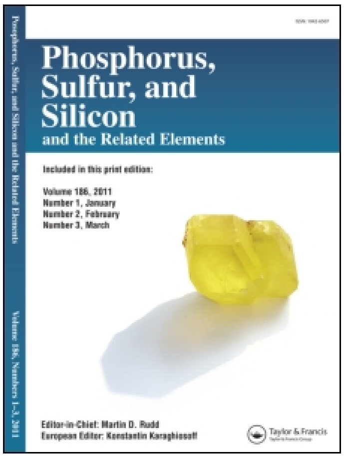

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STUDIES ON PHOSPHONIUM YLIDES XVII. THE BEHAVIOUR OF WITTIG REAGENTS TOWARD 1,4-NAPHTHOQUINONEMONOBENZENESULFONIMINE

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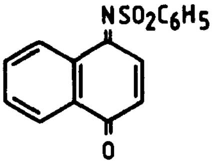
Methylenetriphenylphosphoranes (**IIa, b**) react with 1,4-naphthoquinonemonobenzenesulfonimine (**I**) yielding the new azapropane adduct **IIIa** together with the dimeric adducts **IIIb**, **IIIc**, and **IIId**. Structures of the new products were established by analytical and spectroscopic (IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and MS) results. A mechanism is proposed to explain the formation of compounds **III**.

Key words: 1,4-Naphthoquinonemonobenzenesulfonimine (**I**); Carbmethoxymethylenetriphenylphosphorane (**IIa**); Carbethoxymethylenetriphenylphosphorane (**IIb**); the new azapropane adduct **IIIa**; the dimeric products **IIIb**, **IIIc** and **IIId**.

INTRODUCTION

In previous publications we examined the action of phosphonium ylides on *o*-, and *p*-quinonediimines.[1–4] The present work is an extension on the behaviour of 1,4-naphthoquinonemonobenzene-sulfonimine (**I**) towards Wittig reagents (**II**). This is to establish whether it would undergo a preferential oxygen or nitrogen attack by these reagents and for the production of new phosphonium ylides.



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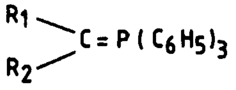
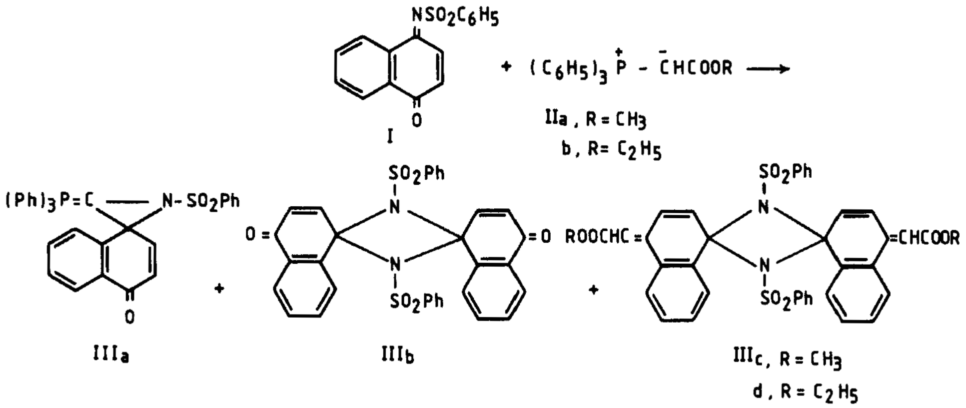


$R_1R_2C=P(C_6H_5)_3$

IIa, R_1 = H ; R_2 = $COOCH_3$
b, R_1 = H ; R_2 = $COOC_2H_5$

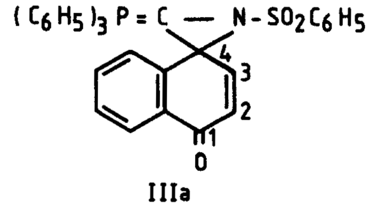
RESULTS AND DISCUSSION

We have found that the reaction of 1,4-naphthoquinonemonobenzenesulfonimine (**I**) with one mole equivalent of carbmethoxymethylenetriphenylphosphorane (**IIa**), in dry benzene, proceeds at room temperature to give three pure adducts formulated as **IIIa**, **IIIb** and **IIIc**, respectively, (cf. Scheme I). Triphenylphosphine oxide (TPPO) was also isolated from the reaction medium. Elemental and mass spectral analyses for compound **IIIa** corresponded to an empirical formula of $C_{35}H_{26}NO_3PS$. Its IR spectrum, in KBr, revealed the presence of the carbonyl absorption band at 1675 cm^{-1} in the starting quinone (**I**). On the other hand, the C=N band present at



