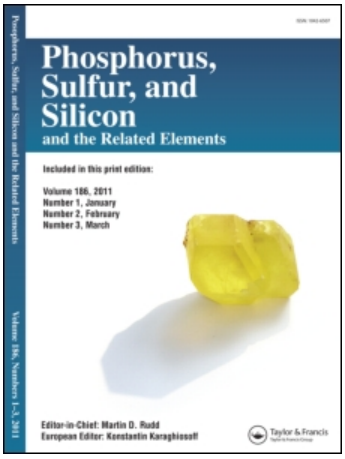

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A Simple Synthesis of Stable Phosphoranes Derived from Imides or Acetanilide Derivatives

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A SIMPLE SYNTHESIS OF STABLE PHOSPHORANES DERIVED FROM IMIDES OR ACETANILIDE DERIVATIVES

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Department of Chemistry, University of Tarbiat Modarres, Tehran, Iran;[a] *Department of Chemistry, University of Sistan and Baluchestan, Zahedan, Iran;*[b] *and Department of Chemistry, University of Shahid Beheshti, Tehran, Iran*[c]

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Stable crystalline phosphorus ylides are obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine, dialkyl acetylenedicarboxylates, and strong NH-acids, such as acetanilide, 4-methylacetanilide, 2-cyanoacetanilide, 4-bromoacetanilide, 4-methoxyacetanilide, succinimide, malimide, or phthalimide. These stabilized phosphoranes exist 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; NH-acid; stable phosphorus ylide; triphenylphosphine

INTRODUCTION

Development of simple synthetic routes for widely-used organic compounds from readily available reagents is one of the major tasks in organic chemistry.[1] Phosphorus ylides are reactive systems, which take part in many valuable reactions in organic synthesis.[2–4] These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually obtained from the phosphine and an alkyl halide.[2–10] Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefines among other methods.[2–4] We describe here an efficient synthesis of acetanilide- or

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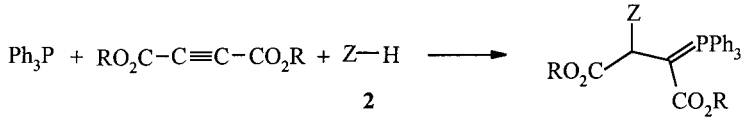
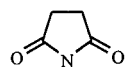
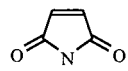
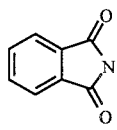
imide-containing stable phosphorus ylides. Thus, reaction of triphenylphosphine with dialkyl acetylenedicarboxylates **1** in the presence of strong NH-acids **2** leads to the corresponding phosphorane **3** in excellent yields (Scheme 1).



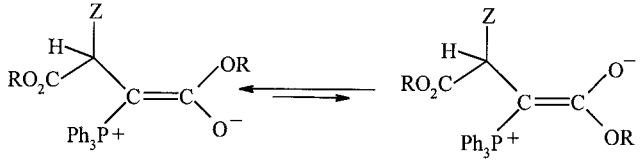
1	R
a	Me
b	^{t}Bu

3	Z	R	%Yield
a	C_6H_5-N-$COCH_3$	Me	90
b		^{t}Bu	95
c	4-CH_3-C_6H_4-N-$COCH_3$	Me	96
d		^{t}Bu	95
e	4-CH_3O-C_6H_4-N-$COCH_3$	^{t}Bu	95
f	4-Br-C_6H_4-N-$COCH_3$	^{t}Bu	94
g	2-CN-C_6H_4-N-$COCH_3$	Me	95
h		Me	95
i		Me	92
j		Me	96

SCHEME 1

RESULTS AND DISCUSSION

The reaction of acetanilide derivatives or imides with dialkyl acetylenedicarboxylates **1** in the presence of triphenylphosphine proceeded at room temperature in ethyl acetate, and was finished after 24 h. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of phosphorane **3**. Any product other than **3** could not be detected by NMR spectroscopy. The structures of compounds **3a–j** were deduced from their elemental analyses and IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of these stable ylides displayed

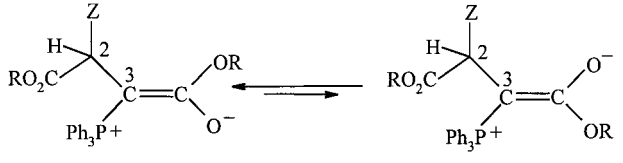


SCHEME 2

molecular ion peaks at appropriate *m/z* values. Any initial fragmentation involves loss from or complete loss of the side chains.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **3a–j** are consistent with the presence of two isomers. The ylide moiety of these compounds

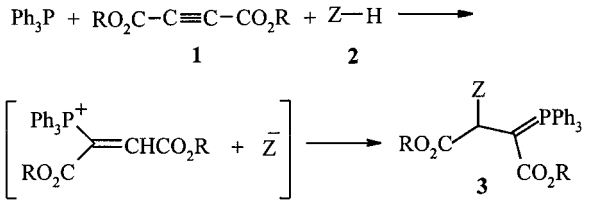
TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-2, OR, CO_2R, C-2, and C-3 in the Major (M) and Minor (m) Diastereoisomers of Compounds **3a–j**



