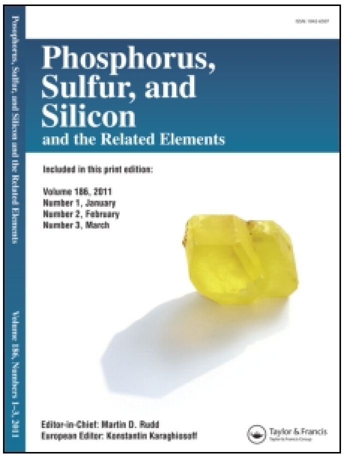

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REACTION OF PHOSPHONIUM YLIDES WITH 3,5-DI-TERT-BUTYL-1,2-BENZOQUINONE

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The reactions of quinone **1** with several Wittig reagents have been studied. When **1** was added to excess of **2**, the corresponding 1,1,2,2-tetrabromocyclobutene derivative **4** was obtained. Reaction of **1** with moderate-stabilized ylides **5a,b** at room temperature afforded the monosubstituted α,β-unsaturated esters **6**, while carrying out the reaction in boiling benzene led to the formation of coumarin-derivatives **8**. On the contrary, the reaction of **1** with resonance-stabilized ylides **5c,d** takes place, only at higher temperature to give disubstituted α,β-unsaturated ketones **9**.

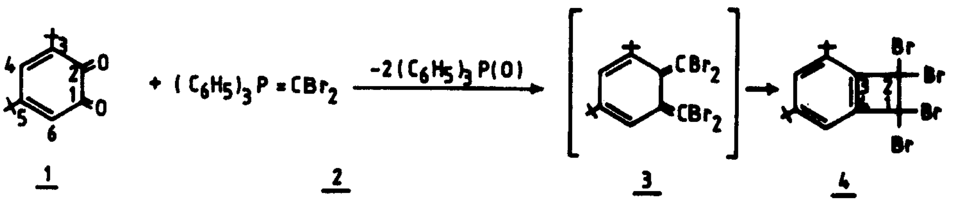
Key words: 3,5-Di-tert-butyl-1,2-benzoquinone; *o*-quinones; ylide-phosphoranes.

INTRODUCTION

The reactions of phosphonium ylides with *o*-quinones have been studied in considerable detail by several investigators.[1–5] They take remarkable interesting courses. Surprisingly, not much attention has been paid to the study of the reactivity of ylides toward 3,5-di-tert-butyl-1,2-benzoquinone (**1**). In earlier papers[6–8] we have studied the behavior of quinone **1** toward alkyl phosphites. In the present communication, it is aimed to examine the reaction of several phosphonium ylides with **1** under different conditions to determine if its reaction differed from those of other substituted *o*-benzoquinones.[2] This has been done and indeed significant departures from the usual behavior have been noted.

RESULTS AND DISCUSSION

Slow addition of **1** to excess of dibromomethylenetriphenylphosphorane (**2**), prepared in situ, in methylene chloride at low temperature affords the corresponding tetrabromocyclobutene derivative-accompanied by triphenylphosphine oxide (Scheme 1). The reaction was instantaneous as judged from the disappearance of the red color of the *o*-quinone. Structure **4** was in accord with the elemental and spectral



Scheme 1

data, a) Elemental analysis for **4** corresponds to $C_{16}H_{20}Br_4$. b) Its MS displayed a molecular ion at m/z 531 (M^+). c) Its IR spectrum lacks any absorption in the $\rangle C{=}O$ region (1650–1750). d) The ^1H-NMR spectrum of **4** showed only the feature of quinone **1**, aromatic protons gave two doublets at δ 7.46 and 8.56, while protons of the tert-butyl groups appeared as two singlets at δ 1.23 (9H) and 1.26 (9H).[9]

Actually, structure **4** could only be verified by ^{13}C-NMR analysis. In the ^{13}C-NMR[10] spectrum of **4**, signals were observed at: δ 31.8 and 32.1 ($\text{—}C(\underline{C}H_3)_2$), 35.09 and 35.69 ($\text{—}\underline{C}\text{—}CH_3$). Moreover, the cyclobutene ring was attested by the presence of signals at 52.5, 53.2 ppm $\left(\rangle\underline{C}\text{—}Br_2\right)$ and at 137.5, 142.2 regards to $\underline{C}$-3 and $\underline{C}$-4, respectively.

