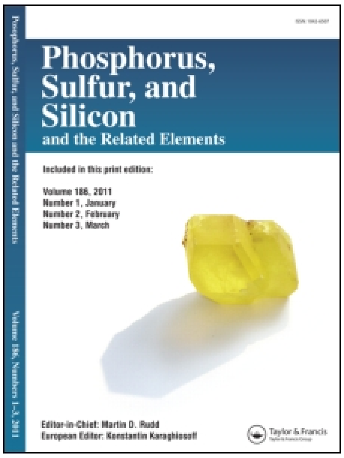

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STUDIES ON PHOSPHONIUM YLIDS—X. THE BEHAVIOUR OF *N,N'*-2,5-CYCLOHEXADIENE-1,4-DIYLIDENEBIS [BENZAMIDE] TOWARDS WITTIG REAGENTS

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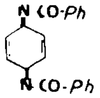
Methylenetriphenylphosphoranes (**2a–b**) react with *N,N'*-2,5-cyclohexadiene-1,4-diylidenebis [benzamide] (**1**) yielding the new ylid-phosphorane adducts **3a** and **3b**, respectively. Quinoneimine 1 is reduced mainly to *p*-phenylenedibenzamide (**7**) when treated with ylid **2c** under similar conditions. Structures of the new products were established by analytical and Spectroscopic (IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and MS) results. A mechanism is proposed to explain the formation of compounds **3**.

Key words: *N,N'*-2,5-cyclohexadiene-1,4-diylidenebis(benzamide) **1**; Carbmethoxymethylenetriphenylphosphorane **2a**; Carbethoxymethylenetriphenylphosphorane **2b**; benzoylmethylenetriphenylphosphorane **2c**; Methyl-2,5-bis(benzoylamino)-α-(triphenylphosphoranylidene) benzeneacetate **3a**; Ethyl 2,5-bis(benzoyl-amino)-α-triphenylphosphoranylidene) acetate **3b**.

INTRODUCTION

Although the action of phosphonium ylids on o-quinoneimines is well established,[1] their action on *p*-quinoneimines has hitherto not been investigated. This besides our current interest in the chemistry of phosphonium ylids,[1-9] has stimulated us to investigate the behaviour of *N,N'*-2,5-cyclohexadiene-1,4-diylidenebis [benzamide] (1) towards a number of Wittig reagents of type **2**.

Nomenclature is in the line of recent Chemical Index Names.



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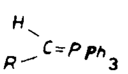
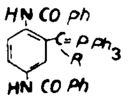


