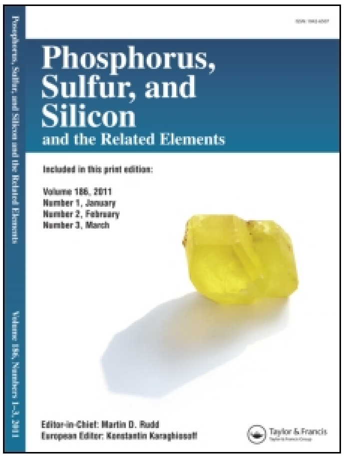

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THE BEHAVIOUR OF *p*-QUINONES TOWARDS WITTIG-HORNER REAGENTS

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THE BEHAVIOUR OF *p*-QUINONES TOWARDS WITTIG-HORNER REAGENTS

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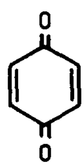
Triethylphosphonoacetate (I) reacts with *p*-quinones (1, 2) to give the corresponding 4-hydroxyl-β-hydroxy-succinic acid diethyl acetate **4** and **5**, respectively. On the other hand, the reaction of Wittig-Horner reagent (I) with *p*-chloranil (**3**) afforded 2,3,5,6-tetrachloro-4-hydroxyphenyl-β-hydroxy-succinic acid diethyl acetate (**7**) and the diethyl phosphonate adduct (**6**). Possible reaction mechanisms are considered and the structural assignments are based on compatible analytical and spectroscopic results.

Key words: triethylphosphonoacetate (I); *p*-quinones **1–3**; 4-hydroxy-phenyl-β-hydroxy-succinic acid diethylacetate (**4**); 4-hydroxynaphthyl-β-hydroxysuccinic acid diethyl acetate (**5**); 2,3,5,6-tetrachloro-4-hydroxyphenyl-β-hydroxy-succinic acid diethyl acetate (**7**); and the diethylphosphonate adduct (**6**).

INTRODUCTION

The Wittig and Wittig-Horner reactions are versatile synthetic methods whereby the latter has the advantage of requiring less expensive starting materials and a simpler product separation.[1–3] Although the reaction of *p*-quinones with Wittig reagents has been extensively studied,[4,5] their behaviour towards Wittig-Horner reagents has not yet been reported. Therefore we examined the reactivity of *p*-quinones **1–3** towards triethylphosphonoacetate (I).



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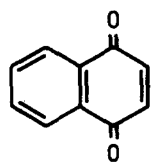

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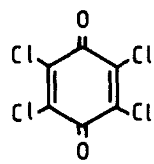


