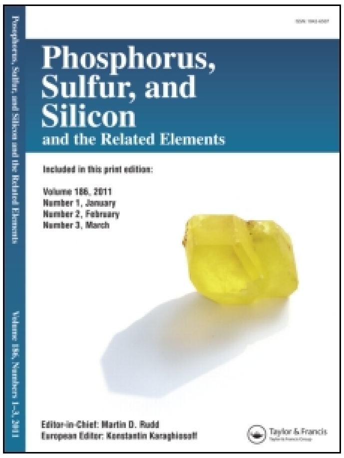

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STUDIES ON PHOSPHONIUM YLIDS. XI. ON THE REACTION OF WITTIG REAGENTS WITH p-BENZOQUINONEDIMETHANE-SULFONIMINES. A NEW 1,2-ADDITION REACTION ON p-QUINONEIMINES

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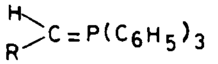
(Received April 14, 1989; in final form May 22, 1989)

The reaction of carbmethoxymethylene (**Ia**)-, carbethoxymethylene (**Ib**)-, acetylmethylene (**Ic**)-, and benzoylmethylene (**Id**)-triphenylphosphoranes with *N,N′*-2,5-cyclohexadiene-1,4-diylidenebis (methanesulfonamide) (**IIa**) and its 2-chloro-derivatives **IIb** afforded the new ylid-phosphoranes **IIIa–g** via 1,2-addition reaction. Structural reasoning for compounds **III** was based on compatible analytical and spectral data (IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and MS). The mechanism that accounts for formation of adducts **III** is discussed.

Key words: Wittig reagents (**I**); *N,N′*-2,5-cyclohexadiene-1,4-diylidene-bis(methanesulfonamide) (**IIa**); *N,N′*-(2-chloro-2,5-cyclohexadiene-1,4-diylidene)bis(methanesulfonamide) (**IIb**); alkyl 1-[(methylsulfonyl)amino]-4-[(methylsulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIa,b**); *N*-[4-[(methylsulfonyl)amino]-4-[2-oxo-1-(triphenylphosphoranylidene)-propyl]-2,5-cyclohexadien-1-ylidene] methanesulfonamide (**IIIc**); *N*-[4-[(methylsulfonyl)amino]-4-[2-oxo-2-phenyl-1-(triphenylphosphoranylidene)ethyl]-2,5-cyclohexadien-1-ylidene] methanesulfonamide (**IIId**).

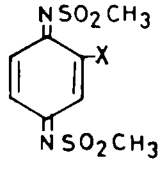
INTRODUCTION

In continuation of our work on the behaviour of o-, and p-quinoneimines towards Wittig reagents,[1,2] the action of phosphonium ylids (**I**) on p-quinonedimethane-sulfonimines (**II**) has now been investigated.



$$\overset{H}{\underset{R}{>}}C=P(C_6H_5)_3$$

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



II a , X = H
b , X = Cl

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† Thanks are due to W. Schätzke and J. Guentner (Institute of Organic Chemistry, FAU, Universität Erlangen-Nürnberg, FRG) for recording of ^{1}H, ^{13}C, ^{31}P NMR, and Mass Spectra. Thanks are also forwarded to the Alexander von Humboldt Stiftung since this work was partly accomplished during the grant period offered to the first author.

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

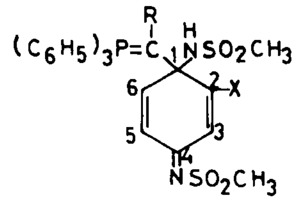
RESULTS AND DISCUSSION

We have found that the reaction of carbmethoxymethylene (**Ia**)-, carbethoxymethylene (**Ib**)-, acetylmethylene (**Ic**)-, and benzolymethylene (**Id**)-, triphenylphosphoranes with *N,N'*-2,5-cyclohexadiene-1,4-diylidenebis [methanesulfonamide] (**IIa**), in benzene, proceeds at room temperature to give chromatographically pure 1:1 adducts formulated as (**IIIa–d**), respectively. Triphenylphosphine and/or triphenylphosphine oxide were neither isolated nor identified in the reaction medium by (TlC) in each case.

Structure elucidation for ethyl 1-[(methylsulfonyl)amino]-4-[(methylsulfonyl)-imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIb**), taken as example, was attested by the following evidence:

(a) Elemental analysis and molecular weight determination (MS) for compound (**IIIb**) corresponds to $C_{30}H_{31}N_2S_2O_6P$.

