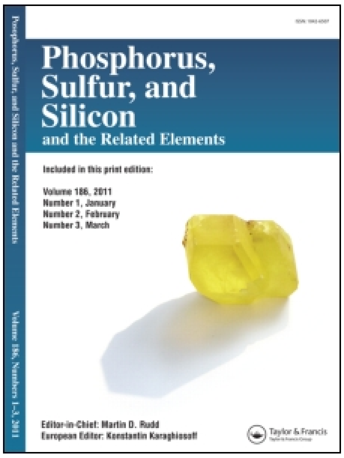

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STUDIES ON PHOSPHONIUM YLIDS—VIII. WITTIG REACTION WITH *N,N'*-3,5-CYCLOHEXADIENE-1,2-DIYLIDENEBIS[BENZAMIDE]

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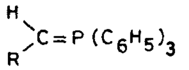
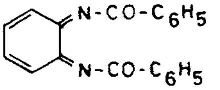
The reaction of methylenetriphenylphosphoranes (**1**) with *N,N'*-3,5-cyclohexadiene-1,2-diylidenebis [benzamide] (**2**) afforded new ylid-phosphoranes of type **3**. The mechanism that accounts for formation of adducts **3** is discussed. Structural reasoning for compounds **3** was based on compatible analytical, chemical and spectroscopic results.

INTRODUCTION

The behaviour of o-quinones[1–3] towards Wittig reagents has been extensively studied. To the best of our knowledge, however, the behaviour of *N,N'*-3,5-cyclohexadiene-1,2-diylidenebis [benzamide] (**2**)† towards the same reagents (**1**) has as yet not been reported.


$HRC{=}P(C_6H_5)_3$

1 a, R = $COOCH_3$
b, R = $COOC_2H_5$
c, R = COC_6H_5
d, R = $COCH_3$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RESULTS AND DISCUSSION

We have found that methylenetriphenylphosphranes **1a–d** react with *N,N'*-3,5-cyclohexadiene-1,2-diylidenebis [benzamide] **2**, in dry benzene, to give colourless 1:1 adducts formulated as **3a–d**, respectively. Triphenylphosphine oxide (TPPO) was neither isolated nor identified in the reaction medium by (TLC) in each case. Compounds **3** are chromatographically pure and possess sharp melting points. Structure **3** was attested by the following evidence: (a) Correct elementary analyses and molecular weight determination by (MS) were obtained for all the products. (b) Adducts **3** 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.[4–7] (c) The IR spectra of these adducts (in KBr), reveal the presence of two strong –NH absorption bands around 3300

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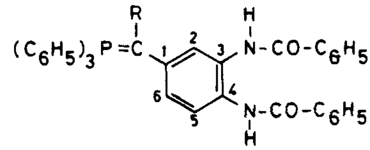
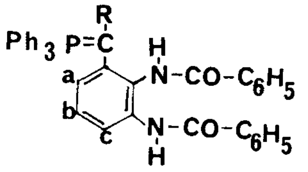
† Nomenclature is in the line of recent Chemical Abstract Index Names.



3 a , R = $COOCH_3$
b , R = $COOC_2H_5$
c , R = COC_6H_5
d , R = $COCH_3$

and 3160 cm^{-1}, respectively. Moreover, the IR spectra of adducts **3** exhibit strong absorption bands around 1680 and 1505 cm^{-1} characteristic for the $>C{=}P$ group absorption[4] and around 1400 cm^{-1} for the $>P{-}C$ (phenyl) absorption.[8] (d) The ^1H NMR spectrum of methyl 3,4-bis(benzoylamine)-α-(triphenylphosphoranylidene)benzeneacetate (**3a**), taken as example, showed signals at $\delta = 3.27$ (3H, OCH_3, s); and at 7.58–7.2 (25H, aromatic, m). The two NH protons gave two singlet (exchangeable with D_2O) at $\delta = 9.33$ and 8.87 ppm. It also shows a doublet centered at $\delta = 6.72$ ppm with $J_{H2H6} = 2.3$ Hz ascribed to the C-2 proton. This value is in full accord with the value expected for aromatic protons in meta position to each other.[9] The two ortho methine protons at C-5 and C-6 appear as a pair of doublets at $\delta = 7.91$ and 7.86 ppm with coupling constant values of $J_{H5H6} = 7.3$ Hz and $J_{H6H2} = 2.3$ Hz which are identical with those values cited for the aromatic protons in ortho,[9,10] and in meta position to each other.[9] These data are most adequately accommodated in structure **3** since alternatively in a formula such as **5** having the three protons a, b, and c adjacent, proton a would be coupled with proton b in (7–10 Hz) and with proton c in (1–3 Hz).[11] Also, if it were an a, b, c system then long range coupling would be expected with the phosphorus atom with ultimate appearance of a maximum with 8 lines. Moreover, proton b would have appeared as a doublet of doublets due to the ortho coupling with a and c. Furthermore, proton c would have behaved also in a fashion similar to proton a. This is not the case since only one doublet appeared at $\delta = 6.72$ with ($J_{H2H6} = 2.3$ Hz) which is in favour of structure **3**.