3

$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}-CH_2-COOC_2H_5$$

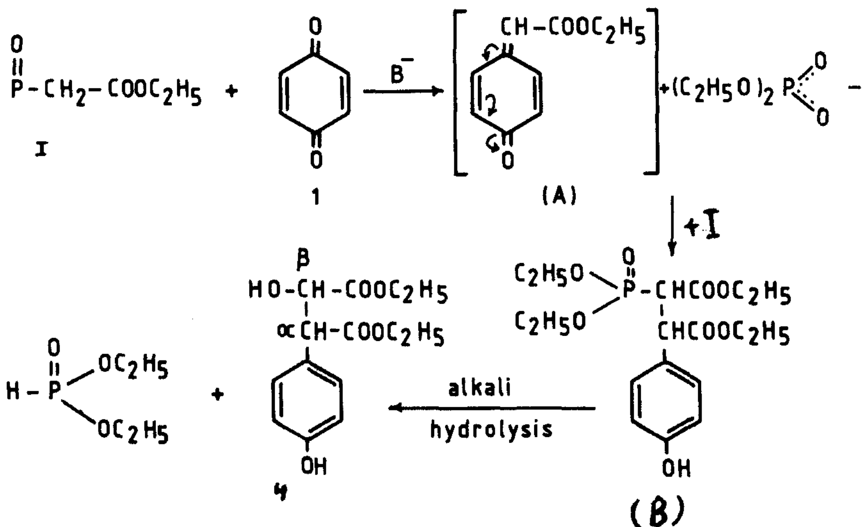
I

RESULTS AND DISCUSSION

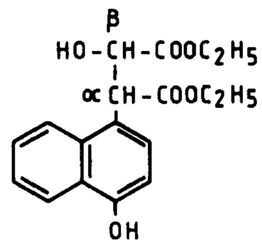
When *p*-benzoquinone (**1**) was treated with one equivalent of triethylphosphonoacetate (I) in the presence of alcoholic sodium ethoxide solution at 60–70°C for two hours, adduct (**4**) and *p*-benzoquinone (**1**) were isolated. Carrying out the reaction using two moles of the phosphonate anion (I) instead of one, lead to the formation of adduct **4** in good yields. The structure of the new compound **4** is assignable from its analysis, IR, ^1H NMR and mass spectral data. The IR spectrum of adduct **4**, in KBr, reveals the presence of strong absorption bands at 1735 and

1745 cm^{-1} ascribed to the ester carbonyl bands. Moreover, the IR spectrum of adduct 4 exhibits strong absorption bands at 3480 and 3500 cm^{-1} characteristic for the two —OH absorption bands. The ^1H NMR spectrum of adduct **4** showed signals at 0.85 ppm (3H, ethoxy-CH_3, *t*), 4.00 (2H, ethoxy-CH_2, *q*), 1.20 (3H, ethoxy-CH_3, *t*), 4.58 (2H, ethoxy-CH_2, *q*) attributed for the two ethoxyl groups. The two >CH—CH< groups appeared as two doublets centered at 2.8 and 2.9 ppm (2H, CH—CH, *d*), respectively. The exchangeable (D_2O) protons (OH) appeared as two singlets at 5.1 and 10 ppm. Also, the aromatic protons appeared as multiplet at 6.80–7.4 ppm (*m*, 4H). Actually, the mass spectrum of adduct **4** by Field Ionization Method yielded a prominent ion peak M^+ at 282 which supports structure (**4**). The mechanism proposed to account for the formation of adduct (**4**) is shown in (Scheme A). Adduct **4** can be obtained via carbonyl olefination by one mole of Wittig-Horner reagent (I) to give the intermediate (A) which reacts with another molecule of triethylphosphonoacetate (I) to give the phosphonate intermediate (B). Under the influence of the base present in the reaction medium, phosphonate **B** is hydrolysed in the conventional manner to give dialkylphosphite and the final product **4**.[6,7]

Similarly, the reaction of triethylphosphonoacetate (I) with 1,4-naphthoquinone (2) proceeds in alcoholic sodium ethoxide solution to give a chromatographically pure adduct assigned structure (5). Compound (**5**) is equally obtained irrespective whether one or two mole equivalents of the phosphonate anion (I) were used. Reasons for structure (5) were: (a) Correct elemental analysis, (b) IR spectrum of adduct (**5**) shows bands at 1730, 1735 (C=O, ester), a broad band at 3490 (two OH groups). The ^1H NMR spectrum of adduct (**5**) showed signals at δ = 0.85 (3H, ethoxy-CH_3, *t*), 3.45 (2H, ethoxy-CH_2, *q*), 1.20 (3H, ethoxy-CH_3, *t*), 3.7 (2H, ethoxy-CH_2, *q*), and at 7.4–8.2 (*m*, 6H, aromatic protons). The two >CH—CH< groups appeared as two doublets centered at 3.05 and 3.15 ppm



