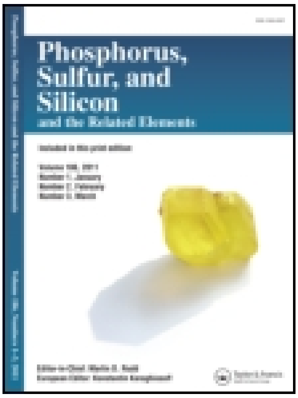

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

A Facile, One-Pot Synthesis of Azoic Compounds and Anthraquinone Derivatives Containing Dialkyl Phosphoryl Moieties in Multicomponent Reactions

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To cite this article: Ghasem Marandi , Malek Taher Maghsoodlou , Reza Heydari , Sayyed Mostafa Habibi-Khorassani , Roya Kabiri , Zahra Gharechahi , Mahbobe Ghahramaninezhad & Belghais Adrom (2010): A Facile, One-Pot Synthesis of Azoic Compounds and Anthraquinone Derivatives Containing Dialkyl Phosphoryl Moieties in Multicomponent Reactions, Phosphorus, Sulfur, and Silicon and the Related Elements, 185:7, 1395-1403

To link to this article: http://dx.doi.org/10.1080/10426500903061517

Phosphorus, Sulfur, and Silicon, 185:1395–1403, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903061517

A FACILE, ONE-POT SYNTHESIS OF AZOIC COMPOUNDS AND ANTHRAQUINONE DERIVATIVES CONTAINING DIALKYL PHOSPHORYL MOIETIES IN MULTICOMPONENT REACTIONS

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Protonation of the reactive 1:1 intermediates produced in the reactions between triphenylphosphine and dialkyl acetylenedicarboxylates by 1-amino-anthraquinone or 1,5-diphenylcarbazone as a core dye leads to vinyl phosphonium salts, which undergo Michael addition with conjugate base of NH compounds to produce stable phosphorus ylides as novel dyes in fairly good yields. These ylides can exist in two geometrical isomers (Z) and (E) for 3, because the negative charge of the ylide moiety of these compounds are strongly conjugated with the adjacent carbonyl group. Rotation around the carbon–carbon double bond is slow in the (Z) and (E) geometrical isomers on the NMR time scale at ambient temperature. These compounds are assigned by their IR, ^{1}H, ^{13}C NMR spectral data as well as their mass spectroscopic data.

Keywords 1-Amino-anthraquinone; azoic dyes; dialkyl acetylenedicarboxylate; 1,5-diphenylcarbazone; geometrical isomers; stable phosphorus ylides

INTRODUCTION

Dyes have been the subject of much interest in recent years because of increasingly stringent restriction on the organic content of industrial effluents. Many industries (plastics, paper, textile, and cosmetics) use dyes in order to color their products. Over 100,000 commercially available dyes exist, and more than 7 × 10^5 tons are produced annually.[1, 2] Azoic dyes, 9,10-anthraquinone, and its derivatives constitute the largest group of commonly available dyes and pigments.[3–5] Due to their colors, azoic dyes are used as pigments, indicators of solvent polarity, of molecular environments, and of chemical environments; they are also widely used as histological stains and in the colorimetric analysis of pharmaceuticals.[6–11] The widespread applications of the azoic dyes as chromophoric and metallo

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Received 28 February 2009; accepted 22 May 2009.

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

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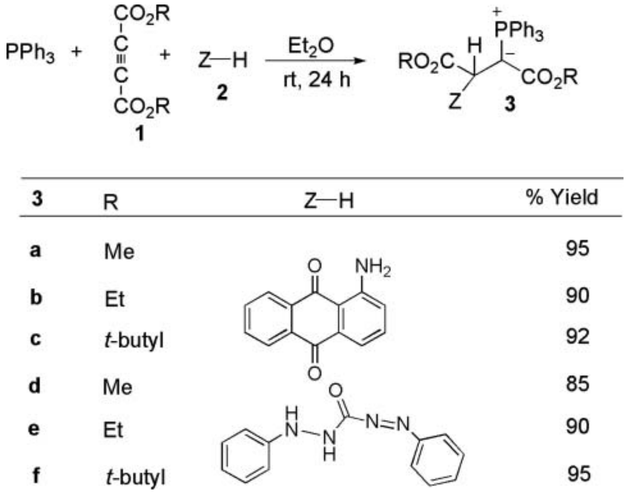
chromic reagents,[12–17] photochromic materials,[18, 19] colorants,[20, 21] nonlinear optics,[22–25] photosensitizers,[26] and sensors[27, 28] have attracted the interest of many electrochemists.[29–33]

Amino anthraquinones are the basic structural units of disperse dyes,[34, 35] which are an important class of dye, characterized by good fastness properties and brightness on hydrophobic fibers, such as poly(ethylene terephthalate), on which they provide mostly bright red to blue hues; also are included acylamino-anthraquinones, which furnish mainly yellow and orange dyes. In addition, anthraquinones have become recently very important due to their application in high technology electronics. Some amino anthraquinone derivatives are used in transfer printing toners, and others are used in thermal printing.[36, 37]

In continuation of our current interest in the development of new routes to heterocyclic and carbocyclic systems,[38–45] in this article we report a simple, one-pot synthesis of stable azo compounds and also anthraquinone derivatives containing dialkyl phosphoryl groups as novel dyes in fairly good yields (see Scheme 1).