		^{1}H NMR data			^{13}C NMR data		
Compound	Isomer (%)	H-2 ($^{3}J_{PH}$)	OR	CO_2R	C-3 ($^{1}J_{PC}$)	C-2 ($^{2}J_{PC}$)	^{31}P NMR
3a	M (70)	5.35 (21)	3.05	3.75	40.6 (134)	58.4 (17)	26.20
	m (30)	5.28 (18)	2.80	3.87	38.3 (126)	59.4 (20)	25.60
3b	M (76)	5.17 (19)	0.76	1.63	38.9 (127)	60.9 (17)	
	m (24)	5.10 (22)	1.11	1.61	42.0 (134)	59.8 (19)	
3c	M (70)	5.35 (20)	3.07	3.85	41.0 (134)	58.9 (17)	26.24
	m (30)	5.28 (18)	2.85	3.75	38.7 (127)	58.2 (18)	25.65
3d	M (70)	5.16 (20)	0.78	1.60	38.2 (126)	60.1 (16)	
	m (30)	5.10 (22)	1.18	1.78	42.0 (134)	60.0 (14)	
3e	M (77)	5.09 (19)	0.76	1.60	39.1 (127)	60.8 (17)	
	m (23)	5.10 (22)	1.13	1.73	41.9 (134)	59.7 (21)	
3f	M (82)	5.87 (19)	0.76	1.61	39.5 (128)	60.8 (19)	25.97
	m (18)	5.02 (22)	1.13	1.60	40.8 (134)	59.9 (18)	25.36
3g	M (55)	5.18 (19)	2.68	3.80	40.3 (125)	61.4 (17)	
	m (45)	5.34 (21)	3.04	3.74	42.0 (132)	60.3 (17)	
3h	M (66)	4.66 (16)	3.09	3.69	38.3 (138)	55.3 (17)	22.68
	m (34)	4.70 (17)	3.58	3.81	36.5 (131)	55.1 (16)	22.50
3i	M (52)	4.60 (16)	3.14	3.73	38.8 (139)	54.7 (17)	22.56
	m (48)	4.61 (18)	3.60	3.70	37.2 (130)	54.2 (17)	22.43
3j	M (56)	4.79 (13)	3.16	3.74	39.0 (139)	55.0 (17)	23.03
	m (44)	4.83 (15)	3.63	3.71	37.3 (130)	54.3 (16)	22.86

is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in **3-**(*E*) and **3-**(*Z*) 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 **3a–j** are shown in Table I. Assignment of configuration (*Z*) to the minor geometrical isomer is based on the ^{1}H chemical shift of the OR moiety, which is expected to be shielded as a result of the anisotropic effect of the phenyl groups.

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 **2**. Then, the positively charged ion is attacked by the nitrogen atom of the conjugate base of the NH-acid to form phosphorane **3** (Scheme 3).



SCHEME 3

In summary, we have prepared novel acetanilide- or imide-containing phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong NH-acids such as acetanilide derivatives or imides. 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. Acetanilide- or imide-containing phosphorus ylides **3a–j** 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 for C, H, and N 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 with a BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz, respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Triphenylphosphine, dialkyl acetylenedicarboxylates, acetanilides, and imides were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

Preparation of Dimethyl 2-(Acetanilide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3a)

General Procedure

To a magnetically stirred solution of acetanilide (0.27 g, 2 mmol) and triphenylphosphine (0.52, 2 mmol) in ethyl acetate (10 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in ethyl acetate (4 mL) at $-10^{\circ}C$ over 10 min. The reaction mixture was then allowed to warm up to room temperature and stand for 24 h. The solvent was removed under reduced pressure and the solid residue was washed with cold diethyl ether (2×5 mL) and the product was obtained as colorless crystals, m.p. 190–192°C, yield 0.96 g, 90%. IR (KBr) (ν_{max}, cm^{-1}): 1744 and 1746 (C=O), 1610 (C=C). MS (*m/z*, %): 539 (M^{+}, 2); 405 (10); 262 (100); 183 (55); 93.2 (75); 43.2 (55). Anal. Calcd for $C_{32}H_{30}O_5NP$ (539.5): C, 71.24; H, 5.50; N, 2.60. Found: C, 71.2; H, 5.5; N, 2.6%.

Major isomer (70%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.72 (3H, s, $COCH_3$); 3.05 (3H, s, P–C–CO_2Me); 3.75 (3H, s, CH–CO_2*Me*); 5.35 (1H, d, $^{3}J_{HP}$ 20.8 Hz, CH) 7.20–7.80 (20H, m, 4 C_6H_5). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 22.84 (CH_3 amide); 40.65 (d, $^{1}J_{CP}$ 134.0 Hz, P–C); 48.86 and 51.63 (2 OMe); 58.42 (d, $^{2}J_{CP}$ 17.3 Hz, P–C–*C*H); 123.99, 127.29 (2 CH, C_6H_5N); 128.16 (d, $^{1}J_{CP}$ 86.6 Hz, C_{ipso}); 128.23 (d, $^{3}J_{CP}$ 11.6 Hz, C_{meta}); 128.59 (CH, C_6H_5N); 131.81 (d, $^{4}J_{CP}$ 2.0 Hz, C_{para}); 133.15 (d, $^{2}J_{CP}$ 10.3 Hz, C_{ortho}); 140.12 (C, C_6H_5N); 168.04 (d, $^{3}J_{CP}$ 12.8 Hz, C=O ester); 169.35 (C=O amide); 172.51 (d, $^{2}J_{CP}$ 13.7 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 26.20 (Ph_3P^{+}–C).

