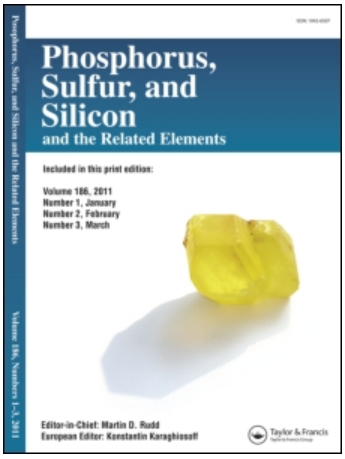

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ACTION OF WITTIG-HORNER REAGENTS ON o-QUINONES

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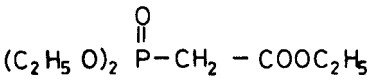
When 3,4,5,6-tetrachloro-1,2-benzoquinone (**1**) was reacted with two molar amounts of triethylphosphonoacetate (**I**), the corresponding 5,6,7,8-tetrachlorocoumarin-4-carbethoxy-3-diethylphosphonate (**4**) was obtained. Moreover, phenanthrene-9,10-quinone (**2**) was converted by reaction of Wittig-Horner reagent (**I**) into 2,3-dicarbethoxy-phenanthro[9,10-b]dihydrofuran (**5**) and the dimeric form (**6**). On the other hand, adducts (**7**) and (**8**) were isolated from the reaction of acenaphthenequinone (**3**) with triethylphosphonoacetate (**I**). Possible reaction mechanisms are considered and the structure of the new compounds (**4**), (**5, 6**) and (**7, 8**) was confirmed on the basis of the elemental analysis and spectral studies.

Key words: Triethylphosphonoacetate (**I**); o-quinones (**1–3**); 5,6,7,8-tetrachlorocoumarin-4-carbethoxy-3-diethylphosphonate (**4**); 2,3-dicarbethoxy-phenanthro[9,10-b]dihydrofuran (**5**); the dimeric form (**6**); 2,2′-diacenaphthylene-dicarbethoxycyclobutane-1,1′-dione (**7**); and 2,2′-diacenaphthylene-dicarbethoxycyclobutane-1-hydroxy-1-carbethoxymethyl-1′-one (**8**).

INTRODUCTION

The preparation of olefins by a convenient, general procedure has long been of interest. The Wittig reaction has proved to be quite versatile in this respect. The phosphonate modification of the Wittig reaction has proved to be useful in preparing sensitive olefins not preparable by standard Wittig synthesis.[1–4] In continuation of our work on the behavior of p-quinones towards Wittig-Horner reagents,[5] the action of triethylphosphonoacetate (**I**) on o-quiones (**1–3**) has now been investigated.



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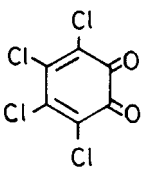

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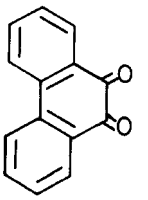

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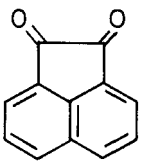

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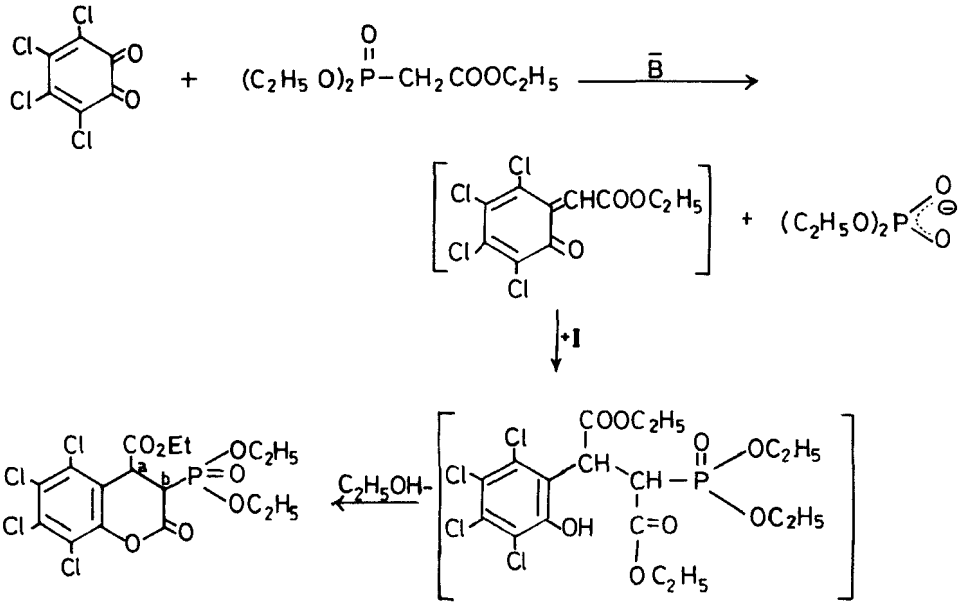
RESULTS AND DISCUSSION

