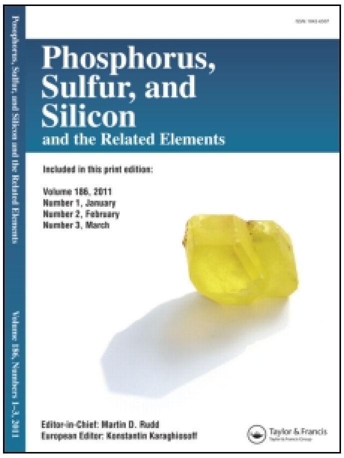

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

An Efficient Synthesis of Stable Phosphorus Ylides Derived from Triphenylphosphine, Dialkyl Acetylenedicarboxylates, and an NH-Acid

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To cite this Article Maghsoodlou, Malek Taher , Hazeri, Norollah , Khorassani, Sayyed Mostafa Habibi , Heydari, Reza , Nassiri, Mahmoud , Marandi, Ghasem , Moeeni, Zohreh , Niromand, Uranous and Torbaghan, Zahra Eskandari(2006) 'An Efficient Synthesis of Stable Phosphorus Ylides Derived from Triphenylphosphine, Dialkyl Acetylenedicarboxylates, and an NH-Acid', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 4, 865 — 877

To link to this Article: DOI: 10.1080/10426500500272111

URL: http://dx.doi.org/10.1080/10426500500272111

Phosphorus, Sulfur, and Silicon, 181:865–877, 2006
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500272111

An Efficient Synthesis of Stable Phosphorus Ylides Derived from Triphenylphosphine, Dialkyl Acetylenedicarboxylates, and an NH-Acid

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Zahedan, Iran

Stable crystalline phosphorus ylides were 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 benzotriazole, 5-methylbenzotriazole, 5-chlorobenzotriazole, pyrrole, 2-acetylpyrrole, pyrrole-2-carboxaldehyde, 4-nitroacetanilide, 4-methoxyacetanilide, 4-bromoacetanilide, 4-methylacetanilide, 2-methylacetanilide, and 2,6-dimethylacetanilide. These stable ylides exist in a solution as a mixture of two geometrical isomers as a result of the restricted rotation around the carbon–carbon partial double bond resulting from the conjugation of the ylide moiety with the adjacent carbonyl group.

Keywords Acetylenic ester; geometrical isomers; NH-acids; stable phosphorus ylides; triphenylphosphine

INTRODUCTION

Phosphorus ylides are reactive systems, which take part in many valuable reactions of organic synthesis.[1–11] These are most often

Received May 10, 2005; accepted June 9, 2005.

We gratefully acknowledge financial support from the Research Council of University of Sistan and Baluchestan.

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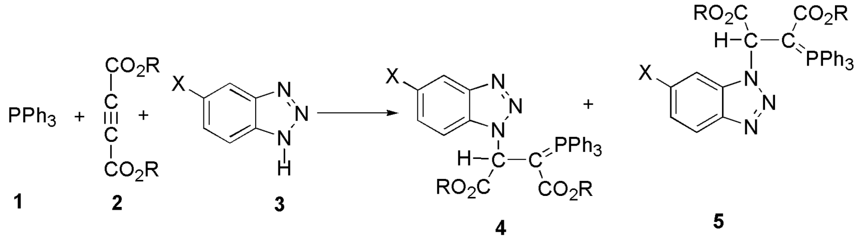
prepared by the treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from phosphine and an alkyl halide,[1–5] and they are also obtained by a Michael addition of phosphorus nucleophiles to activated olefins.[1,2] Here we whish to describe an efficient synthetic route of stable phosphorus ylides **4**, **5**, **7**, and **8** using triphenylphosphine **1**, dialkyl acetylenedicarboxylates **2**, and strong NH-acids **3**, **6** (see Schemes 1, 2, and 3). Benzotriazole is a very useful synthetic auxiliary.[12] The benzotriazole, pyrrole, and acetanilide derivatives are widely used in making medicines, and they also have biological activity.[11,13,14]