3	R	Z—H	% Yield
a	Me		95
b	Et		90
c	*t*-butyl		92
d	Me		85
e	Et		90
f	*t*-butyl		95

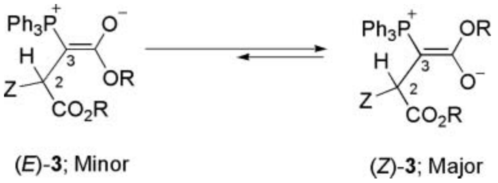
Scheme 1

RESULTS AND DISCUSSION

The reactions of 1-amino-anthraquinone or 1,5-diphenylcarbazone with dialkyl acetylenedicarboxylates **1** in the presence of triphenylphosphine were carried out in Et_2O solvent at room temperature and were finished within a few hours. The ^1H and ^{13}C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **3**.

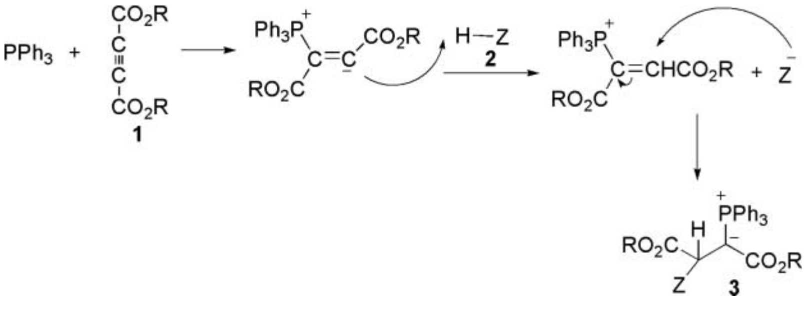
Any products other than **3** could not be detected by NMR spectroscopy. The structures of compounds **3a**–**f** were deduced from their IR, ^1H, ^{13}C, and ^{31}P NMR spectra. Their mass spectra displayed molecular ion peaks at appropriate *m/z* values. Any initial fragmentations involve the missing parts or complete loss of the side chains and scission of the ring system. The ^1H, ^{13}C, and ^{31}P NMR spectra of ylides **3a**–**f** are consistent with the presence of two isomers. The ^1H NMR spectra of **3a** showed two sharp lines (δ 3.19 and 3.73) arising from the methoxy groups in *Z*-diastereoisomer and two single sharp resonances at 3.73 and 3.82 ppm for methoxy groups in *E*-diastereoisomer. In this spectra, the characteristic methine proton appeared at 5.28 and 4.41 ppm for major and minor stereoisomers, respectively.

All of the aromatic protons resonated at δ 6.28–8.31 for major and minor isomers. The ^{1}H NMR spectrum of compound **3a** exhibited a N–H proton as a doublet at 10.11 ppm and a doublet at 10.33 ppm for major and minor, respectively. Other partial assignments of compound **3a** have been presented in the Experimental section. The ylide moieties of these compounds are strongly conjugated with the adjacent carbonyl group, and rotation around the partial double bond in (*E*)-**3** and (*Z*)-**3** geometrical isomers is slow on the NMR time scale at ambient temperature (see Scheme 2). Selected ^{1}H-, ^{13}C-, and ^{31}P NMR chemical shifts and coupling constants are shown in Table I.



Scheme 2

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[46–51] 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 NH-compounds to form phosphoranes **3** (see Scheme 3).



Scheme 3

Briefly, we have prepared novel stable phosphorus ylides as a novel dyes, using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 1-amino-anthraquinone or 1,5-diphenylcarbazone. 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. 1-Amino-anthraquinone and 1,5-diphenylcarbazone-containing phosphorus ylides **3a**–**f** may be considered as potentially useful synthetic intermediates. It seems that the procedure described here may be employed as an acceptable method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points and IR spectra 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 $CDCl_3$

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–f**

		^{1}H NMR spectroscopic data			^{13}C NMR data		
Compd	Isomer%	H-2 ($^3J_{PH}$)	OR	CO_2R	C-2 ($^2J_{PC}$)	C-3 ($^1J_{PC}$)	^{31}P NMR
3a	M (59)	5.28 (24.0)	3.19	3.73	55.8 (12.0)	43.0 (124.9)	20.7
3a	m (41)	4.41 (18.8)	3.73	3.82	55.3 (11.8)	44.0 (135.1)	22.5
3b	M (57)	5.26 (24.1)	3.74–3.85		55.8 (13.4)	42.6 (127.5)	20.7
3b	m (43)	4.37 (18.9)	4.10–4.23		55.8 (13.4)	42.6 (127.5)	22.4
3c	M (63)	5.08 (24.8)	0.99	1.48	56.2 (13.5)	42.0 (125.0)	19.9
3c	m (37)	5.08 (24.8)	1.55	1.57	55.3 (12.7)	43.3 (124.2)	22.4
3d	M (61)	5.13 (18.5)	3.07	3.82	60.6 (17.6)	40.7 (126.2)	23.8
3d	m (39)	5.02 (16.8)	3.16	3.84	61.5 (17.1)	40.3 (126.6)	23.9
3e	M (57)	5.12 (18.4)	4.21–4.44		61.7 (17.8)	40.0 (126.8)	23.8
3e	m (43)	5.18 (18.6)	4.15–4.44		62.2 (17.7)	40.4 (126.0)	23.9
3f	M (79)	5.00 (18.3)	0.88	1.61	61.4 (17.8)	39.9 (126.3)	23.5
3f	m (21)	4.87 (18.9)	1.43	1.55	61.4 (17.8)	36.9 (126.9)	23.6

as a solvent at 500.1, 125.8, and 202.4 MHz, respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. In addition, the mass spectra were recorded on a Shimadzu GC/MS QP 1100 EX mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates, triphenylphosphine, 1-amino-anthraquinone, and 1,5-diphenyl carbazone were purchased from Fluka and were used without further purification.

