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The Reaction of Organophosphorus Reagents with Substituted-1,3-Diphenylpropanetrione: New Synthesis of Azaphospholene Derivatives

L. S. Boulos and M. H. N. Arsanious

Department of Pesticide Chemistry, National Research Centre, Dokki, Cairo, Egypt

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ABSTRACT: *The reaction of 1,3-diphenyl-2-(phenylimino)-3-(ylidenemethyl-acetate)-1-propanone* **(5)** *with trisdialkylaminophosphines* **(6a,b)** *in refluxing toluene afforded the new oxazaphospholene products* **(7a–b)**. *On the other hand, the cyclic azaphospholene adducts* **8a–b** *were isolated from the reaction of* **5** *with* **6a,b** *without solvent. Trialkyl phosphites* **1b–c** *react with compound* **5** *to give the respective dialkyl phosphate products* **(9a,b)**. *Moreover, trisdialkylaminophosphines* **(6a,b)** *react with* **2a** *and* **2b** *to give the dipolar adducts* **10a,b** *and the phosphonate products* **11a,b,** *respectively. Possible reaction mechanisms are considered, and the structural assignments are based on compatible analytical and spectroscopic results*. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:511–517, 2001

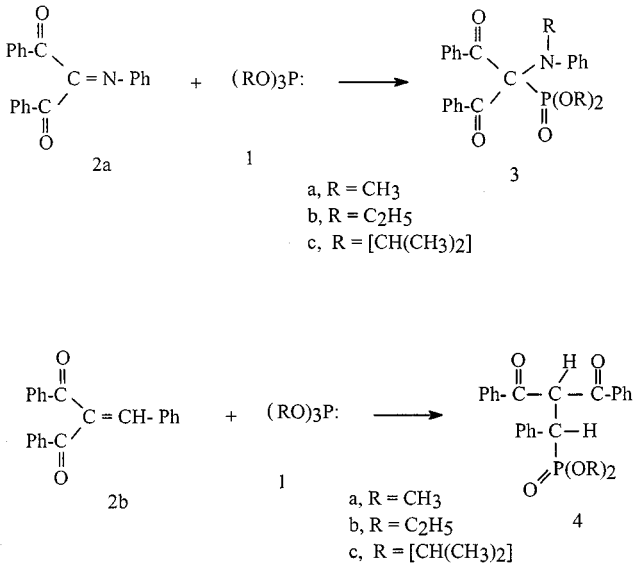
INTRODUCTION

We have reported [1] that trialkyl phosphites **(1a–c)** react with 2-(phenylimino)-1,3-diphenylpropanedione **(2a)** and 2-(phenylmethylene)-1,3-diphenylpropane dione **(2b)** to give the corresponding phosphonate adducts **(3a–c)** and **(4a–c)**, respectively (Scheme 1). As part of our continuing interest in organophosphorus syntheses [2–10], we describe here the reactivity of 1,3-(phenylimino)-3-(ylidenemethylacetate)-1-propanone **(5)** toward trisdialkylaminophosphines **(6a,b)** and trialkyl phosphites **(1a–c)**. The purpose of this study was to determine the preferential site of attack by these reagents. A comparative study on the behavior of **2a** and **2b** toward trisdialkylaminophosphines **(6a,b)** is also reported (Scheme 2).

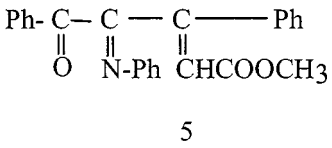
Correspondence to: L. S. Boulos

RESULTS AND DISCUSSION

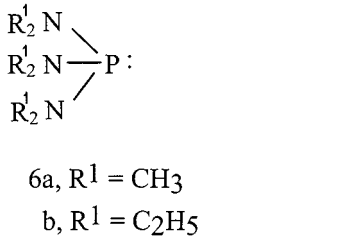
We have found that 1,3-diphenyl-2-(phenylimino)-3-(ylidenemethylacetate)-1-propanone **(5)** [1] reacts with trisdimethylaminophosphine **6a** in refluxing toluene to give a chromatographically pure adduct formulated as **7a** (Scheme 3). Structure elucidation of product **7a** is based on the following evidence: elemental analyses and molecular weight determination (MS) of **7a** support the molecular formula $C_{26}H_{25}N_2O_4P$ (460.46); accordingly, MS : $m/z = 460$ (M^+, 100% base peak). Its IR spectrum, in KBr, exhibits an intense band at 1240 cm^{-1} corresponding to the P=O absorption [11], two bands at 1320 cm^{-1} and 860 cm^{-1} due to the absorptions of P–$N(CH_3)_2$ [12] and at 1710 (C=O, ester). Moreover, the IR spectrum of oxazaphospholene product **7a** revealed the absence of the absorption bands at 1580 (C=N), 1660 (C=O, Ar) and also the characteristic absorption band attributable to the stretching frequency of the enolate carbonyl function [13]. The ^1H NMR spectrum (in $CDCl_3$) of the adduct showed a doublet centered at $\delta = 2.65$ ($J_{HP} = 11.07$ Hz) due to the 6H of the dimethylamino group, a singlet at 3.55 (s, 3H, $COO\underline{CH_3}$), and a singlet at 6.45 (s, 1H, $=\underline{CH}COOCH_3$). The aromatic protons appeared



SCHEME 1



5



SCHEME 2

as multiplets at $\delta = 7.05$–6.65 (15H). The ^{31}P NMR spectrum of product **7a** gave one signal at $\delta = +40.9$ that support the cyclic oxazaphospholene structure [14].