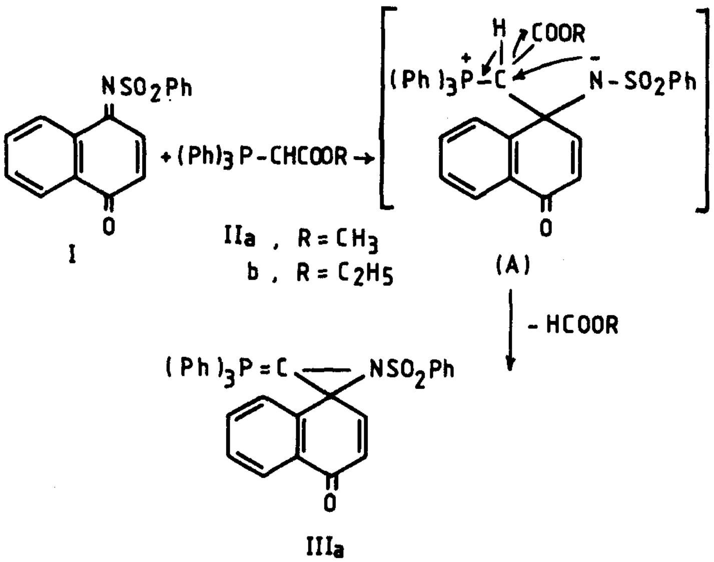
(Scheme I)

1580 cm^{-1} in the spectrum of I was absent in the IR spectrum of **IIIa**, Moreover, the IR spectrum of **IIIa** exhibits strong absorption bands at 1335, 1175 cm^{-1} (SO_2), at 1680, 1505 cm^{-1} characteristic for the $>C{=}P$ group absorption[5] and at 1410 cm^{-1} denoting the $\geq P{-}C$ (phenyl) absorption.[6] Adduct **IIIa** possesses ylide-phosphorane structure since it exhibits a positive shift in its ^{31}P NMR spectrum ($\delta = +19.714$, vs. 85% H_3PO_4) and absorbs in the region characteristic for this class of compounds.[7] The ^1H NMR spectrum (200 MHz) of **IIIa** showed two protons doublets centered at $\delta = 6.90$ (H-2 and H-3) and at 8.40 (H-3 and H-2) with coupling constant values of $J_{2,3} = J_{3,2} = 8$ Hz.[8] The spectrum also revealed a complex pattern due to the aromatic protons (24H, m) in the region 7.25–7.7 ppm. Actually, the ^{13}C NMR spectrum (200 MHz) provided strong evidence in support of the ylide-phosphorane linkage incorporated in structure **IIIa**. ^{13}C NMR of 4-benzosulfonyl-4-azacyclopropyl-α-(triphenylphosphoranylidene)-1-oxo-1,4-dihydronaphthaline (**IIIa**), in ($CDCl_3$), shows doublets at 60.78 ppm $\left(>P{=}C,\ J = 141\ \text{Hz}\right)^9$ and at 178.35 (C=O, quinone) with a coupling constant value of $J = 3.5$ Hz.[9] The mass spectrum of compound **IIIa** yielded a prominent ion peak at m/e 571 (M^+, 12%), 416 (M^+-$NSO_2C_6H_5$, 25%), 388 (M^+-NSO_2Ph-CO, 40%) and at 262 (TPP, 95%).



IIIa

A possible explanation of the course of the reaction of phosphonium ylide (**IIa**) with 1,4-naphthoquinonemonobenzene-sulfonimine (**I**) is shown in (Scheme II). Adduct **IIIa** can be obtained via 1:1 addition of ylides **IIa** or **IIb** to the starting

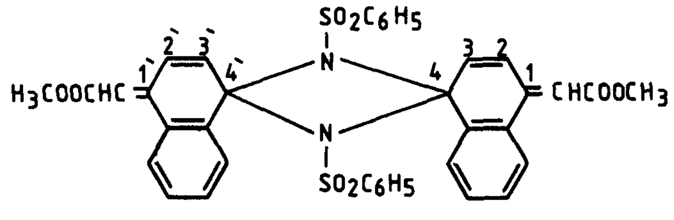


(Scheme II)

