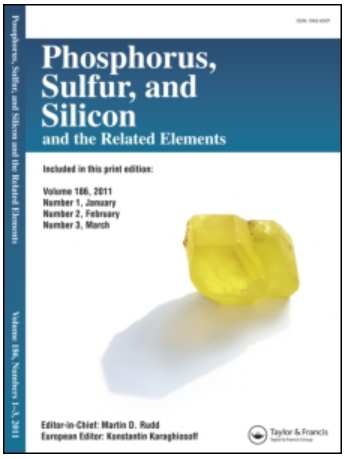

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STUDIES ON PHOSPHONIUM YLIDES–XIII THE REACTIVITY OF N,N'-2,5-CYCLOHEXADIENES-1,4-DIYLIDENEBIS [BENZENESULFONAMIDE] TOWARDS WITTIG REAGENTS

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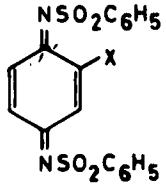
Cyanomethylenetriphenylphosphorane (**IIa**) reacts with N,N'-2,5-cyclohexadiene-1,4-diylidenebis [benzenesulfonamide] (**Ia**) affording the new azacyclopropane adduct **IIIa**. On the other hand, methylenetriphenylphosphoranes (**IIb–d**) react with quinoneimine (**Ia**) and its 2-chloro-derivative (**Ib**) yielding the corresponding ylid-phosphorane adducts **IIIb–g**. Structural reasoning for compounds **III** was based on compatible analytical and spectral data (IR, ^{1}H, ^{31}P, ^{13}C, NMR and MS). A mechanism is proposed to explain the formation of compounds **III**.

Key words: N,N'-2,5-Cyclohexadiene-1,4-diylidenebis [benzenesulfonamides] (**Ia,b**); Wittig reagents (**II**); azacyclopropane adduct (**IIIa**); alkyl-1-[(benzenesulfonyl)amino]-4-2,5-cyclohexadiene-1-acetate (**IIIb,c**); N-4-(benzenesulfonyl)amino]-4-[2-oxo-2-phenyl-1-(triphenylphosphoranylidene)ethyl-2,5-cyclohexadien-1-ylidene] benzenesulfonamide (**IIId**).

INTRODUCTION

In previous publications we examined the action of phosphonium ylides on o-, and p-quinoneimines.[1–3] The present work is an extension on the the behaviour of N,N'-2,5-cyclohexadiene-1,4-diylidenebis [benzenesulfonamide] (**Ia**) and its 2-chloro-derivative (**Ib**) towards Wittig reagents (**II**). This is to determine the preferential site of attack by these reagents and for the production of new phosphonium ylides.



I a, X = H
b, X = Cl

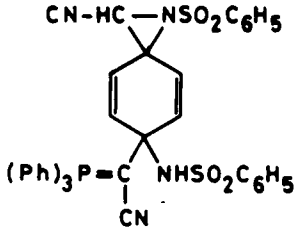
$(C_6H_5)_3\overset{+}{P}-\bar{C}HR$

II a, R = CN
b, R = $COOCH_3$
c, R = $COOC_2H_5$
d, R = COC_6H_5

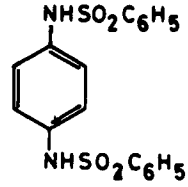
RESULTS AND DISCUSSION

When p-quinoneimine (**Ia**) was treated with one equivalent of cyanomethylenetriphenylphosphorane (**IIa**) in benzene at room temperature for one hour, adducts **IIIa**, p-phenylenedibenzenesulfonamide **IIIa'**, and triphenylphosphine were iso-

lated. Carrying out the reaction using two moles of phosphonium ylides instead of one, lead to the formation of adduct **IIIa** and triphenylphosphine in good yields.