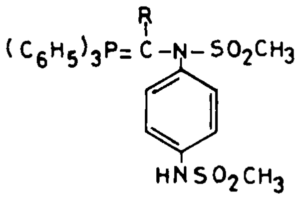
(b) The IR spectrum of adduct (**IIIb**), in KBr, reveals the presence of strong —NH absorption band at 3400 cm^{-1}. The strong absorption band at 1575 cm^{-1} recorded[3] for the C=N absorption band in quinoneimine (**IIa**) is still present in the IR spectrum of adduct (**IIIb**). Moreover, the IR spectrum of adduct (**IIIb**) exhibits strong absorption bands at 1680 and 1505 cm^{-1} characteristic for the >C=P group absorption[4] at 1400 cm^{-1} denoting the >P—C< (phenyl) absorption,[5] and at 1626 cm^{-1} which corresponds to shifted ester >C=O bands.[6]



III a , X = H ; R = $COOCH_3$
b , X = H ; R = $COOC_2H_5$
c , X = H ; R = $COCH_3$
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

(c) Adduct (**IIIb**) possesses ylid-phosphorane structure since it exhibits a positive shift in its ^{31}P NMR spectrum ($\delta = +20.543$, vs. 85% H_3PO_4) and absorbs in the region characteristic for this class of compounds.[4,7–9]

(d) ^1H NMR spectrum (400 MHz) of (**IIIb**) showed signals at $\delta = 0.68$ (3H, ethoxy-CH_3, t); 3.80 (2H, ethoxy—CH_2, q), 3.1 (3H, $NHSO_2$—$\underline{CH}_3$, s) and at 2.49 (3H, $C{=}NSO_2\underline{CH}_3$, s). The exchangeable ($D_2O$) proton (NH) appears as broad singlet at $\delta = 8.15$. This spectrum also showed two proton doublets at $\delta = 6.74$, 6.76 with coupling constant value of 8.54 Hz (H-2 and H-6) and another pair of doublets at $\delta = 7.22$ and 7.24 (H-3 and H-5) with coupling constant value of 8.57 Hz[10,11]



IVa, $R = COOCH_3$
b, $R = COOC_2H_5$
c, $R = COCH_3$
d, $R = COC_6H_5$

These data are most adequately accommodated in structure (**IIIa–d**) since in the alternative formula like (**IVa–d**) 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).

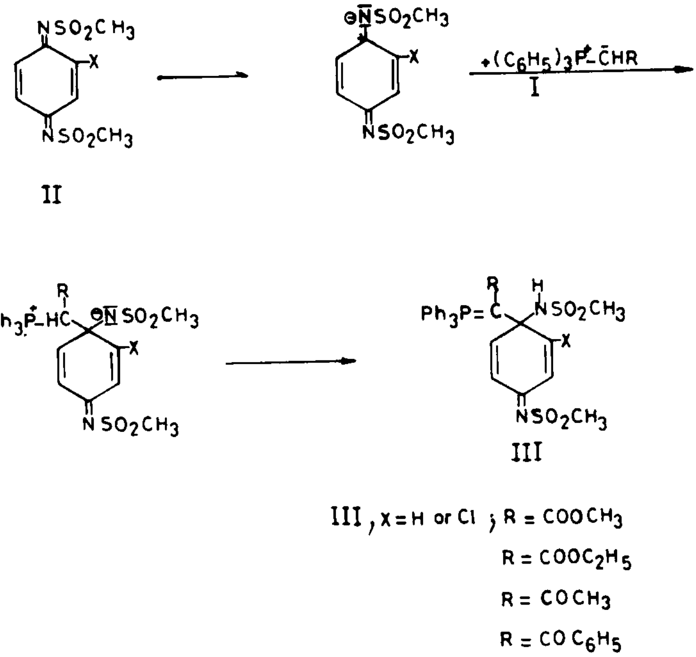
Actually the ^{13}C NMR spectra (400 MHz) provided strong evidence in support of the ylid-phosphorane linkage incorporated in structure (**III**). ^{13}C NMR of ethyl 1-[(methylsulfonyl)amino]-4-[(methylsulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIb**) (in $CDCl_3$), taken as example, shows a doublet at 52.55 ppm ($>P{=}C$, $J = 130$ Hz),[12] doublet at $\delta = 169.053$ ($C{=}O$, ester) with coupling constant ($J = 13.7$ Hz),[13] singlet at 13.946 ppm ($\underline{CH}_3$ of ethoxy group), and a signal at 57.057 ppm (CH_2 of the ethoxy group). The carbon atoms of the SO_2CH_3 groups gave signals at 38.035 ($HNSO_2CH_3$) and 40.64 ppm ($C{=}NSO_2\underline{CH}_3$), respectively. Actual investigation of ^{13}C NMR spectrum of compound (**IIIb**) proved that C-1 appears at 58.482 (d, $J = 141.530$ Hz) corresponding to the quatenary carbon atom (head bridged saturated carbon) and C-4 appears at 136.092 ppm ($C{=}N$).[13] These values are in full accord of structure (**III**).