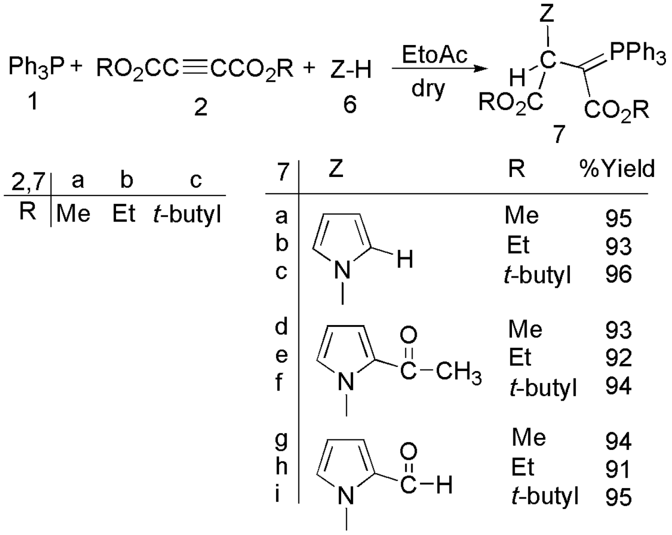
2	R
a	Me
b	Et
c	*t*-butyl

4,5	X	R	%Yield
4a	H	Me	94
4b	H	Et	92
4c	H	*t*-butyl	95
4d	Me	Me	60
5e	Me	Me	40
4f	Me	Et	55
5g	Me	Et	45
4h	Me	*t*-butyl	57
5i	Me	*t*-butyl	41
4j	Cl	Et	46
5k	Cl	Et	54
4l	Cl	*t*-butyl	42
5m	Cl	*t*-butyl	58

SCHEME 1

RESULTS AND DISCUSSION

The reaction of benzotriazole, 5-methylbenzotriazole, 5-chlorobenzotriazole, pyrrole, 2-acetylpyrrole, pyrrole-2-carboxaldehyde, 4-nitroacetanilide, 4-methoxyacetanilide, 4-bromoacetanilide, 4-methylacetanilide, 2-methylacetanilide, and 2,6-dimethylacetanilide with dialkyl acetylenedicarboxylates **2** in the presence of triphenylphosphine **1** proceeded at r.t. in ethyl acetate as a solvent, and it was finished within a

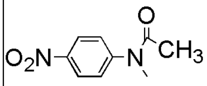
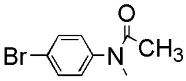
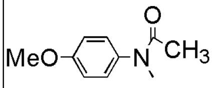
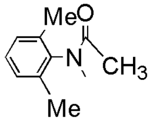
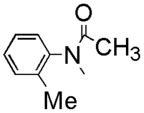
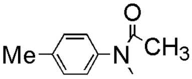


SCHEME 2

few hours. The ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of stable phosphorus ylides **4**, **5**, **7**, and **8**. Any products other than **4**, **5**, **7**, and **8** could not be detected by NMR spectroscopy. The structures of compounds **4a–5m**, **7a–i**, and **8a–l** were deduced from their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of them displayed molecular ion peaks at appropriate *m/z* values. Any initial fragmentations involve the missing parts or complete loss of the side chains and the scission of the aromatic ring system. The ^{1}H, ^{13}C, and ^{31}P NMR spectrum of ylides **4a**, **4b**, **4d**, **5e**, **4f**, **5g**, **4j**, **5k**, **7a**, **7b**, **7d**, **7e**, **7g**, **7h**, **8a**, **8b**, **8d**, **8e**, **8f**, **8g**, **8h**, **8j**, and **8l** are consistent with the presence of two isomers. The ylides moiety of these compounds are strongly conjugated with the adjacent carbonyl group, and the rotation about the partial double bond is slow in (***E***)-***4***, (***Z***)-***4***, (***E***)-***5***, (***Z***)-***5***, (***E***)-***7***, (***Z***)-***7***, (***E***)-***8***, and (***Z***)-***8*** geometrical isomers on the NMR time scale at an ambient temperature (see Schemes 4, 5, and 6). 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 **4a**, **4b**, **4d**, **5e**, **4f**, **5g**, **4j**, **5k**, **7a**, **7b**, **7d**, **7e**, **7g**, **7h**, **8a**, **8b**, **8d**, **8e**, **8f**, **8g**, **8h**, **8j**, and **8l** are shown in Tables I, II, and III. As can be seen, only one geometrical isomer was observed for the di-*tert*-butyl derivative of **4**, **5**, **7**, and **8** presumably, because of the bulky *tert*-butyl groups.