General Procedures for Preparation of Stable Phosphorus Ylides

To a magnetically stirred solution of triphenylphosphine (0.26 g,1 mmol) and NH compound (1 mmol) in diethyl ether 10 mL, a mixture of dimethyl acetylenedicarboxylates (0.14 g,1 mmol) in diethyl ether 3 mL was added dropwise over 10 min at room temperature. After 24 h stirring at room temperature, the product was filtered off and recrystallized from ethyl acetate.

Dimethyl-2-(*N*-1-aminoanthraquinon-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3a). Red powder (0.45 g), yield 95%, mp 176–179°C. IR (KBr) (λ_{max}, cm^{-1}): 1620, 1648 (2 C=O), 1730 ($C{=}O_{ester}$), 3400 (N—H). MS (*m*/*z*,%): 627 (M^+, 1), 500 (8), 453 (53), 277 (100), 262 (13), 223 (16), 183 (26), 77 (18). Anal. Calc. for $C_{38}H_{30}NO_6P$ (627.62): C, 72.73; H, 4.78; N, 2.23%; Found: C, 73.08; H, 4.82; N, 2.15%.

***Major isomer* (*Z*)-3a** (59%): ^{1}H NMR: 3.19 and 3.73 (6H, 2s, 2 OCH_3), 5.28 (1H, dd, $^3J_{HH} = 5.4$ Hz, $^3J_{HP} = 24.0$ Hz, P = C—C*H*), 6.28–8.31 (22H, m, 3 C_6H_5 and $C_{14}H_9NO_2$), 10.11 (1H, d, $^3J_{HH} = 6.0$ Hz, CH—N*H*). ^{13}C NMR: 43.0 (d, $^1J_{PC} = 124.9$ Hz, P=C), 49.4 and 52.5 (2s, 2 OCH_3), 55.8 (d, $^2J_{PC} = 12.0$ Hz, P=C—*C*H), 113.2, 115.5, 117.0, 118.1, 119.9, 123.5 (6C, $C_{14}H_9NO_2$), 126.3 (d, $^1J_{PC} = 89.5$ Hz, C_{ipso} of 3 C_6H_5), 128.5 (d, $^3J_{PC} = 12.0$ Hz, C_{meta} of 3 C_6H_5), 132.1 (C_{para} of 3 C_6H_5), 133.0, 133.2, and 133.4 (3C, $C_{14}H_9NO_2$), 133.7 (d, $^2J_{PC} = 9.9$ Hz, C_{ortho} of 3C_6H_5), 149.6, 150.2 and 151.4 (3C, $C_{14}H_9NO_2$), 170.2 (d, $^3J_{PC} = 12.7$, $C{=}O_{ester}$), 173.6 (d, $^2J_{PC} = 17.2$, P—C=*C*), 184.0 and 185.0 (2 C=O, $C_{14}H_9NO_2$). ^{31}P NMR: 20.7 (Ph_3P^+—C).

***Minor isomer* (*E*)-3a** (41%): ^{1}H NMR: 3.73 and 3.82 (6H, 2s, 2OCH_3), 4.41 (1H, dd, $^3J_{HH} = 6.8$ Hz, $^3J_{HP} = 18.8$ Hz, P=C—C*H*), 6.20–8.31 (22H, m, 3 C_6H_5 and $C_{14}H_9NO_2$), 10.33 (1H, d, $^{3}J_{HH} = 7.0$ Hz, CH—N*H*). ^{13}C NMR: 44.0 (d, $^{1}J_{PC} = 135.1$ Hz, P=C), 50.4 and 52.4 (2s, 2 OCH_3), 55.3 (d, $^{2}J_{PC} = 11.8$ Hz, P=C—*C*H), 113.2, 115.5, 117.0, 118.2, 119.9, 123.5 (6C, $C_{14}H_9NO_2$), 125.9 (d, $^{1}J_{PC} = 92.3$ Hz, C_{ipso} of 3 C_6H_5), 128.6 (d, $^{3}J_{PC} =$ 12.4 Hz, C_{meta} of 3 C_6H_5), 132.0 (C_{para} of 3 C_6H_5), 133.0, 133.2 and 133.4 (3C, $C_{14}H_9NO_2$), 133.8 (d, $^{2}J_{PC} = 9.8$ Hz, C_{ortho} of 3 C_6H_5), 149.6, 150.1 and 151.4 (3C, $C_{14}H_9NO_2$), 170.2 (d, $^{3}J_{PC} = 12.7$, C=O_{ester}), 173.6 (d, $^{2}J_{PC} = 17.2$, P—C=*C*), 183.7 and 184.1 (2 C=O, $C_{14}H_9NO_2$). ^{31}P NMR: 22.5 (Ph_3P^+—C).

Diethyl-2-(*N*-1-aminoanthraquinon-1-yl)-3-(triphenylphosphoranylidene) butanedioate (3b). Red powder (0.45 g), yield 90%, mp 126–129°C. IR (KBr) (λ_{max}, cm^{-1}): 1620, 1664 (C=O), 1738, 1742 (C=O_{ester}), 3422 (N—H). MS (*m*/*z*,%): 655 (M^+, 2), 485 (3), 277 (8), 223 (100), 77 (8). Anal. Calc. for $C_{40}H_{34}NO_6P$ (655.67): C, 73.28; H, 5.19; N, 2.14%; Found: C, 73.53; H, 5.25; N, 2.20%.