Minor isomer (30%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.70 (3H, s, $COCH_3$); 2.80 (3H, s, P–C–CO_2Me); 3.87 (3H, s, CH–CO_2*Me*); 5.28 (1H, d, $^{3}J_{HP}$ 18.3 Hz, CH); 7.20–7.80 (20 H, m, 4 C_6H_5). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 22.90 (CH_3 amide); 38.31 (d, $^{1}J_{CP}$ 125.8 Hz, P–C); 59.44 (d, $^{2}J_{CP}$ 20.2 Hz, P–C–*C*H); 48.25 and 51.87 (2 OMe); 124.48, 127.30 (2 CH, C_6H_5N); 127.82 (d, $^{1}J_{CP}$ 91.8 Hz, C_{ipso}); 128.23 (d, $^{3}J_{CP}$ 11.6 Hz, C_{meta}); 128.59 (CH, C_6H_5N); 131.81 (d, $^{4}J_{CP}$ 2.0 Hz, C_{para}); 132.58 (d, $^{2}J_{CP}$ 10.3 Hz, C_{ortho}); 140.48 (C, C_6H_5N); 168.33 (d, $^{3}J_{CP}$

12.8 Hz, C=O ester); 170.17 (C=O amide); 172.51 (d, $^2J_{CP}$ 13.7 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 26.20 (Ph_3P^+–C).

*Selected Data for Di-*tert*-butyl 2-(Acetanilide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3b)*

White solide, m.p. 196–198°C, yield 1.18 g, 95%. IR (KBr) (ν_{max}, cm^{-1}): 1730 and 1630 (C=O); 1506 (C=C). MS (*m/z*, %): 623 (M^+, 2); 406 (13); 377 (10); 262 (100); 183 (36); 109 (12); 57 (9). Anal. Calcd for $C_{38}H_{42}O_5NP$ (623.7): C, 73.18; H, 6.79; N, 2.25. Found: C 73.1; H, 6.7; N, 2.2%.

Major isomer (76%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.76 and 1.63 (18H, 2 s, 2 CMe_3); 1.76 (3H, s, $COCH_3$); 5.17 (1H, d, $^3J_{HP}$ 19.4 Hz, CH); 7.30–7.80 (20H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.87 (CH_3 amide); 28.45 and 28.85 (6 C, 2 C*Me*$_3$), 38.86 (d, $^1J_{CP}$ 126.8 Hz, P–C); 60.88 (d, $^2J_{CP}$ 17.1 Hz, P–C–*C*H); 77.06 and 80.46 (2 *C*Me$_3$); 120.23, 123.62, 127.28 (3 CH, C_6H_5N); 127.78 (d, $^1J_{CP}$ 91.0 Hz, C_{ipso}); 128.23 (d, $^3J_{CP}$ 12.0 Hz, C_{meta}); 131.98 (d, $^4J_{CP}$ 2.0 Hz, C_{para}); 133.28 (d, $^2J_{CP}$ 10.0 Hz, C_{ortho}); 141.62 (C, C_6H_5N); 167.62 (d, $^3J_{CP}$ 12.8 Hz, C=O ester); 169.75 (C=O amide); 171.50 (d, $^2J_{CP}$ 13.7 Hz, P–C=*C*).

Minor isomer (24%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.11 and 1.61 (18H, 2 s, 2 CMe_3); 1.66 (3H, s, $COCH_3$); 5.10 (1H, d, $^3J_{HP}$ 22.2 Hz, CH); 7.30–7.80 (20H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.52 (CH_3 amide); 28.57 and 29.01 (6 C, 2 C*Me*$_3$); 41.98 (d, $^1J_{CP}$ 134.6 Hz, P–C); 59.76 (d, $^2J_{CP}$ 18.7 Hz, P–C–*C*H); 80.59 and 82.05 (2 *C*Me$_3$); 120.12, 123.47, 127.76 (3 CH, C_6H_5N); 127.95 (d, $^1J_{CP}$ 91.0 Hz, C_{ipso}); 128.22 (d, $^3J_{CP}$ 12.0 Hz, C_{meta}); 131.96 (d, $^4J_{CP}$ 2.0 Hz, C_{para}); 133.30 (d, $^2J_{CP}$ 10.8 Hz, C_{ortho}); 141.62 (C, C_6H_5N); 169.67 (C=O amide); 170.83 (d, $^3J_{CP}$ 18.4 Hz, C=O ester); 171.81 (d, $^2J_{CP}$ 14.0 Hz, P–C=*C*).

Selected Data for Dimethyl 2-(p-Methylacetanilide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3c)

Colorless crystals, m.p. 178–180°C, yield 1.05 g, 95%. IR (KBr) (ν_{max}, cm^{-1}): 1733 and 1706 (C=O); 1637 (C=C). MS (*m/z*, %): 553 (M^+, 2); 405 (5); 262 (100); 183 (30); 107 (75); 43 (55). Anal. Calcd for $C_{33}H_{32}O_5$ (553.6): C, 71.59; H, 5.83; N, 2.53. Found: C, 71.2; H, 5.7; N, 2.5%.

