—C), 60.7 (C_{spiro}), 126.4 (d, $^1J_{PC}$ = 88 Hz, P—C), 128.5 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.0 (C_{para}), 133.6 (d, $^3J_{PC}$ = 9 Hz, C_{ortho}), 156.6 (N—CO—N), 169.0 (d, $^3J_{PC}$ = 12 Hz, C=O), 171.4 (d, $^2J_{PC}$ = 13 Hz, P—C=*C*), 175.9 (N—C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.84 (Ph_3P^+—C).

Minor isomer (*Z*)-**3g** (49%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 1.34–1.92 (10 H, m, 5 CH_2), 3.58 and 3.76 (6 H, 2 s, 2 OCH_3), 4.59 (1 H, d, $^3J_{PH}$ = 17.1 Hz, CH), 6.50 (1 H, s, NH), 7.0–7.5 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 21.7–33.6 (5 CH_2), 38.6 (d, $^1J_{PC}$ = 135 Hz, P—C), 50.3 and 52.5 (2 OCH_3), 55.2 (d, $^2J_{PC}$ = 17 Hz, P—C), 60.8 (C_{spiro}), 127.1 (d, $^1J_{PC}$ = 92 Hz, P—C), 128.8 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.1 (C_{para}), 133.6 (d, $^3J_{PC}$ = 9 Hz, C_{ortho}), 157 (N—CO—N), 169 (d, $^3J_{PC}$ = 12 Hz, C=O), 172 (d, $^2J_{PC}$ = 13 Hz, P—C=*C*), 176 (N—C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 22.55 (Ph_3P^+—C).

Diethyl 2-(2,5-dioxo-1,3-diaza-spiro[4.5]dec-3-yl)-3-(triphenylphosphanylidene)-succinate 3h

Colorless crystals, m.p. 182–184°C, yield 1.12 g, 93. IR (KBr) (ν_{max}, cm^{-1}): 3190 (N–H), 1731, 1699, 1650 (C=O), 1585 (C=C). Analyses: Calc. for $C_{34}H_{37}N_2O_6P$ (600.64): C, 67.99; H, 6.21; N, 4.66%. Found C, 67.77; H, 6.32; N, 4.49%. MS (*m/z*, %): 600 (M, 1); 361 (M-heterocycle and CO_2Me, 2); 262 (PPh_3, 85); 167 (heterocycle, 20); 108 (PPh, 85); 77 (Ph, 7).

Major isomer (*E*)-**3h** (53%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.44 and 1.28 (6 H, 2 t, $^3J_{HH}$ = 7.1 Hz, 2 CH_3), 1.26–1.90 (10 H, m, 5 CH_2), 3.63 (2 H, ABX_3 system, OCH_2), 4.01 (2 H, ABX_3 system, OCH_2), 4.57 (1 H, d, $^3J_{PH}$ = 16.1 Hz, CH), 6.17 (1 H, s, NH), 7.3–7.8 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14 and 14.1 (2 CH_3), 21.4–33.6 (5 CH_2), 58.0 (d, $^1J_{PC}$ = 125 Hz, P–C), 54.4 (d, $^2J_{PC}$ = 17 Hz, CH), 60.4 (C_{spiro}), 60.7 and 61.3 (2 OCH_2), 126.7 (d, $^1J_{PC}$ = 93 Hz, P–C), 128.7 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.1 (C_{para}), 133.3 (d, $^3J_{PC}$ = 10 Hz, C_{ortho}), 156.8 (N–CO–N), 168.5 (d, $^3J_{PC}$ = 13 Hz, C=O), 170.7 (d, $^2J_{PC}$ = 13 Hz, P–C=*C*), 176 (N–CO). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.67 (Ph_3P^+–C).

Minor isomer (*Z*)-**3h** (47%): ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 1.17 and 1.23 (6 H, 2 t, $^3J_{HH}$ = 7.1 Hz, 2 CH_3), 1.26–1.90 (10 H, m, 5 CH_2), 3.78 (2 H, ABX_3 system, OCH_2), 4.26 (2 H, ABX_3 system, OCH_2), 4.58 (1 H, d, $^3J_{PH}$ = 17.5 Hz, CH), 6.61 (1 H, s, NH), 7.3–7.8 (15 H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 14.0 and 14.8 (2 CH_3), 21.7–33.6 (5 CH_2), 38.1 (d, $^1J_{PC}$ = 125 Hz, P–C), 55.2 (d, $^2J_{PC}$ = 17.1 Hz, CH), 60.4 (C_{spiro}), 60.6 and 61.2 (2 OCH_2), 127.4 (d, $^1J_{PC}$ = 92 Hz, P–C), 128.5 (d, $^3J_{PC}$ = 12 Hz, C_{meta}), 132.0 (C_{para}), 133.3 (d, $^3J_{PC}$ = 11 Hz, C_{ortho}), 156.91 (N–CO–N), 168.5 (d, $^3J_{PC}$ = 13 Hz, C=O), 170.8 (d, $^2J_{PC}$ = 14 Hz, P–C=*C*), 176.2 (N–CO). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.73 (Ph_3P^+–C).

Di-*tert*-buthyl 2-(2,5-dioxo-1,3-diaza-spiro[4.5]dec-3-yl)-3-(triphenylphosphanylidene)-succinate 3i

Colorless crystals, m.p. 131–132°C, yield 1.20 g, 91%. IR (KBr) (ν_{max}, cm^{-1}): 3230 (N–H), 1760, 1724 and 1638 (C=O), 1649 (C=C). Analyses: Calc. for $C_{34}H_{37}N_2O_6P$ (656.75) C, 69.49; H, 6.91; N, 4.27%. Found C, 69.67; H, 6.97; N, 4.48%. MS (*m/z*, %): 656 (M, 1); 369 ($MeO_2CC{=}PPh_3$, 2); 262 (PPh_3, 50).

Major isomer (*E*)-**3i**, ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.94 and 1.53 (18 H, 2 s, C*Me*$_3$), 1.02–1.89 (10 H, m, 5 CH_2), 4.37 (1 H, d, $^3J_{PH}$ = 17.2 Hz, CH), 6.60 (1 H, s, NH), 7.3–7.8 (15 H, m, 3 C_6H_5). ^{13}C NMR

(125.8 MHz, $CDCl_3$) δ 28.2 and 28.4 (2 C*Me*$_3$), 21.8–33.6 (5 CH_2), 35.9 (d, $^1J_{PC} = 132$ Hz, P–C), 56.1 (d, $^2J_{PC} = 17$ Hz, CH), 60.6 (C_{spiro}), 76.8 and 80.6 (2 *C*Me$_3$), 127.9 (d, $^1J_{PC} = 92$ Hz, P–C), 128.5 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.1 (C_{para}), 133.8 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 156.9 (N–CO–N), 167.6 (d, $^2J_{PC} = 13$ Hz, P–C=*C*), 169.6 (d, $^3J_{PC} = 12$ Hz, C=O), 175.6 (N–C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.02 (Ph_3P^+–C).

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