2a, $R = COOCH_3$
b, $R = COOC_2H_5$
c, $R = CO\,Ph$

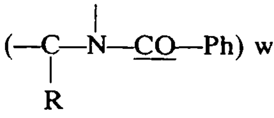


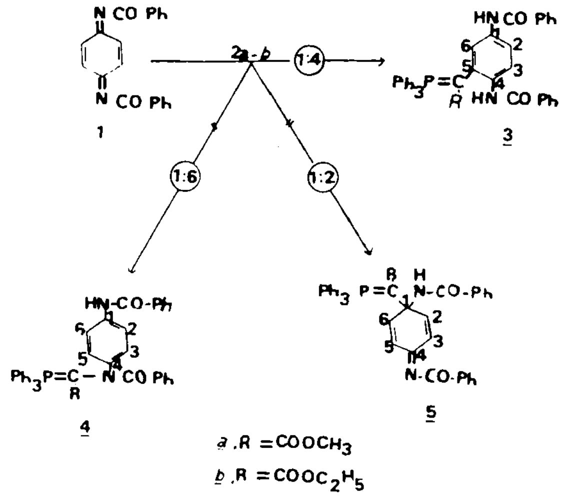
3a, $R = COOCH_3$
b, $R = COOC_2H_5$

RESULTS AND DISCUSSION

We have found that when *N,N'*-2,5-cyclohexadiene-1,4-diylidenebis (benzamide) (**1**) was allowed to react with methoxy-, ethoxymethylene-triphenylphosphoranes (**2a–b**), in dry benzene, colourless crystalline 1:1 adducts (**3a–3b**) are formed in almost quantitative yields. Triphenylphosphine and/or triphenylphosphine oxide were neither isolated nor identified in the reaction medium by (TLC) in each case. Compounds **3** are chromatographically pure and possess sharp melting points. These adducts are formulated as alkyl-2,5-bis (benzoylamino)-α-(triphenylphosphoranylidene) benzeneacetate (**3a**, **b**) based on the following proofs: (1) Correct elemental analysis and molecular weight determination (MS) were obtained for each product. (2) The IR spectra of these adducts (**3a–b**) reveal the presence of two strong -NH absorption bands around 3340 and 3100 cm^{-1}, respectively. Moreover, the strong C=N absorption band appearing at 1580 cm^{-1} with quinoneimine **1**, vanished completely in the spectra of both **3a** and **3b**. The IR spectra of adducts 3 exhibit strong absorption bands around 1680 and 1505 cm^{-1} characteristic for the $>$C=P group absorption[10], around 1400 cm^{-1} denoting the $>$P—C≡ (phenyl absorption)[11], and around 1626 cm^{-1} which corresponds to shifted ester $>$C=O bands[12] (cf. Experimental). (3) Adducts **3a–b** possess ylid phosphorane structure since they exhibit a positive shift in their ^{31}P NMR spectra (vs. 85% H_3PO_4) and absorb in the region characteristic for this class of compounds.[10,13–15] (4) ^{1}H NMR spectrum (400 MHz) of ethyl-2,5-bis (benzoylamino)-α-(triphenylphosphoranylidene) benzeneacetate (**3b**), taken as example, showed signals at $\delta = 0.53$ (3H, ethoxy-CH_3, t); 3.80 (2H, ethoxy-CH_2, q) and at 8.25–7.11 (28H, aromatic, m). The two NH protons gave two singlets (exchangeable with D_2O) at 10.06 and 9.20 ppm. This spectrum also showed a doublet centered at 8.24 ppm (J H2H3 = 6.7 Hz) ascribed to the C-2 proton (Scheme 1). H-3 appeared as a doublet centered at 8.09 ppm with coupling constant value of (J H3H2 = 6.7 Hz) which are identical with those values cited for the aromatic protons in ortho[16,17] position to each other, in addition to one proton at 7.43 ppm(s) attributed to H-6. These data are most adequately accommodated in structure **3** since in the alternative formula **4** obtainable via 1:6-addition reaction, the P-NMR spectra would have given an AA'BB' system due to H-2,3,5, and 6 (24 lines) accompanied with the appearance of only one NH group (Scheme 1).

On the other hand, structure like **5** is also excluded since its P-NMR would have given two protons doublets at ≃6.7 ppm (H-2 & H-6) and another pair of doublets at about 7.1 ppm (H-3 & H-5)[16,17] in addition to only one NH group (Scheme 1).

Actually, the ^{13}C NMR spectra (400 MHz) offered strong evidence in support of the ylid-phosphorane linkage incorporated in structure **3**. The ^{13}C NMR of compound **3b** (in CD_2Cl_2), taken as example, exhibited a doublet at 52.31 ppm ($\geqslant$P=C, $J = 130$ Hz)[18] and two (—NH—$\underline{\mathrm{CO}}$—Ph) carbonyl groups at 165.33 and 164.87 ppm, respectively. These values are in accord with structure **3** since in a formula like **4**, one carbonyl group  $(\text{—}\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}\text{—}\overset{|}{\mathrm{N}}\text{—}\underline{\mathrm{CO}}\text{—Ph})$ would have appeared in the range of 180–190 ppm and the other carbonyl in the range 160 to 170 ppm.[19] Also in a formula like **5** there would have been one carbonyl group (—NH—$\underline{\mathrm{CO}}$—Ph) in the range of 160 to 170 ppm[11] and another one (=N—$\underline{\mathrm{CO}}$—Ph) at about 200 ± (10 ppm).[11] As regards C-1 and C-4, in formula **5**, these would have appeared at 55–60 ppm and at 145–160 ppm, respectively.[11,19–20]



SCHEME 1

Actual investigation of ^{13}C NMR spectra of compounds **3** ($R = COOCH_3/R = COOC_2H_5$) proved that C-1 appears at (131.25/131.28) and C-4 appears at (131.10/131.16) which is only in full accord of structure **3** (cf. Table I).

The mass spectrum of compound **3b** yielded a prominant ion peak at m/e 662 (M^+, 25%), 616 (662-HOEt, 14%), 542 (662—Ph—CO—NH, 3%), 512 (662—Ph—COOEt, 4%), 400 (662—$C_{18}H_{15}P$, 18%), 384 (662—$C_{18}H_{15}PO$, 96%), 278 ($C_{18}H_{15}PO$, 96%), and 262 (TPP).

A possible explanation of the course of the reaction of phosphonium ylids **2** with *N*,*N*′-2,5-cyclohexadiene-1,4-diylidenebis (benzamide) (**1**) is shown in Scheme 2.

Adducts (**3**) can be obtained by 1:4 addition of ylids **2** to the starting quinoneimine **1** affording the stable ylid phosphoranes (**3**) possibly via rearrangement of an intermediate like (**6**) (Scheme 2).