We have found that the reaction of triethylphosphonoacetate (**I**) with 3,4,5,6-tetrachloro-1,2-benzoquinone (**1**), in the presence of alcoholic sodium ethoxide solution, proceeds at room temperature to give a chromatographically pure adduct formulated as (**4**) (Scheme I).

Elemental and mass spectral analyses for compound (**4**) corresponded to an empirical formula of $C_{16}H_{17}O_7PCl_4$. Its IR spectrum, in KBr, reveals the presence of strong absorption bands at 1720 and 1740 cm^{-1} ascribed to the ester and lactone carbonyl bands.[6] Moreover, the IR spectrum of adduct (**4**) exhibits strong absorption bands at 1230 cm^{-1} (P═O, bonded)[7] and at 1050 cm^{-1} (P—O—C_2H_5). The ^{1}H-NMR spectrum (200 MHz) of compound (**4**), in $CDCl_3$, disclosed the presence of signals at δ = 0.82 (3H, CH_3-ethoxy, t), 4.0 (2H, CH_2-ethoxy, q) corresponding to the carbethoxyl group. The two ethoxy groups attached to the phosphorus atom appeared as a triplet centered at 1.23 (6H, CH_3, t) and as a quinted centered at 4.22 (4H, CH_2, q). Moreover, the ^{1}H-NMR spectrum of adduct (**4**) showed signals centered at δ = 2.95 (dd with J_{HP} = 10 Hz, J_{HH} = 7.5 Hz) and at 3.05 (dd with J_{HP} = 12 Hz, J_{HH} = 7.5 Hz) corresponding to the two methine protons at position *a* and *b*, respectively (Scheme I). The mass spectrum of compound (**4**) showed the molecular ion peak at m/e 495.

A possible explanation of the course of the reaction of triethylphosphonoacetate (**I**) with o-chloranil (**1**) is shown in (Scheme I). o-Chloranil reacts with two moles of triethylphosphonoacetate to give the stable phosphonate derivative (**4**), possibly through loss of ethanol.



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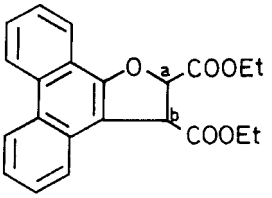
SCHEME I

The reaction of phenanthrene-9,10-quinone (**2**) with triethylphosphonoacetate (**I**) was also investigated. When (**I**) was allowed to react with two mole equivalents of (**2**) at 60–70° for eight hours, adducts 5 and 6 were isolated in good yields. Compounds 5 and 6 are equally obtained irrespective whether one or two equivalents of the carbanion reagent was used. Structure elucidation of 2,3-dicarbethoxyphenanthro[9,10-b]dihydrofuran (**5**) was attested by the following evidence:



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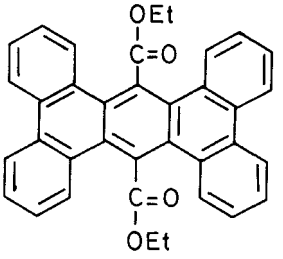

