Heteroatom Chemistry
Volume 11, Number 1, 2000

The Behavior of 2-Substituted-1,3-Diphenylpropane-1,3-tione toward Organophosphorus Reagents

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Received 5 March 1999; revised 25 August 1999

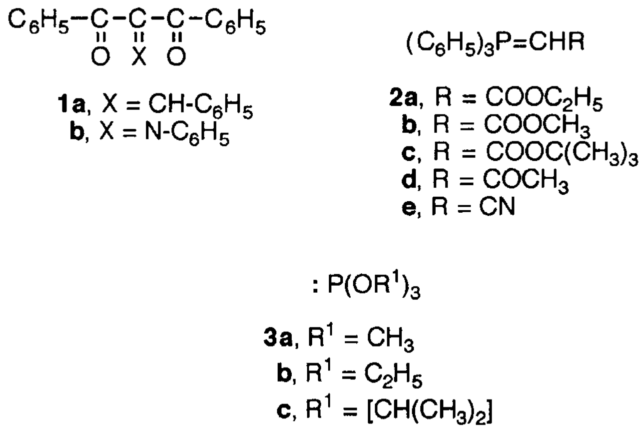
ABSTRACT: *The reaction of 2-benzylidene-1,3-diphenylpropanetrione (***1a***) with phosphorus ylides* **2a–c** *afforded the new phosphonium ylides* **4a–c**. *Trialkyl phosphites* **3a–c** *react with* **1a** *to give the respective dialkyl phosphonate products* **5a–c**. *On the other hand, the olefinic compounds* **6** *and* **7** *were isolated from the reaction of* **1b** *with Wittig reagents* **2**. *Moreover, trialkyl phosphites reacted with* **1b** *to give products* **8a–c**. *Possible reaction mechanisms are considered, and the structural assignments are based on analytical and spectroscopic evidence.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:57–64, 2000

INTRODUCTION

Although the action of phosphonium ylides and trialkyl phosphites on diphenyl-1,2,3-propanetrione is well established [1,2], their action on 2-substituted-1,3-diphenylpropanetrione (**1**) has hitherto not been investigated. This, together with our interest in organophosphorus chemistry [3–8], has stimulated us to investigate the behavior of 1,3-diphenyl-2-(phenylmethylene)-1,3-propanedione (**1a**) and 1,3-diphenyl-2-(phenylimino)-1,3-propanedione (**1b**) toward a number of Wittig reagents of types **2a–e**. A comparative study of the behavior of **1a,b** toward trialkyl phosphites **3a–c** is also reported (Scheme 1).

RESULTS AND DISCUSSION

We have found that carbethoxymethylenetriphenylphosphorane (**2a**) reacts with 1,3-diphenyl-2-(phenylmethylene)-1,3-propanedione (**1a**), in boiling tetrahydrofuran, to give the new phosphorane product **4a** as the sole reaction product. Triphenylphosphine and/or triphenyl phosphine oxide are neither isolated nor detected in the reaction medium (Scheme 2). Compound **4a** consists of chromatographically pure crystals and has a sharp melting point. Structure elucidation of the new phosphorus ylide **4a** is based on the following evidence: elemental analyses and molecular weight determination (MS) of **4a** support the molecular formula $C_{44}H_{37}O_4P$ (660.7); accordingly, MS: *m/z* = 660 (M^+, 100%, base peak). Its



SCHEME 1

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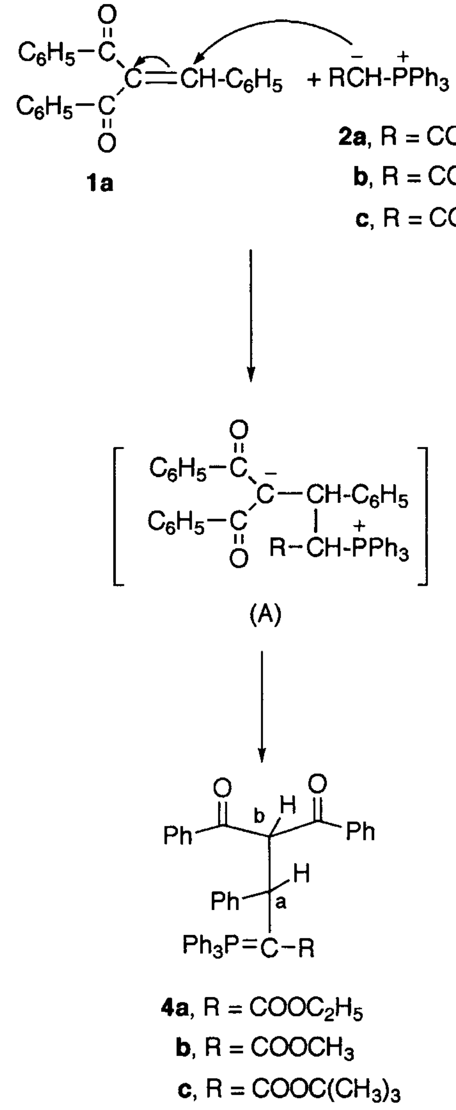