As it has been noted earlier, the phosphorus ylide enables to carry out an intramolecular Wittig reaction.[15,16] In the current work, the

2	R
a	Me
b	Et
c	*t*-butyl

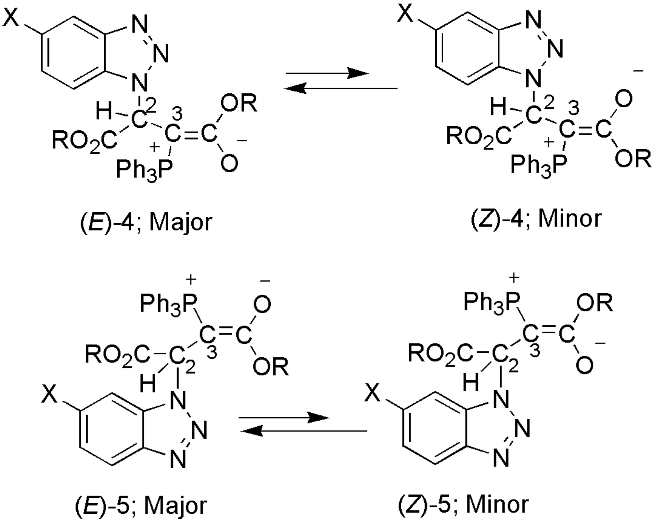
8	Z	R	%Yield
a		Me	91
b		Et	91
c		*t*-butyl	94
d		Me	95
e		Et	98
f		Me	95
g		Et	91
h		Et	91
i		*t*-butyl	91
j		Et	95
k		*t*-butyl	94
l		Et	96

SCHEME 3

stable phosphorus ylide **7a–c** successfully undergo an intramolecular Wittig reaction to generate compound **9** (see Scheme 7) after refluxing in toluene solvent for 12 h. In contrast to that, the phosphoranes **7d–f** do not undergo the intramolecular Wittig reaction (compound **10** was not observed).

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[1–5] it is reasonable to assume that phosphorus ylides **4**, **5**, **7**, and **8** result from the initial addition of triphenylphosphine to the acetylenic ester and subsequent of the 1:1 adduct by the NH-acid to form phosphoranes **4**, **5**, **7**, and **8** (see Scheme 8).

Briefly, we have prepared novel stable phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong NH-acids such as benzotriazole,



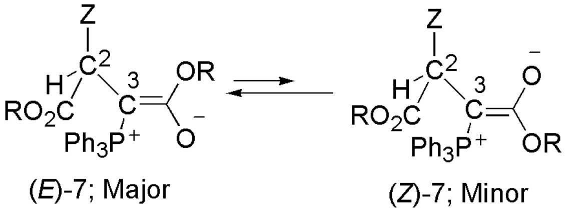
(*E*)-4; Major

(*Z*)-4; Minor

(*E*)-5; Major

(*Z*)-5; Minor

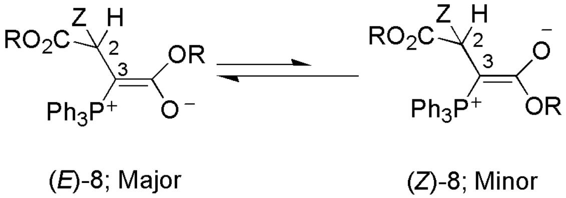
SCHEME 4



(*E*)-7; Major

(*Z*)-7; Minor

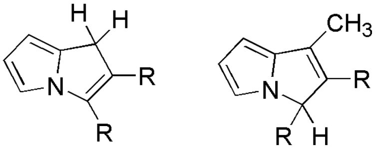
SCHEME 5



(*E*)-8; Major

(*Z*)-8; Minor

SCHEME 6



9

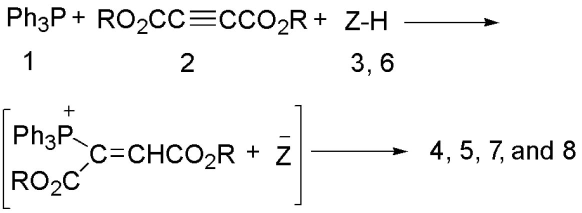
10

SCHEME 7

TABLE I Selected ^1H, ^{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) Diasteroisomers of Compounds 4a–5m