The mass spectrum of compound (**IIIb**) yielded a prominent ion peak at m/e 610 (M^+, 5%), 565 ($M—OC_2H_5$, 8%), 486 ($M^+—OC_2H_5$, $—SO_2CH_3$, 35%), 407 ($M^+—OC_2H_5$, $—SO_2CH_3$, $—SO_2CH_3$, 25%), and 262 (TPP, 95%).

Further, this study was extended to include the reaction of *N,N'*-2-chloro-2,5-cyclohexadiene-1,4-diylidenebis [methanesulfonamide] (**IIb**) with the same Wittig reagents (**I**) to determine whether it would behave in a similar manner.

We have found that carbmethoxymethylene (**Ia**)-, carbethoxymethylene (**Ib**)-, and benzoylmethylene (**Id**)-triphenylphosphoranes react with 2-chloro-derivative (**IIb**) in a similar manner to give colourless crystalline 1,2-addition compounds assigned structures (**IIIe–g**), respectively. Correct analytical values were obtained for the new compounds (**IIIe, f** and **g**) and their molecular weights (MS) corresponded to monomeric formulae (cf. **IIIe–g**).

Compatible analytical and spectral data (IR, ^1H, ^{31}P, ^{13}C NMR and MS) were equally obtained for the new products (cf. Experimental).



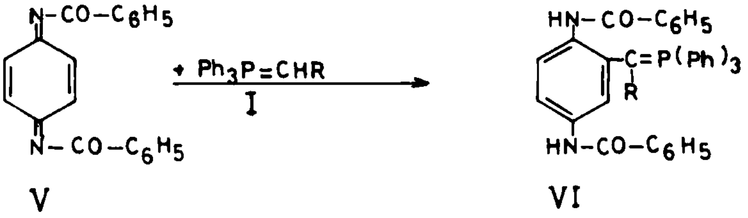
SCHEME 1

A possible explanation of the course of the reaction of phosphonium ylids (**I**) with *N,N′*-2,5-cyclohexadiene-1,4-diylidenebis (methanesulfonamide) (**IIa**) and its 2-chloro-derivative (**IIb**) is shown in "Scheme I".

Adducts (**III**) can be obtained via 1:2-addition of ylids (**I**) to the starting quinoneimines (**II**) affording the stable ylid-phosphoranes (**III**).

Worth-mentioning is that quinoneimines (**II**) yield only the mono-ylid phosphorane adducts (**IIIa–g**) even when it is allowed to react with two equivalents of the ylid-reagent. This is equally true, when the formed adduct e.g. (**IIIa**) was further reacted with a mole of ylid (**Ia**) under similar conditions.

The results of the present investigation allow certain interesting conclusions to be drawn. While *N,N′*-2,5-cyclohexadiene-1,4-diylidenebis [benzamide] (**V**) reacts with phosphonium ylids (**I**) to yield the normal 1:4-addition products (**VI**),[2] a different behaviour is noted with *N,N′*-2,5-cyclohexadiene-1,4-diylidenebis-[methanesulfonamide] (**IIa**) and its 2-chloro derivative.



The latter compounds (**IIa**) and (**IIb**) gave with the same reagents the respective 1,2-addition products.

This finding, which represents a novel route to (**III**), supplements to the expanded utility of Wittig reagents (**I**) for the production of certain ylid-phosphoranes (cf. **III**). This constitutes a remarkable usefulness in obtaining new 1,2-addition products via Wittig reagents.