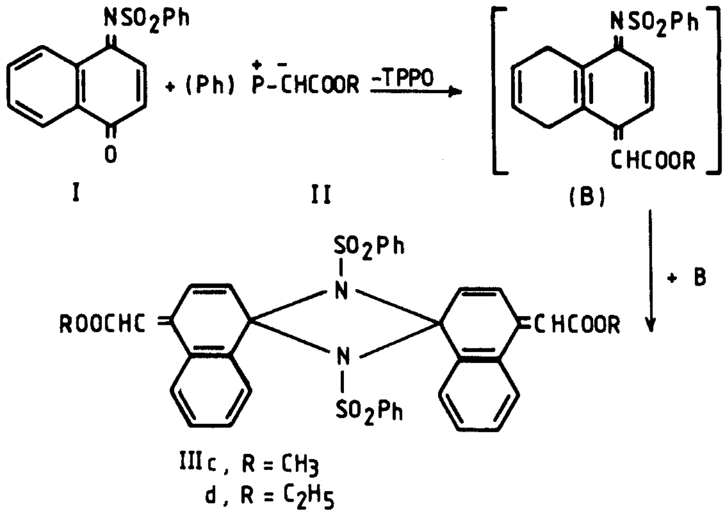
quinonemonoimine **I** affording the intermediate (A) which gives adduct **IIIa** through ejection of methyl (R = CH_3) or ethyl (R = C_2H_5) formate.

The structure of compound **IIIb** was deduced only from elemental analyses, IR and mass spectral data (Field Ionization Method) owing to its scarce solubility in most organic solvents. (cf. Experimental).

The identity of the other isolated product **IIIc** was attested by compatible analytical and mass spectroscopic results. The IR spectrum of adduct **IIIc** lacks both the carbonyl and C=N absorption bands appearing in the starting quinoneimine (I) at 1675 and 1580 cm^{-1}, respectively. Moreover, the IR spectrum of adduct **IIIc** exhibits strong absorption bands at 1630 cm^{-1} (C=C), 1730 and 1735 cm^{-1} (two ester C=O). The ^1H-NMR spectrum of **IIIc** (200 MHz) showed two singlets at 3.75 (3H, $COOCH_3$) and 4 ppm (3H, $COOCH_3$). It also shows two singlets at 6.05 (s, 1H, =CHCOO) and 6.15 (s, 1H, =CHCOO). The ortho methine protons H-2, H-3 and H-2′, H-3′ appear as two doublets centered at 6.65, 8.05 with ($J_{2,3}$ = $J_{3,2}$ = 8 Hz) and at 6.75, 8.1 with ($J_{2',3'}$ = $J_{3',2'}$ = 8 Hz). The aromatic protons appear as multiplet at 7.2–7.8 ppm (18H, m). Actually, the mass spectrum of adduct **IIIc** by (Field Ionization Method) yielded a prominent ion peak M^+ at 706 which supports structure **IIIc**.



IIIc



(Scheme III)

Formation of adduct **IIIc** can be explained in terms of addition of one mole of Wittig reagent **IIa** to the starting quinonemonoimine **I** to give the intermediate (B) through loss of TPPO, followed by dimerization under the experimental condition (tail to tail dimerization) to give the final product **IIIc** (Scheme III).

Similarly, carbethoxymethylenetriphenylphosphorane (**IIb**) reacts with one mole equivalent of 1,4-naphthoquinonemonoimine (**I**) at room temperature to give the dimeric ethylenic compound **IIId** together with both adducts **IIIa** and **IIIb** (cf. Schemes I, II, and III). Triphenylphosphine oxide was also isolated from the reaction medium. Structure **IIId** was deduced from correct microanalysis, IR, ^{1}H-NMR and mass spectral data (cf. Experimental).

Compounds **IIIa–d** are equally obtained, irrespective whether one or two equivalents of the Wittig reagents **IIa, b** were used with respect to one equivalent of quinoneimine **I**.

From the above results, it can be seen that the reaction of 1,4-naphthoquinonemonoimine **I** with ylides **II** leads to different products depending on the nature of the quinoneimine used[2–4] and also on the stability of the addition product. Moreover, it is safe to conclude that 1,4-naphthoquinonemonoimine **I** behaves towards Wittig reagents in a manner different from that already known with *p*-quinones[9] and *p*-quinonediimines.[2–4] 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 the synthesis of the new azacyclopropane adduct **IIIa**.