		^1H NMR spectroscopy			^{13}C NMR data		
Compound	Isomer (%)	H-2($^3J_{PH}$)	OR	CO_2R	C-2($^2J_{PC}$)	C-3($^1J_{PC}$)	^{31}PNMR
4a	M (52)	5.86 (16.1)	3.18	3.71	64.03 (16.0)	42.26 (126.9)	24.07
4a	m (48)	5.77 (17.9)	3.69	3.72	63.28 (15.8)	42.44 (137.5)	24.26
4b	M (64)	5.86 (16.5)	4.19	4.27	64.15 (16.2)	42.08 (126.6)	24.05
4b	m (36)	5.72 (17.9)	3.75	3.86	63.37 (17.9)	42.16 (136.6)	24.60
4c	M	5.70 (17.9)	1.00	1.53	64.81 (16.5)	41.67 (126.6)	23.86
4d	M (68)	5.83 (16.2)	3.20	3.70	63.60 (15.5)	42.24 (133.8)	24.12
4d	m (32)	5.76 (bro)	3.69	3.71	62.93 (15.3)	42.37 (133.7)	24.18
5e	M (65)	5.82 (16.2)	3.18	3.79	63.87 (16.1)	42.92 (128.2)	23.77
5e	m (35)	5.76 (bro)	3.22	3.81	63.23 (16.0)	42.13 (128.3)	24.37
4f	M (73)	5.83 (16.5)	4.18	4.22	63.98 (15.8)	42.02 (126.5)	24.05
4f	m (27)	5.68 (17.0)	3.70	3.83	63.22 (16.2)	42.09 (133.8)	24.61
5g	M (75)	5.81 (17.0)	4.19	4.25	63.75 (15.9)	41.73 (126.9)	23.77
5g	m (25)	5.66 (17.0)	3.81	3.94	62.95 (17.9)	42.06 (128.9)	24.45
4h	M	5.59 (17.4)	1.00	1.51	64.61 (15.9)	41.16 (126.5)	23.89
5i	M	5.62 (19.6)	0.97	1.48	64.59 (15.9)	41.63 (126.8)	23.72
4j	M (59)	5.79 (19.4)	4.18	4.24	64.32 (17.6)	42.06 (127.4)	24.13
4j	m (41)	5.70 (17.1)	3.72	3.88	63.24 (16.5)	42.05 (127.5)	24.74
5k	M (57)	5.83 (17.3)	4.20	4.25	64.46 (16.7)	42.44 (129.6)	23.89
5k	m (33)	5.71 (17.1)	3.80	3.88	63.58 (16.8)	42.42 (127.9)	22.99
4l	M	5.66 (16.9)	0.99	1.54	65.14 (16.1)	41.44 (126.5)	23.88
5m	M	5.59 (16.8)	1.03	1.49	65.10 (15.9)	41.91 (126.2)	23.70

5-methylbenzotriazole, 5-chlorobenzotriazole, pyrrole, 2-acetylpyrrole, pyrrole-2-carboxaldehyde, 4-nitroacetanilide, 4-methoxyacetanilide, 4-bromoacetanilide, 4-methylacetanilide, 2-methylacetanilide, and 2,6-dimethylacetanilide. The present method carries the advantage that not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modifications. In addition, stable phosphorus ylides **4a–5m**, **7a–i**, and **8a–l** may be considered potentially useful synthetic intermediates. It seems that the