SCHEME 2

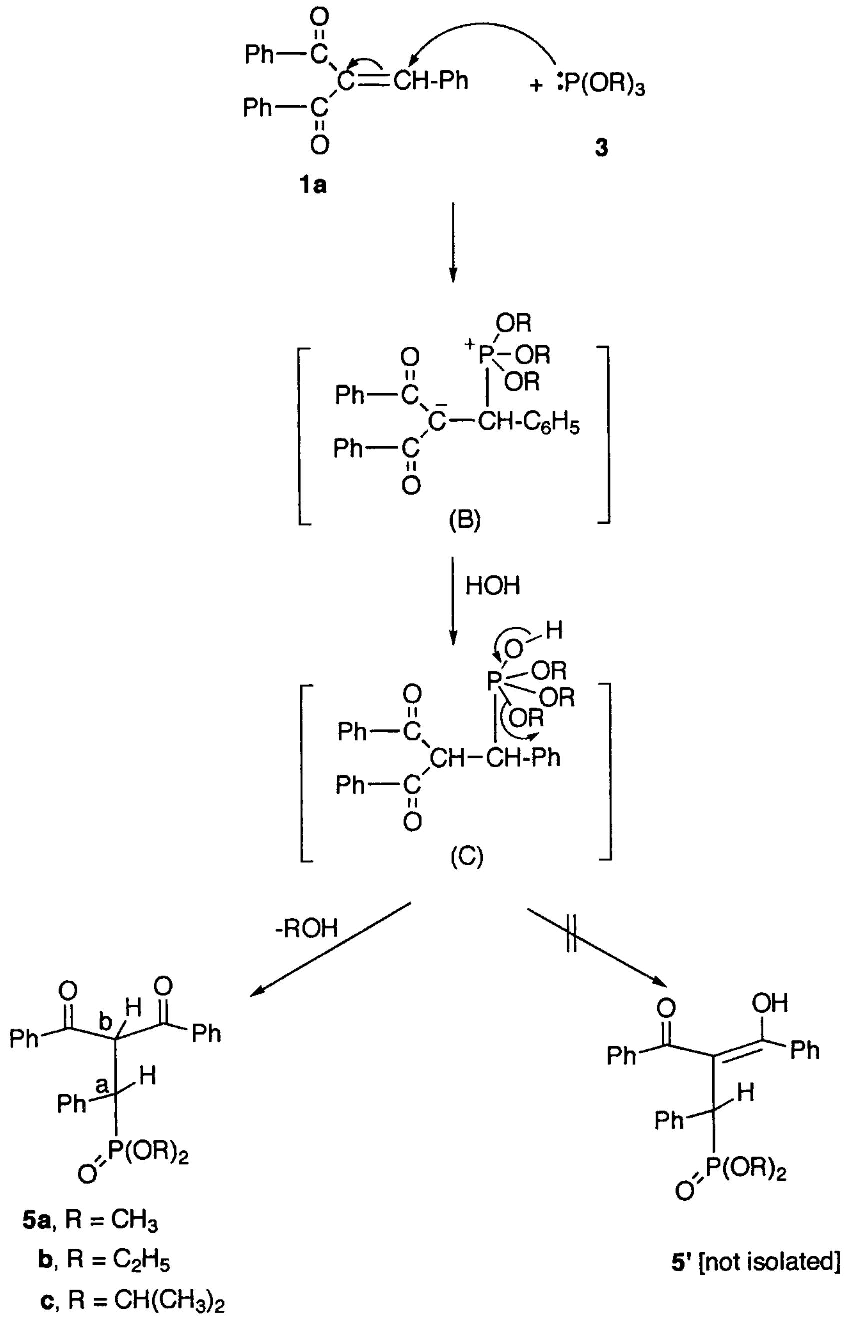
IR spectrum, in KBr, exhibits strong absorption bands at 1689 cm^{-1} (C = O, ester), 1656 cm^{-1} (C = O, Ar), 1626, 1510 cm^{-1} (C = P), and at 1436, 990 cm^{-1} (P-C, phenyl) [9]. ^{31}P NMR δ = +24.4, a value that falls in the range frequently recorded for this class of compounds [9,10]. The ^{1}H NMR spectrum of **4a** in CDCl$_3$ discloses the presence of signals at δ = 0.43 (t, 3H, ethoxy-CH$_3$), and 3.65 (q, 2H, OCH$_2$). Moreover, its ^{1}H NMR spectrum shows two signals at δ = 4.15 (dd, $^3J_{HP}$ = 16.6 Hz, J_{HH} = 10.8 Hz) and at δ = 6.85 (dd, $^4J_{HP}$ = 6.2 Hz, J_{HH} = 10.8 Hz) corresponding to the exocyclic methine protons $\underline{a}$ and $\underline{b}$, respectively (Scheme 2). The aromatic protons (30H) appeared as a multiplet at 7.25–8.25 ppm. Actually, the structure assigned for compound **4a** is based on ^{13}C NMR spectroscopy, which indicates the presence of signals at 195.90 and 195.63 ppm ascribed to the two C = O groups attached to the phenyl groups, at 169.32 (d, $^2J_{CP}$ = 13.4 Hz) and allocated to the C = O of the ester group, at 13.82 ppm (ethoxy-$\underline{C}$H$_3$), 57.05 ppm (ethoxy-CH$_2$), 57.92 ppm (d, $^3J_{CP}$ = 8.5 Hz, $\underline{C}$Hb), 45.80 ppm (d, $^2J_{CP}$ = 14.6 Hz, $\underline{C}$Ha) and at 125.98 (d, $^1J_{CP}$ = 105 Hz, P = C) [11].

The reaction product of **1a** with carbomethoxymethylenetriphenylphosphorane **2b** and *tert*-butoxycarbonylmethylenetriphenylphosphorane **2c** was assigned analogous structures **4b** and **4c** on the basis of comparable spectroscopic arguments (c.f. Experimental section).

Products **4a–c** are presumably formed via Michael addition of the ylide species **2a–c** to the active methine carbon in compound **1a** to afford the intermediate (A). Transfer of a proton from the α- to the γ-carbon atom leads to the formation of the new phosphonium ylides **4a–c** (Scheme 2) [12,13].