III a



III a'

The structure of the new compound **IIIa** is deduced from its analysis, IR, ^{1}H-NMR, ^{31}P-NMR, and mass spectral data. Elemental and mass spectral analyses of adduct **IIIa** [by Field Ionization Method] corresponded to an empirical formula of $C_{40}H_{31}N_4O_4PS_2$. IR spectrum of adduct **IIIa** (in KBr) reveals the presence of strong —NH absorption band at 3250 cm^{-1}. The strong absorption band at 1575 cm^{-1} recorded[4] for the C=N in quinoneimine (**Ia**) is absent in the IR spectrum of adduct **IIIa**. Moreover, the IR spectrum of **IIIa** exhibits strong bands at 1670 and 1500 cm^{-1} characteristic for the $\diagdown$C=P$\diagup$ group absorption[5] and at 1410 cm^{-1} for the $\diagdown$P—C—(phenyl)$\diagup$ absorption.[6] Adduct **IIIa** possesses ylid-phosphorane structure since it exhibits a positive shift in its ^{31}P-NMR spectrum (δ = +25.35, vs. 85% H_3PO_4) and absorbs in the region characteristic for this class of compounds.[5,7-9].

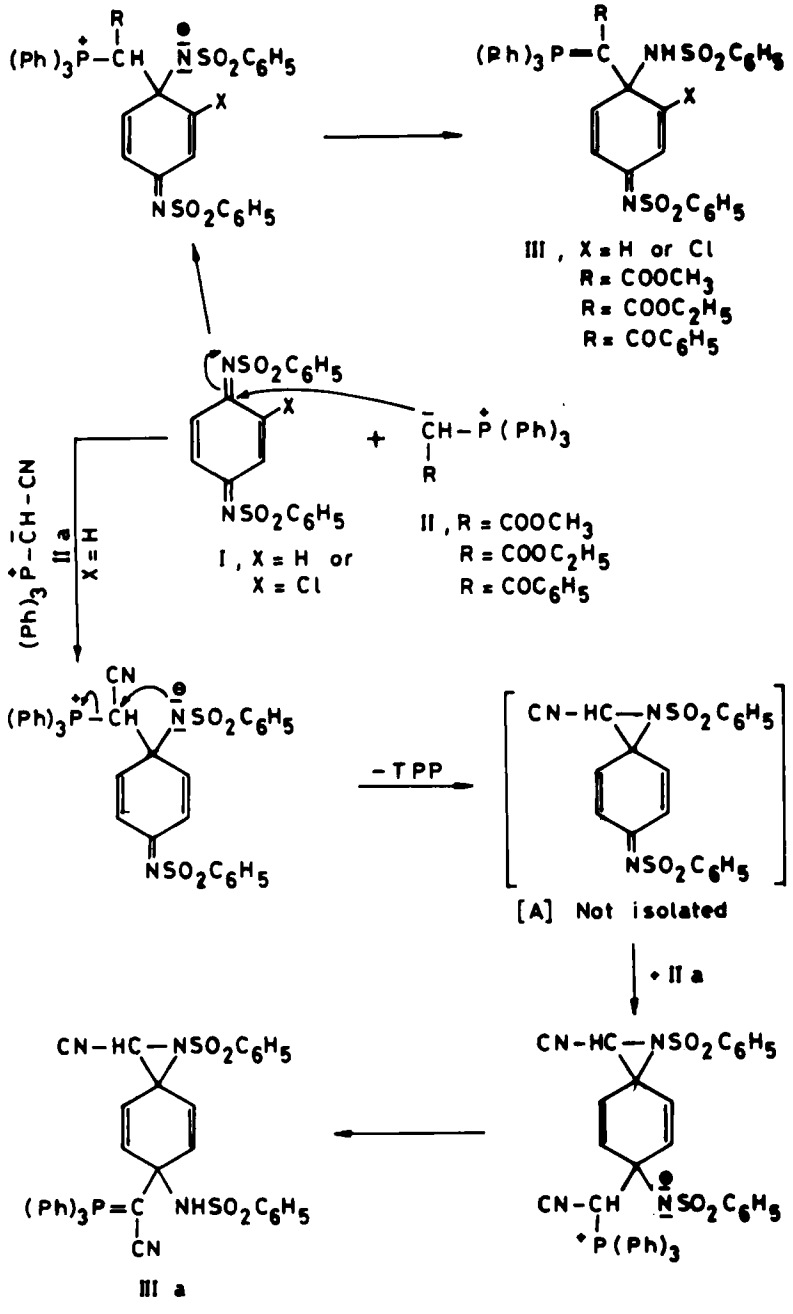
^{1}H-NMR spectrum (200 MHz) of **IIIa** showed two protons doublets at δ = 6.78 and 6.82 with coupling constant value of 7.5 Hz (H-2 and H-6) and another pair of doublets at δ = 6.9 and 6.94 (H-3 and H-5) with coupling constant value of 7.5 Hz.[10,11] The exchangeable (D_2O) proton (NH) appears at δ = 8.19. Moreover, the ^{1}H-NMR spectrum of adduct **IIIa** showed a singlet at δ = 6.25 corresponding to the CH proton of the spiro azapropane ring. Actually, the mass spectrum of adduct **IIIa** by Field Ionization Method yielded a prominent ion peak M^+ at 726 which supports structure **IIIa**.