SCHEME 8

TABLE II 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 7a–i

Compound	Isomer (%)	^{1}H NMR spectroscopy H-2($^{3}J_{PH}$)	OR	CO_2R	^{13}C NMR data C-2($^{2}J_{PC}$)	C-3($^{1}J_{PC}$)	^{31}PNMR
7a	M (68)	4.53 (16.0)	3.20	3.78	62.05 (15.6)	44.86 (136.2)	24.31
7a	m (32)	4.60 (17.7)	3.64	3.75	61.40 (15.4)	44.97 (126.2)	25.17
7b	M (71)	4.51 (18.2)	0.52	1.31	61.31 (15.8)	44.09 (127.5)	23.43
7b	m (29)	4.56 (19.8)	1.25	1.38	62.01 (15.1)	44.64 (135.3)	23.87
7c	M	4.36 (19.8)	1.03	1.59	62.49 (16.0)	43.62 (128.3)	23.79
7d	M (65)	5.77 (19.2)	3.58	3.71	60.76 (17.3)	44.55 (135.0)	25.15
7d	m (35)	5.83 (17.8)	3.19	3.72	60.85 (17.7)	43.63 (126.2)	24.40
7e	M (74)	5.65 (18.3)	0.50	1.30	61.14 (13.4)	43.42 (128.6)	24.41
7e	m (26)	5.76 (19.7)	1.15	1.33	62.11 (16.2)	43.92 (134.6)	25.30
7f	M	5.73 (18.6)	0.98	1.53	61.22 (18.2)	43.45 (126.7)	23.83
7g	M (76)	5.75 (17.8)	3.21	3.73	60.42 (16.3)	43.55 (135.4)	24.13
7g	m (24)	5.70 (19.3)	3.60	3.72	60.74 (15.8)	43.24 (127.1)	23.96
7h	M (70)	5.74 (17.8)	0.50	1.24	59.52 (17.1)	43.07 (126.8)	22.67
7h	m (30)	5.68 (19.3)	1.16	1.29	60.06 (16.4)	43.15 (127.4)	22.73
7i	M	5.65 (18.1)	0.99	1.52	61.22 (17.1)	44.45 (126.8)	24.12

procedure described here may be employed as an acceptable method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points and the IR spectrum of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR 460 spectrometer, respectively. Also, the ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained from a Bruker DRX-500 AVANCE instrument with $CDCl_3$ as solvent at 500.1, 125.8, and 202.4 MHz, respectively. In addition, the mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates, triphenylphosphine, and NH-acid compounds were purchased from Fluka (Buchs, Switzerland) and used without further purifications.

Preparation of Dimethyl 2-(Benzotriazole-1-Yl)-3-(Triphenylphosphanylidene)Butanedioate (4a)

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g or 1 mmol) and benzotriazole (0.12 g or 1 mmol) in 10 mL of ethyl acetate, a mixture of dimethyl acetylenedicarboxylates (0.14 g or 1 mmol) in

TABLE III 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$_2$R, C-2, and C-3 in the Major (M) and Minor (m) Diastereoisomers of Compounds 8a–l

		^{1}H NMR spectroscopy			^{13}C NMR data		
Compound	Isomer (%)	H-2($^3J_{PH}$)	OR	CO$_2$R	C-2($^2J_{PC}$)	C-3($^1J_{PC}$)	^{31}PNMR
8a	M (54)	5.29 (19.2)	3.01	3.74	59.34 (15.7)	41.02 (133.6)	24.74
8a	m (46)	5.24 (18.7)	2.82	3.81	60.51 (14.9)	38.91 (125.2)	25.58
8b	M (59)	5.25 (17.8)	3.35	4.22	61.07 (15.6)	40.96 (133.3)	24.63
8b	m (41)	5.19 (16.4)	3.63	4.35	60.48 (15.1)	38.82 (126.3)	25.72
8c	M	5.09 (14.8)	0.68	1.53	61.04 (16.3)	38.71 (124.8)	24.18
8d	M (62)	5.27 (20.1)	3.06	3.74	57.60 (16.1)	40.36 (136.7)	25.32
8d	m (38)	5.20 (18.5)	2.86	3.82	58.75 (17.6)	39.52 (125.2)	24.54
8e	M (55)	5.25 (20.6)	3.33	4.16	57.68 (18.2)	40.92 (133.6)	25.46
8e	m (45)	5.20 (18.9)	3.45	4.25	58.84 (19.1)	38.57 (126.9)	24.45
8f	M (66)	5.23 (20.0)	3.05	3.73	58.83 (17.6)	41.11 (134.7)	25.23
8f	m (34)	5.18 (19.2)	2.82	3.77	59.91 (17.1)	38.81 (126.5)	24.71
8g	M (59)	5.25 (20.6)	3.34	4.18	58.46 (17.7)	41.34 (134.1)	25.31
8g	m (41)	5.19 (19.0)	3.66	4.34	59.77 (17.5)	39.63 (125.4)	24.57
8h	M (53)	5.19 (18.7)	3.17	3.40	57.54 (16.8)	40.91 (132.3)	25.14
8h	m (47)	5.12 (19.3)	2.96	3.78	59.01 (17.4)	39.17 (125.1)	24.38
8i	M	4.62 (20.2)	0.60	1.56	61.20 (19.6)	37.13 (128.4)	25.34
8j	M (68)	5.19 (19.6)	3.23	3.73	57.64 (18.2)	40.62 (133.6)	25.17
8j	m (32)	5.13 (19.8)	3.38	3.54	58.80 (17.6)	39.67 (126.1)	25.43
8k	M	4.95 (20.1)	0.64	1.61	60.54 (18.2)	37.94 (127.1)	24.03
8l	M (69)	5.27 (20.6)	3.25	3.66	58.52 (17.7)	40.79 (134.7)	25.23
8l	m (31)	5.22 (19.0)	3.32	3.43	59.71 (17.0)	38.39 (126.7)	24.40