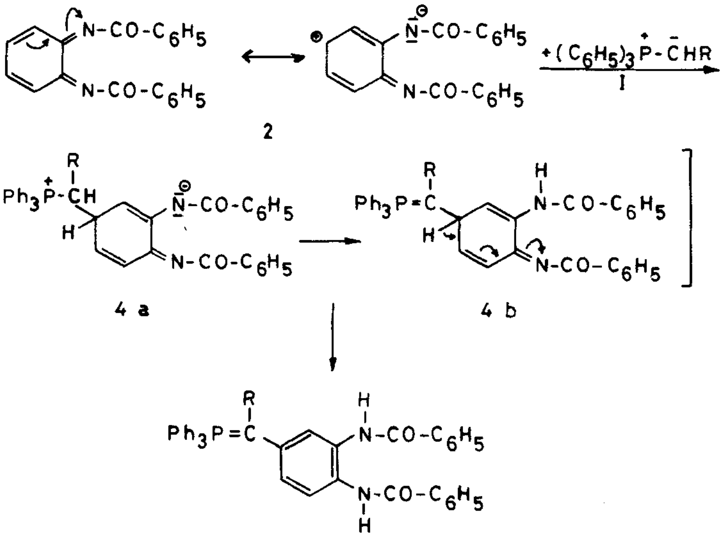


5a , R = $COOCH_3$
b, R = $COOC_2H_5$
c , R = COC_6H_5
d , R = $COCH_3$

Actually the ^{13}C NMR spectrum offered strong evidence in support of the ylid-phosphorane linkage incorporated in structure **3**. ^{13}C NMR of compound **3a** (in $CDCl_3$) taken as example shows a doublet at $\delta = 52.3125$ ppm ($>$P=C, $J = 130$ Hz),[12] doublet at $\delta = 192.35$ ppm (C=O, ester) with coupling constant $J = 80$ Hz,[12] and a singlet at 50.720 ppm (s, $-OCH_3$).[12]

The mass spectrum of compound **3a** gives a prominent ion peak at m/e 648 (^+M, 3%), 386 ($648-C_{18}H_{15}P$, 6%), and 262 ($C_{18}H_{15}P$, 90%).

A possible explanation for the course of the reaction of phosphonium ylids **1** with *N,N'*-3,5-cyclohexadiene-1,2-di-ylidenebis[benzamide] (**2**) is shown in "Scheme I". Adducts (**3**) can be obtained by 1:4-addition of ylids (**1**) to the starting quinoneimine (**2**) affording the stable ylid-phosphoranes (**3**), possibly via rearrangement of an intermediate like (**4**) (Scheme I).



3 a, R = $COOCH_3$
b, R = $COOC_2H_5$
c, R = COC_6H_5
d, R = $COCH_3$

SCHEME I

Worthy to mention is that quinoneimine **2** yields only the mono-ylid phosphorane adducts (**3a–d**) 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 a mole of ylid **1a** under similar conditions.

Although stabilised ylids[1] of type **1** react with o-quinones according to the Wittig mechanisms,[1-3] yielding the respective ethylene and TPPO, a different course is observed in the reaction of the same reagent with quinoneimine **2** where 1:4-addition reaction takes place to form a new type of ylid-phosphoranes **3**.

The present study clearly shows that o-quinonedimines behave similar to the reaction of 1-methyl-benzoquinol-(1,2)-acetate (**1**) with benzylidene-triphenylphosphorane where 1,4-addition takes place.[13]

The results of the present investigation are of particular significance since they report on a novel route for the production of certain ylid-phosphorane (cf. 3) by the utilization of Wittig reagents.

EXPERIMENTAL

All melting points are uncorrected. The benzene used was dried over Na. Carbmethoxymethylene,[14] carbethoxymethylene,[14] benzoylmethylene,[15] and acetylmethylene-triphenylphosphorane[15,16] were prepared according to established procedures. The IR spectra were measured in KBr, on Perkin–Elmer Infracord Spectrometer Model 157 G (Grating). The ^{1}H NMR spectra were taken in $CDCl_3$ or CD_2Cl_2 on a Varian A-60, T-60, HA-400 Spectrometers. The ^{31}P-NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 (vs. H_3PO_4 as external standard) on Varian CFT 20, 32 MHz Spectrometer. The mass spectra were run at 70 eV on Kratos MS 50 equipment and/or Varian MAT 711 Spectrometer.

Methyl 3,4-bis(benzoylamino)-α-(triphenylphosphoranylidene)-benzeneacetate (**3a**)
To a suspension of quinoneimine **2**[17] (0.31 g, 0.001 mole) in dry benzene (10 ml), was added ylid **1a** 0.33 g, 0.001 mole) in benzene (10 ml) and the reaction mixture was left at room temperature for 24 hr. The colourless precipitated material was filtered off, washed with benzene (2 ml) and recrystallized from chloroform-benzene to give **3a** as colourless crystals (0.58; 89%), mp. 229°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, 75.87; H, 5.20; N 4.37; P, 4.72%, Mol. wt. (MS) = 648.