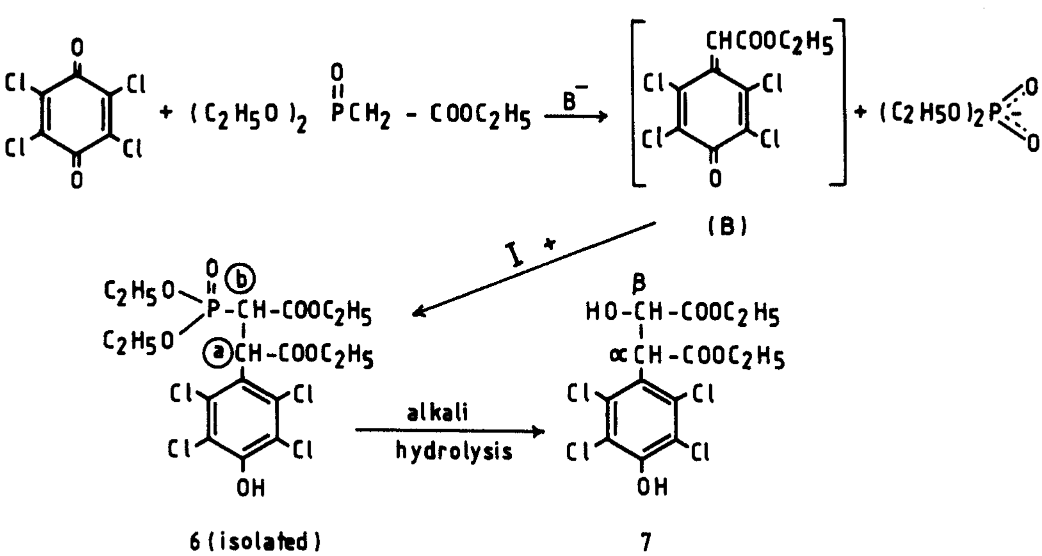
(Scheme A)



5

(2H, CH—CH, *d*), respectively. The exchangeable (D_2O) protons (OH) appeared as two singlets at 5.3 and 10.3 ppm. The mass spectrum of compound **5** yielded a prominent ion peak at m/e = 332.

We have found that triethylphosphonoacetate (I) reacts with *p*-chloranil (**3**) to give two pure adducts assigned structures **6** and **7**, respectively (cf. Scheme B). Elemental and mass spectral analyses for compound **6** corresponded to an empirical formula of $C_{18}H_{23}O_8PCl_4$. Its IR spectrum, in KBr, reveals the presence of two —OH absorption bands, at 3450, 3470 cm^{-1}. Moreover, the IR spectrum of adduct **6** exhibits strong absorption bands at 1230 cm^{-1} (P═O, bonded)[8] and at 1050 cm^{-1} (P—O—C_2H_5). The ^1H NMR spectrum (200 MHZ) of compound (**6**) (Scheme B), in $CDCl_3$, disclosed the presence of signals at δ = 0.85 (3H, CH_3 ethoxy, *t*), 1.4 (3H, CH_3-ethoxy, *t*), 4.45 (2H, CH_2-ethoxy, *q*), 4.55 (2H, CH_2-ethoxy, *q*) corresponding to the two carbethoxy groups. The two ethoxy groups attached to the phosphorus atom appeared as a triplet centered at 1.25 (6H, CH_3, *t*) and as a quintet centered at 4.2 (4H, CH_2, *q*). Moreover, the ^1H NMR spectrum of compound **6** showed signals centered at δ = 2.95 (*dd* with J_{HP} = 10 Hz, J_{HH} = 7.5



(Scheme B)

Hz) and at 3.03 (*dd* with J_{HP} = 12 Hz, J_{HH} = 7.5 Hz corresponding to the two methine protons ⓐ and ⓑ, respectively. The exchangeable (D_2O) proton (OH) appears as broad singlet at 10.12 ppm. The mass spectrum of compound **6** showed the molecular ion peak at m/e 540. The identity of the other isolated product **7**, (cf. Scheme B) was inferred from its correct analytical, mass spectroscopic analyses, and IR spectrum which reveals the presence of OH absorption bands at 3490, 3500 cm^{-1}, respectively.

The ^{1}H NMR spectrum of adduct **7** showed signals at 0.95 (3H, CH_3, *t*), 3.95 (2H, CH_2, *q*), 1.15 (3H, CH_3, *t*) and at 4.15 (2H, CH_2, *q*) corresponded to the two carbethoxyl groups. The two methine protons appeared as two doublets centered at 2.9 (1H, *d*) and at 3.1 ppm (1H, *d*) with J_{HH} = 7 Hz, respectively. The exchangeable (D_2O) protons (OH) appeared as a broad signal at 7.6 ppm.