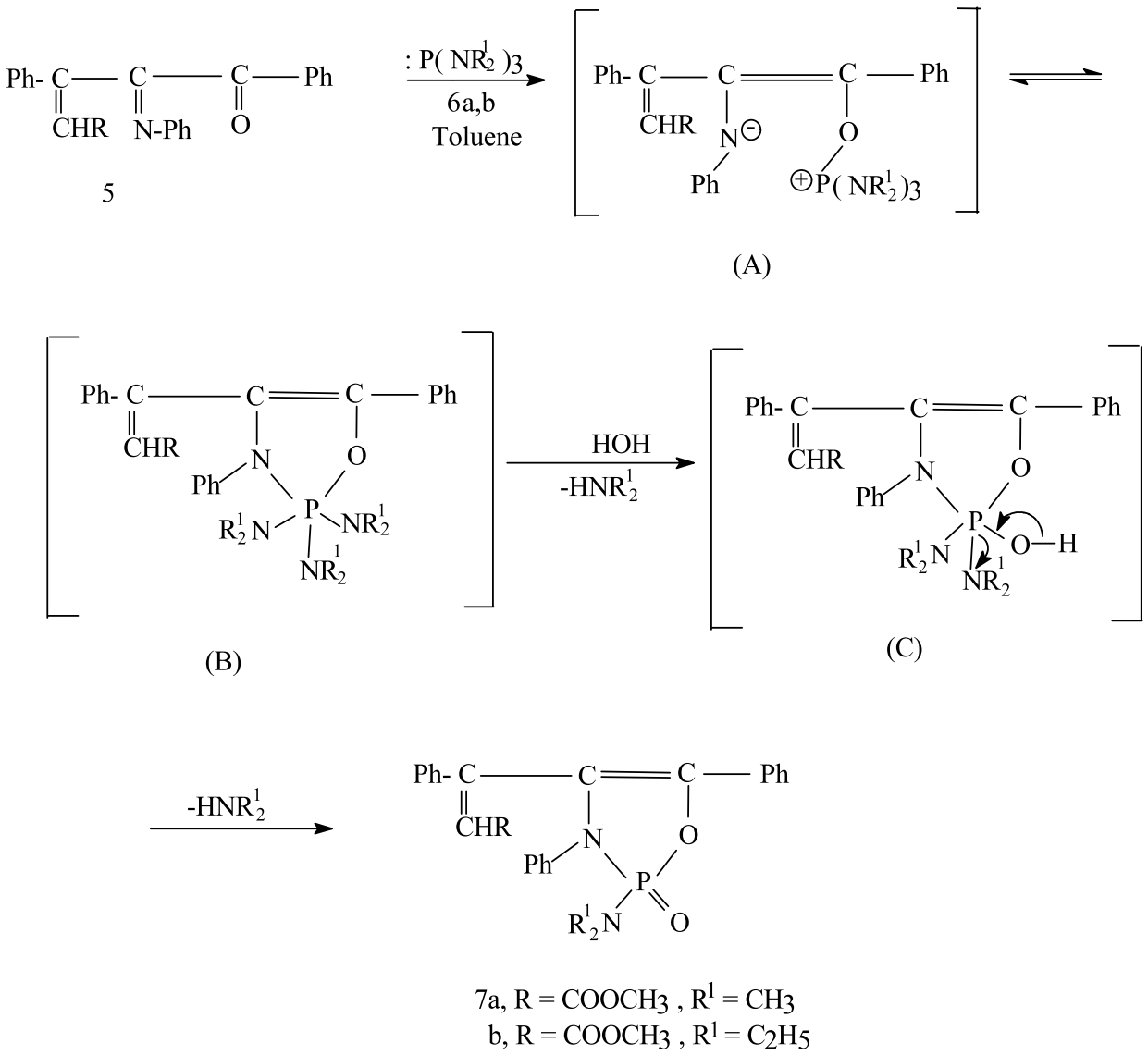
Similarly, compound **5** reacts with trisdiethylaminophosphine **6b** in refluxing toluene to give a yellow crystalline compound formulated as **7b** (Scheme 3). Compatible analytical and spectral data (IR,^{1}H, ^{13}C NMR, and MS) were obtained for the new cyclic oxazaphospholene product **7b** (cf. Experimental section).