EXPERIMENTAL

All melting points are uncorrected. The benzene used was dried over Na. Carbmethoxymethylene-, carbethoxymethylene-, acetylmethylene-, and benzoylmethylene-triphenylphosphoranes 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-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 1-[(methylsulfonyl)amino]-4-[(methylsulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (IIIa). To a suspension of quinoneimine (**IIa**) (0.26 g; 0.001 mole)[14] in dry benzene (10 ml), was added ylid (**Ia**) (0.33 g, 0.001 mole) in benzene (10 ml) and the reaction mixture was left at room temperature under stirring for 12 h. The colourless precipitated material was filtered off, washed with benzene (2 ml) and recrystallized from benzene to give (**IIIa**) as colourless crystals (0.45 g, 76%), mp. 242°C.

Anal. cald. for $C_{29}H_{29}N_2O_6S_2P$ (596.663): C, 58.38; H, 4.89; N, 4.69; S, 10.75 P, 5.19%.

Found: C, 58.31; H, 4.9; N, 4.7; S, 10.8; P, 5.2% Mol. Wt (MS) = 596.

IR Spectrum of (**IIIa**), in KBr, bands at 3290 (NH), 1570 (C=N), 1675, 1510 ($>$C=P), 1395 ($\geq$P—C-phenyl), 1626 (acyl ylid, $>$C=O) and 1310 cm^{-1} (C—O, stretching). ^{1}H NMR (in $CDCl_3$ and expressed in δ-scale ppm): signals at 3.68 (3H, $O\underline{CH}_3$, s), 3.1 (3H, $NHSO_2\underline{CH}_3$, s), 2.68 (3H, $C{=}NSO_2\underline{CH}_3$, s), 7.5–7.7 (15H, aromatic, m). The exchangeable (D_2O) proton (NH) appear as broad singlet at 8.43 ppm. A pair of doublets at 6.74, 6.76 (d, H-2 and H-6, $J = 8.54$ Hz) and at 7.22, 7.24 (d, H-3 and H-5, $J = 8.57$ Hz). ^{31}P NMR (in $CDCl_3$, vs 85% H_3PO_4); +20.125 ppm (MS) m/e (relative intensity %) 596 (5), 565 (M^+—OCH_3) (8), 486 (M^+—OCH_3, —SO_2CH_3) (22), 407 (M^+—OCH_3, —$2SO_2CH_3$) (37), 262 (TPP) (95).

Similarly, the reaction of quinoneimine (**IIa**) with carbethoxymethylenetriphenylphosphorane (**Ib**), acetylmethylenetriphenylphosphorane (**Ic**), and benzoylmethylenetriphenylphorphorane (**Id**) afforded **IIIb**, **IIIc** and **IIId**, respectively. The colourless crystals of ethyl 1-[(methylsulfonyl)amino]-4-[(methylsulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIb**) were obtained (85%) from chloroform, mp. 138°C. Anal. calcd. for $C_{30}H_{31}N_2S_2O_6$ P (610.69) C, 59.00; H, 5.12; N, 4.59; S, 10.50,; P, 5.07.

Found: C, 59.12; H, 5.23; N, 4.60; S. 10.60; P, 5.13% Mol. Wt. (MS) = 610.

IR: bands at 3400 (NH), 1575 (C=N), 1680, 1505 ($>$C=P), 1400 ($\geq$P—C (Phenyl), 1626 ($>$C=O, acyl ylid), and 1295 cm^{-1} (C—O, stretching. ^{1}H NMR in $CDCl_3$, expressed in δ-ppm: signals at 0.68 (3H, ethoxy-CH_3, t); 3.80 (2H, ethoxy-CH_2, q), 3.1 (3H, $NHSO_2(\underline{CH}_3$, s), 2.49 (3H, $C{=}NSO_2\underline{CH}_3$, s), 8.15 (NH, one singlet exchangeable with D_2O), 6.74, 6.76 (2H, pair of doublets with $J_{HH} = 8.54$ Hz (H-2 and H-6), 7.22 and 7.24 (2H, pair of doublets with $J_{HH} = 8.57$ Hz (H-3 and H-5). ^{31}P NMR in $CDCl_3$ expressed in δ-ppm = +20.543 (MS) *m/e* (relative intensity %) 610 (5), 565 (8), 486 (35), 407 (25), 262 (95)%.