Major isomer **(*E*)-3b** (57%): ^{1}H NMR: 0.46 and 1.28 (6H, 2t, $^{3}J_{HH} = 7.0$ Hz, 2OCH_2CH_3), 3.74–3.85 (4H, m, 2 ABX_3 system, 2 OCH_2CH_3), 5.26 (1H, dd, $^{3}J_{HH} = 5.1$ Hz, $^{3}J_{HP} = 24.1$ Hz, P=C—CH), 6.24–8.35 (22H, m, 3 C_6H_5 and $C_{14}H_9NO_2$), 10.14 (1H, d, $^{3}J_{HH} = 5.7$ Hz, CH—N*H*). ^{13}C NMR: 14.1 and 14.2 (2s, 2 OCH_2CH_3), 42.6 (d, $^{1}J_{PC} =$ 127.5 Hz, P=C), 55.8 (d, $^{2}J_{PC} = 13.4$ Hz, P=C—*C*H), 58.0 and 61.3 (2s, 2 OCH_2CH_3), 113.2, 113.5, 115.3, 117.1, 120.1 and 123.5 (6 C, $C_{14}H_9NO_2$), 126.3 (d, $^{1}J_{PC} = 94.1$ Hz, C_{ipso} of 3 C_6H_5), 128.6 (d, $^{3}J_{PC} = 11.1$ Hz, C_{meta} of 3 C_6H_5), 132.0 (C_{para} of 3 C_6H_5), 132.5, 133.0 and 133.2 (3 C, $C_{14}H_9NO_2$), 133.8 (d, $^{2}J_{PC} = 9.9$ Hz, C_{ortho} of 3 C_6H_5), 149.7, 150.2 and 151.3 (3 C, $C_{14}H_9NO_2$), 165.0 (d, $^{3}J_{PC} = 12.6$ Hz, C=O_{ester}), 173.0 (d, $^{2}J_{PC} =$ 14.6, P—C=*C*), 183.6 and 184.2 (2 C=O, $C_{14}H_9NO_2$). ^{31}P NMR: 20.7 (Ph_3P^+—C).

Minor isomer **(*Z*)-3b** (43%): ^{1}H NMR: 1.21 and 1.32 (6H, 2t, $^{3}J_{HH} = 6.9$ Hz, 2 OCH_2CH_3), 4.10–4.23 (4H, 2m, 2ABX_3 system, 2 OCH_2CH_3), 4.37 (1H, dd, $^{3}J_{HH} = 7.1$ Hz, NH-C*H*, $^{3}J_{HP} = 18.9$ Hz, P=C—CH), 6.24–8.35 (22H, m, 3 C_6H_5 and $C_{14}H_9NO_2$), 10.41 (1H,d, $^{3}J_{HH} = 7.1$ Hz, CH—N*H*). ^{13}C NMR: 14.2 and 15.3 (2s, 2 OCH_2CH_3), 42.6 (d, $^{1}J_{PC} = 127.5$ Hz, P=C), 55.8 (d, $^{2}J_{PC} = 13.4$ Hz, P=C—*C*H), 58.7 and 61.4 (2s, 2 OCH_2CH_3), 113.2, 113.5, 115.3, 117.1, 120.1 and 123.5 (6 C, $C_{14}H_9NO_2$), 126.6 (d, $^{1}J_{CP}$ = 91.6 Hz, C_{ipso} of 3 C_6H_5), 128.6 (d, $^{3}J_{PC} = 11.1$ Hz, C_{meta} of 2 C_6H_5), 132.0 (C_{para} of 3 C_6H_5), 132.5, 133.0 and 133.2 (3 C, $C_{14}H_9NO_2$), 133.7 (d, $^{2}J_{PC} = 9.9$ Hz, C_{ortho} of 3 C_6H_5), 149.7, 150.2 and 151.3 (3 C, $C_{14}H_9NO_2$), 165.0 (d, $^{3}J_{PC} = 12.6$ Hz, C=O_{ester}), 173.0 (d, $^{2}J_{PC} = 14.6$ Hz, P—C=*C*), 183.8 and 185.1 (2 C=O, $C_{14}H_9NO_2$). ^{31}P NMR: 22.4 (Ph_3P^+—C).

Di-*tert*-butyl-2-(*N*-1-aminoanthraquinon-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3c). Red powder (0.53 g), yield 92%, mp 162–165°C. IR (KBr) (λ_{max}, cm^{-1}): 1598, 1631 (C=O), 1730 (C=O_{ester}), 3425 (N—H). MS (*m*/*z*,%): 711 (M^+, 1), 684 (25), 402 (17), 277 (100), 262 (7), 223 (15), 183 (24), 77 (18), 57 (47). Anal. Calc. for $C_{44}H_{42}NO_6P$ (711.78): C, 74.26; H, 5.91; N, 1.97%; Found: C, 74.35; H, 6.02; N, 1.89%.

Major isomer **(*E*)-3c** (63%): ^{1}H NMR: 0.99 and 1.48 (18H, 2s, 2 C*Me*$_3$), 5.08 (1H, dd, $^{3}J_{HH} = 5.5$ Hz, $^{3}J_{HP} = 24.8$ Hz, P=C—CH), 6.92–8.31 (22H, m, 3 C_6H_5 and $C_{14}H_9NO_2$), 10.02 (1H, d, $^{3}J_{HH} = 5.5$ Hz, CH—N*H*). ^{13}C NMR: 28.0 and 28.4 (2s, 2 C*Me*$_3$), 42.0 (d, $^{1}J_{PC} = 125.0$ Hz, P=C), 56.2 (d, $^{2}J_{PC} = 13.5$ Hz, P=C—*C*H), 78.0 and 81.7 (2s, 2 *C*Me_3), 113.0, 113.6, 115.1, 117.2, 120.4 and 123.2 (6C, $C_{14}H_9NO_2$), 127.3 (d, $^{1}J_{PC} = 90.6$ Hz, C_{ipso} of 3 C_6H_5), 128.5 (d, $^{3}J_{PC} = 10.2$ Hz, C_{meta} of 2 C_6H_5), 131.9 (C_{para} of 3 C_6H_5), 133.1, 133.2 and 133.3 (3C, $C_{14}H_9NO_2$), 133.9 (C_{ortho} of 3 C_6H_5), 149.8, 150.2 and 151.2 (3C, $C_{14}H_9NO_2$), 169.2 (d, $^{2}J_{PC} = 12.3$ Hz, C=O_{ester}), 171.9 (d, $^{2}J_{PC} = 14.0$ Hz, P—C=*C*), 184.3 and185.2 (2C, $C_{14}H_9NO_2$). ^{31}P NMR: 19.9 (Ph_3P^+—C).