A possible explanation for the reaction of compound **5** with trisdialkylaminophosphines **6a,b** is shown in Scheme 3. Thus, initial attack of aminophosphines **6** on the most reactive center of compound **5** leads to the formation of the dipolar adduct (A) that undergoes ring closure giving compound (B). The latter could collapse [15] to the most stable form **7** through the rapid hydrolysis of (B) (by the presence of unavoidable moisture) to give the intermediate (C), which undergoes further decomposition [15], yielding the cyclic structure **7** (through expulsion of two moles of dimethylamine).

On the other hand, we have found that the reaction of 1,3-diphenyl-2-(phenylimino)-3-(ylidenemethylacetate)-1-propanone **(5)** with excess of **6a**, employed as a solvent, was completed after heating at 80°C for one hour (thin-layer chromatography [TLC]). The reaction product was subjected to column chromatography to afford adduct **8a** (75% yield) as the sole reaction product (Scheme 4). The structure of the isolated compound **8a** is deduced from its analysis, IR, ^{1}H,^{31}P,^{13}C NMR, and mass spectral data. Elemental and mass spectral analyses for compound **8a** corresponded to an empirical formula $C_{29}H_{33}N_4O_2P$. Its IR spectrum reveals the absence of both C=O (ester) and C=N absorption bands recorded for **5** at 1710 and 1580 cm^{-1}, respectively. The spectrum shows, however, strong absorption bands at 2220 cm^{-1} (C=C=O), 1660 (C=O, Ar), 1325, and 862 cm^{-1} [P-N(CH$_3$)$_2$] [12]. The ^{1}H NMR spectrum of **8a** exhibits the absence of both singlets at $\delta = 3.55$, and 6.45, recorded for the methyl (=CHCOOCH$_3$) and methine (=CHCOO-CH$_3$) protons in the ^{1}H NMR spectrum of **5**. Moreover, the ^{1}H NMR spectrum of **8a** disclosed the presence of doublet at $\delta = 2.45$ with $J_{HP} = 11.10$ Hz, corresponding to the 18H of the three magnetically equivalent dimethylamino groups attached to the phosphorus atom P[N(CH$_3$)$_2$]$_3$ [16], and multiplet at 6.85–7.35 (m, 15H, Ar). Compound **8a** exhibits $\delta = -29.14$ in its^{31}P NMR spectrum, which is in full accord with the cyclic azaphospholene structure [14]. Actually, the mass spectrum of compound **8a** provided strong evidence in support of the cyclic azaphospholene adduct **8a**. The mass spectrum of **8a** yielded a prominent peak for M$^+$ at *m/e* 500 (100%).

Similarly, trisdiethylaminphosphine **6b** reacts with **5** at 90°C to yield product **8b** in 70% yield (Scheme 4).This compound has been identified on the basis of its elemental analysis, IR, ^{1}H,^{13}C,^{31}P NMR, and mass spectral data (cf. Experimental section).

We propose the reaction course depicted in Scheme 4. The reaction was assumed to proceed through nucleophilic attack of the phosphorus reagents at the α-carbon of the α,β-unsaturated ester group. The reaction was accompanied by elimination of one molecule of alcohol under the applied reaction conditions to afford the cyclic azaphospholene derivatives **8a,b** (Scheme 4).