A possible explanation of the course of the reaction of triethylphosphonoacetate (I) with *p*-chloranil is shown in (Scheme B). *p*-Chloranil reacts with two moles of triethylphosphonoacetate to give the stable phosphonate derivative **6**. Alkali hydrolysis of adduct **6** results in the formation of compound **7**. Although *p*-quinones have been reported[4] to react with two equivalents of Wittig reagents to yield the corresponding 2-(4-hydroxyaryl)-1,2-dialkoxycarbonyl ethylidene-triphenylphosphorane derivatives, a different behaviour is observed in the reaction of *p*-quinones **1–3** with Wittig-Horner reagent (I). From the results of the present investigation it could be concluded that the reaction of triethylphosphonoacetate (I) with *p*-quinones **1–3** lead to different products depending on the structure of *p*-quinones as well as on the stability of the addition products.

EXPERIMENTAL

All melting points are uncorrected. Triethylphosphonoacetate was prepared by means of the Michaelis-Arbuzov reaction.[9] The IR spectra were measured in KBr, on a Perkin-Elmer Infracord Spectrometer Model 157 (Grating). The ^{1}H NMR spectra were run on a Varian spectrometry at 200 MHz, using TMS as an internal reference. The MS spectra were run at 70 eV on a Kratos MS-50 equipment provided with a data system.

The reaction of triethylphosphonoacetate (I) *with p-benzoquinone* (**1**) *and/or 1,4-naphthoquinone* (**2**). A solution of 2 moles of sodium ethoxide in absolute ethanol was treated with an equimolar amount of the phosphonate I, after a while 1 mole of the quinone was added and the resulting reaction mixture was allowed to heat on a water bath at 60–70°C for 2 hr. The reaction mixture was allowed to cool to room temperature, then poured on a small amount of water, extracted with ethyl acetate, and the extract evaporated in a vacuum. The residual material was recrystallized from ethanol to give compounds **4** and/or **5**.

The coloured crystals of compound **4** were obtained (83%) from ethanol, mp. 320°C. Anal. Calcd. for $C_{14}H_{18}O_6$ (282.298) C, 58.33; H, 6.43. Found: C, 58.30; H, 6.48% Mol. wt. (MS) = 282. Similarly, compound **5** was obtained from ethanol (78%) mp. 275°C.
Anal. Calcd. for $C_{18}H_{20}O_6$ (332.358) C, 65.05; H, 6.07. Found: C, 65.08; H, 6.10% Mol. wt. (MS) = 332.

Action of triethylphosphonoacetate (I) on p-chloranil (**3**). To a suspension of chloranil **3** (0.245 g, 0.001 mol) in ethanol (10 ml), was added phosphonate (I) (0.448 g, 0.002 mol) and an equimolecular amount of sodium ethoxide. The reaction mixture was refluxed on a water bath for 2 hr, then cooled to room temperature, poured on a small amount of water, extracted with chloroform. The extract was evaporated to dryness and the residue was recrystallized from *n*-pentane to give adduct (**6**) as shiny orange crystals in 43% yield, mp. 85°C.
Anal. Calcd for $C_{18}H_{23}Cl_4O_6P$ (508.168) C, 42.54; H, 4.56; Cl, 27.91; P, 6.70. Found: C, 42.50; H, 4.60; Cl, 27.90; P, 6.73%. Mol. wt. (MS) = 508.

The water layer was extracted with ethyl acetate, the extract evaporated to dryness whereby a brown

material was obtained which was filtered off and recrystallized from alcohol/petroleum ether to give adduct **7** as brown crystals (48%), mp. 45°C. (Dialkyl phosphite was detected in the water layer by the development of a violet color on addition of 3,5-dinitrobenzoic acid).[10]
Anal. Calcd. for $C_{14}H_{14}Cl_4O_6$ (420.08) C, 40.03; H, 3.36; Cl, 33.76. Found: C, 40.00; H, 3.40; Cl, 33.78% Mol. wt. (MS) = 420.

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