4 mL of ethyl acetate at −5°C over 10 min was added, dropwise. After approximately 6 h stirring at r.t. the product was filtered and recrystallized from the diethyl ether, and it was obtained as colorless crystals; m.p. 143–145°C, Yield 0.49 g, IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1750, 1748, (C=O), 1646 (N=N). MS (m/z, %): 523 (M$^+$, 7), 464 (14), 405 (31), 262 (79), 183 (78), 108 (24).

Diethyl 2-(Benzotriazole-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (4b)

Colorless crystals; m.p. 147–149°C, IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1747, 1745 (C=O), 1633 (N=N). MS (m/z, %): 478 (2), 433 (1), 262 (96), 183 (76), 108 (19).

Di-tert-buthyl 2-(Benzotriazole-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (4c)

White powder; m.p. 155–157°C, IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1744, 1742 (C=O), 1643 (N=N). MS (*m/z*, *%*): 607 (M$^+$, 2), 506 (18), 489 (12), 262 (85), 183 (47), 108 (12).

Dimethyl 2-(5(6)-methylbenzotriazole-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (4d and 5e)

Colorless crystals; m.p. 163–165°C, IR (KBr) (υ_{max}, cm^{-1}): 1753, 1750, (C=O), 1632 (N=N). MS (m/z, %): 537 (M$^+$, 14), 478 (76), 405 (10), 262 (78), 183 (79), 108 (78).

Diethyl 2-(5(6)-methylenzotriazole-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (4f and 5g)

Colorless crystals; m.p. 147–149°C, IR (KBr) (υ_{max}, cm^{-1}): 1747, 1722 (C=O), 1652 (N=N). MS (m/z, %): 492 (28), 433 (64), 262 (78), 183 (78), 132 (7), 108 (77), 77 (59).

Di-tert-buthyl 2-(5(6)-methylbenzotriazole-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (4h and 5i)

White powder; m.p. 165–167°C, IR (KBr) (υ_{max}, cm^{-1}): 1737, 1735 (C=O), 1636 (N=N). MS (*m/z*, %): 621 (M$^+$, 16); 520 (16); 489 (3), 262 (79), 183 (78), 108 (64), 132 (3), 77 (38).

Diethyl 2-(5(6)-Chlorobenzotriazole-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (4j and 5k)

Colorless crystals; m.p. 118.5–120°C, IR (KBr) (υ_{max}, cm^{-1}): 1722, 1747 (C=O), 1652 (N=N). MS (m/z, %): 585 (M$^+$, 14); 512 (55); 433 (55); 262 (76); 183 (78); 108 (79).

Di-tert-buthyl 2-(5(6)-Chlorobenzotriazole-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (4l and 5m)

White powder; m.p. 170–172°C, IR (KBr) (υ_{max}, cm^{-1}): 1734, 1737 (C=O), 1636 (N=N). MS (*m/z*, %): 641 (M$^+$, 24), 540 (38), 489 (7), 262 (78), 183 (78); 108 (55).