The reaction of 1,3-diphenyl-2-(phenylmethylene)-1,3-propanedione (**1a**) with trialkyl phosphites **3a–c** was also investigated. We have found that the reaction of trimethyl-, triethyl-, and triisopropyl phosphites **3a–c** with **1a**, in dry toluene, proceeds at reflux temperature to give chromatographically pure 1:1 adducts formulated as **5a–c** (Scheme 3). Structure elucidation for compound **5a**, taken as an example, was attested by the following evidence: (a) elemental analyses and a molecular weight determination (MS) for compound **5a** correspond to $C_{24}H_{23}O_5P$; (b) the IR spectrum of **5a**, in KBr, exhibits strong absorption bands at 1670, 1695 cm^{-1} (2C=O), 1240 cm^{-1} (P=O), and at 1045 cm^{-1} (P-O-CH$_3$) [14]; (c) Compound **4a** responds negatively to the ferric chloride test and does not dissolve in 10% aqueous alkali, which indicates the absence of an enolic OH; (d) The ^{1}H NMR spectrum of compound **5a** reveals signals at δ = 3.45 [2d, 6H, J_{HP} = 11 Hz, P(OCH$_3$)$_2$], 4.50 (dd, 1H, $^2J_{HP}$ = 23 Hz, J_{HH} = 10.5 Hz, H-a), 6.45 (dd, 1H, $^3J_{HP}$ = 11 Hz, J_{HH} = 10.5 Hz, H-b), and at 7.02–8.20 ppm (m, 15H, Ar.). The ^{13}C NMR spectrum furnishes strong evidence in support of the phosphonate structure **5a**. The ^{13}C NMR spectrum of **5a**, in CDCl$_3$, shows two doublets at δ = 44.4 with coupling constant $^1J_{CP}$ = 136.7 Hz and at 55.3 ppm with $^2J_{CP}$ = 35.5 Hz ascribed to CH$\underline{a}$ and CH$\underline{b}$ attached to phosphorus. The spectrum of **5a** also shows signals at 53.25 ppm [P(O$\underline{C}$H$_3$)$_2$] and at 192.15 ppm (d, J_{CP} = 17.1 Hz) for the two C=O groups. Worthy of mention is the fact that the ^{1}H and ^{13}C NMR spectra of compound **5a** are in favor of the phosphonate structure **5** and rule out the other possible alternative form **5′** (Scheme 3). The mass spectrum of **5a** yielded a prominent peak for M$^+$ at *m/z* 422 (22%), 390 (100, base peak).

Triethyl- and triisopropyl-phosphites **3b,c**, on



SCHEME 3

the other hand, reacted with **1a** in the conventional manner to give the corresponding dialkyl phosphonate products **5b** and **5c**, respectively. The structures of **5b,c** are deduced from their analysis, IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data (c.f. Experimental section). The formation of compounds **5a–c** involves Michael addition [16,17] by a tertiary phosphite ester on the active methine carbon in **1a** to give the dipolar intermediate (B). Addition of water (unavoidable moisture) to intermediate (B) produces a transient intermediate (C) with pentacovalent phosphorus [18]. The latter collapses to give the dialkyl phosphonate products **5a–c** (Scheme 3).

The present study clearly shows that 2-benzylidene-1,3-diphenyl-propanetrione **1a** behaves in a different manner than that of 3-benzylidene-2,4-pentanedione with trialkyl phosphites where 1,4-addition takes place to form the tetraalkoxyalkylphosphoarne derivatives [19].

Since 1,3-diphenyl-2-(phenylimino)-1,3-propanedione (**1b**) bears both the carbonyl and imino-functions, it appeared, therefore, of interest to examine its behavior toward the same phosphorus ylides (**2**) and phosphite reagents (**3**) to prove if the carbonyl or the imino center is preferentially attacked by phosphorus.

When 1,3-diphenyl-2-(phenylimino)-1,3-propanedione (**1b**) was treated with one equivalent of carbethoxymethylenetriphenylphosphorane (**2a**) in tetrahydrofuran at reflux temperature for 6 hours, adduct **6a** and triphenylphosphine oxide were isolated in good yields (Scheme 4). The IR spectrum of 1,3-diphenyl-1-ethoxycarbonylmethylene-2-phenylimino-3-propanone (**6a**) revealed the presence of strong absorption bands at 1580 cm^{-1} (C=N), 1660 cm^{-1} (C=O, Ar), 1710 cm^{-1} (C=O, ester), and at 1615 cm^{-1} (C=C). The ^{1}H NMR spectrum of **6a** exhibits signals at $\delta = 1.01$ (t, 3H, ethoxy-CH_3), 3.95 (q, 2H, ethoxy-CH_2), 6.40 (s, 1H, =CH), 6.7–7.7 ppm (m, 15H, Ar.). The mass spectrum of **5a** yields a prominent ion peak at *m/z* 383 (M^+).

When **1b** was treated with two equivalents of ylide **2a** in refluxing toluene, the new olefin **7a** was isolated together with triphenylphosphine oxide. Compound **7a** can also be obtained via the reaction of **6a** with ylide **2a** in an equal molar ratio (Scheme 5, Experimental section). The elemental analysis, IR, ^{1}H NMR, ^{13}C NMR spectra, and molecular weight determination (MS) were in good agreement with structure **7a** (Experimental section).