IR bands at 3260, 3160 (NH), 1680, 1505 (C=P), 1490, 1115 (P—C (phenyl)), 1670, 1650 cm^{-1} (C=O, amidic), 1630 (C=O, acyl ylide),[18] and 1310 cm^{-1} (C—O, stretching).

^{1}H NMR (in CD_2Cl_2 and expressed in δ-scale ppm): signals at 3.27 (3H, OCH_3, s), 7.58–7.2 (25H, aromatic, m), and 9.33, 8.87 (NH, two s, exchangeable with D_2O).

^{31}P NMR (in CD_2Cl_2, vs. 85% H_3PO_4): +19.41 ppm. (MS) m/e (relative Intensity %) 648 (3), 386 (6), 316 (32), 262 (90), and 183 (38).

Similarly, the reaction of compound **2** with ethoxymethylenetriphenylphosphorane (**1b**), benzoylmethylenetriphenylphosphorane (**1c**), and acetylmethylenetriphenylphosphorane (**1d**) afforded (**3b**), (**3c**), and (**3d**), respectively.

The colourless crystals of ethyl 3,4-bis (benzoylamino)-α-(triphenylphosphoranylidene) benzeneacetate (**3b**) were obtained (85%) from chloroform-benzene, mp. 232°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, 76.12; H, 5.38; N, 4.32; P, 4.7% Mol. Wt. (MS) = 662.

IR: bands at 3240, 3165 (NH), 1680, 1505 (>C–P), 1485, 1105 (>p–C, phenyl), 1655, 1640 (C=O, amidic), 1635 (C=O, acyl ylid), and 1295 cm^{-1} (C—O, stretching).

^{1}H NMR in $CDCl_3$, expressed in δ-ppm: Signals at 3.67 (3H, ethoxy-CH_3), 1.79 (2H, ethoxy-CH_2, q), 9.43, 9.10 (NH, two singlet exchangeable with D_2O), 6.81 (1H, d with $J_{HH} = 2.6$ Hz), 7.90, 7.87 (2H, pair of doublets with $J_{HH} = 7.9$; $J_{HH} = 2.6$ Hz).

^{31}P NMR in DMSO-d_6, expressed in δ-ppm; +18.68 ppm (MS) m/e (relative Intensity) 662 (1), 400 (26), 372 (4), 316 (45), 262 (97), and 183 (93)%.

N,N'] [4-[2-Oxo-2-phenyl-1-(triphenylphosphoranylidene) = ethyl]-1,2-phenylene] bis [benzamide] (**3c**) was obtained in 80% yield as colourless crystals from chloroform-benzene, mp. 230°C. Anal. Calcd. for $C_{46}H_{35}N_2O_3P$ (694.81) C, 79.51: H, 5.07; N, 4.03; P, 4.46. Found: C, 79.55; H, 5.1; N, 4.09; P, 4.45%, Mol. Wt. (MS) = 694.

IR: bands at 3270, 3150 (NH), 1680, 1505 (C=P), 1480, 1115 (P—C (phenyl)), 1660, 1665 (C=O, amidic), 1635 (C=O, acyl ylide), and 1320 cm^{-1} (C—O, stretching).

^{1}H NMR (in DMSo-d_6 and expressed in δ-scale ppm): signals at 10.10, 9.20 (NH, two s, exchangeable with D_2O), and 8.10–7.50 (30H, aromatic, m).

^{31}P NMR in $CDCl_3$, expressed in δ-ppm: +16.5 ppm (MS) m/e (relative Intensity) 694 (1), 432 (9), 416 (85), 400 (5), 262 (98), and 183 (88)%.

N,N'-[4-[2-Oxo-1-(triphenylphosphoranylidene)propyl]-1,2-phenylene]bis[benzamide] (**3d**) was obtained in 85% yield as colourless crystals from chloroform-benzene, mp. 265°C. Anal. calcd. for $C_{41}H_{33}N_2O_3P$ (632.75), C, 77.82; H, 5.25; N, 4.43; P, 4.89. Found: C, 77.87; H, 5.30; N, 4.45; P, 4.91%, Mol. Wt. (MS) = 632.

IR: bands at 3250, 3170 (NH), (C=O, acyl ylid) at 1630 cm^{-1}, C=C, aromatic) at 1610 cm^{-1}, 1680, 1500 (C=P), and 1325 cm^{-1} (C—O, stretching).

^{1}H NMR in CD_2Cl_2 and expressed in δ-scale: Signals at 3.5 (3H, s, $COCH_3$), 9.75, 9.1 (NH, two s, exchangeable with D_2O), ^{31}P NMR in $CDCl_3$, and expressed in δ-scale: +17.67 ppm (MS) m/e (relative Intensity) % 632 (3), 370 (8), 262 (85), and 183 (90)%.

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