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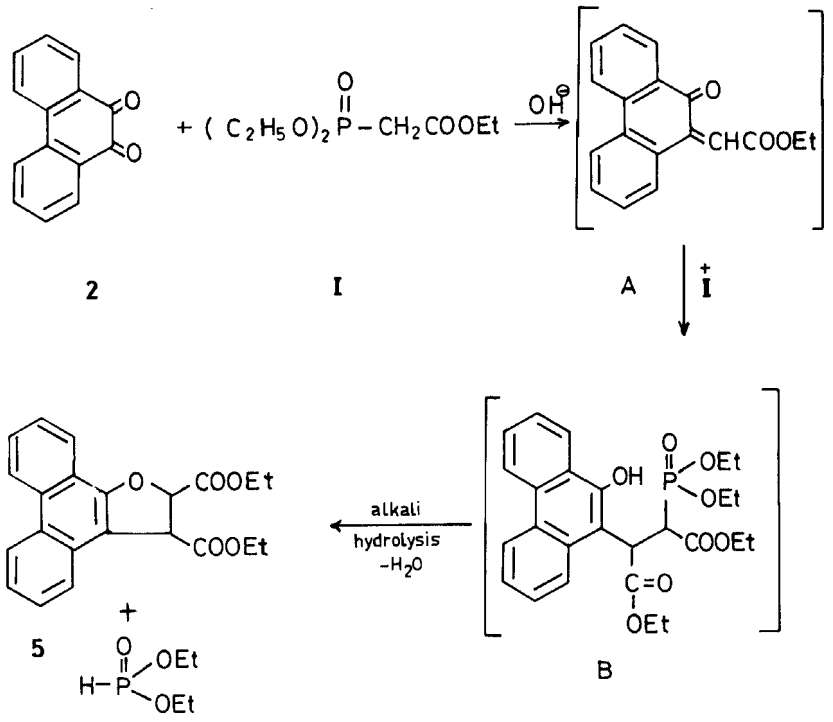
(a) Correct elemental analysis and molecular weight determination by (MS), (b) the IR spectrum of (**5**), in KBr, reveals the presence of strong absorption bands at 1705 cm^{-1} (C=O, ester), 1605 (C=C, aromatic) and at 1225 (C—O, stretching).

The strong absorption band at 1680 cm^{-1} recorded for the C=O in quinone (**2**) is absent in the IR spectrum of adduct (**5**). In the ^{1}H-NMR spectrum of (**5**), signals appeared at δ = 0.9 (3H, ethoxy-CH_3, t), 3.5 (2H, ethoxy-CH_2, q), 1.3 (3H, ethoxy-CH_3, t), 4.2 (2H, ethoxy-CH_2, q). Protons of the dihydrofuran nucleus appeared as two doublets each with J_{HH} = 4 Hz at δ = 3.15 (1H, proton b) and at 4.45 (1H, proton a). The spectrum also revealed a complex pattern due to the aromatic protons (8H, m) in the region 7.84–8.60 ppm. The mass spectrum of compound (**5**) yielded a prominent ion peak at m/e 364 (M^+, 11%), 319 (M^+-oEt, 15%), 274 (M^+-2 OEt, 30%) and at 218 (M^+-2 OEt-2CO, 45%).

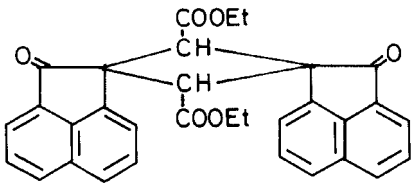
The mechanism proposed to account for the formation of adduct (**5**) is shown in (Scheme II). Adduct (**5**) can be obtained via carbonyl olefination by one mole of Wittig-Horner reagent (**I**) to give the intermediate (**A**) which reacts with another molecule of triethylphosphonoacetate (**I**) to give the phosphonate intermediate (**B**). Under the influence of the base present in the reaction medium, phosphonate (**B**) is hydrolysed in the conventional manner[8,9] to give dialkyl phosphite and the final product (**5**), possibly through elimination of water (Scheme II).

The identity of the other isolated product (**6**) was inferred from its correct analytical, mass spectroscopic analyses, and IR spectrum which reveals the presence of strong absorption bands at 1730, 1735 cm^{-1} (C=O, ester), 1580, 1550 (C=C, aromatic) and at 1620, 1625 (C=C, conjugated with aromatic ring).[10] The ^{1}H-NMR spectrum of adduct **6** showed signals at 1.2 (6H, ethoxy-CH_3, t), 4.15 (4H, ethoxy-CH_2, q), 7.2–9.2 (16H, m). Actually, the mass spectrum of the dimeric product **6** by Field Ionization Method yielded a prominent ion peak M^+ at 522 which supports structure **6**. Next, the reaction of acenaphthenequinone (**3**) with triethylphosphonoacetate (**I**) was performed in 1:2 molar ratio at 60–70° to give two chromatographically pure adducts formulated as (**7**) and (**8**), respectively.