Similarly, **1b** reacts with methylenetriphenylphosphoranes **2b–e** in a 1:1 molar ratio to give products formulated as **6b–e,** respectively. Triphenylphosphine oxide (TPPO) was also isolated and identified in each case. Compatible analytical and spectral data (IR, ^{1}H, ^{13}C NMR and MS) were obtained for the new products (cf. Experimental section). These findings clearly indicate that Wittig reagents preferentially attack the carbonyl group in **1b.**

Furthermore, this study has been extended to include the reaction of **1b** with alkyl phosphites **3a–c** to establish whether they would behave in a similar manner. We have found that 1,3-diphenyl-2-(phenylimino)-1,3-propanedione (**1b**) reacts with excess trimethyl phosphite **3a** to give the phosphonate product **8a** in 65% yield (Scheme 5). The phosphonate structure **8a** has been determined on the basis of the following findings: (1) The microanalysis of 1,3-diphenyl-2-(1,1-methylphenylimino)-2-dimethylphosphonate-1,3-propanedione (**8a**) corresponds to an empirical formula of $C_{24}H_{24}NO_5P$; (2) Strong bands are found at 1640 cm^{-1} (C=O, Ar), 1268 cm^{-1} (P=O), 1050 cm^{-1} (P-O-CH_3), and at 1600 cm^{-1} (C=C, aromatic), and moreover, the C=N absorption band at 1586 cm^{-1} observed in the spectrum of **1b** is absent in the spectrum of **8a**; (3) The ^{1}H NMR spectrum of product **8a** shows signals at $\delta = 3.12$ (s, 3H, N-CH_3), 3.81 ppm (d, 6H, $P(OCH_3)_2$, $J_{HP} = 12$ Hz), and at 6.81–7.65 ppm (m, 15 H, Ar). The ^{13}C NMR of **8a** indicates signals at $\delta = 123.7$ [(d, $\underline{C}$-$PO(OCH_3)_2$, $^1J_{CP} = 95.7$ Hz], 55.4 [$P(O\underline{C}H_3)_2$], 28.3 (N-$\underline{C}H_3$) and at $\delta = 196.6$ (2C=O, Ar.). The mass spectrum of compound **8a** exhibits a prominent ion peak at *m/z* = 347 (100%).

When **1b** is allowed to react with triethyl- and triisopropyl phoshites (**3b–c**), the phosphonate products **8b** and **8c** are obtained. Compatible analytical and spectral data (IR, ^{1}H, ^{13}C NMR, and MS) have been recorded for the new products.

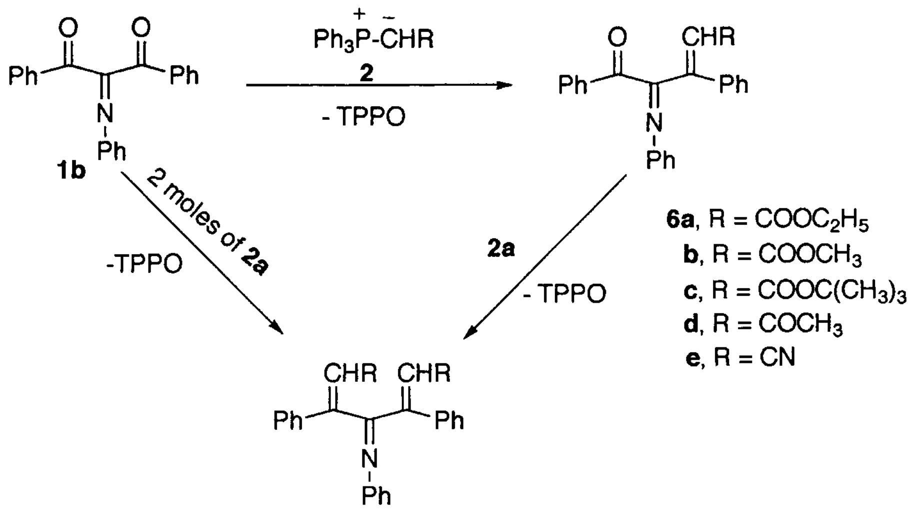
Compounds **8** are possibly obtained via Michael addition of trialkyl phosphites to the most reactive C=N group followed by group translocation (N-alkylation).

CONCLUSION

From the results of the present investigation, it could be concluded that Wittig reagents **2** and trialkyl phosphites **3** preferentially attacked the α,β-unsaturated carbon rather than the carbonyl carbon in **1a**. Also, it is important to note that 2-benzylidene-1,3-diphenylpropanetrione **1a** reacts with both phosphorus ylides and trialkyl phosphites via the Michael addition reaction to give the new phosphonium ylides **4a–c** and the respective dialkyl phosphonate adducts **5a–c**. Meanwhile, it has been found that the reaction of **1b** with Wittig reagents proceeds according to the Wittig reaction to give the olefinic products **6** and **7**, whereas, in the reaction of **1b** with trialkyl phosphites; the dialkyl phosphonate adducts **8a–c** are the sole reaction products.

EXPERIMENTAL

All melting points are uncorrected. Benzene (thiophene-free) and petroleum ether (boling range 60–80 °C) were dried with sodium. Wittig reagents **2a–e** were prepared according to established procedures [20–22]. The trialkyl phosphites were prepared according to established procedures and were purified by treatment with sodium followed by fractional distillation [23,24]. The IR spectra were measured in KBr, on a Perkin Elmer Infracord Spectrophotometer model 157 (Grating). The ^{1}H NMR spectra were recorded in $CDCl_3$ on a JNM-GX-400 Fa Jeol Spectrometer. The ^{31}P NMR spectra were recorded in $CDCl_3$ (vs. H_3PO_4 as external standard) on a TNM-PS-100Fa Spectrometer. ^{13}C NMR spectra were taken in $CDCl_3$ on a varian Spectrometer at 200 MHz. The mass spectra were run at 70 eV on Kratos MS equipment and/or an Varian MAT 311 A Spectrometer.