A possible explanation for the course of the reaction of cyanomethylenetriphenylphosphorane (**IIa**) with 1,4-benzoquinonedibenzenesulfonimine (**Ia**) is shown in "Scheme I".

Adduct (**IIIa**) can be obtained via 1:2-addition of ylide **IIa** to the starting quinoneimine **Ia** affording the intermediate [A] (possibly through loss of triphenylphosphine) which reacts with another molecule of ylide **IIa** to give the stable ylid-phosphorane adduct **IIIa** (cf. Scheme I).

The reaction of carbmethoxymethylene (**IIb**)-, carbethoxymethylene (**IIc**)-, and benzoylmethylene (**IId**)-, triphenylphosphoranes with N,N'-2,5-cyclohexadiene-1,4-diylidenebis [benzenesulfonamide] (**Ia**) and its 2-chloro-derivative (**Ib**) was also investigated.

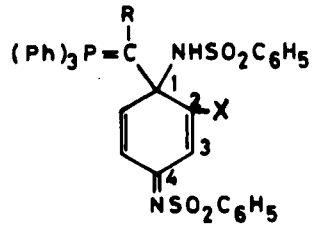
We have found that the reaction of phosphonium ylides (**IIb–d**) with quinoneimines (**Ia,b**), in benzene, proceeds also at room temperature to give colourless 1:1 adducts formulated as (**IIIb–g**), respectively.



Scheme I

Triphenylphosphine and/or triphenylphosphine oxide were neither isolated nor identified in the reaction medium by (TLC) in each case. Under similar conditions, however, compounds (**IIIb–g**) were obtained even when two equivalents of the phosphoranes (**IIb–d**) were used. On the basis of IR, ^{1}H, ^{31}P, ^{13}C, NMR, MS,

and elemental analyses, the structure of compounds (**IIIb–g**) were deduced (cf. Experimental). In the ^{1}H-NMR spectrum of **IIIc**, taken as example, signals appeared at δ = 1.15 (3H, ethoxy-CH_3, t), 3.43 (2H, ethoxy-CH_2, q). The exchangeable (D_2O) proton (NH) appears as broad singlet at 8.73 ppm.



III b, X = H ; R = $COOCH_3$
c, X = H ; R = $COOC_2H_5$
d, X = H ; R = COC_6H_5
e, X = Cl ; R = $COOCH_3$
f, X = Cl ; R = $COOC_2H_5$
g, X = Cl ; R = COC_6H_5

This spectrum also showed two proton doublets centered at 6.25 ppm with coupling constant value of 7.2 Hz (H-2 and H-6) and another pair of doublets centered at δ = 6.92 (H-3 and H-5) with coupling constant value of 7.2 Hz.[10,11] Actually, the ^{13}C-NMR spectra (400 MHz) provided strong evidence in support of the ylid-phosphorane linkage incorporated in structure (**IIIb–g**). ^{13}C-NMR of ethyl-1-[(phenylsulfonyl) amino]-4-[(phenylsulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIc**) in ($CDCl_3$), taken as example, shows a doublet at 46.85 ppm (—P=C, J = 130 Hz),[12] doublet at 169.61 ppm (C=O, ester) with coupling constant (J = 13.7 Hz),[13] singlet at 14.38 ($\underline{CH_3}$ of ethoxy group), and a singlet at 59.02 ppm (CH_2 of ethoxy group).