Although *p*-benzoquinone has been reported[21] to react with two equivalents of ylid **2a** yielding 2-(4-hydroxyphenyl)-1,2-dimethoxycarbonylethylidenetriphenylphosphorane, a different behaviour is observed in this work in the reaction of *p*-quinoneimine 1 with the same reagent where 1:4-addition reaction takes place to form a new type of ylid-phosphoranes (**3**).

Worthy to mention is that quinoneimine 1 yields only the mono-ylid phosphorane adducts (**3a–b**) even when it is allowed to react with two equivalents of the ylid-reagent. This is equally true, when the formed adduct e.g. 3a was further reacted with one mole of ylid **2a** under similar conditions.

This finding, which represents a novel route to (**3**) supplements to the expanded utility of reagent **2** for the production of new ylid phosphorane adducts.

On the other hand quinoneimine **1** is reduced mainly to *p*-phenylenedibenzamide (**7**), when treated with benzoylmethylenetriphenylphosphorane **2c** under similar conditions.†

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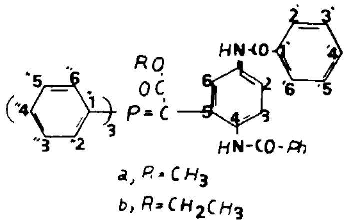
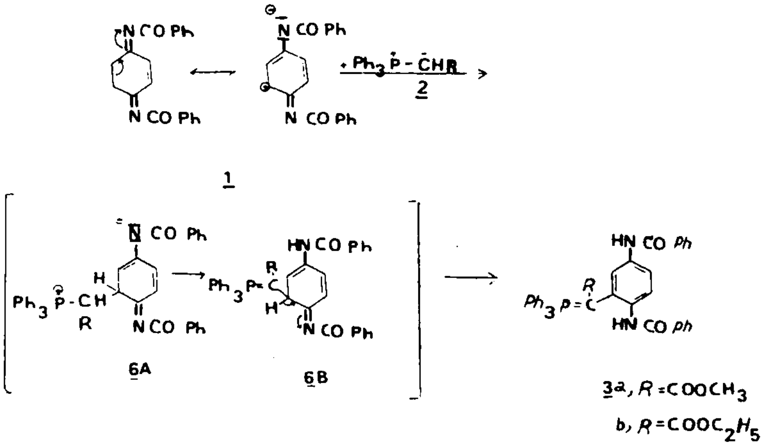
† In many miscellaneous addition reactions, reduction occurred to a greater or lesser extent in presence of reagents which are normally not considered to have reducing properties.[22]

TABLE I

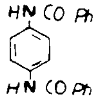
^{13}C NMR of 3a and 3b



No.	a. (ppm)	b. (ppm)
NH—CO	165.31 and 164.81	165.33 and 164.87
1′	135.411	135.24
4′	135.214	135.26
1″	134.630 ($^{1}J_{C-P} = 92.6$ Hz)	134.61 ($^{1}J_{C-P} = 95.6$ Hz)
2″/6″	133.66 ($^{2}J_{C-P} = 9.5$ Hz)	133.53 ($^{2}J_{C-P} = 9.1$ Hz)
4″	131.78	131.78
1	131.25	131.28
4	131.10	131.16
5	130.62 ($^{2}J_{C-P} = 12.2$ Hz)	130.66 ($^{2}J_{C-P} = 12.2$ Hz)
3″/5″	128.26 ($^{3}J_{C-P} = 9.1$ Hz)	128.43 ($^{3}J_{C-P} = 9.1$ Hz)
2′/6′	127.36	127.401
3′/5′	127.000	127.000
6	120.12	120.306
3	119.27	118.93
2	118.000	115.30
CH_3	50.47	14.01
CH_2	—	58.27



SCHEME 2



7

From the results of the present investigation, it could be noticed that the reaction between quinoneimine **1** and phosphonium ylids (**2a–c**) depends upon the nature of the ylid reagent. Moreover, the present study clearly shows that *p*-quinoneimine **1** behaves in a similar manner to that reaction of *o*-quinoneimine with Wittig reagents where 1,4-addition takes place.[1]

EXPERIMENTAL

All melting points are uncorrected. The benzene used was dried over Na. Carbmethoxyethylene,[23] carbethoxymethylene,[23] and benzoylmethylene-triphenylphosphorane[24] were prepared according to established procedures. The IR spectra were measured in KBr, on Perkin-Elmer Infracord Spectrometer Model 157 (Grating). The ^{1}H NMR spectra were taken in CD_2Cl_2 or $CDCl_3$ on JNM-GX-400 Fa Jeol, Tokio, Spectrometer. The ^{31}P-NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 (vs. H_3PO_4 as external standard) on JNM-PS-100 Fa, Jeol Spectrometer. ^{13}C NMR spectra were taken in $CDCl_3$ or CD_2Cl_2 on JNM-PS-100 Fa Jeol and JNM-GX-400 Fa Jeol Spectrometer. The mass spectra were run at 70 eV on Kratos MS equipment and/or Varian MAT 311 A Spectrometer.