6a, R = $COOC_2H_5$
b, R = $COOCH_3$
c, R = $COOC(CH_3)_3$
d, R = $COCH_3$
e, R = CN

7a, R = $COOC_2H_5$

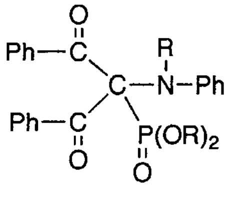
SCHEME 4

Reaction of Carbethoxymethylenetriphenylphosphorane 2a *with 1,3-Diphenyl-2-(phenylmethylene)-1,3-propanedione* 1a

A mixture of **1a** (0.31 g, 0.001 mol) [25], the ylide **2a** (0.34 g, 0.001 mol) and dry tetrahydrofuran (30 mL) was stirried magnetically at reflux temperature until no more of the starting material could be detected (TLC), (12 hours). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to a silica gel column using as the eluent ethyl acetate/petroleum ether (40:60, v:v) to give **4a** as pale yellow crystals, m.p. 165–166°C, yield (0.44 g, 66.6%). Anal. Calcd for $C_{44}H_{37}O_4P$ (660.74): C, 79.98; H, 5.64; P, 4.68%; Found: C, 79.74; H, 5.78; P, 4.55%.

Reaction of Carbomethoxymethylenetriphenylphosphorane 2b *with 1,3-Diphenyl-2-(phenylmethylene)-1,3-Propanedione* 1a

A mixture of **1a** (0.31 g, 0.001 mol), the ylide **2b** (0.33 g, 0.001 mol), and dry tetrahydrofuran (30 mL) as the solvent was stirred magnetically at reflux temperature until no more of the starting material could be detected (TLC, 12 hours). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to a silica gel column using as the eluent ethyl acetate/petroleum ether (35:65, v:v) to give **4b** as pale yellow crystals, m.p. 162–163°C, yield (0.48 g, 74.2%). Anal. Calcd for $C_{43}H_{35}O_4P$ (646.72): C, 79.86; H, 5.45; P, 4.78%; Found: C, 79.58; H, 5.29; P, 4.91%. IR (cm^{-1}, group): 1700 (C=O, ester), 1660 (C=O, Ar), 1630, 1515 (C=P), 1435, 990 (P-C, phenyl). MS: *m/e* (%, rel. int.): 646 (M^+, <5), 333 $[(Ph_3P{=}C\text{-}COOCH_3)^+$, 100, base peak], 302 $[(Ph_3P{=}C\text{-}CO)^+$, 70], 105 $[(C_6H_5CO]^{\pm}$, 29]. ^{1}H NMR ($CDCl_3$: δ = 3.10 ppm (s, 3H, $COOCH_3$), 4.10 ppm (dd, 1H, $^3J_{HP}$ = 15.5 Hz, J_{HH} = 10.5 Hz), 6.81 ppm (dd, $^4J_{HP}$ = 6.1 Hz, J_{HH} = 10.5 Hz), 7.10–8.26 (m, 30H, aromatics).



8a, R = CH_3
b, R = C_2H_5
c, R = $[CH(CH_3)_2]$

SCHEME 5

Reaction of Carbo-t-Butoxymethylenetriphenylphosphorane 2c *with 1,3-Diphenyl-2-(phenylmethylene)-1,3-propanedione* 1a

A mixture of **1a** (0.31 g, 0.001 mol), the ylide (0.37 g, 0.001 mol) and dry toluene (30 mL) was refluxed for 12 hours. The volatile materials were evaporated under reduced pressure. The residual substance was recrystallized from petroleum ether at 60–80°C to give **4c** as colorless crystals, m.p. 170–171°C, yield

(0.38 g, 55.2%). Anal. Calcd for $C_{46}H_{41}O_4P$ (688.80): C, 80.21; H, 5.99; P, 4.49%; Found: C, 79.98; H, 6.02; P, 4.55%. IR (cm^{-1}, group): 1705 (C=O, ester), 1655 (C=O), 1620, 1510 (C=P), 1438, 995 (P-C, phenyl). MS: *m/e* (% rel. int.) 688 (M^+, 18), 587 (M^+-COOC$(CH_3)_3$, < 5), 276 (M^+-C_6H_5-OC$(CH_3)_3$-TPP, 100, base peak), 262 (TPP, 33). ^{1}H NMR ($CDCl_3$): δ = 0.75 ppm (s, 9H, -C$(CH_3)_3$), 4.32 ppm (dd, 1H, $^3J_{HP}$ = 16 Hz, J_{HH} = 10.5 Hz), 6.75 (d, $^4J_{HP}$ = 6 Hz, J_{HH} = 10.5 Hz), 7.10–8.32 ppm (m, 30H, aromatics). ^{13}C NMR: 28.2 ppm (s, 3$\underline{C}H_3$ of *t*-butyl group), 195.01, 196.07 (2s, two C=O groups), 169.1 (d, C=O, ester, $^2J_{CP}$ = 13 Hz), 57.9 (d, $^3J_{CP}$ = 7.2 Hz, $\underline{C}$Hb), 46.7 (d, $^2J_{CP}$ = 13.5 Hz, $\underline{C}$Ha), 126.1 ppm (d, $^1J_{CP}$ = 105 Hz, P=C).

Reaction of Trimethyl Phosphite **3a** *with 1,3-Diphenyl-2-(phenylmethylene)-1,3-propanedione* **1a**

A mixture of **1a** (0.31 g, 0.001 mol), trimethyl phosphite (0.37 g, 0.003 mol), and dry toluene (30 mL) was refluxed for 4 hours. The volatile materials were evaporated under reduced pressure, and the residual substance was applied to a silica gel column using as the eluent acetone/petroleum ether (20:80, v:v) to give **5a** as colorless crystals, m.p. 155–156 °C, yield (0.28 g, 66.3%). Anal. Calcd for $C_{24}H_{23}O_5P$ (422.415): C, 68.24; H, 5.48; P, 7.33%; Found: C, 68.11; H, 5.54; P, 7.20%.