Moreover, the ^{13}C-NMR spectrum of **IIIc** proved that C-1 appears at 66.05 (d, J = 141.5 Hz) corresponding to the quatenary carbon atom (head bridged saturated carbon) and C-4 appears at 138.092 ppm (C=N).[13] These values are in full accord with the structure **IIIc**.

A possible explanation of the course of the reaction of phosphonium ylides (**IIb–d**) with p-quinoneimine (**Ia**) and its 2-chloro-derivative (**Ib**) is shown in (Scheme I).

Adducts (**IIIb–g**) can be obtained via 1:2 addition of ylides (**IIb–d**) to the starting quinoneimines (**Ia,b**) giving rise to the stable phosphoranes (**IIIb–g**).

From the results of the present investigation, it could be noticed that the reaction between quinoneimines **I** and phosphonium ylides **II** depends upon the nature of the ylid-reagent. Moreover, the present study clearly shows that p-quinonedibenzenesulfonimine **I** behaves in a similar manner to that reaction of p-quinonedimethanesulfonimine with Wittig reagents where 1,2-addition takes place.[3]

The significance of these findings is not only the discovery of a new pattern for Wittig reaction but also the establishment of a novel method for preparing the new azacyclopropane adduct **IIIa**.

EXPERIMENTAL

All melting points are uncorrected. The benzene used was dried over Na. Cyanomethylene-,[12] carbmethoxymethylene-,[13] carbethoxymethylene-,[13] and benzoylmethylenetriphenylphosphoranes[14] were prepared according to established procedures. The IR spectra were measured in KBr, on Perkin-Elmer Infracord Spectrophotometer Model 157 (Grating). The ^{1}H-NMR spectra were taken in $CDCl_3$ on JNM-GX-400 FA Jeol, Tokio, Spectrometer. The ^{31}P-NMR spectra were recorded in $CDCl_3$ (vs. H_3PO_4 as external standard) on JNM-PS-200 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.

Azacyclopropane adduct **IIIa**. To a solution of quinoneimine **Ia** (0.38 g; 0.001 mole)[15] in dry benzene (20 ml), was added ylid **IIa**[12] (0.31; 0.001 mole) in benzene and the reaction mixture was left at room temperature under stirring for 1 h. The coloured precipitated material was filtered off, washed with pet-ether, then benzene and recrystallized from benzene to give (**IIIa**) as violet crystals (0.3 g; 83%) m.p. 250°C.

Anal. Calcd for $C_{40}H_{31}N_4O_4PS_2$ (726.82): C, 66.10; H, 4.29; N, 7.71; S, 8.82; P, 4.26.
Found: C, 66.2; H, 4.3; N, 7.8; S, 8.76; P, 4.3%.
The benzene filtrate afforded triphenylphosphine and dibenzenesulfonamide (**IIIa'**) in almost quantitative yield.

Methyl-1-[(phenylsulfonyl) amino]-4-[(phenylsulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIb**). To a solution of quinoneimine **Ia** (0.38 g; 0.001 mole) in dry benzene (10 ml), was added ylid **IIb** (0.33 g; 0.001 mole) in benzene (10 ml) and the reaction mixture was left at room temperature under stirring for 3 h. The colourless precipitated material was filtered off, washed with benzene (10 ml) and recrystallized from chloroform to give colourless crystals (0.70 g; 97%), m.p. 244°C.

Anal. Calcd. for $C_{39}H_{33}N_2O_6PS_2$ (720.81): C, 64.99; H, 4.61; N, 3.89; S, 8.90; P, 4.30.
Found: C, 64.92; H, 4.63; N, 3.9; S, 8.91; P, 4.33% Mol. wt (MS) = 720.