***Minor isomer* (Z)-3c** (37%): ^{1}H NMR: 1.55 and 1.57 (18H, 2s, 2 C*Me*$_3$), 4.20 (1H, dd, $^3J_{HH}$ = 5.3 Hz, $^3J_{HP}$ = 24.5 Hz, P=C—CH), 6.97–8.31 (22H, m, 3 C_6H_5 and $C_{14}H_9NO_2$), 10.54 (1H, d, $^3J_{HH}$ = 5.5 Hz, CH—N*H*). ^{13}C NMR: 28.8 and 29.3 (2s, 2 C*Me*$_3$), 43.3 (d, $^1J_{PC}$ = 124.2 Hz, P=C), 55.3 (d, $^2J_{PC}$ = 12.7 Hz, P=C—*C*H), 80.7 and 81.1 (2s, 2 *C*Me$_3$), 114.8, 117.2, 118.0, 119.6 120.4 and 124.7 (6C, $C_{14}H_9NO_2$), 126.4 (d, $^1J_{PC}$ = 92.3 Hz, C$_{ipso}$ of 3 C_6H_5), 128.2 (d, $^3J_{PC}$ = 9.8 Hz, C$_{meta}$ of 2 C_6H_5), 130.2 (C$_{para}$ of 3 C_6H_5), 132.4, 133.6 and 132.9 (3C, $C_{14}H_9NO_2$), 133.9 (C$_{ortho}$ of 3C_6H_5), 149.9, 151.3 and 151.0 (3C, $C_{14}H_9NO_2$), 170.4 (d, $^2J_{PC}$ = 11.6 Hz, C=O$_{ester}$), 171.7 (d, $^2J_{PC}$ = 13.7 Hz, P—C=*C*), 183.5 and 183.8 (2C, $C_{14}H_9NO_2$). ^{31}P NMR: 22.4 (Ph$_3$P$^+$—C).

Dimethyl-2-(1,5-diphenylcarbazone-1-yl)-3-(triphenylphosphoranylidene) butanedioate (3d). Yellow powder (0.60 g), yield 94%, mp 115–118°C. IR (KBr) (λ_{max}, cm^{-1}): 1588 (N=N), 1636, 1735 (C=O$_{ester}$), 3430 (N—H). MS (*m/z*,%): 646 (M$^+$+2, 54), 277 (58), 92 (33), 77 (100), 57 (33). Anal. Calc. for $C_{37}H_{33}N_4O_5P$ (644.66): C, 68.94; H, 5.12; N, 8.70%; Found: C, 69.05; H, 5.18; N, 8.68%.

***Major isomer* (Z)-3d** (59%): ^{1}H NMR: 3.07 and 3.82 (6H, 2s, 2 OCH$_3$), 5.13 (1H, d, $^3J_{HP}$ = 18.5 Hz, P=C—CH), 1.30 (1H, br, N*H*), 6.86–7.91 (25H, m, 5 C_6H_5). ^{13}C NMR: 40.7 (d, $^1J_{PC}$ = 126.2 Hz, P=C), 49.3 and 52.5 (2 OCH$_3$), 60.6 (d, $^2J_{PC}$ = 17.6 Hz, P=C—*C*H), 113.3, 113.6, 114.2, 117.8, 120.5, 123.1 and 128.7 (7C, $(C_6H_5)_2N_4HCO$), 126.1 (d, $^1J_{PC}$ = 92.1 Hz, C$_{ipso}$), 128.7 (d, $^3J_{PC}$ = 12.7 Hz, C$_{meta}$), 132.1 (d, $^4J_{PC}$ = 3.2 Hz C$_{para}$), 133.4 (d, $^2J_{PC}$ = 9.9 Hz, C$_{ortho}$), 146.1, 149.0, 149.9, 152.2 and 160. 4 (5C, $(C_6H_5)_2N_4HCO$), 167.0 (1C, O=C—N), 171.4 (d, $^3J_{PC}$ = 12.9 Hz, C=O$_{ester}$), 173.38 (d, ^{2}J$_{PC}$ = 11.32Hz, P—C=*C*). ^{31}P NMR: 23.8 (Ph$_3$P$^+$—C).

***Minor isomer* (*E*)-3d** (41%): ^{1}H NMR: 3.16 and 3.84 (6H, 2s, 2 OCH$_3$), 5.02 (1H, d, $^3J_{HP}$ = 16.8 Hz, P=C—CH), 1.30 (1H, br, N*H*), 6.80–7.55 (25H, m, 5C_6H_5). ^{13}C NMR: 40.3 (d, $^1J_{PC}$ = 126.6 Hz, P=C), 52.5 and 52.9 (2 OCH$_3$), 61.5 (d, $^2J_{PC}$ = 17.1 Hz, P=C—*C*H), 113.2, 113.4, 114.0, 118.2, 120.1, 124.1 and 129.1 (7C, $(C_6H_5)_2N_4HCO$), 126.0 (d, $^1J_{PC}$ = 92.1 Hz, C$_{ipso}$), 128.6 (d, $^3J_{PC}$ = 12.1 Hz, C$_{meta}$), 132.0 (d, $^4J_{PC}$ = 3.2 Hz, C$_{para}$), 133.5 (d, $^2J_{PC}$ = 9.8 Hz, C$_{ortho}$), 147.3, 148.9, 149.4, 151.5 and 160.3 (5C, $(C_6H_5)_2N_4HCO$), 165.4 (1C, O=C—N), 171.0 (d, $^3J_{PC}$ = 12.7 Hz, C=O$_{ester}$), 172.3 (d, $^2J_{PC}$ = 10.3 Hz, P—C=*C*). ^{31}P NMR: 23.9 (Ph$_3$P$^+$—C).