Major isomer (70%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.05 (3H, s, $COCH_3$); 2.40 (3H, s, Ar-CH_3); 3.07 (3H, s, P–C–CO_2Me); 3.85 (3H, s, CH–CO_2*Me*); 5.35 (1H, d, $^3J_{HP}$ 20.2 Hz, CH); 7.40–7.80 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 21.17 (Ar-CH_3); 23.13 (CH_3 amide); 40.98 (d, $^1J_{CP}$ 134.0 Hz, P–C); 49.19 and 51.96 (2 OMe); 58.90 (d, $^2J_{CP}$ 17.5 Hz, P–C–*C*H); 124.44 (CH, C_6H_4N); 127.86 (d, $^1J_{CP}$ 90.5 Hz, C_{ipso}); 128.65 (d, $^3J_{CP}$ 11.9 Hz, C_{meta}); 131.28, (CH, C_6H_4N);

132.10 (d, $^4J_{CP}$ 2.0 Hz, C_{para}), 133.64 (d, $^2J_{CP}$ 9.1 Hz, C_{ortho}); 137.15 (C, C_6H_4N); 137.92 (*C*—Me); 168.3 (d, $^3J_{CP}$ 12.8 Hz, C=O ester); 169.76 (C=O amide); 172.97 (d, $^2J_{CP}$ 13.7 Hz, P—C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 26.24 (Ph_3P^+—C).

Minor isomer (30%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.75 (3H, s, $COCH_3$); 2.45 (3H, s, Ar-CH_3); 2.85 (3H, s, P—C—CO_2Me); 3.75 (3H, s, CH—CO_2*Me*); 5.28 (1H, d, $^3J_{HP}$ 17.7 Hz, CH); 7.40–7.80 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 20.76 (Ar-CH_3); 23.94 (CH_3 amide); 38.66 (d, $^1J_{CP}$ 126.8 Hz, P—C); 48.54 and 51.95 (2 OMe); 58.20 (d, $^2J_{CP}$ 17.8 Hz, P—C—*C*H); 124.93 (CH, C_6H_4N); 127.72 (d, $^1J_{CP}$ 90.8 Hz, C_{ipso}); 128.35 (d, $^3J_{CP}$ 10.2 Hz, C_{meta}); 130.51, (CH, C_6H_4N); 132.10 (d, $^4J_{CP}$ 2.0 Hz, C_{para}), 132.54 (d, $^2J_{CP}$ 9.1 Hz, C_{ortho}); 136.70 (C, C_6H_4N); 138.25 (*C*—Me); 169.2 (d, $^3J_{CP}$ 12.8 Hz, C=O ester); 170.6 (C=O amide); 172.97 (d, $^2J_{CP}$ 12.8 Hz, P—C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 25.65 (Ph_3P^+—C).

*Selected Data for Di-*tert*-butyl 2-(p-Methylacetanilide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3d)*

White solide, m.p. 209–211°C, yield 1.20 g, 95%. IR (KBr) (ν_{max}, cm^{-1}): 1729 and 1630 (C=O); 1605 (C=C). MS (*m/z*, %): 638 (M^+, 0.005); 262 (100); 183 (30); 149 (38); 107 (38); 57 (42). Anal. Calcd for $C_{39}H_{44}O_5NP$ (637.7): C, 73.45; H, 6.95; N, 2.19. Found: C, 73.2; H, 6.9; N, 2.2%.

Major isomer (70%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.78 and 1.60 (18H, 2 s, 2 CMe_3); 2.40 (3H, s, Ar-CH_3); 1.60 (3H, s, $COCH_3$); 5.16 (1H, d, $^3J_{HP}$ 19.8 Hz, CH); 7.30–7.80 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 20.80 (CH_3 amide); 23.04 (Ar-CH_3); 27.65 and 28.09 (6 C, 2 C*Me*$_3$), 38.18 (d, $^1J_{CP}$ 126.0 Hz, P—C); 60.10 (d, $^2J_{CP}$ 16.3 Hz, P—C—*C*H); 76.14 and 79.48 (2 *C*Me$_3$); 125.33 (CH, C_6H_4N); 127.36 (d, $^1J_{CP}$ 90.6 Hz, C_{ipso}); 127.80 (d, $^3J_{CP}$ 11.8 Hz, C_{meta}); 131.37 (CH, C_6H_4N); 131.58 (d, $^4J_{CP}$ 2.0 Hz, C_{para}); 133.64 (d, $^2J_{CP}$ 10.8 Hz, C_{ortho}); 136.09 (C, C_6H_4N); 138.24 (*C*-Me); 166.80 (d, $^3J_{CP}$ 12.7 Hz, C=O ester); 169.68 (C=O amide); 170.85 (d, $^2J_{CP}$ 13.6 Hz, P—C=*C*).