SCHEME II

Elemental and mass spectral analyses for compound (**7**) corresponded to an empirical formula of $C_{36}H_{24}O_6$. Its IR spectrum, in KBr, revealed the presence of the carbonyl absorption band at 1700 cm^{-1} recorded for the starting quinone (**3**). Moreover, the IR spectrum of (**7**) exhibits strong absorption band at 1730 cm^{-1} characteristic for the ester carbonyl absorption bands. The ^{1}H-NMR spectrum (200 MHz) of (**7**) showed signals at δ = 0.85 (3H, ethoxy-CH_3, t), 4.20 (2H, ethoxy-CH_2, q), 1.32 (3H, ethoxy-CH_3, t), 4.30 (2H, ethoxy-CH_2, q) and at 1.45 (1H, s) and 1.83 (1H, s) for the two methine protons of the cyclobutane ring. The mass spectrum of compound (**7**) yielded a prominent ion peak at m/e 504.



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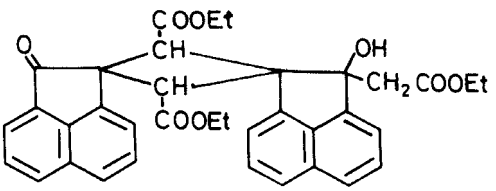

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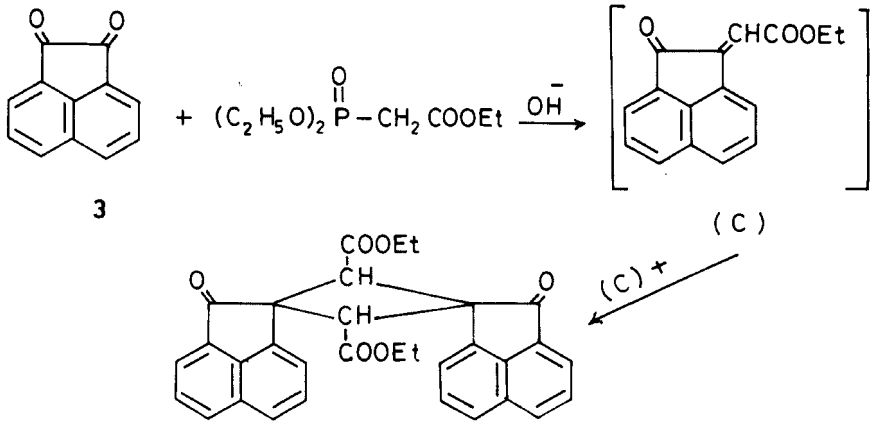
Adduct (**7**) can be obtained via carbonyl olefination by one mole of Wittig-Horner reagent (**I**) to give the intermediate (**C**) followed by dimerization under the experimental condition (tail to tail dimerization) to give the final product **7** (Scheme III).



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SCHEME III

The structure of the other isolated compound (**8**) is assignable from elemental analysis, IR, ^{1}H-NMR and mass spectral data. The IR spectrum of adduct (**8**), in KBr, reveals the presence of strong absorption bands at 1700 and 1740 cm^{-1} ascribed to the C=O of the quinone and the ester carbonyl absorption bands, respectively. Moreover, the IR spectrum of adduct (**8**) exhibits strong absorption band at 3480 cm^{-1} characteristic for the —OH absorption band. The ^{1}H-NMR spectrum of adduct (**8**) showed signals at 0.89 (3H, ethoxy-CH_3, t), 4.20 (2H, ethoxy-CH_2, q), 1.32 (3H, ethoxy-CH_3, t), 4.23 (2H, ethoxy-CH_2, q), 1.42 (3H, ethoxy-CH_3, t), 4.23 (2H, ethoxy-CH_2, q) and at 1.09 (CH_2, s). The two methine protons of the cyclobutane ring appeared as two singlets at 1.48 and 1.85 cm^{-1}. The exchangeable (D_2O) proton (OH) appeared as singlet at 5.2 ppm. Also, the aromatic protons appeared as multiplet at 7.5–8.7 (12H, m). The mass spectrum of adduct (**8**) by Field Ionization Method yielded a prominent ion peak at 592 which supports structure (**8**).