N-[4-[(Methylsulfonyl)amino]-4-[2-oxo-1-(triphenylphosphoranylidene)propyl]-2,5-cyclohexadien-1-ylidene methanesulfonamide (**IIIc**) was obtained in 80% yield as colourless crystals from benzene, mp. 134°C.

Anal. calcd. for $C_{29}H_{29}N_2S_2O_5P$ (580.664) C, 59.99; H, 5.03; N, 4.82, S, 11.04; P, 5.33.

Found: C, 59.9; H, 5.1; N, 4.9; S, 11.1; P, 5.4%, Mol. Wt (MS) = 580.

IR: bands at 3280 (NH), 1575 (C=N), 1670, 1505 ($>$C=P), 1400 ($\geq$P—C (phenyl)), 1630 ($>$C=O, acyl ylid), and 1320 cm^{-1} (C—O, stretching). ^{1}H NMR (in $CDCl_3$ and expressed in δ-scale ppm) signals: 2.20 (3H, $CO\underline{CH}_3$, s), 2.50 (3H, $C{=}N{-}SO_2{-}\underline{CH}_3$, s), 2.85 (3H, $NHSO_2{-}\underline{CH}_3$, s), 9.3 (NH, one s, exchangeable with D_2O) and 7.5–7.7 (15H, aromatic, m). ^{31}P NMR in $CDCl_3$, expressed in δ-ppm = +20.32 ppm (MS) *m/e* (relative intensity %) 580 (8), 537 (15), 458 (35), 379 (45), 262 (95)%.

N-[4-[(Methylsulfonyl)amino]-4-[2-oxo-2-phenyl-1-(triphenylphosphoranylidene)ethyl]-2,5-cyclohexadien-1-ylidene]methane sulfonamide] (**IIId**) was obtained in 85% yield as colourless crystals from chloroform, mp. 218°C.

Anal. calcd. for $C_{34}H_{31}N_2S_2O_5P$ (642.735) C, 63.54; H, 4.86; N, 4.36; S, 9.97; P, 4.82.
Found: C, 63.6; H, 4.9; N, 4.4; S, 10.1; P, 4.9% Mol. Wt (MS) = 642.
IR: bands at 3300 (NH), 1570 (C=N), 1670, 1495 ($>$C=P), 1410 ($\geq$C—P (phenyl)), 1620 ($>$C=O, acyl ylid). ^1H NMR in $CDCl_3$ and expressed in δ-scale signals: 2.60 (3H, C=NSO_2—CH_3, s), 2.9 (3H, $NHSO_2$—CH_3, s), 8.8 ppm (NH, one singlet exchangeable with D_2O), and 7.5–7.7 (20H, aromatic, m) ^{31}P NMR in $CDCl_3$ expressed in δ-ppm +20.287 ppm (MS) *m/e* (relative intensity %) 642 (5), 614 (20), 535 (27), 456 (35), 262 (95%).

Methyl 2-chloro-1-[(methylsulfonyl)amino]-4-[(methylsulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIe**). To a suspension of quinoneimine (**IIb**) (0.29 g, 0.001 mole), in dry benzene (10 ml), was added ylid (**Ia**) (0.33 g, 0.001 mole) in benzene (10 ml) and the reaction mixture was left at room temperature for 10 h. The colourless precipitated material was filtered off, washed with benzene (5 ml) and recrystallized from benzene to give (**IIIe**) as colourless crystals in 85% yield, mp. 174°C).
Anal. calcd. for $C_{29}H_{28}N_2S_2O_6PCl$ (631.11) C, 55.19; H, 4.47; N, 4.44; S, 10.16; P, 4.91; Cl, 5.62.
Found: C, 55.23; H, 4.52; N, 4.5; S, 10.2; P, 4.98; Cl, 5.65%, Mol. Wt. (MS) = 631.
IR: bands at 3300 (NH), 1570 (C=N), 1670, 1495 ($>$C=P), 1410 ($\geq$C—P (phenyl)), 1620 ($>$C=O, acyl ylid). ^1H NMR (400 MHz) (in $CDCl_3$ and expressed in δ-scale ppm): signals at 3.39 (3H, $O\underline{CH_3}$, s), 3.16 (3H, $NHSO_2$—$\underline{CH_3}$, s), 2.55 (3H, C=$NSO_2\underline{CH_3}$, s). Proton H-3 appears as singlet at 6.50 ppm, protons H-5, H-6 appear as two doublets centered at 7.15, 7.18 with coupling constant value of *J* H5H6 = *J* H6H5 = 8 Hz, signal at 8.25 ppm (NH, one singlet exchangeable with D_2O). ^{31}P NMR in $CDCl_3$ expressed in δ-ppm = +20.452 ppm. (MS) *m/e* (relative intensity %) 631 (12), 600 (35), 521 (40), 442 (45), 262 (95)% ^{13}C NMR of (**IIIe**) (400 MHz) in $CDCl_3$ and expressed in δ-ppm signals at 38.885 (C=NSO_2—$\underset{\cdot}{C}H_3$), 40.403 ($NHSO_2$—$\underset{\cdot}{C}H_3$), 49.951 ($COO\underset{\cdot}{C}H_3$), 169.125 (d, C=O, ester with J = 13.7 Hz), 51.35 ppm (d, C=P, J = 130 Hz), 58.345 (C-1, d with J = 141.356 Hz), 137.505 (C-4, C=N).