Dimetyl-2-(pyrrole-1-Yl)-3-(triphenylphosphoranilidene) Butanedioate (7a)

Cololess crystals; m.p. 147–149°C, yield 0.45 g, IR (KBr) (ν/cm^{-1}) = 1750 and 1715 (C=O), 1625 (C=C); MS: *m/z* (%) = 471 (M$^+$, 7), 412 (45), 405 (100), 262 (56), 183 (100), 108 (46), 77 (4).

Diethyl-2-(pyrrole-1-Yl)-3-(triphenylphosphoranilidene) Butanedioate (7b)

White solide; m.p. 129–131°C, Yield 0.46 g, IR (KBr) (ν/cm^{-1}): 1756 and 1725 (C=O), 1620 (C=C). MS: *m/z (%)* = 499 (M$^+$, 3), 454 (18), 426 (87), 437 (63), 262 (37), 183 (66) 108 (17).

Di-tert-butyl-2-(pyrrole-1-Yl)-3-(triphenylphosphoranilidene) Butanedioate (7c)

White powder; m.p. 161–163°C, yield 0.53 g, IR (KBr) (ν_{max}/cm^{-1}): 1737 and 1725 (C=O), 1620 (C=C). MS: *m/z (%)* = 555 (M$^+$, 5), 489 (100), 454 (62), 262 (45), 183 (72), 108 (21), 77(19), 66 (49).

Dimetyl-2-(2-acetylpyrrole-1-Yl)-3-(triphenylphosphoranilidene) Butanedioate (7d)

Yellow powder; m.p. 176–178°C, yield 0.47 g, IR (KBr) (ν_{max}/cm^{-1}): 1733 and 1706 (C=O), 1618 (C=C). MS: *m/z (%)* = 513 (M$^+$, 5), 482 (27), 454 (100), 405 (100), 262 (100), 183(55), 108 (75).

Diethyl-2-(2-acetylpyrrole-1-Yl)-3-(triphenylphosphoranilidene) Butanedioate (7e)

White solid; m.p. 163–165°C, yield 0.50 g. IR (KBr) (ν_{max}/cm^{-1}): 1733 and 1706 (C=O), 1625 (C=C).). MS: *m/z (%)* = 541 (M$^+$, 4), 464 (4), 433 (100), 358 (23), 262 (100), 183 (30), 108 (54).

Di-tert-butyl-2-(N-2-acetylpyrrole-1-Yl)-3-(triphenylphosphoranilidene) Butanedioate (7f)

White solid; m.p. 196–198°C, yield 0.56 g, IR (KBr) (ν_{max}/cm^{-1}): 1738 and 1729 (C=O), 1635 (C=C). MS: *m/z (%)* = 597 (M$^+$, 4), 524 (8), 496 (26), 489 (17), 262(100), 183 (16), 108(36).

Dimethyl-2-(pyrrole-2-caboxaldehyde)-3-(triphenylphosphoranilidene) Butanedioate (7g)

Yellow powder; m.p. 178–180°C, yield 0.56 g, IR (KBr) (ν_{max}/cm^{-1}): 1725 and 1638 (C=O), 1635 (C=C). MS: *m/z (%)* = 499 (M$^+$, 5), 468 (7), 440 (37), 393 (76), 262 (100), 183 (19), 108 (34), 77 (54).

Diethyl-2-(pyrrole-2-caboxaldehyde)-3-(triphenylphosphoranilidene) Butanedioate (7h)

Yellow powder; m.p. 154–156°C, yield 0.48 g, IR (KBr) ($\nu_{\max}$/cm^{-1}): 1720 and 1642 (C=O), 1630 (C=C). MS: *m/z (%)* = 527 (M^{+}, 5), 454 (28), 433 (32), 262 (100), 183 (30), 108 (42), 94 (54).

Di-tert-butyl-2-(pyrrole-2-caboxaldehyde)-3-(triphenylphosphoranilidene) Butanedioate (7i)

White solid; m.p. 191–193°C, yield 0.55 g, IR (KBr) ($\nu_{\max}$/cm^{-1}): 1720 and 1654 (C=O), 1640 (C=C). MS: *m/z (%)* = 583 (M^{+}, 6), 489 (18), 482 (43), 262 (100), 183 (56), 108 (85).