Minor isomer (30%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.18 and 1.78 (18H, 2 s, 2 CMe_3); 2.40 (3H, s, Ar-CH_3); 1.60 (3H, s, $COCH_3$); 5.10 (1H, d, $^3J_{HP}$ 22.0 Hz, CH); 7.30–7.80 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 20.80 (CH_3 amide); 22.71 (Ar-CH_3); 27.65 and 28.09 (6 C, 2 C*Me*$_3$), 42.02 (d, $^1J_{CP}$ 134.0 Hz, P—C); 59.97 (d, $^2J_{CP}$ 14.0 Hz, P—C—*C*H); 76.20 and 79.60 (2 *C*Me$_3$); 125.05 (CH, C_6H_4N); 127.36 (d, $^1J_{CP}$ 91.0 Hz, C_{ipso}); 127.70 (d, $^3J_{CP}$ 12.0 Hz, C_{meta}); 130.71 (CH, C_6H_4N); 130.72 (d, $^4J_{CP}$ 2.0 Hz, C_{para}); 133.19 (d, $^2J_{CP}$ 10.8 Hz,

C_{ortho}); 136.70 (C, C_6H_4N); 137.96 (*C*–Me); 169.85 (C=O amide); 170.21 (d, $^3J_{CP}$ 16.0 Hz, C=O ester); 170.55 (d, $^2J_{CP}$ 15.7 Hz, P–C=*C*).

*Selected Data for Di-*tert*-butyl 2-(p-Methoxyacetanilide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3e)*

White solide, m.p. 154–156°C, yield 1.20 g, 95%. IR (KBr) (ν_{max}, cm^{-1}): 1735 and 1642 (C=O); 1506 (C=C). MS (*m/z*, %): 653 (M^+, 2); 262 (100); 183 (70); 108 (80). Anal. Calcd for $C_{39}H_{44}O_6NP$ (653.7): C, 71.65; H, 6.78; N, 2.14. Found: C 71.6; H, 6.8; N, 2.1%.

Major isomer (77%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.76 and 1.60 (18H, 2 s, 2 CMe_3); 1.73 (3H, s, $COCH_3$); 3.87 (3H, s, Ar-OCH_3); 5.09 (1H, d, $^3J_{HP}$ 19.4 Hz, CH); 7.30–7.80 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.80 (CH_3 amide); 28.71 and 28.79 (6 C, 2 C*Me*$_3$); 39.06 (d, $^1J_{CP}$ 127.3 Hz, P–C); 60.76 (d, $^2J_{CP}$ 17.2 Hz, P–C–*C*H); 77.05 and 80.40 (2 *C*Me_3); 113.54, 121.87 (2 CH, C_6H_4N); 128.17 (d, $^1J_{CP}$ 91.2 Hz, C_{ipso}); 128.70 (d, $^3J_{CP}$ 11.0 Hz, C_{meta}); 132.31 (d, $^4J_{CP}$ 2.0 Hz, C_{para}); 133.15 (C, C_6H_4N); 134.20 (d, $^2J_{CP}$ 10.0 Hz, C_{ortho}); 158.99 (*C*–OMe); 167.66 (d, $^3J_{CP}$ 12.8 Hz, C=O ester); 171.12 (C=O amide); 171.55 (d, $^2J_{CP}$ 13.6 Hz, P–C=*C*).

Minor isomer (23%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.13 and 1.73 (18H, 2 s, 2 CMe_3); 1.64 (3H, s, $COCH_3$); 3.89 (3H, s, Ar-OCH_3); 5.10 (1H, d, $^3J_{HP}$ 22.2 Hz, CH); 7.30–7.80 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.53 (CH_3 amide); 28.57 and 29.01 (6 C, 2 C*Me*$_3$); 41.86 (d, $^1J_{CP}$ 134.5 Hz, P–C); 59.70 (d, $^2J_{CP}$ 20.8 Hz, P–C–*C*H); 80.53 and 82.03 (2 *C*Me_3); 114.77, 121.67 (2 CH, C_6H_4N); 127.83 (d, $^1J_{CP}$ 91.2 Hz, C_{ipso}); 128.91 (d, $^3J_{CP}$ 12.2 Hz, C_{meta}); 132.30 (d, $^4J_{CP}$ 2.0 Hz, C_{para}); 132.92 (C, C_6H_4N); 134.41 (d, $^2J_{CP}$ 10.8 Hz, C_{ortho}); 159.53 (*C*–OMe); 170.88 (d, $^3J_{CP}$ 18.2 Hz, C=O ester); 169.34 (C=O amide); 171.46 (d, $^2J_{CP}$ 14.0 Hz, P–C=*C*).

*Selected Data for Di-*tert*-butyl 2-(p-Bromoacetanilide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3f)*

White solide, m.p. 148–150°C, yield 1.31 g, 94%. IR (KBr) (ν_{max}, cm^{-1}): 1730 and 1638 (C=O). MS (*m/z*, %): 704 (M^+ 2, 2); 702 (M^+, 2); 387 (20); 377 (20); 262 (80); 57 (100). Anal. Calcd for $C_{38}H_{41}O_5BrNP$ (702.6): C, 64.95; H, 5.88; N, 1.99. Found: C 64.1; H, 6.1; N, 1.8%.