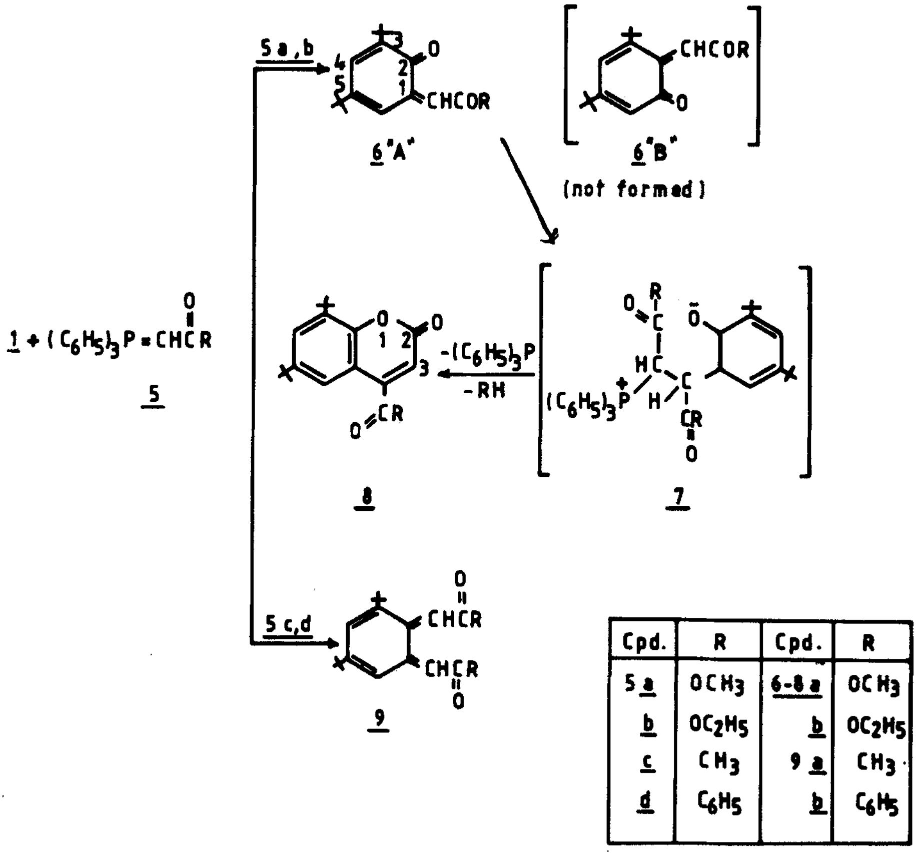
We can presume tentatively that formation of **4** (Scheme 1) was due to the rearrangement of the prior instable intermediate **3**. Such observation has been stated before by Sullivan *et al.*[3] for the reaction product of **9,10**-phenanthraquinone with **2**.

Next, the reaction of **1** with resonance-stabilized phosphoranes (**5**) was also investigated. The reaction of **1** with methoxy-(**5a**) and ethoxycarbonylmethylene-triphenylphosphorane (**5b**) at room temperature in benzene gave the corresponding monosubstituted α,β-unsaturated esters **6** as yellow crystals in fairly good yields. Triphenylphosphine oxide was isolated and identified in each case. Compounds **6** are equally obtained, irrespective whether one or two mole equivalents of the Wittig reagent **5a,b** were used. Reasons for structure **6** were: a) Correct elemental analyses and molecular weight determinations (MS) were obtained for both products. b) The IR spectra of these adducts **6a,b** reveal the presence of two strong absorption bands around 1740 and 1670 cm^{-1} for the ester- and aryl-carbonyl absorptions. Presence of $\rangle C{=}O$ groups in **6a** were also attested by signals at δ 179.6 and 169.5 ppm in its ^{13}C-NMR spectrum attributed to the aryl- and the estercarbonyl groups respectively. Meanwhile, presence of $\text{—}\overset{O}{\searrow}\!CO\underline{CH_3}$ group in **6a** was supported by a singlet at δ 3.84 (3H) in its PMR spectrum as well as by a signal at δ 58.82 at its ^{13}C-NMR. Moreover, the exocyclic vinyl proton resonated at δ 6.81 (1H) in its PMR spectrum.

Structure **6"A"**, however, seems to represent the reaction products more adequately than the other possible alternative form **6"B"** for the following reasons: a) The aryl-carbonyl band present in the IR spectrum of **6a** at 1675 cm^{-1}, agrees with the value that has been reported[11] for $\text{—}\overset{O}{\searrow}\!\underline{C}\text{—}2$ $\left(\text{while } \text{—}\overset{O}{\searrow}\!\underline{C}\text{—}1 \text{ has a stretching frequency at } 1695^{11};\ 2\right)$ ^{13}C-NMR spectrum of **6a** also showed a signal at δ 176.4 ppm a value which coincides with a chemical shift recorded[10] for $\text{—}\overset{O}{\searrow}\!\underline{C}\text{—}2$ in this quinone. 3) It has been established[8,11] that the initial nucleophilic attack, may be for steric reasons, is on the carbonyl-carbon-1 of quinone **1**.