IR spectrum (**IIIb**), in KBr, bands at 3295 (NH), 1575 (C=N), 1670, 1515 ($\diagdown$C=P$\diagup$), 1400 ($\diagdown$—P—C-phenyl$\diagup$), 1626 (acyl ylid, C=O) and 1315 cm^{-1} (C—O, stretching). ^{1}H-NMR (in $CDCl_3$ and expressed in δ-scale ppm): signals at 3.68 (3H, OCH_3, s), 7.35–7.98 (25H, aromatic, m). The exchangeable (D_2O) proton (NH) appear as broad singlet at 8.55 ppm. A pair of doublets centered at 6.35 (d, H-2 and H-6, J = 7 Hz) and at 6.85 (d, H-3 and H-5, J = 7 Hz). ^{31}P-NMR (in $CDCL_3$, vs 85% H_3PO_4); + 25.1 ppm · (MS) m/e (relative intensity %) 720 (1), 689 (M^+—OCH_3) (75), 533 (M^+—OCH_3—$NHSO_2C_6H_5$) (35), 378 (M^+—OCH_3—$NHSO_2C_6H_5$—$NSO_2C_6H_5$) (12), 262 (TPP) (95).

Similarly, the reaction of quinoneimine (**Ia**) with carbethoxymethylenetriphenylphosphorane (**IIc**), and benzoylmethylenetriphenylphosphorane (**IId**) afforded **IIIc** and **IIId**, respectively.

The colourless crystals of ethyl-1-[(benzenesulfonyl)amino]-4-[(benzenesulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIc**) were obtained (0.54 g, 73.9%) from chloroform, m.p. 222°C.

Anal. Calcd. for $C_{40}H_{35}N_2O_6PS_2$ (734.84): C, 65.38; H, 4.80; N, 3.81; S, 8.73; P, 4.21.
Found: C, 65.40; H, 4.85; N, 3.85; S, 8.75; P, 4.23% Mol. Wt (MS) = 734.

N-[4-[2-oxo-2-phenyl-1-(triphenylphosphoranylidene) ethyl]-4-[(phenylsulfonyl) amino]-2,5-cyclohexadiene-1-ylidene] benzenesulfonamide (**IIId**) was obtained in 74% as colourless crystals from chloroform, m.p. 252°C.

Anal. Calcd. for $C_{44}H_{35}N_2O_5PS_2$ (766.88): C, 68.91; H, 4.60; N, 3.65; S, 8.36; P, 4.04.
Found: C, 68.95; H, 4.66; N, 3.66; S, 8.38; P, 4.07%.

IR: bands at 3290 (NH), 1570 (C=N), 1670, 1505 ($\diagdown$C=P$\diagup$), 1405 [$\diagdown$P—C-(phenyl)$\diagup$], 1630 (C=O, acyl ylid), 1320 cm^{-1} (C—O, stretching). ^{1}H-NMR (in $CDCl_3$ and expressed in δ-scale ppm). 8.47 ppm (NH, one singlet exchangeable with D_2O), and 7.35–8.2 (30H, aromatic, m), two doublets centered at 6.63 (d, H-2 and H-6, J = 7.2 Hz) and at 6.85 (d, H-3 and H-5, J = 7.2 Hz). ^{31}P-NMR in $CDCl_3$ expressed in δ-ppm + 25.9 ppm.

Methyl-2-chloro-1-[(phenylsulfonyl) amino]-4-[(phenylsulfonyl) imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIe**). To a solution of quinoneimine (**Ib**) (0.42 g; 0.001 mole), in dry benzene (10 ml), was added ylid (**IIb**) (0.33 g; 0.001 mole) in benzene (10 ml) and the reaction mixture was left at room temperature for 2 h. The colourless precipitated material was filtered off, washed with benzene (5 ml), and recrystallized from chloroform-benzene to give (**IIIe**) as colourless crystals, m.p. 208°C.