Major isomer (82%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.76 and 1.61 (18H, 2 s, 2 CMe_3); 1.75 (3H, s, $COCH_3$); 5.87 (1H, d, $^3J_{HP}$ 19.2 Hz, CH); 7.20–7.80 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.78 (CH_3 amide); 28.75 and 28.84 (6 C, 2 C*Me*$_3$); 39.50 (d, $^1J_{CP}$ 127.9 Hz, P–C); 60.81 (d, $^2J_{CP}$ 19.0 Hz, P–C–*C*H); 77.31 and 80.68

(2 *C*Me$_3$); 121.24 (CH, C$_6$H$_4$N); 127.85 (d, $^1J_{CP}$ 90.6 Hz, C$_{ipso}$); 128.80 (d, $^3J_{CP}$ 11.0 Hz, C$_{meta}$); 129.02 (CH, C$_6$H$_4$N); 132.40 (C$_{para}$); 133.34 (C, C$_6$H$_4$N); 134.11 (C$_{ortho}$); 140.81 (C—Br); 167.75 (d, $^3J_{CP}$ 18.0 Hz, C=O ester); 169.42 (C=O amide); 171.55 (d, $^2J_{CP}$ 13.6 Hz, P—C=*C*). ^{31}P NMR (202.4 MHz, CDCl$_3$): δ 25.97 (Ph$_3$P$^+$—C).

Minor isomer (18%): ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 1.13 and 1.60 (18H, 2 s, 2 CMe$_3$); 1.66 (3H, s, COCH$_3$); 5.02 (1H, d, $^3J_{HP}$ 22.1 Hz, CH); 7.20–7.80 (19H, m, 3 C$_6$H$_5$ and C$_6$H$_4$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 23.50 (CH$_3$ amide); 28.57 and 29.01 (6 C, 2 C*Me*$_3$); 40.80 (d, $^1J_{CP}$ 134.0 Hz, P—C); 59.95 (d, $^2J_{CP}$ 18.0 Hz, P—C—CH); 80.82 and 82.15 (2 *C*Me$_3$); 121.75 (CH, C$_6$H$_4$N); 127.65 (d, $^1J_{CP}$ 91.9 Hz, C$_{ipso}$); 128.60 (d, $^3J_{CP}$ 10.0 Hz, C$_{meta}$); 130.34 (CH, C$_6$H$_4$N); 132.20 (C$_{para}$); 133.12 (C, C$_6$H$_4$N); 134.11 (C$_{ortho}$); 140.41 (C—Br); 140.81 (C—Br); 169.3 (C=O amide); 170.75 (d, $^3J_{CP}$ 18.0 Hz, C=O ester); 171.10 (d. $^2J_{CP}$ 14.0 Hz, P—C=*C*). ^{31}P NMR (202.4 MHz, CDCl$_3$): δ 25.36 (Ph$_3$P$^+$—C).

Selected Data for Dimethyl 2-(o-Cyanoacetanilide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3g)

Colorless crystals, m.p. 190–192°C, yield 1.06 g, 95% IR (KBr) (ν_{max}, cm^{-1}): 1740 and 1663 (C=O); 1642 (C=C); 2270 (CN). Anal. Calcd for C$_{33}$H$_{29}$O$_5$N$_2$P (564.5): C, 70.21; H, 5.18; N, 4.96. Found: C, 70.4; H, 5.1; N, 5.0%.

Major isomer (55%): ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 1.76 (3H, s, COCH$_3$); 2.68 (3H, s, P—C—CO$_2$Me); 3.80 (3H, s, CO$_2$Me); 5.18 (1H, d, $^3J_{HP}$ 19.2 Hz, CH); 7.40–8.40 (19H, m, 3 C$_6$H$_5$ and C$_6$H$_4$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 23.31 (CH$_3$ amide); 40.28 (d, $^1J_{CP}$ 124.8 Hz, P—C); 48.97 and 52.84 (6 C, 2 s, 2 OMe); 61.42 (d, $^2J_{CP}$ 17.4 Hz, P—C—*C*H); 115.72 (CN); 118.13 (*C*—CN); 126.52 (d, $^1J_{CP}$ 90.6 Hz, C$_{ipso}$); 128.88 (CH, C$_6$H$_4$N); 129.18 (d, $^3J_{CP}$ 12.4 Hz, C$_{meta}$); 132.13 (d, $^4J_{CP}$ 2.0 Hz, C$_{para}$); 132.56 (d, $^2J_{CP}$ 11.9 Hz, C$_{ortho}$); 132.60, 133.80, 133.94 (3 CH, C$_6$H$_4$N); 144.32 (C, C$_6$H$_4$N); 169.18 (d, $^3J_{CP}$ 12.4 Hz, C=O ester); 170.01 (C=O amide); 173.70 (d, $^2J_{CP}$ 12.44 Hz, P—C=*C*).