Reaction of Triethyl Phosphite **3b** *with 1,3-Diphenyl-2-(phenylmethylene)-1,3-propandione* **1a**

To a solution of **1a** (0.312 g, 0.001 mol) in dry toluene (30 mL) was added triethyl phosphite (0.5 g, 0.003 mol) and the reaction mixture was refluxed for 4 hours. The reaction mixture was evaporated on silica gel under reduced pressure and then applied to a silica gel column using as the eluent acetone/petroleum ether (25:75, v:v) to give **5b** as colorless crystals, m.p. 150–151 °C, yield (0.31 g, 68.8%). Anal. Calcd for $C_{26}H_{27}O_5P$ (450.469): C, 69.32; H, 6.04; P, 6.87%; Found: C, 69.19; H, 5.88; P, 6.90%. IR (cm^{-1}, group): 1710, 1690 (2C=O), 1248 (P=O), 1600 (C=C, aromatics), 1045 (P-O-C_2H_5). MS: *m/e* (% rel. int.) 451 (M^{+1}, 63), 345 (M^+-C_6H_5-C=O$\rceil^{\pm}$, 100, base peak), 105 ($C_6H_5CO\rceil^{\pm}$, 92). ^{1}H NMR ($CDCl_3$): δ = 0.92 (2t, 6H, the two ethoxy-CH_3), 3.41–3.80 ppm (m, 4H, two ethoxy-CH_2), 4.40 (dd, 1H, $^2J_{HP}$ = 25 Hz and J_{HH} = 10 Hz), 6.51 ppm (dd, 1H, $^3J_{HP}$ = 10.6 Hz, J_{HH} = 10 Hz), 7.01–8.22 (m, 15H, aromatics). ^{13}C NMR: 44.9 ppm (d, $^1J_{CP}$ = 138 Hz, $\underline{C}$Ha), 56.42 (d, $^2J_{CP}$ = 35.5 Hz, $\underline{C}$Hb), 191.8 (d, $^3J_{CP}$ = 17.1 Hz, C=O), 61.79 (d, J_{CP} = 8.5 Hz, P-$\underline{C}H_2$), 15.78 (d, J_{CP} = 6.1 Hz, P-O-CH_2-$\underline{C}H_3$).

Reaction of Triisopropyl Phosphite **3c** *with* **1a**

A mixture of **1a** (0.31 g, 0.001 mol), triisopropyl phosphite (0.62 g, 0.003 mole), and dry toluene (30 mL) was refluxed until no more of the starting material could be detected (TLC), (3 hours). The reaction mixture was worked up as previously described. Acetone/petroleum ether (20:80, v:v) was used as eluent to give **5c** as colorless crystals, m.p. 152–153 °C, yield (0.34 g, 71.1%). Anal. Calcd for $C_{28}H_{31}O_5P$ (478.522): C, 70.28; H, 6.52; P, 6.47%; Found: C, 70.22; H, 6.61; P, 6.29%. IR (cm^{-1}, group): 1700, 1675 (2C=O), 1245 (P=O), 1594 (C=C, aromatics), 1050 (P-O-CH). MS: *m/e* (% rel. int.) 479 (M^{+1}, 26), 373 (M^+-C_6H_5-C=O$\rceil^{\pm}$, 100, base peak), 105 (C_6H_5-CO$\rceil^{\pm}$, <5). ^{1}H NMR ($CDCl_3$): δ = 0.70 ppm (2d, 6H, J_{HH} = 5.9 Hz, two CH_3 of isopropyloxy groups), 1.11 (2d, 6H, two CH_3 of isopropyloxy groups), 4.10 (m, 1H, isopropyloxy CH), 4.45 (m, 2H, isopropyloxy CH + H$\underline{a}$), 6.41 (dd, 1H, $^3J_{HP}$ = 11 Hz, J_{HH} = 10.6 Hz, CH$\underline{b}$), 7.01–8.25 (m, 15H, aromatics).

Reaction of Carbethoxymethylenetriphenylphosphorane **2a** *with 1,3-diphenyl-2-(phenylimino)-1,3-propanedione* **1b**

A mixture of **1b** (0.31 g, 0.001 mol) [26], the ylide **2a** (0.34 g, 0.001 mole) and dry tetrahydrofuran (30 mL) was refluxed until no more of the starting material could be detected (TLC, 6 hours). The reaction mixture was worked up as previously described. The eluent used was ethyl acetate/petroleum ether (6:94, v:v) to give **6a** as yellow crystals, m.p. 120–121 °C, yield (0.24 g, 62.6%). Anal. Calcd for $C_{25}H_{21}NO_3$ (383.445): C, 78.30; H, 5.51; N, 3.65%; Found: C, 78.21; H, 5.47; N, 3.48%.