Diethyl-2-(1,5-diphenylcarbazone-1-yl)-3-(triphenylphosphoranylidene) butanedioate (3e). Yellow crystal (0.60 g), yield 90%, mp 177–180°C. IR (KBr) (λ_{max}, cm^{-1}): 1620 (N=N), 1720, 1732 (C=O$_{ester}$), 3433 (N—H). MS (*m/z*,%): 672 (M$^+$+2, 13), 446 (10), 277 (100), 199 (24), 183 (22), 152 (14), 134 (10), 92 (25), 77 (59). Anal. Calc. for $C_{39}H_{37}N_4O_5P$ (672.71): C, 69.64; H, 5.51; N, 8.33%; Found: C, 69.71; H, 5.48; N, 8.38%.

***Major isomer* (Z)-3e** (67%): ^{1}H NMR: 0.43 and 1.39 (6H, 2t, $^3J_{HH}$ = 7.1 Hz 2 OCH$_2$CH$_3$), 1.70 (1H, br, N*H*), 4.21–4.44 (4H, m, 2 ABX$_3$ system, 2 OCH$_2$CH$_3$), 5.12 (1H, d, $^3J_{HP}$ = 18.4 Hz, P=C—CH), 6.84–7.80 (25H, m, 5 C_6H_5). ^{13}C NMR: 14.0 and 14.3 (2s, 2 OCH$_2$CH$_3$), 40.0 (d, $^1J_{PC}$ = 126.8 Hz, P=C), 58.0 and 61.8 (2 OCH$_2$CH$_3$), 61.7 (d, $^2J_{PC}$ = 17.8 Hz, P=C—CH), 113.0, 113.3, 113.8, 117.9, 122.5, 123.1 and 124.1 (7C, $(C_6H_5)_2N_4HCO$), 126.2 (d, $^1J_{PC}$ = 92.1 Hz, C$_{ipso}$), 128.7 (d, $^3J_{PC}$ = 11.9 Hz, C$_{meta}$), 132.9 (d, $^4J_{PC}$ = 2.6 Hz, C$_{para}$), 133.6 (d, $^2J_{PC}$ = 10.0 Hz, C$_{ortho}$), 146.0, 148.9, 149.9, 152.2 and 160.9 (5C, $(C_6H_5)_2N_4HCO$), 167.3 (1C, O=C—N), 170.7 (d, $^3J_{PC}$ = 12.8Hz, C=O$_{ester}$), 172.8 (d, $^2J_{PC}$ = 11.6 Hz, P—C=C). ^{31}P NMR: 23.8 (Ph$_3$P$^+$—C).

***Minor isomer* (E)-3e** (33%): ^{1}H NMR: 1.26 and 1.29 (6H, 2t, $^3J_{HH}$ = 7.0 Hz, 2OCH$_2$CH$_3$), 1.70 (1H, br, N*H*), 4.15–4.44 (4H, m, 2 ABX$_3$ system, 2 OCH$_2$CH$_3$), 5.18

(1H, d, $^3J_{HP} = 18.6$ Hz, P=C—CH), 6.84–7.80 (25H, m, 5 C_6H_5). ^{13}C NMR: 13.8 and 14.1 (2 OCH_2CH_3), 40.4 (d, $^1J_{PC} = 126.0$ Hz, P=C), 58.4 and 61.3 (2 OCH_2CH_3), 62.2 (d, $^2J_{PC} = 17.7$ Hz, P=C—*C*H), 113.2, 113.6, 114.3, 118.1, 121.4, 123.1 and 125.4 (7C, $(C_6H_5)_2N_4HCO$), 126.3 (d, $^1J_{PC} = 92.1$ Hz, C_{ipso}), 128.6 (d, $^3J_{PC} = 11.8$ Hz, C_{meta}), 131.9 (d, $^4J_{PC} = 2.6$ Hz C_{para}), 133.5 (d, $^2J_{PC} = 10.3$ Hz, C_{ortho}), 147.2, 149.1, 150.1, 151.4 and 160.5 (5C, $(C_6H_5)_2N_4HCO$), 165.0 (1C, O=C—N), 170.7 (d, $^3J_{PC} = 12.7$ Hz, C=O_{ester}), 171.7 (d, $^2J_{PC} = 10.4$ Hz, P—C=C). ^{31}P NMR: 23.9 (Ph_3P^+—C).

Di-*tert*-buthyl-2-(1,5-diphenylcarbazone-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3f). Pale white powder (0.70 g), yield 96%, m.p. 172–175°C. IR (KBr) (λ_{max}, cm^{-1}): 1598 (N=N), 1688, 1728 (C=O_{ester}), 3427 (N—H). MS (*m/z*,%): 728 (M^+, 4), 489 (21), 377 (40), 277 (40), 262 (98), 183 (100), 152 (22), 108 (53), 93 (95), 57 (58). Anal. Calc. for $C_{43}H_{45}N_4O_5P$ (728.81): C, 70.88; H, 6.18; N, 7.69%; Found: C, 70.91; H, 6.09; N, 7.75%.