Minor isomer (45%): ^{1}H NMR (500.1 MHz, CDCl$_3$): δ 1.74 (3H, s, COCH$_3$); 3.04 (3H, s, P—C—CO$_2$Me); 3.74 (3H, s, CO$_2$Me); 5.34 (1H, d, $^3J_{HP}$ 20.8 Hz, CH); 7.40–7.80 (19H, m, 3 C$_6$H$_5$ and C$_6$H$_4$). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 23.36 (CH$_3$ amide); 42.01 (d, $^1J_{CP}$ 131.9 Hz, P—C); 48.96 and 52.84 (6 C, 2 s, 2 OMe); 60.28 (d, $^2J_{CP}$ 17.4 Hz, P—C—*C*H); 116.35 (CN); 117.91 (*C*—CN); 126.25 (d, $^1J_{CP}$ 91.5 Hz, C$_{ipso}$); 128.88 (CH, C$_6$H$_4$N); 129.18 (d, $^3J_{CP}$ 12.4 Hz, C$_{meta}$); 132.13 (d, $^4J_{CP}$ 2.0 Hz, C$_{para}$); 132.54 (d, $^2J_{CP}$ 11.9 Hz, C$_{ortho}$); 132.63, 133.41, 133.80 (3 CH, C$_6$H$_4$N); 143.99 (C, C$_6$H$_4$N); 169.78 (C=O amide); 170.12 (d, $^3J_{CP}$ 18.2 Hz, C=O ester); 173.70 (d, $^2J_{CP}$ 11.2 Hz, P—C=*C*).

Selected Data for Dimethyl 2-(Succinimide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3h)

Orange powder, m.p. 45–47°C, yield 0.95 g, 95%. IR (KBr) (ν_{max}, cm^{-1}): 1705 and 1757 (C=O), 1579 (C=C). Anal. Calcd for $C_{28}H_{26}NO_6P$ (503.5): C, 66.79; H, 5.20; N, 2.78. Found: C, 66.5; H, 5.3; N, 2.7%. MS (*m/z*, %): 503 (M^+, 0.1); 447 (1); 405 (1); 332 (2); 262 (100); 183 (15); 108 (13); 77 (7).

Major isomer (66%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.56 (4H, s, 2 CH_2), 3.09 and 3.69 (6H, 2 s, 2 OCH_3), 4.66 (1H, d, $^3J_{PH}$ 15.8 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 27.97 (2 CH_2), 38.25 (d, $^1J_{PC}$ 138.0 Hz, P–C), 49.10 and 52.70 (2 OCH_3), 55.26 (d, $^2J_{PC}$ 17.0 Hz, P–C–*C*H), 126.95 (d, $^1J_{PC}$ 91.6 Hz, C_{ipso}), 128.51 (d, $^3J_{PC}$ 12.0 Hz, C_{meta}), 132.07 (d, $^4J_{PC}$ 2.0 Hz, C_{para}), 133.67 (d, $^3J_{PC}$ 10.0 Hz, C_{ortho}), 168.75 (d, $^3J_{PC}$ 13.0 Hz, C=O ester), 170.85 (C=O imide), 171.70 (d, $^2J_{PC}$ 14.0 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.68 (Ph_3P^+–C).

Minor isomer (34%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.71 (4H, s, 2 CH_2), 3.58 and 3.81 (6H, 2 s, 2 OCH_3), 4.70 (1H, d, $^3J_{PH}$ 17.2 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 29.60 (2 CH_2), 36.51 (d, $^1J_{PC}$ 131.0 Hz, P–C), 52.80 and 53.10 (2 OCH_3), 55.05 (d, $^2J_{PC}$ 16.0 Hz, P–C–*C*H), 126.30 (d, $^1J_{PC}$ 91.4 Hz, C_{ipso}), 128.77 (d, $^3J_{PC}$ 12.1 Hz, C_{meta}), 132.15 (d, $^4J_{PC}$ 2.0 Hz, C_{para}), 133.67 (d, $^3J_{PC}$ 10.0 Hz, C_{ortho}), 170.94 (C=O imide), 171.67 (d, $^3J_{PC}$ 13.0 Hz, C=O ester), 171.86 (d, $^2J_{PC}$ 14.0 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 22.50 (Ph_3P^+–C).

Selected Data for Dimethyl 2-(Maleimide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3i)

Orange powder, m.p. 125–127°C, yield 0.46 g (92%). IR (KBr) (ν_{max}, cm^{-1}): 1710 (C=O), 1611 (C=C). Anal. Calcd for $C_{28}H_{24}NO_6P$ (501.4): C, 67.07; H, 4.82; N, 2.79. Found: C, 67.1; H, 4.8; N, 2.8%. MS (*m/z*, %): 501 (M^+, 0.01); 456 (0.2); 345 (0.5); 272 (100); 262 (16); 183 (19); 78 (16); 44 (28).

Major isomer (52%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.14 and 3.73 (6H, 2 s, 2 OCH_3), 4.60 (1H, d, $^3J_{PH}$ 15.7 Hz, CH), 6.54 (2H, s, HC=CH), 7.31–7.51 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 38.85 (d, $^1J_{PC}$ 138.9 Hz, P–C), 49.07 and 52.71 (2 OCH_3), 54.75 (d, $^2J_{PC}$ 16.9 Hz, P–C–*C*H), 126.86 (d, $^1J_{PC}$ 92.0 Hz, C_{ipso}), 128.80 (d, $^3J_{PC}$ 12.2 Hz, C_{meta}), 132.01 (C_{para}), 133.55 (d, $^3J_{PC}$ 9.6 Hz, C_{ortho}), 133.94 (HC=CH), 169.19 (d, $^3J_{PC}$ 13.2 Hz, C=O), 170.17 (C=O imide), 171.31 (d, $^2J_{PC}$ 12.5 Hz, P–C=C). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.56 (Ph_3P^+–C).