Reaction of Carbethoxymethylenetriphenylphosphorane **2a** *with* **1b** *using a 2:1 Molar Ratio*

A mixture of **1b** (0.31 g, 0.001 mol), the ylide (0.7 g, 0.002 mol), and dry toluene (30 mL) was refluxed until no more of the starting material could be detected (TLC, 15 hours). The reaction mixture was purified as previously described using as the eluent ethyl acetate/petroleum ether (8:92, v:v) to give **7a** as reddish brown crystals, m.p. 116–117 °C, yield (0.3 g, 66%). Anal. Calcd for $C_{29}H_{27}NO_4$ (453.536): C, 76.80; H, 6.00; N, 3.08%; Found: C, 76.68; H, 5.87; N, 3.02%. IR (cm^{-1}, group): 1578 (C = N), 1726, 1706 (2C = O, acyl ylide), 1602, 1623 (2C = C). MS: *m/e* (% rel. int.) 453 (M^+, 24), 380 (M^+-$COOCH_2CH_3$, 56), 334 (M^+-$COOC_2H_5$-C_2H_5O-H, 79), 306 (M^+-$2COOC_2H_5$-H, 100, base peak). ^1H NMR ($CDCl_3$): δ = 1.02 ppm (t, 3H, ethoxy-CH_3), 1.31 (t, 3H, ethoxy-CH_3), 4.10 ppm (q, 2H, ethoxy-CH_2), 4.31 ppm (q, 2H, ethoxy-CH_2), 6.41 (s, 1H, = CH), 6.50 (s, 1H, = CH), 6.80–7.51 (m, 15H, aromatics).

Reaction of **6a** *with* **2a** (*Another way to Prepare* **7a**)

A mixture of **6a** (0.38 g, 0.001 mol), the ylide **2a** (0.34 g, 0.001 mol), and dry toluene (30 mL) in the presence of one drop of triethylamine was refluxed for 12 hours. The reaction mixture was evaporated on silica gel under reduced pressure and applied to a silica gel column using as the eluent ethyl acetate/petroleum ether (8:92, v:v) to give reddish brown crystals, m.p. 116–117°C, yield (0.15 g, 33.1%). Found: C, 76.59; H, 5.91; N, 2.98% (comparative IR, ^1H NMR with **7a**).

Reaction of Carbomethoxymethylenetriphenylphosphorane **2b** *with 1,3-Diphenyl-2-(phenylimino)-1,3-propanedione* **1**

A mixture of **1b** (0.31 g, 0.001 mol), the ylide **2b** (0.33 g, 0.001 mol), and dry tetrahydrofuran (30 mL) was refluxed until no more of the starting material could be detected (TLC, 6 hours). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to a silica gel column using ethyl acetate/petroleum ether (6:94, v:v) as the eluent to give **6b** as yellow crystals, m.p. 118–119 °C, yield (0.27 g, 73.05%). Anal. Calcd for $C_{24}H_{19}NO_3$ (369.41): C, 78.03; H, 5.18; N, 3.79%; Found: C, 77.85; H, 5.01; N, 3.72%. IR (cm^{-1}, group): 1577 (C = N), 1666 (C = O, acyl ylide), 1697 (C = O), 1606 (C = C). MS: *m/e* (% rel. int.) 369 (M^+, 12), 338 (M^+-OCH_3, < 5), 278 (M^+-C_6H_5N, 15.7), 264 (M^+-C_6H_5-C = O, 100, base peak), 208 (M^+-Ph-C = CH-$COOCH_3$)$\rceil^{\pm}$, 14), 105 ($C_6H_5CO\rceil^{\pm}$, 53). ^1H NMR ($CDCl_3$): δ = 3.50 (s, 3H, $COO\underline{C}H_3$), 6.41 (s, 1H, = CH), 6.65–7.73 (m, 15H, aromatics).

Reaction of Carbo-t-butoxymethylenetriphenylphosphorane **2c** *with* **1b**

A mixture of **1b** (0.31 g, 0.001 mol), the ylide **2c** (0.37 g, 0.001 mol), and dry tetrahydrofuran (30 mL) was refluxed for 5 hours. The reaction mixture was worked up as previously described. The eluent used was ethyl acetate/petroleum ether (6:94, v:v) to give **6c** as yellow crystals, m.p. 135–136 °C, yield (0.32 g, 77.8%). Anal. Calcd for $C_{27}H_{25}NO_3$ (411.499): C, 78.80; H, 6.12; N, 3.40%; Found: C, 78.64; H, 6.03; N, 3.29%. IR (cm^{-1}, group): 1577 (C = N), 1665 (C = O, acyl ylide), 1698 (C = O), 1607 (C = C). MS: *m/e* (% rel. int.) 411 (M^+, 32), 338 (M^+-$OC(CH_3)_3$, < 5), 249 (M^+-C_6H_5CO-$C(CH_3)_3$, 100 base peak). ^1H NMR ($CDCl_3$): δ = 1.25 ppm (s, 9H, $COOC(CH_3)_3$), 6.35 (s, 1H, = CH), 6.71–7.72 (m, 15H, aromatics). ^{13}C NMR: signals at δ = 196.4 (s, C = O, Ar), 167.5 (C = O, ester), 164.6 (C = N), 119.8 (C = $\underline{C}$H), 135.1 ($\underline{C}$ = CH), 81.5 ($\underline{C}(CH_3)_3$), and at 27.5 ppm (s, ($\underline{C}H_3)_3$).

Reaction of Acetylmethylenetriphenylphosphorane **2d** *with* **1b**

A mixture of **1b** (0.31 g, 0.001 mole), the ylide (0.32 g, 0.001 mol), and dry tetrahydrofuran (30 mL) was refluxed until no more of the starting material could be detected (TLC, 12 hours). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to a silica gel column using ethyl acetate/petroleum ether (4:96, v:v) to give **6d** as brown crystals, m.p. 115–116 °C, yield (0.22 g, 62.2%). Anal. Calcd for $C_{24}H_{19}NO_2$ (353.419): C, 81.56; H, 5.41; N, 3.96%; Found: C, 81.32; H, 5.33; N, 3.80%. IR (cm^{-1}, group): 1575 (C = N), 1660, 1680 (2C = O), 1605 (C = C). MS: *m/e* (% rel. int.) 354 (M^{+1}, 100, base peak), 248 (M^+-C_6H_5-$CO\rceil^{\pm}$, 10), 105 (C_6H_5-$CO\rceil^{\pm}$, < 5). ^1H NMR ($CDCl_3$): δ = 2.11 ppm (s, 3H, $COCH_3$), 5.80 (s, 1H, = CH), 7.10–7.80 (m, 15H, aromatics).