Methyl-2,5-bis(benzylamino)-α-(triphenylphosphoranylidene)-benzeneacetate (**3a**). To a suspension of quinoneimine **1** (0.31 g, 0.001 mole)[25] in absolute benzene (10 ml), was added ylid **2a** (0.33 g, 0.001 mole) in benzene (10 ml) and the reaction mixture was left at room temperature under stirring for 24 hr. The colourless precipitated material was filtered off, washed with benzene (2 ml) and recrystallized from benzene to give **3a** as colourless crystals (0.60 g, 93%), m.p. 236°C. Anal. Calcd. for $C_{41}H_{33}N_2O_4P$ (648.74) C, 75.90; H, 5.12; N, 4.32; P, 4.77. Found: C, 75.88; H, 5.19; N, 4.37; P, 4.8% Mol. Wt. (MS) = 648 IR bands at 3310, 3280 cm^{-1} (NH), 1680, 1505 (C═P), 1490, 1115 (P—C(phenyl)), 1670, 1650 cm^{-1} (C═O, amidic), 1625 (C═O, acyl ylid), and 1310 cm^{-1} (C—O, stretching).

^{1}H NMR (in CD_2Cl_2 and expressed in δ-scale ppm): signals at 3.55 (3H, OCH_3, s), 8.25–7.2 (28 H, aromatic, m), 10.06, 9.17 (NH, two sharp singlets, exchangeable with D_2O), H-2 (8.24, d), and H-3 at 8.07 with $J_{H2\,H3} = J_{H3\,H2} = 8$ Hz). H-6 (7.37, s).

^{31}P NMR (in CD_2Cl_2, vs 85% H_3PO_4): +20.35 ppm (MS) m/e (relative intensity %) 648(22), 616(M^+—CH_3OH), 570 ($M^+ - 78$), 528 (M^+—Ph—CO—NH), 512 (M^+—ph—$COOCH_3$), 386 (M^+—TPP)(80), 370 (M^+—TPPO) (96), and 316 (Ph—CO—NH)$_2$—C_6H_4].

Ethyl 2,5-bis(benzoylamino)-α-(triphenylphosphoranylidene benzeneacetate (**3b**). Quinoneimine **1** (0.31 g, 0.001 mole) in dry benzene (10 ml), was added to a suspension of ethoxymethylenetriphenylphosphorane **2b** (0.34 g, 0.001 mole) in dry benzene (10 ml) and the reaction mixture was left under stirring at room temperature for 24 hr. The colourless precipitated material was filtered off, washed with benzene (2 ml) and recrystallized from benzene to give **3b** as colourless crystals in 92% yield. m.p. 238°C Anal. Calcd for $C_{42}H_{35}N_2O_4P$ (662.774) C, 76.11; H, 5.32; N, 4.22; P, 4.67. Found: C, 76.15; H, 5.32; N, 4.3; P, 4.68 % Mol. Wt (MS) 662.

IR: bands at 3340, 3280 cm^{-1} (NH), 1680, 1505 (C═P), 1485, 1105 (P—C, phenyl), 1650, 1645 cm^{-1} (C═O, amidic), 1625 cm^{-1} (C═O, acyl ylid) and at 1290 cm^{-1} (C—O, stretching). ^{1}H NMR in $CDCl_3$, expressed in δ ppm: Signals at 0.53 (3H, ethoxy—CH_3, t), 3.80 (2H, ethoxy CH_2, q), 10.05, 9.20 (NH, two singlets exchangeable with D_2O), 8.24 (1H, d with $J_{H2\,H3} = 6.7$ Hz), 8.09 (1H, d, with $J_{H3\,H2} = 6.7$ Hz), and 7.43 (1H, s (H-6)).

^{31}P NMR in $CDCl_3$ = +20.845 ppm (MS) m/e 662, 616 ($M^+ -$ HOEt), 584 (M^+—C_6H_6), 542 (662—Ph—CO—NH), 512 (662—Ph—COOEt), 400, 384, 356, 278, and 262.

Action of ylid **2c** *on quinoneimine* **1**. Quinoneimine **1** (0.001 mole) in 10 ml dry benzene was added to a suspension of ylid **2c** in dry benzene (10 ml) and the reaction mixture was left under stirring at room temperature for 24 hr. The colourless crystalline product was filtered off, washed with ethanol, dried, crystallized from dimethylformamide and proved to be p-phenylenedibenzamide (m.p., mixed m.p. and comparative IR spectra).[25] The filtrate was evaporated and proved to be TPPO (mixed m.p. with authentic sample).

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