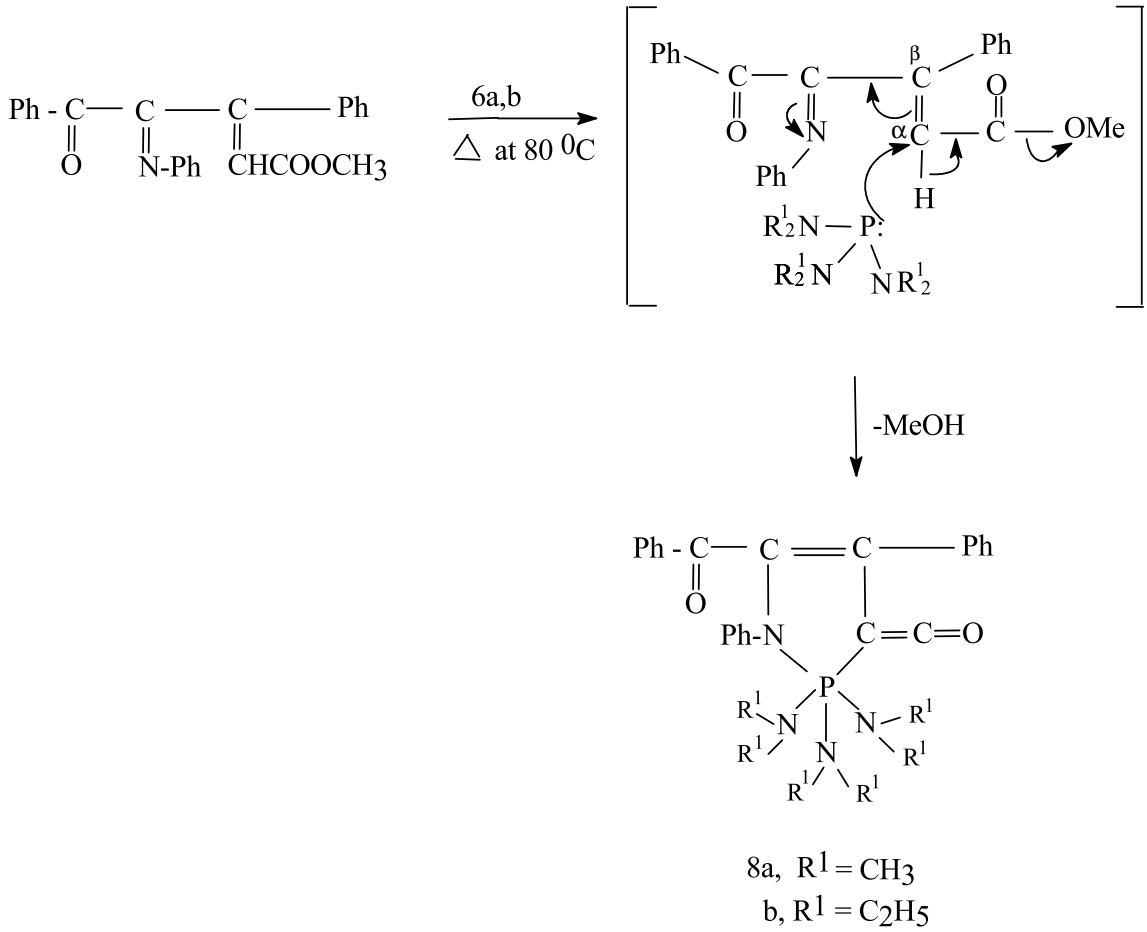


SCHEME 3

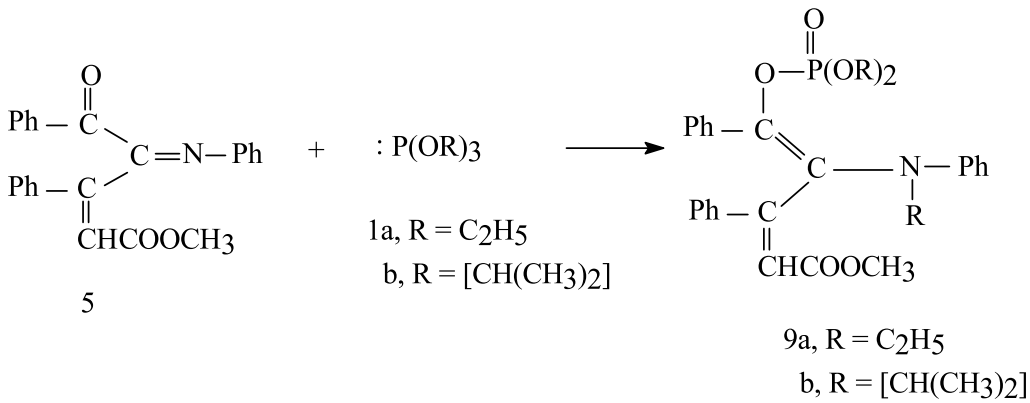
Next, the reaction of 1,3-diphenyl-2-(phenylimino)-3-(ylidenemethylacetate)-1-propanone **(5)** with trialkyl phosphites **1b,c** was also investigated. We have found that the reaction of triethyl phosphites and triisopropyl phosphites **1b,c** with **5**, in dry toluene, proceeds at reflux temperature to give chromatographically pure 1:1 adducts formulated as the dialkyl phosphate products **9a** and **9b**, respectively (Scheme 5). The structures of **9a** and **9b** are deduced from their elemental analysis, IR, ^{1}H, ^{13}C, and ^{31}P NMR, and mass spectral data (cf. Experimental section). Products **9a** and **9b** are presumably formed via addition of trialkyl phosphites to the most reactive center in compound **5** followed by group translocation (N-alkylation) (Scheme 5).

Furthermore, this study has been extended to include the behavior of **2a** and **2b** toward trisdialkylaminophosphines **6a,b** to determine the preferential site of attack.

Trisdimethylaminophosphine **6a** reacts with 1,3-diphenyl-2-(phenylimino)-1,3-propanedione **(2a)** at room temperature to give pure adducts assigned the open dipolar structure **10a** (Scheme 6) based on the following evidence: elemental and a molecular weight determination (MS) for **10a** support the molecular formula $C_{27}H_{33}N_4O_2P$. The IR spectrum of **10a** exhibits strong absorption bands at 1640 (C=O, Ar), 1312 cm^{-1}, and at 860 cm^{-1} $P[N(CH_3)_2]_3$. Moreover, its IR spectrum lacks both the C=N and P=O absorption bands at 1580 cm^{-1} and 1240 cm^{-1},