***Major isomer* (Z)-3f** (79%): ^{1}H NMR: 0.88 and 1.61 (18H, 2s, 2 CMe_3), 5.00 (1H, d, $^3J_{HP} = 18.3$ Hz, P=C—CH), 1.28 (1H, br, N*H*), 6.80–7.92 (25H, m, 5 C_6H_5).^{13}C NMR: 28.3 and 28.4 (2 C*Me*$_3$), 39.9 (d, $^1J_{PC} = 126.3$ Hz, P=C), 61.4 (d, $^2J_{PC} = 17.8$ Hz, P=C—*C*H), 77.5 and 81.2 (2 O*C*Me$_3$), 113.2, 113.4, 119.9, 120.0, 121.2 and 123.2 (6C, $(C_6H_5)_2N_4HCO$), 126.7 (d, $^1J_{PC} = 92.0$ Hz, C_{ipso}), 128.5 (d, $^3J_{PC} = 12.0$ Hz, C_{meta}), 132.0 (C_{para}), 133.7 (d, $^2J_{PC} = 9.5$ Hz, C_{ortho}), 147.2, 149.0, 149.2, 150.0, 159.6 and 160.7 (6C, $(C_6H_5)_2N_4HCO$), 164.4 (1C, O=C—N), 170.5 (d, $^3J_{PC} = 12.1$ Hz, C=O_{ester}), 172.0 (d, $^2J_{PC} = 11.9$ Hz, P—C=*C*). ^{31}P NMR: 23.5 (Ph_3P^+—C).

***Minor isomer* (E)-3f** (23%): ^{1}H NMR: 1.43 and 1.55 (18H, 2s, 2 C*Me*$_3$), 4.87 (1H, d, $^3J_{HP} = 18.9$ Hz, P=C—CH), 1.22 (1H, br, N*H*), 6.80–7.92 (25H, m, 5 C_6H_5). ^{13}C NMR: 28.0 and 28.1 (2 C*Me*$_3$), 39.6 (d, $^1J_{PC} = 126.9$ Hz, P=C), 61.4 (d, $^2J_{PC} = 17.8$ Hz, P=C—*C*H), 81.7 and 82.0 (2 O*C*Me$_3$), 113.3, 113.8, 120.3, 120.6, 123.7 and 124.1 (6C, $(C_6H_5)_2N_4HCO$), 126.7 (d, $^1J_{PC} = 92.0$ Hz, C_{ipso}), 128.4 (d, $^3J_{PC} = 12.3$ Hz, C_{meta}), 132.0 (C_{para}), 133.6 (d, $^2J_{PC} = 9.5$ Hz, C_{ortho}), 148.4, 149.0, 151.4, 152.1, 159.6 and 161.1 (6C, $(C_6H_5)_2N_4HCO$), 167.4 (1C, O=C—N), 170.5 (d, $^3J_{PC} = 12.1$ Hz, C=O_{ester}), 170.6 (d, $^2J_{PC} = 10.5$ Hz, P—C=*C*). ^{31}P NMR: 23.6 (Ph_3P^+—C).

REFERENCES

1. G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I. M. Banat, R. Marchant, and W. F. Smyth, *Appl. Microbiol. Biotecnol.*, **56,** 81 (2001).
2. C. I. Pearce, J. R. Lloyd, and J. T. Guthrie, *Dyes Pigm.*, **58,** 179 (2003).
3. S.S. Nathan and S. K. Murthy, *Organic Chemistry Made Simple* (W. H. Allen, London, 1968).
4. M. Matsui, *Dyes Pigm.*, **40,** 21 (1998).
5. B. V. Rao, V. Choudhary, and I. K. Varma, *J. Soc. Dyers Colour.*, **106,** 388 (1990).
6. W. Herbst, K. Hunger, *Industrial Organic Pigments: Production, Properties, Applications*, 3rd ed, (Wiley-VCH, Weinheim, Germany, 2004), chapter 2.
7. V. Buss and L. Eggers, In *Encyclopedia of Spectroscopy and Spectrometry*, J. C. Lindon, G. E. Tranter, J. L. Holmes, eds. (Academic Press, New York, 2000), p. 389e96.
8. N. M. Rageh, *Spectrochim. Acta, Part A*, **60,** 103 (2004).
9. A. C. Bratton and J. E. K. Marshall, *J. Biol. Chem.*, **128**, (2), 537 (1939).
10. P. Nagaraja, H. S. Yathirajan, C. R. Raju, R. A. Vasantha, M. S. Nagendra, and M. S. Hemantha Kumar, *IL Farmaco*, **58,** 1295 (2003).
11. H. D. Revanasiddappa and B. Manju, *IL Farmaco*, **56,** 615 (2001).
12. S. M. B. Fraga, M. S. T. Goncalves, J. C. V. P. Moura, and K. Rani, *Eur. J. Org. Chem.*, **8,** 1750 (2004).