Minor isomer (48%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.60 and 3.70 (6H, 2 s, 2 OCH_3), 4.61 (1H, d, $^3J_{PH}$ 17.6 Hz, CH), 6.62 (2H, s, HC=CH),

7.35–7.75 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 37.21 (d, $^1J_{PC}$ 130.0 Hz, P–C), 50.35 and 52.48 (2 OCH_3), 54.16 (d, $^2J_{PC}$ 16.7 Hz, P–C–*C*H), 126.16 (d, $^1J_{PC}$ 92.1 Hz, C_{ipso}), 128.83 (d, $^3J_{PC}$ 12.3 Hz, C_{meta}), 132.09 (C_{para}), 133.60 (d, $^2J_{PC}$ 10.0 Hz, C_{ortho}), 134.86 (HC=CH), 170.21 (C=O imide), 171.08 (d, $^2J_{PC}$ 17.4 Hz, C=O ester), 171.41 (d, $^2J_{PC}$ 13.0 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.43 (Ph_3P^+–C).

Selected Data for Dimethyl 2-(Phtaleimide-N-yl)-3-(triphenylphosphanylidene)-butanedioate (3j)

Orange-red solid, m.p. 125–127°C, yield 1.10 g, 96%. IR (KBr) (ν_{mix}, cm^{-1}): 1734 and 1702 (C=O), 1635 (C=C). Anal. Calcd for $C_{32}H_{26}NO_6P$ (551.5): C, 69.68; H, 4.75; N, 2.54. Found: C, 69.8; H, 4.8; N, 2.5%. MS (*m/z*, %): 551 (M^+, 3); 492 (23); 262 (100); 230 (13); 183 (11); 76 (8).

Major isomer (56%): ^1H NMR (500.1 MHz, $CDCl_3$): δ 3.16 and 3.74 (6H, 2 s, 2 OCH_3), 4.79 (1H, d, $^3J_{PH}$ 13.5 Hz, CH), 7.41–7.61 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 38.98 (d, $^1J_{PC}$ 139.0 Hz, P–C), 49.04 and 52.76 (2 OCH_3), 54.97 (d, $^2J_{PC}$ 17.2 Hz, P–C–*C*H), 123.22 (2 CH, C_6H_4), 127.01 (d, $^1J_{PC}$ 92.0 Hz, C_{ipso}), 128.78 (C_{meta}), 132.04 (C_{para}), 132.89 (2 C, C_6H_4), 133.59 (d, $^2J_{PC}$ 10.8 Hz, C_{ortho}), 133.96 (2 CH, C_6H_4), 165.38 (d, $^3J_{PC}$ 24.0 Hz, C=O ester), 167.53 (C=O imide), 171.39 (d, $^2J_{PC}$ 12.0 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.03 (Ph_3P^+–C).

Minor isomer (44%): ^1H NMR (500.1 MHz, $CDCl_3$): δ 3.63 and 3.71 (6H, 2 s, 2 OCH_3), 4.83 (1H, d, $^3J_{PH}$ 14.8 Hz, CH), 7.60–7.80 (19H, m, 3 C_6H_5 and C_6H_4). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 37.27 (d, $^1J_{PC}$ 130.0 Hz, P–C), 50.40 and 52.51 (2 OCH_3), 54.34 (d, $^2J_{PC}$ 16.5 Hz, P–C–*C*H), 124.07 (2 CH, C_6H_4), 126.28 (d, $^1J_{PC}$ 92.0 Hz, C_{ipso}), 128.31 (C_{meta}), 132.21 (C_{para}), 133.37 (2 C, C_6H_4), 133.54 (C_{ortho}), 134.62 (2 CH, C_6H_4), 168.37 (C=O imide), 169.18 (d, $^3J_{PC}$ 12.7 Hz, C=O ester), 171.12 (d, $^2J_{PC}$ 17.1 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.86 (Ph_3P^+–C).

REFERENCES

[1] P. Laszlo, *Organic Reactions: Simplicity and Logic* (Wiley, New York, 1995).
[2] J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis* (Academic Press, New York, 1979).
[3] R. Engel, *Synthesis of Carbon-Phosphorus Bonds* (CRC Press, Boca Raton, FL, 1988).
[4] L. D. Quin, *A Guide to Organophosphorus Chemistry* (Wiley-Interscience, New York, 2000).

[5] H. R. Hudson, *In The Chemistry of Organophosphorus Compounds, Vol. 1. Primery, Secondary and Tertiary Phosphines and Heterocyclic Organophosphorus (III) Compounds*, edited by F. R. Hartley (Wiley, New York, 1990), pp. 382–472.
[6] D. E. C. Corbridge, *Phosphorus. An Outline of Chemistry, Biochemistry and Technology* (Elsevier, Amsterdam, 1995), 5th ed.
[7] A. W. Johnson, *Ylid Chemistry* (Academic Press, New York, 1966).
[8] Y. Shen, *Acc. Chem. Res.*, **31,** 384 (1998).
[9] O. I. Kolodiazhnyi, *Russ. Chem. Rev.*, **66,** 225 (1997).
[10] R. A. Cherkasov and M. A. Pudovik, *Russ. Chem. Rev.*, **63,** 1019 (1994).