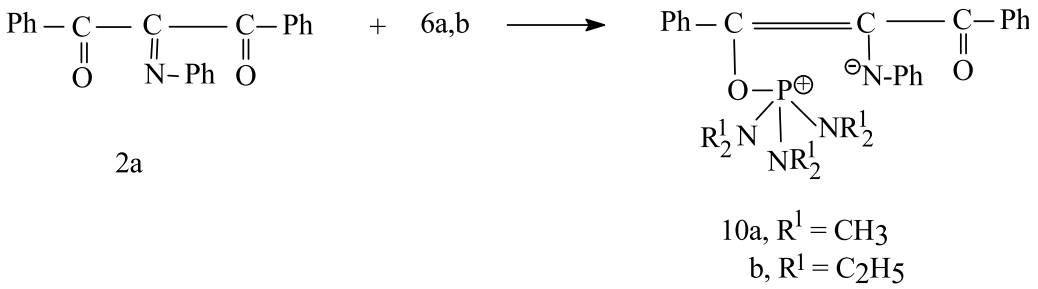
SCHEME 4



SCHEME 5

respectively. The ^{31}P NMR spectrum of **10a** showed a signal at $\delta = +40.62$, a value that falls in the range frequently recorded for the open dipolar structure. ^{1}H NMR, ^{13}C NMR, and mass spectral data of compound **10a** provided strong evidence in support of the dipolar ion structure **10a** (cf. Experimental).

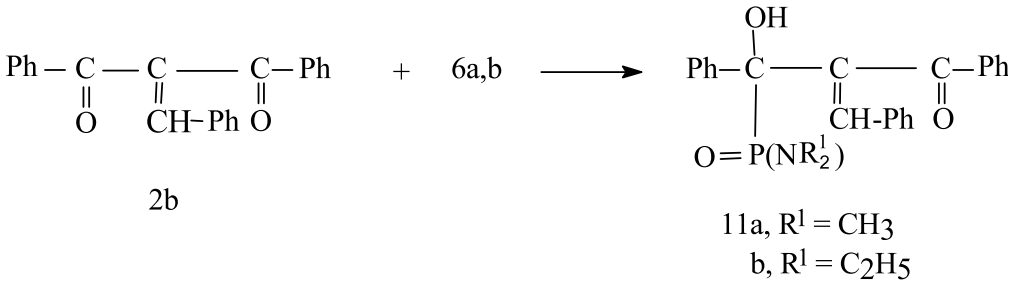
Similarly, trisdiethylaminophosphine **6b** reacts with **2a** to give the open dipolar structure **10b**. The



2a

10a, $R^1 = CH_3$
b, $R^1 = C_2H_5$

SCHEME 6



2b

11a, $R^1 = CH_3$
b, $R^1 = C_2H_5$

SCHEME 7

structure of **10b** is deduced from its analysis, IR, ^1H, ^{13}C, ^{31}P NMR, and mass spectral data (cf. Experimental section) (Scheme 6).

On the other hand, the reaction of trisdialkylaminophosphines **6a,b** with 1,3-diphenyl-2-(phenylmethylene)-1,3-propanedione **2b** proceeds, in refluxing benzene, to give the corresponding dialkylaminophosphonate adducts **11a** and **11b**, respectively (Scheme 7). The strctures of **11a,b** are indicated by their analyses, ^1H, ^{31}P, and ^{13}C NMR and mass spectral data (cf. Experimental section).

Whereas trisdialkylaminophosphines **6a,b** react with **2a**, yielding the dipolar adducts **10a,b**, a different behavior is observed when the same reagents react with **2b**, giving rise to the respective dialkyl phosphonate products **11a,b**.

CONCLUSIONS

From the results of the present investigation, it could be concluded that the reaction of 1,3-diphenyl-2-(phenylimino)-3-(ylidenemethylacetate)-1-propanone **(5)** with trisdialkylaminophosphines leads to different products, depending on the reaction conditions as well as the stability of the addition products.

The significance of these findings is not only the discovery of an anomalous behavior of trisdialkylaminophosphines, but also the demonstration of a novel route for the synthesis of new cyclic oxaza phospholene and azaphospholene products **(7,8)**.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were obtained with a Perkin-Elmer Infracord Spectrometer Model 157(Grating) in KBr discs. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ as solvent on a Joel-270 MHz spectrometer, and the chemical shifts were recorded in δ values relative to TMS. The ^{31}P NMR spectra were taken with a Varian CFT-20 (vs. external 85% H_3PO_4 standered). The mass spectra were performed at 70 eV on a shimadzu GCS-OP 1000 Ex spectrometer provided with a data system.