Dimethyl 2-(4-nitroacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8a)

Pale white crystals; m.p. 195–197°C, yield 0.53 g, IR (KBr)($\upsilon_{\max}$, cm^{-1}): 1756, 1640, (C=O). MS: *m/z (%)* = 584 (M^{+}, 1), 262 (80), 108 (60), 43 (100).

Diethyl 2-(4-Nitroacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8b)

Pale white crystals; m.p. 174–176°C, yield 0.58 g, IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1747, 1636, (C=O). MS: *m/z (%)* = 612 (M^{+}, 1), 433 (11), 262 (80), 183 (57), 108 (41), 43 (100).

Di-tert-butyl-2-(4-nitroacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8c)

Pale white crystals; m.p. 172–175°C, yield 0.63 g, IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1747, 1636, (C=O). MS: *m/z (%)* = 489 (18), 262 (20), 183 (15), 108 (54), 77(41), 43 (90).

Dimethyl 2-(4-Bromoacetanilide-N-1-Yl)-3-(Triphenylphosphanylidene) Butanedioate (8d)

White crystals; m.p. 190–193°C, yield 0.60 g, IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1735, 1628, (C=O). MS (m/z, %): 617 (M^{+}, 1), 558 (98), 405 (3), 262 (30), 155 (3), 108 (100), 43 (90).

Diethyl 2-(4-Bromoacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8e)

White crystals; m.p. 137–139°C, yield 0.61 g, IR (KBr) (υ_{max}, cm^{-1}): 1745, 1636, (C=O). MS: *m/z* (%) = 645 (M^+, 2), 262 (50), 183 (48), 108 (57), 73 (32).

Dimethyl 2-(4-Methoxyacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8f)

White crystals; m.p. 200–203°C, yield 0.54 g, IR (KBr) (υ_{max}, cm^{-1}): 1747, 1640, (C=O). MS: *m/z* (%) = 569 (M^+, 3), 405 (100), 262 (95), 183 (48), 108 (56).

Diethyl 2-(4-Methoxyacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8g)

Pale white crystals; m.p. 149–152°C, yield 0.54 g, IR (KBr) (υ_{max}, cm^{-1}): 1747, 1636, (C=O). MS: *m/z* (%) = 597 (M^+, 1), 433 (M-C_9H_{10} NO_2, 87), 262 (PPh_3, 20), 183 (PPh2, 48), 108 (PPh, 23).

Diethyl 2-(2,6-Dimethylacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) butanedioate (8h)

White crystals; m.p. 134–136°C, yield 0.54 g, IR (KBr) (υ_{max}, cm^{-1}): 1739, 1622, (C=O). MS: *m/z* (%) = 595 (M^+, 1), 522 (28), 262 (30), 183 (76), 43 (90).

Di-tert-butyl-2-(2,6-dimethylacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8i)

White crystals; m.p. 160–162°C, yield 0.59 g, IR (KBr) (υ_{max}, cm^{-1}): 1731, 1627, (C=O). MS: *m/z* (%) = 651 (M^+, 1), 389 (5), 262 (95), 183 (100), 108 (45), 101 (18).

Diethyl 2-(2-Methylacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8j)

White crystals; m.p. 151–154°C, yield 0.55 g, IR (KBr) (υ_{max}, cm^{-1}): 1745, 1638, (C=O). MS: *m/z* (%) = 581 (M^+, 1), 508 (20), 262 (95), 183 (100), 73 (34), 43 (5).

Di-tert-butyl-2-(2-methylacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8k)

White crystals; m.p. 155–157°C, yield 0.60 g, 94%. IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1747, 1636, (C=O). MS: *m/z* (%) = 149 (5), 91 (5), 77 (100), 43 (40).

Diethyl 2-(4-Methylacetanilide-N-1-Yl)-3-(triphenylphosphanylidene) Butanedioate (8l)

White crystals; m.p. 154–156°C, yield 0.56 g, IR (KBr) ($\upsilon_{\max}$, cm^{-1}): 1752, 1640, (C=(O). MS: *m/z* (%) = 581 (M^+, 1), 432 (3), 262 (70), 149 (3).

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