Anal. Calcd. for $C_{39}H_{32}ClN_2O_6PS_2$ (755.25); C, 62.02; H, 4.27; N, 3.71; S, 8.49; P, 4.10; Cl, 4.69. Found: C, 62.07; H, 4.3; N, 3.75; S, 8.5; P, 4.15; Cl, 4.7% Mol. wt (MS) = 755.

IR: bands at 3300 (NH), 1570 (C=N), 1670, 1495 (>C=P), 1410 [—P—C (phenyl)], 1620 (C=O, acyl ylid). ^{1}H-NMR (in $CDCl_3$ and expressed in δ-scale ppm): signals at 3.75 (3H, OCH_3; s). Proton H-3 appears as singlet at 6.61 ppm, protons H-5, H-6 appear as two doublets centered at 6.91, 6.95 with coupling constant value of H5H6 = JH6H5 = 7.5 Hz. ^{31}P-NMR in $CDCl_3$ expressed in δ-ppm = +25.97. ^{31}C-NMR of (**IIIe**) (400 MHz) in $CDCl_3$ and expressed in δ-ppm; singals 55.92 ($COO\underline{C}H_3$), 168.61 (d, C=O, ester with J = 13.7 Hz), 52.35 ppm (d, >C=P, J = 130 Hz), 78.52 (C-1, d with J = 141.35 Hz), 138.5 (C-4, C=N).

Similarly, the reaction of compound (**Ib**) with carbethoxymethylenetriphenylphosphorane (**IIc**) and benzoylmethylenetriphenylphosphorane (**IId**) afforded (**IIIf**) and (**IIIg**), respectively.

The colourless crystals of ethyl-2-chloro-1-[(benzenesulfonyl) amino]-4-[(benzenesulfonyl) imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIf**) were obtained (83%) from chloroform m.p. 220°C.

Anal. Calcd. for $C_{40}H_{34}ClN_2O_6PS_2$ (769.28): C, 62.45; H, 4.46; N, 3.64; S, 8.34; P, 4.03; Cl, 4.61. Found: C, 62.5; H, 4.5; N, 3.65; S, 8.4; P, 4.08; Cl, 4.6% Mol. wt (MS) = 769.

IR: bands at 3300 (NH), 1570 (C=N), 1680, 1510 (>C=P), 1405 [—P—C (phenyl)], 1620 (C=O, acyl ylid). ^{1}H-NMR of (**IIIf**) in $CDCl_3$ and expressed in δ-scale ppm: signals at 0.65 (3H, CH_3 of ethoxy, t), 3.75 (2H, CH_2 of ethoxy, q), H-3 appears at δ = 6.25, singlet and H-5, H-6 appear as two doublets centered at 6.93, 6.97 with JH5H6 = JH6H5 = 7.5 Hz and at 8.47 (NH one singlet exchangeable with D_2O). ^{31}P-NMR of (**IIIf**) in $CDCl_3$ = +26.01 ppm.

N-[2-chloro-4-[2-oxo-2-phenyl-1-(triphenylphosphoranylidene)-ethyl]-4-[(phenylsulfonyl)amino]-2,5-cyclohexadien-1-ylidene] benzenesulfonamide (**IIIg**) was obtained in 80% yield as colourless crystals from benzene m.p. 188°C.

Anal. Calcd. for $C_{44}H_{34}ClN_2O_5PS_2$ (801.33): C, 65.95; H, 4.28; N, 3.49; S, 8.00; P, 3.86; Cl, 4.42. Found: C, 65.9; H, 4.3; N, 3.5; S, 8.03; P, 3.8; Cl, 4.45% Mol. wt (MS) = 801.

IR: band at 3305 (NH), 1580 (C=N), 1670, 1505 (>C=P), 1410 [—P—C (phenyl)], 1630 (C=O), acyl ylid). ^{1}H-NMR in $CDCl_3$ and expressed in ppm signals at 8.51 ppm (NH one singlet exchangeable with D_2O). ^{31}P-NMR of (**IIIg**) in $CDCl_3$ = +25.83 ppm.

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