Reaction of Cyanomethylenetriphenylphosphorane **2e** *with* **1b**

A mixture of **1b** (0.31 g, 0.001 mol), the ylide (0.30 g, 0.001 mol), and dry tetrahydrofuran (30 mL) was refluxed until no more of the starting material could be detected (TLC, 6 hours). The product was purified by column chromatography using ethyl acetate/petroleum ether (10:90, v:v) as the eluent to give **6e** as colored crystals, m.p. 35–36 °C, yield (0.225 g, 66.9%). Anal. Calcd for $C_{23}H_{16}N_2O$ (336.392): C, 82.12; H, 4.79; N, 8.32%; Found: C, 81.98; H, 4.85; N, 8.16%. IR (cm^{-1}, group): 1577 (C = N), 1700 (C = O), 1600 (C = C), 2255 (CN). MS: *m/e* (% rel. int.) 337 (M^{+1}, 100, base peak), 310 (M^+-CN, 12), 231 (M^+-$C_6H_5CO\rceil^{\pm}$, 27). ^1H NMR ($CDCl_3$): δ = 6.11 ppm (s, 1H, = CH), 6.80–8.21 (m, 15H, aromatics).

Reaction of Trimethyl Phosphite **3a** *with 1,3-Diphenyl-2-(phenylimino)-1,3-propanedione* **1b**

A mixture of **1b** (0.31 g, 0.001 mol), trimethyl phosphite (0.37 g, 0.003 mol), and dry benzene (30 mL) was refluxed until no more of the starting material could be detected (TLC, 8 hours). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to silica gel column chromatography using ethyl acetate/petroleum ether (30:70, v:v) as the eluent to give **8a** as colorless crystals, m.p. 161–162 °C, yield (0.3 g, 68.5%). Anal. Calcd for $C_{24}H_{24}NO_5P$ (437.43): C, 65.89; H, 5.52; N, 3.20; P, 7.08%; Found: C, 65.65; H, 5.61; N, 3.12; P, 7.01%.

Reaction of Triethyl Phosphite **3b** *with* **1b**

A mixture of **1b** (0.31 g, 0.001 mol), triethyl phosphite (0.5 g, 0.003 mol) and dry benzene (30 mL) was refluxed until no more of the starting material could be detected (TLC, 8 hours). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to silica gel column chromatography using ethyl acetate/petroleum ether (30:70, v:v) as the eluent to give **8b** as pale yellow crystals, m.p. 155–156 °C, yield (0.30, 62.6%). Anal. Calcd for $C_{27}H_{30}NO_5P$ (479.51): C, 67.63; H, 6.30, N, 2.92; P, 6.45%; Found: C, 67.52; H, 6.38; N, 2.78; P, 6.41%. IR (cm^{-1}, group): 1650 (C=O), 1270 (P=O), 1055 (P-O-C_2H_5), 1600 (C=C, aromatic), 1590 (C=N). MS: *m/e* (% rel. int.) 480 (M^{+1}, 10), 451 (7), 366 (25), 382 (100, base peak). ^1H NMR ($CDCl_3$): $\delta = 1.0$–1.6 ppm (m, 9H, 3CH_3 groups), 3.8–4.2 (m, 6H, 3CH_2 groups), 7.0–8.1 (m, 15H, aromatic).

Reaction of Triisopropyl Phosphite **3c** *with* **1b**

A mixture of **1b** (0.31 g, 0.001 mol), triisopropyl phosphite (0.62 g, 0.003 mol), and dry toluene (30 mL) was refluxed until no more of the starting material could be detected (TLC, 8 hours). The reaction mixture was evaporated on silica gel under reduced pressure and then applied to silica gel column chromatography using ethyl acetate/petroleum ether (35:65, v:v) as the eluent to give **8c** as pale yellow crystals, m.p. 157–158 °C, yield (0.38 g, 72.8%). Anal. Calcd for $C_{30}H_{36}NO_5P$ (521.591): C, 69.08; H, 6.95; N, 2.68; P, 5.93%; Found: C, 68.89; H, 7.01; N, 2.62; P, 5.86%. IR (cm^{-1}, group): 1650 (C=O), 1266 (P=O), 1054 (P-O-CH), 1600 (C=C, aromatic), 1595 (C=N). MS: *m/e* (% rel. int.) 522 (M^{+1}, 10), 479 (100, base peak). ^1H NMR ($CDCl_3$): $\delta = 1.21$ (m, 18H, isopropyl CH_3 groups), 4.51 (m, 3H, isopropyl CH), 6.60–8.1 (m, 15H, aromatics). ^{13}C NMR: $\delta = 194.6$ (C=O, Ar), 160.1 ($\underline{C}$=N), 23.88 (d, $J_{CP} = 4.9$ Hz), 23.53 (d, $J_{CP} = 4.9$ Hz), P-(O-CH($\underline{C}H_3)_2)_2$, 23.7 (N-CH-($\underline{C}H_3)_2$), 73.9 ppm (d, $^1J_{CP} = 136.7$, $\underline{C}$-P(O)(OCH$(CH_3)_2$), 120.7 ppm (d, $^2J_{CP} = 12.2$ Hz, $\underline{P}$(O$\underline{C}$H-$(CH_3)_2)_2$), 116.6 (N-CH$(CH_3)_2$.

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