13. S. Przeszlakowski and H. Wydra, *Chromatographia*, **15,** 301 (1982).
14. S. H. Ashuto, N. D. Pandey, and J. K. Mehrotra, *Colourage*, **26,** 25 (1979).
15. L. Sommer and V. Koblizko, *Collect. Czech. Chem. Commun.*, **39,** 396, (1974).
16. C. Woodward and H. Freiser, *Talanta*, **20,** 417 (1973).
17. M. R. Islami, F. Mollazehi, and Z. Hassani, *Russ. Chem. Bull.*, **56,** 532, (2007).
18. P. J. Coelho, L. M. Carvalho, A. M. C. Fonseca, and M. M. M. Raposo, *Tetrahedron Lett.*, **47,** 3711 (2006).
19. M. Serwadczak and S. Kucharski, *J. Sol-Gel Sci. Technol.*, **37,** 57 (2006).
20. A. D. Towns, *Dyes Pigm.*, **42,** 3 (1999).
21. G. Hallas and A. D. Towns, *Dyes Pigm.*, **33,** 215 (1997).
22. S. Yin, H. Xu, W. Shi, L. Bao, Y. Gao, Y. Song, and B. Z. Tang, *Dyes Pigm.*, **72,** 119 (2007).
23. M. M. M. Raposo, A. M. R. C. Sousa, A. M. C. Fonseca, and G. Kirsch, *Tetrahedron*, **61,** 8249 (2005).
24. A. Carella, R. Centore, A. Sirigu, A. Tuzi, Quatela A, S. Schutzmann, and M. Casalboni, *Macromol. Chem. Phys.*, **205,** 1948 (2004).
25. A. M. Albu, B. Marculescu, and D. Vasilescu, *Eur. Polym. J.*, **35,** 2203 (1999).
26. F. Ruyffelaere, V. Nardello, R. Schmidt, and J. M. Aubry, *J. Photochem. Photobiol., A*, **183,** 98 (2006).
27. A. Grafe, K. Haupt, and G. J. Mohr, *Anal. Chim. Acta*, **565,** 42 (2006).
28. D. Zhang, M. Zhang, Z. Liu, M. Yu, F. Li, T. Yi, and C. Huang, *Tetrahedron Lett.*, **47,** 7093 (2006).
29. N. Menek and Y. Karaman, *Dyes Pigm.*, **68,** 101 (2006).
30. N. Menek and Y. Karaman, *Dyes Pigm.*, **67,** 9 (2005).
31. F. S. De Paula, A. G. Cioletti, J. F. Da Silva, and A. E. G. Santana, *J. Electroanal. Chem.*, **544,** 25 (2003).
32. R. Jain, M. Bhargava, and N. Sharma, *Ind. Eng. Chem. Res.*, **42,** 243 (2003).
33. M. M. Ghoneim, Y. M. Issa, E. M. Mabrouk, and T. Amerah, *J. Electrochem. Soc.*, **133,** C133 (1986).
34. H. M. Smith, ed., *High Performance Pigments* (Wiley-VCH, Weinheim, Germany, 2002), pp. 188–190.
35. S. Patai and Z. Rappaport, ed., *The Chemistry of Quinonoid Compounds*, vols. 1 and 2, (Wiley-Interscience, New York, 1988).
36. S. Miki, R. Noda, and K. Fukunishi, *J. Chem. Soc., Chem. Commun.*, 925 (1997).
37. P. Boldt, S. Zippel, and G. Haucke, *J. Chem. Res., Synop.*, 386 (1997).
38. I. Yavari, N. Zabarjad-Shiraz, M. T. Maghsoodlou, and N. Hazeri. *Phosphorus, Sulfur, and Silicon.*, **177,** 759 (2002).
39. M. T. Maghsoodlou, S. M. Habibi-Khorassani, R. Heydari, A. Hassankhani, G. Marandi, M. Nassiri, and E. Mosaddeg, *Mol. Divers.*, **11,** 87 (2007).
40. M. T. Maghsoodlou, N. Hazeri, S. M. Habibi-Khorassani, R. Heydari, M. Nassiri, G. Marandi, Z. Moeeni, U. Niromand, and Z. E. Torbaghan, *Phosphorus, Sulfur, and Silicon*, **181,** 865 (2006).
41. M. T. Maghsoodlou, S. M. Habibi-Khorassani, N. Hazeri, and M. Nassiri, *Phosphorus, Sulfur, and Silicon*, **181,** 1363 (2006).
42. I. Yavari and K. Karimi, *Phosphorus, Sulfur, and Silicon*, **182,** 595 (2007).
43. M. T. Maghsoodlou, N. Hazeri, R. Kakaei, and M. Nassiri, *Phosphorus, Sulfur, and Silicon*, **181,** 25 (2006).
44. S. M. Habibi-Khorassani, M. T. Maghsoodlou, N. Hazeri, M. Nassiri, G. Marandi, and A. G. Shahzadeh, *Phosphorus, Sulfur, and Silicon*, **181,** 567 (2006).
45. S. M. Habibi-Khorassani, M. T. Maghsoodlou, A. Ebrahimi, H. Roohi, M. Zakarianezhad, H. R. Dasmeh, and M. Moradian, *Phosphorus, Sulfur, and Silicon*, **181,** 1103 (2006).
46. P. J. Murphy, *Organophosphorus Reagents*, 1st ed. (Oxford University Press: Oxford, UK, 2004), Chapters 1 and 2.

47. O. I. Kolodiazhnyi, *Phosphorus Ylides*: *Chemistry and Application in Organic Synthesis* (Wiley-VCH, Weinheim, Germany, 1999).
48. I. Gosney and A. G. Rowley, *Organophosphorus Reagents in Organic Synthesis*, J. I. G. Cadogan, ed. (Academic Press: London, 1979), pp. 17–153.
49. R. Engel and J. I. Cohen, *Synthesis of Carbon-Phosphorus Bonds*, 2nd ed. (CRC Press, Boca Raton, FL, 2004), Chapters 1–3.
50. H. R. Hudson, *The Chemistry of Organophosphorus Compounds*, Vol. 1: Primary, Secondary, and Tertiary Phosphates and Heterocyclic Organophosphorus (III) Compounds, F. R. Hartley, ed. (Wiley, New York, 1990), pp. 382–472.
51. D. E. C. Corbridge, In *Topics in Phosphorus Chemistry*, M. Grayson and J. Griffith, eds. (Interscience, New York, 1969), vol. 6, pp. 235–365.