Reaction of 1,3-Diphenyl-2-(phenylimino)-3-(ylidenemethylacetate)-1-propanone **(5)** *with Trisdimethylaminophosphine* **(6a)**

Trisdimethylaminophosphine **6a** (0.32;0.002 mol) was added dropwise to a solution of compound **5** [1] (0.36 g, 0.01 mol) in dry toluene (30 ml) and the reaction mixture was refluxed for 4 hours. After evaporation of the volatile materials under

reduced pressure, the residue was applied to silica gel column chromatography using acetone/ petroleum ether (12:78, v:v) as eluent to give **7a** as yellow crystals, m.p. 173°C (yield 68%). Anal. Calcd. for $C_{26}H_{25}N_2O_4P$(460.46): C, 67.81; H, 5.47; N, 6.08; P, 6.72. Found: C, 67.84; H, 5.45; N, 6.05; P, 6.68. IR(KBr): 1240,1320,860,1710 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.62$\{d, 6H, J_{HP} =11.07 Hz, P[N(CH_3)$_2$]\}, 3.55 (s, 1H, =CHCOOCH$_3$), 6.45 (s, 1H, =CHCOOCH_3), and at 7.05–6.65 (m,15H,Ar.). ^{31}P NMR: δ = +40.89. ^{13}C NMR($CDCl_3$): $\delta = 163.5$ (COOCH$_3$), 135.1(C=CH), 119.8 (C=CH), 25.7 (COOCH$_3$), 147.5 (=CO, $^2J_{CP} = 13.01$ Hz), 132.34 (=C–N, $^2J_{CP} = 13.53$ Hz), 38.5 \{P[N(CH_3)$_2$]\}. MS: *m/z* (%) 460 (100) [M^+].

Similarly, **7b** was obtained as yellow crystals, m.p. 165°C (yield 65%). Anal. Calcd. for $C_{28}H_{29}N_2O_4P$(488.52): C, 68.84; H, 5.98; N, 5.73; P, 6.34. Found: C, 68.80; H, 6.01; N, 5.71; P, 6.30. IR (KBr): 1712 (C=O, ester), 1325, 865 (P–N–C), and 1242 cm^{-1} (P=O). ^1H NMR ($CDCl_3$): $\delta = 1.10$ (t, 6H, P[N-(CH_2CH_3)$_2$], 2.85 (q, 4H, P[N(CH_2CH_3)$_2$], 3.55 (s, 3H, COOCH$_3$), 6.45 (s, 1H, =CHCOOCH$_3$) and 7.10–8.01 (m, 15H,Ar.). MS: *m/z* (%) 488(100) [M^+].

Reaction of Compound **5** *with Trisdimethylaminophosphine* **6a** *(without solvent)*

A suspension of compound 5 (0.36 g, 0.001 mol), in 1 mL of trisdimethylaminophosphine **6a** was heated in an oil bath at 80°C for 1 hour. The reaction mixture was evaporated under reduced pressure, and the residue was subjected to silica gel column chromatography, using acetone/ petroleum ether (85:15, v:v) as eluent to give **8a** as orange crystals, m.p. 200°C (yield 75%). Anal. Calcd. for $C_{29}H_{33}N_4O_2P$ (500.28): C, 69.62; H, 6.65; N, 11.20; P, 6.19. Found: C, 69.60; H, 6.67; N, 11.17; P, 6.15. IR(KBr): 2220 (C=C=O), 1660, 1325, 862 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.45$\{d, 18H, P[N(CH3)$_2$]$_3$, J_{HP} =11.10 Hz\} and at 6.85–7.35 (m, 15H, Ar.) ^{31}P NMR: $\delta = -29.41$. ^{13}C NMR($CDCl_3$): $\delta = 196.6$ (C=O, Ar), 138.7 (N-C=, $^2J_{CP} = 12.80$ Hz), 135.89 (C=C-Ph, $^2J_{CP} = 12.80$ Hz), 141.08 (C=C=O, $^1J_{CP} = 145.21$ Hz), 184.81 (C=C=O, $^2J_{CP} = 20.2$ Hz), 37.36\{P[N(CH_3)$_2$]$_3$, J_{CP} = 6.1 Hz). MS: *m/z* (%) 500 (100) [M^+].

Similarly, trisdiethylaminophosphine **6b** was reacted with **5** at 90°C (temperature of oil bath), using ethyl acetate/petroleum ether (80:20, v:v) as eluent to give **8b** as yellow crystals, m.p. 188°C, (yield 70%). Anal. Calcd. for $C_{35}H_{45}N_4O_2P$ (584.75): C, 71.89; H, 7.75; N, 9.58; P, 5.29. Found: C, 71.85; H, 7.78; N, 9.56; P, 5.27. IR(KBr): 2230 (C=C=O),1660, 1325, 862 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.05$\{t, 18H, P[N(CH_2 CH_3)$_2$]$_3$\}, 2.90\{q, 12H, P[N(CH_2CH_3)$_2$]$_3$\}, and at 7.35–6.90 (m, 15H, Ar.) ^{31}P NMR: $\delta = -29.35$. ^{13}C NMR ($CDCl_3$): δ =144.5 (C=C=O, $^1J_{CP} = 141.07$ Hz), 187.0 (C=C=O, $^2J_{CP} = 20.4$ Hz), 41.2 \{P[N(CH_2CH_3)$_2$]$_3$, $^2J_{CP} = 4.9$ Hz), 14.4 \{P[N(CH_2CH_3)$_2$]$_3$\}. MS: *m/z* (%) 584(100) [M^+].