Similarly, the reaction of compound (**IIb**) with carbethoxymethylenetriphenylphosphorane (**Ib**) and benzoylmethylenetriphenylphosporane (**Id**) afforded (**IIIf**) and (**IIIg**), respectively.

The colourless crystals of ethyl 2-chloro-1-[(methylsulfonyl)amino]-4-[(methylsulfonyl)imino]-α-(triphenylphosphoranylidene)-2,5-cyclohexadiene-1-acetate (**IIIf**) were obtained (85%) from chloroform, mp. 203°C. Anal. Calcd for $C_{30}H_{30}N_2S_2O_6PCl$ (645.14) C, 55.85; H, 4.69; N, 4.34; S, 9.94; P, 4.80; Cl, 5.49%.
Found: C, 55.9; H, 4.7; N, 4.4; S, 9.97; P, 4.9; Cl, 5.5% Mol. Wt (MS) = 645.
IR: bands at 3305 (NH), 1570 (C=N), 1680, 1510 ($>$C=P), 1405 ($\geq$P—C (Phenyl)), 1620 ($>$C=O, acyl ylid).
^1H NMR in CDCl expressed in δ-ppm: signals at 0.72 (3H, CH_3 of ethoxy, t), 3.85 (2H, CH_2 of ethoxy, q), 2.59 (3H, C=NSO_2CH_3, s), 3.15 (3H, $NHSO_2$—CH_3, s), H-3 appears at δ = 6.25, s and H-5, H-6 appear as two doublets centered at 7.46, 7.48 with *J* H5H6 = *J* H6 H5 = 6.7 Hz and at 8.30 ppm (NH one singlet exchangeable with D_2O).
^{31}P NMR of (**IIIf**) in $CDCl_3$ and expressed δ-scale ppm = +20.543 ppm. (MS) *m/e* (relative intensity %) 645 (8), 600 (20), 521 (35), 442 (45), 262 (95)%.

N-[3-Chloro-4-[(methylsulfonyl)amino]-4-[2-oxo-2-phenyl-1-(triphenylphosphoranylidene)ethyl]-2,5-cyclohexadiene-1-ylidene] methanesulfonamide (**IIIg**) was obtained in 80% yield as colourless crystals from toluene mp. 250°C. Anal. Calcd for $C_{34}H_{30}N_2S_2O_5PCl$ (677.18) C, 60.30; H, 4.47; N, 4.14; S, 9.96; P, 4.57; Cl, 5.23.
Found: C, 60.35, H, 4.48; N, 4.2; S, 9.98; P, 4.6; Cl, 5.3% Mol. Wt (MS) = 677.
IR: bands at 3300 (NH) 1580 (C=N), 1670, 1505 ($>$C=P), 1410 ($\geq$P—C (phenyl)), 1630 (C=P, acyl ylid). ^1H NMR in $CDCl_3$ and expressed in ppm: signals; 2.63 (3H, C=NSO_2CH_3, s), 2.95 (3H, $NHSO_2$—CH_3, s) and at 8.5 ppm (NH one singlet exchangeable with D_2O). ^{31}P NMR of (**IIIg**) in $CDCl_3$ and expressed in δ-scale = +20.553 ppm. (MS) *m/e* (relative intensity %) 677 (3), 649 (10), 570 (35), 491 (50), 262 (95)%.

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