On the other hand, when **1** was treated with two mole equivalents of **5a** and/or **5b** in boiling benzene for 6 h, a colorless product **8**, triphenylphosphine oxide and triphenylphosphine were isolated. Remarkably, heating the reaction product **6** with one mole of ylide **5a** and/or **5b** led also to the formation of **8** accompanied by triphenylphosphine. Proof of structure **8** was accomplished by: a) Elemental and spectral analyses for **8a** agree with the formula $C_{19}H_{24}O_4$. b) Its IR spectrum exhibited a strong band at 1765 cm^{-1} denoting the presence of a coumarin-carbonyl having —C—H grouping.[9] Strong bands at 1740 (C=O, ester), and at 1235 cm^{-1} (C—O, stretching) were also present in the IR spectrum of **8a**. The ^{1}H-NMR (δ, ppm) spectrum of **8a** had signals at δ 1.23, 1.29 (18H, 2s, tert-butyl), 3.9 (3H, s, OC$\underline{H}_3$), 6.65 (1H, s, coumarin-ring-H) and at 6.23, 6.99 ppm (2H, 2d, Ar-H).

On the basis of the isolated products, the conditions applied, and several leading mechanisms discussed in the literature for Wittig reactions,[1-5] we propose for the formation of **6** and **8**, the mechanism shown in Scheme 2. Following this, the initial nucleophilic attack by the carbanion centre in the ylide **5a,b** on the more reactive carbonyl-carbon-1,[11] to give the primary condensation product monoethylenes, **6** which is reasonably stable at room temperature. However, its stabilization at high



Cpd.	R	Cpd.	R
5a	OCH3	6-8a	OCH3
b	OC2H5	b	OC2H5
c	CH3	9a	CH3
d	C6H5	b	C6H5

Scheme 2

temperature (>70°C) in contact with ylides is not possible due to the resonance of the electronegative ester group, as in former reported cases.[12] Instead compounds **6** are trapped in a Michaelis type addition of the starting ylide, yielding the phosphorus-containing intermediate **7** which is followed by *O*-alkylation with expulsion of triphenylphosphine and a molecule of alcohol to give the final product **8**.

In contrast to the behavior of **1** toward ylides **2** or **5a,b**, no reaction occurred, when **1** was treated with acetonylidene- (**5c**) or phenacylidenetriphenylphosphorane (**5d**) in benzene (or ethyl alcohol) at room temperature, and starting materials were recovered, even after 60 h, practically unchanged. But, carrying out the reaction in boiling benzene (best yield in ethanol), using two mole equivalents of the phosphonium ylides **5c,d**. the Wittig reaction occurred readily to give the corresponding 1,2-di-α,β-unsaturated ketones as orange substances, believed to have structure **9** for the following reasons: a) Elemental analyses and molecular weight (MS) measurements agree with the assigned structure **9**. b) The IR spectrum of **9a** revealed the absence of the aryl-carbonyl absorption in the region 1650–1700. The two acetonylidene-carbonyl functions lie together as a broad absorption band at 1725 cm^{-1}. c) Its ^{1}H-NMR showed signals at δ 1.24, 1.28 (18H, 2s, tert-butyl), 2.2, 2.3 $\left(6H, 2s, -\overset{O}{\overset{\|}{C}}CH_3\right)$, 5.9, 6.1 (2H, 2s, =CH) and at 7.45, 8.10 ppm (2H, 2d, Ar-H).

CONCLUSION

The present study clearly shows that the dione system in **1** behaves toward the Wittig reagents in different interesting courses. However, the electronic nature of the substituents (R) in the ylides **2** and **5** is instrumental in determining the path of the Wittig reaction. Thus, while the highly active ylides of type **2** and the resonance stabilized ylides of type **5c,d** behave similarly (definitely under certain conditions) toward quinone **1**, the moderate stabilized ylides **5a,b** behave differently toward the same compound.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run on a Perkin-Elmer Infracord Spectrometer 157 (Grating) in KBr. The ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker-Model WH90 Spectrometer. The chemical shifts are recorded in δ ppm relative to TMS. The mass spectra were performed at 70 eV on MS-50 Kratos (A.E.I.) Spectrometer. All reactions were carried out under N_2 atmosphere.