Reaction of Triethyl Phosphite **(1a)** *with 1,3-Diphenyl-2-(phenylimino)-3-(ylidenemethylacetate)-1-propanone* **(5)**

Triethyl phosphite **(1a)** (0.32g, 0.002 mol) was added dropwise to a solution of compound **5** (0.36 g, 0.001 mol) in dry toluene (30 mL), and the reaction mixture was refluxed for 6 hours. The reaction mixture was evaporated under reduced pressure, and the residue was subjected to silica gel column chromatography, using ethyl acetate/ petroleum ether (25:75, v:v) as eluent to give **9a** as white crystals, m.p. 89°C (yield 78%). Anal. Calcd. for $C_{30}H_{34}NO_6P$ (535.57): C, 67.28; H, 6.40; N, 2.61; P, 5.78. Found: C, 67.25; H, 6.45; N, 2.59; P, 5.77. IR(KBr): 1742, 1264, 1596, 1018 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 1.10$ (t,3H, NCH$_2$CH$_3$), 3.90 (q, 2H, NCH$_2$CH$_3$), 1.25 [t,6H,(O)P(OCH$_2$CH$_3$)$_2$], 4.05 [q, 4H,(O)P(OCH$_2$CH$_3$)$_2$], 3.52 (s, 3H, =CHCOOCH$_3$), 6.80 (s, 1H, =CHCOOCH$_3$), and at 7.59–8.10 (m, 15H, Ar). ^{31}P NMR: δ = +2.90. ^{13}C NMR ($CDCl_3$): δ = 131.53 (=C-O-P, $^2J_{CP}$ = 19.6 Hz), 141.4 (C=CH),143.9 (C=C-N(C_2H_5),123.8(C=CH),170.1 (CO-OCH$_3$), 63.3 (P-OCH$_2$CH$_3$, $^2J_{CP} = 18.3$ Hz), 16.4 (P-OCH$_2$CH$_3$), 40.5 (N-CH$_2$CH$_3$),16.2 (N-CH$_2$CH$_3$), 30.0 (COOCH$_3$). MS: *m/z* (%) 535 (40) [M^+], 353 (84) [M^+-OP (OC_2H_5)$_2$].

Similarly, 1,3-diphenyl-2-(phenylimino)-3-(ylidenemethylacetate)-1-propanone **(5)** (0.36 g, 0.001 mol) was reacted with triisopropyl phosphite **1c** (0.4g, 0.002 mol) in 30 mL dry toluene to give **9b** as white crystals, m.p. 68°C, yield (75%). Anal. Calcd. for $C_{33}H_{40}NO_6P$ (577.65): C, 68.61; H, 6.98; N, 2.42; P, 5.36. Found: C, 68.60; H, 7.02; N, 2.40; P, 5.35. IR(KBr):1742 (CO,ester),1260,1600, 1053 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.05[d, 6H, CH(CH$_3$)$_2$], 4.55 [q,1H, CH(CH$_3$)$_2$], 1.25\{2d, 12H, P[OCH-(CH$_3$)$_2$]$_2$\}, 4.65\{q, 2H, P[OCH(CH$_3$)$_2$]$_2$\},3.30 (s,3H,COOCH$_3$),6.85 (s,1H, =CHCOOH$_3$) and at 7.95–8.15 (m,15H, Ar.). ^{31}P NMR: δ = +0.90. ^{13}C NMR ($CDCl_3$): δ = 138.6 (=C–O–P, $^2J_{CP}$ = 19.6 Hz),140.4 (C=CH), 143.9 (C=C–N), 123.0 (C=CH),169.4(COOCH$_3$), 71.6 (P-O-CH, $^2J_{CP}$ = 22.0 Hz), 23.1[POCH(CH$_3$)$_2$, $^3J_{CP}$ = 6.1Hz],71.8[N-CH(CH$_3$)$_2$], 22..4[N-CH(CH$_3$)$_2$], 29.45 (COOCH$_3$). MS: *m/z* (%) 577 (5) [M^+], 352 (95){M^+-OP[OCH(CH$_3$)$_2$]$_2$}.

Reaction of 1,3-Diphenyl-2-(phenylimino)-1, 3-propanedione **(5)** *with Trisdimethylaminophosphine* **(6a)**

Trisdimethylaminophosphine **6a** (1 mL) was added dropwise to compound **5** (0.31 g; 0.001 mol), and the reaction mixture was kept at room temperature for 1 hour. The precipitate was filtered off and recrystallized from ethyl acetate to give **10a** as yellow crystals; m.p. 170°C (yield, 80%). Anal. Calcd. for $C_{27}H_{33}N_4O_2P$ (476.56): C, 68.04; H, 6.98; N, 11.76; P, 6.50. Found: C, 68.01; H, 7.01; N, 11.73; P, 6.48. IR(KBr): 1640 cm^{-1} (CO,Ar.),1312, 860 cm^{-1} (P–N–C). ^1H NMR ($CDCl_3$): δ = 2.75 {d, 18H, $P[N(CH_3)_2]_3$, J_{HP} = 13.50 Hz} and at 7.40–6.80 (m, 15H, Ar.). ^{31}P NMR: δ = +40.62. ^{13}C NMR($CDCl_3$): δ = 186.0 (C=O),145.1(P–O–<u>C</u>=, $^2J_{CP}$ = 16.80 Hz), 144.4 (C=<u>C</u>-N, $^3J_{CP}$ = 6.70 Hz), 37.8 {$P[N(\underline{CH}_3)_2]_3$, $^2J_{CP}$ = 4.9 Hz). MS: *m/z* (%) 476 (100) [M^+], 297 (25) {M^+-(O)$P[N(CH_3)_2$}.