EXPERIMENTAL

All melting points are uncorrected. The benzene (thiophene-free) and pet. ethers (40–60°) used were dried over Na. Carbmethoxymethylene and carbethoxymethylene-triphenylphosphoranes were prepared according to established procedures.[10] 1,4-Naphthoquinonemonobenzenesulfonimide[11] was recrystallized and dried before use. The IR spectra were measured in KBr, on Perkin-Elmer Infracord Spectrophotometers 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 standared) on JNM-PS-100 Fa Jeol and JNM-GX-400 Fa Jeol Spectrometers. ^{13}C NMR spectra were taken in $CDCl_3$ 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 Spectrometer. Silicagel (Kieselgel 60, particle size 0.063–0.200 mm, E. Merk, Darmstadt) was used for column chromatography.

Reaction of Carbmethoxymethylenetriphenylphosphorane (**IIa**) *with 1,4-Naphthoquinonemonoimine* (**I**). To a suspension of quinone (**I**) (0.29 g, 0.001 mol) in dry benzene (10 ml), was added ylide (**IIa**) (0.33 g, 0.001 mol) in benzene (10 ml) and the reaction mixture was left at room temperature under stirring for 12 h. The yellowish grey precipitated material was filtered off (filterate A) and washed with benzene (2 ml). This solid material was triturated with chloroform whereby yellow crystals separated, filtered off (filterate B) to give **IIIb**, m.p. above 300°C, yield 25%. Anal. Calcd for $C_{32}H_{22}N_2O_6S_2$ (594.664) C, 64.63; H, 3.73; N, 4.71; S, 10.78. Found: C, 64.61; H, 3.75; N, 4.7; S, 10.75% Mol. Wt (MS) = 594. IR bands at 1730, 1735 (two C=O), 1335, 1175 cm^{-1} (SO_2) and at 1630 cm^{-1} (C=C).

Filterate (B) was evaporated whereas the solid material was washed with pet. ether and recrystallized from chloroform-pet. ether to give **IIIa** as grey crystals in 24% yield m.p. 205°C. Anal. Calcd for $C_{35}H_{26}NO_3PS$ (571.635) C, 73.54; H, 4.58; N, 2.45; P, 5.42; S, 5.61. Found C, 73.50; H, 4.60; N, 2.50, P, 5.40; S, 5.62% Mol. Wt (MS) = 571.

Filterate (A) was evaporated in vacuo and the residue was subjected to column chromatography on silica gel. Chloroform/ether (1:1) eluted **IIIc** as green crystals in 31% yield m.p. 155°C Anal. Calcd. for $C_{38}H_{30}N_2O_8S_2$ (706.792) C, 64.58, H, 4.28; N, 3.96; S, 9.07. Found: C, 64.60; H, 4.30; N, 3.94; S, 9.10% Mol. Wt (MS) = 706.

Reaction of Carbethoxymethylenetriphenylphosphorane (**IIb**) *with Naphthoquinonemonoimine* (**I**). To a suspension of quinone (**I**) (0.3 g, 0.001 mole) in benzene (10 ml), was added ylide (**IIb**) (0.35 g, 0.001 mol) in benzene (10 ml) and the reaction mixture was left at room temperature under stirring for 12 h. Working up of the reaction mixture as above afforded **IIIa**, **IIIb** and **IIId**.

Compound **IIId** was isolated using colulmn chromatography and eluted with chloroform/ether (7:3) as blue crystals in 31% yield m.p. 138°C Anal. Calcd. for $C_{40}H_{34}N_2O_8S_2$ (734.846) C, 65.38; H, 4.66; N, 3.81; S, 8.73. Found: C, 65.40; H, 4.65; N, 3.80; S, 8.75% Mol. Wt. (MS) = 734. **IR** bands at 1730, 1740 (two ester C=O), 1630 (C=C), ^1H NMR in $CDCl_3$, expressed in ppm: signals at 1.25 (3H, ethoxy-CH_3, *t*), 1.47 (3H, ethoxy-CH_3, *t*), 4.25 (2H, ethoxy-CH_2, *q*) 4.55 (2H, ethoxy-CH_2, *q*) 5.35 (1H, =CHCOO, *s*), 5.55 (1H, =CHCOO, *s*).

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