In view of the above results, it can be seen that the reaction of Wittig-Horner reagents with quinones (**1–3**) lead to diverse products depending on the nature of the quinone used and also on the stability of the addition products.

Moreover, it is safe to conclude that o-chloranil, phenanthrenequinone and acenaphthenequinone behave towards Wittig-Horner reagent in a manner different from that already known with Wittig-reagents.[11–14] The significance of these findings is not only the discovery of a new pattern of Wittig-Horner reaction but also the establishment of a novel method for the synthesis of the dimeric products **6, 7** and **8**.

EXPERIMENTAL

All melting points are uncorrected. Triethylphosphonoacetate was prepared by means of the Michaelis-Arburov reaction.[15] The IR spectra were measured in KBr, on a Perkin-Elmer Infracord Spectometer Model 157 (Grating). The ^{1}H-NMR spectra were run on a Varian spectrometer at 200 MHz, using

TMS as internal reference. The MS spectra were run at 70 eV on a Kratos MS-50 equipment provided with a data system.

Reaction of triethylphosponoacetate (**I**) *with 3,4,5,6-Tetrachloro-1,2-benzoquinone* (**1**): To a suspension of chloranil 1 (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 stirred at room temperature for 12 hrs. Ethanol was distilled under reduced pressure and the remaining precipitate was extracted with dry benzene. The benzene evaporated to dryness in the presence of silicagel (8 g). The mixture was then added to a column previously charged with silica gel in petroleum ether (b.p. 60–80°C). Fraction (100% petroleum ether) gave colourless crystals which recrystallized from cyclohexane to give adduct **4** (82%), m.p. 58°C. Anal. Calcd. for $C_{16}H_{17}O_7PCl_4$ (495.286); C, 38.80; H, 3.46; Cl, 28.67; P, 6.46. Found: C, 38.78; H, 3.50; P, 6.50%. Mol. wt. (MS) = 495.

Reaction of triethylphosphonoacetate (**I**) *with phenanthrene-9,10-quinone* (**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 one mole of the quinone was added and the resulting reaction mixture was allowed to heat on a water bath at 60–70°C for 8 hrs. The reaction mixture was allowed to cool to room temperature. Then poured on a small amount of water, extracted with chloroform. The extract was evaporated to dryness and the residue was recrystallized from cyclohexane to give adduct **5** as buff crystals (67%), m.p. 200°C. Anal. Calcd. for $C_{22}H_{20}O_5$ (364.402); C, 72.51; H, 5.53. Found: C, 72.56; H, 5.58%. Mol. wt. (MS) = 364. The water layer was extracted with ethyl acetate, the extract evaportated to dryness whereby a coloured material was obtained and recrystallized from ethanol to give adduct **6** as violet crystals (33%), m.p. > 300°C. Anal. Calcd. for $C_{36}H_{26}O_4$ (522.604); C, 82.74; H, 5.01. Found: C, 82.75; H, 5.2%. Mol. wt. (MS) = 522.

Reaction of acenaphthenequinone (**3**) *with triethylphosphonoacetate* (**I**). As previously, after pouring on water, extracted with chloroform. The extract was evaporated to dryness and the residue was recrystallized from benzene to give compound **7** (75%). m.p. 150°C. Anal. Calcd. for $C_{32}H_{24}O_6$ (504.544); C, 76.18; H, 4.79. Found: C, 76.13; H, 4.78. Mol. wt. (MS) = 504.

The water layer was extracted with ethyl acetate, the extract evaporated to dryness whereby a yellow material was obtained and recrystallized from ethanol to give adduct **8** (25%), m.p. >300°C. Anal. Calcd. for $C_{36}H_{32}O_8$ (592.652); C, 72.96; H, 5.44. Found: C, 72.9; H, 5.50. Mol. wt. (MS) = 592.

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