Similarly, trisdiethylaminophosphine **6b** was reacted with compound **5** at room temperature. The precipitate was filtered off and recrystallized from cyclohexane to give **10b** as yellow crystals; m.p. 166°C (yield, 75%). Anal. Calcd. for $C_{33}H_{45}N_4O_2P$ (560.72): C, 70.68; H, 8.09; N, 9.99; P, 5.52. Found: C, 70.67; H, 8.12; N, 9.96 ; P, 5.50. IR(KBr): 1643 cm^{-1} (C=O, Ar.), 1312, 860 cm^{-1} (P–N–C), 1478 cm^{-1} (C–O–P). ^1H NMR ($CDCl_3$): δ = 1.15{t, 18H, $P[N(CH_2\underline{CH}_3)_2]_3$}, 3.50 {q, 12H, $P[N(\underline{CH}_2\text{-}CH_3)_2]_3$}, and at 7.35–6.85 (m, 15H, Ar.). ^{13}C NMR($CDCl_3$): δ = 189.0(C=O),145.0 (P–O–<u>C</u>=C, $^2J_{CP}$=16.8Hz), 143.0 (=<u>C</u>–N, $^3J_{CP}$ = 6.5 Hz), 42.0 {$P[N(\underline{CH}_2CH_3)_2]_3$), 14.1 {$P[N(CH_2\underline{CH}_3)_2]_3$}. MS: *m/z* (%) 560 (60) [M^+].

Reaction of Trisdimethylaminophosphine **6a** *with 1,3-Diphenyl-2-(phenylmethylene)-1,3-propanedione* **2b**

A mixture of **6a** (0.31 g,0.001 mol), trisdimethylaminophosphine **2b** (0.16, 0.001 mol), and dry benzene were refluxed for 2 hours. The volatile materials were evaporated in vacuo, and the residual substance was subjected to silica gel column chromatography, using acetone/ petroleum ether (40:60, v:v) as eluent to give **11a** as yellow crystals, m.p. 161°C (yield 70%). Anal. Calcd. for $C_{26}H_{29}N_2O_3P$ (448.50): C, 69.62; H, 6.51; N, 6.24; P, 6.90. Found: C, 69.60; H, 6.49; N, 6.22; P, 6.88. IR (KBr): 3400 cm^{-1} (OH), 1657 cm^{-1} (Ph-C=O). ^1H NMR: δ = 2.50 (d,12H, $P[N\text{-}(CH_3)_2]$, 7.05 (s,1H, =CHPh), 8.10–7.21 (m, 15H, Ar.), and at 8.22 (br, 1H, OH, exchangeable with D_2O). ^{31}P NMR: δ = +25.43. ^{31}C NMR: δ = 136.0 (C-P,$^1J_{CP}$ = 101.25 Hz), 194.35(C=O),134.25 (<u>C</u>=CH), 118.07 (C=<u>CH</u>), 35.9{P[N ($\underline{CH}_3)_2]_2$, $^3J_{CP}$ = 3.7 Hz}. MS: *m/z* (%) 448(100) [M^+].

Similarly, trisdiethylaminophosphine **6b** was reacted with compound **2b** to yield **11b** (eluent ethyl acetate/ petroleum ether [20:80, v:v]) as white crystals, m.p. 218°C (yield 70%). Anal. Calcd. for $C_{30}H_{37}N_2O_4P$(504.61): C, 71.40; H, 7.39; N, 5.55; P, 6.31. Found: C, 71.38; H, 7.37; N, 5.52; P, 6.29. IR (KBr): 3449 (OH), 1662 (C=O), 1313, 882 (P–N–C), and 1247 cm^{-1} (P=O). ^1H NMR: δ = 1.10, 0.9 {2t, 12H, $P[N\text{-}(CH_2\underline{CH}_3)_2]_2$}, 2.85, 2.70 (2q, 8H, $P[N(\underline{CH}_2CH_3)_2]_2$), 7.10–8.01 (m, 15H, Ar.), and 8.25 (br, 1H, OH, exchangeable with D_2O). ^{31}C NMR : δ = 132.4 (C–P, $^1J_{CP}$ = 96..4 Hz), 192.6 (<u>C</u>=O),139.2 (C=<u>CH</u>),117.5 (C=CH), 40.6 {$P[N(CH_2\ \underline{CH}_3)_2]_2$}, 14.8 {$P[N(CH_2\underline{CH}_3)_2]_2$}. MS: *m/z* (%) 505(60) [M^+].

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