Action of Dibromomethylenetriphenylphosphorane (**2**) *on Quinone* (**1**). Triphenylphosphine (1 g, 0.004 mol) was added to a well stirred solution of carbontetrabromide (0.6 g, 0.1 ml) in dry methylene chloride (12 ml). When the solution becomes orange (i.e., the dibromomethylenetriphenylphosphorane (**2**) is formed),[13] quinone **1**[14] (0.2 g, 0.001 mol) was added and the mixture was stirred at 5–10°C for 15 min. After evaporation of the volatile materials, the yellow residual substance was recrystallized from pentane to yield **4** as yellow crystals in 75% yield, m.p. 87°C. $C_{16}H_{20}Br_4$ (531.972). Calcd. C 36.12, H 3.79, Br 60.08; found C 36.06, H 3.73, Br 60.12. MS: m/z IR(KBr): 1600 cm^{-1} (arom.). ^{1}H-NMR: δ 1.23, 1.26 (18 H, tert-butyl, 2s) and at δ 7.46, 8.56 ppm (2H, aryl-H, 2d). ^{13}C-NMR: δ 31.8, 32.1 [$C(CH_3)_2$]; 35.09. 35.69 (—C—CH_3); 52.5, 53.2 $\left(>C{-}Br_2\right)$ and at δ 137.5, 142.2 ppm (C-3, C-4). MS: m/z 531 (M^+).

Action of phosphonium ylides **5a,b** *on quinone* **1**.

a) *At room temperature. General procedure.* To a suspension of quinone (**1**, 2.2 g, 0.01 mol) in dry benzene (10 ml) was added a solution of ylide **5a**[15] or **5b**[15] (0.011 mol) in the same solvent (10 ml) and the reaction mixture was stirred at room temperature (25°C) for 48 h. The reaction mixture was then concentrated at 40°C under reduced pressure. The solid product was redissolved in methanol (100 ml) and evaporated to dryness in the presence of silica gel (8 g). The mixture was then added to a column previously charged with silica gel in cyclohexane. The column was developed with cyclohexane containing increasing amounts of diethyl ether. Fraction (up to 8:2 v/v): eluted a yellow substance, recrystallized from suitable solvent to give **6a,b**.

Compound **6a**, yellow crystals (2.1 g, 78%), m.p. 127°C (ether). $C_{17}H_{24}O_3$ (276.379). Calcd. C 73.87, H 8.75; found C 73.79, H 8.71, IR (KBr) cm^{-1}: 1745 (C=O, ester), 1675 (C=O, aryl), 1620 (=CH). ^{1}H-NMR (δ ppm): 1.32, 1.38 (18H, tert-butyl, 2s), 3.84 (3H, O—CH_3, s), 6.81 (1H, =CH, s), 7.42, 8.43 (2H, aryl-H, 2d). MS: m/z 276 (M^+). aryl-H, 2d). ^{13}C-NMR: δ 58.82 $\left(—\overset{\overset{\displaystyle O}{\|}}{C}—O—CH_3\right)$, 169.5 $\left(\rangle C{=}O\text{, ester}\right)$ and at 179.6 ppm (C=O, quinone). MS: m/z 276 (M^+):

Compound **6b**, yellow crystals (2.3 g, 82%), m.p. 118°C (cyclohexane). $C_{18}H_{26}O_3$ (290.406). Calcd. C 74.44, H 9.02; found C 74.38, H 8.97, IR (KBr) cm^{-1}: 1740 (C=O, ester), 1668 (C=O, quinone), 1622 (=CH). ^{1}H-NMR (δ ppm): 1.36, 1.41 (18H, tert-butyl, 2s), 1.38 (3H, —CH_2—CH_3, t, J_{HH} = 7 Hz), 4.35 (2H, OCH_2, q, J_{HH} = 7 Hz), 6.88 (1H, =CH, s), 7.46, 8.26 (2H, aryl-H, 2d). MS: m/z 290 (M^+).

The fraction (up to 6:4 v/v) afforded colorless needles m.p. 156°C (ca. 82% yield) of triphenylphosphine oxide[16] (m.p., mixed m.p. and comparative IR spectra).

Similarly, the reaction of quinone **1** (0.01) with ylides **5a,b** (0.02 mol) at 25°C, afforded the same compounds **6a,b** in almost quantitative yield.

b) *In boiling benzene. General procedure.* A mixture of **1** (2.2 g, 0.01 mol) and ylide **5a,b** (0.0022 mol) in benzene (25 ml) was refluxed for 6 h. The volatile materials were then evaporated *in vacuo* and the residue so obtained (yellow oil) was chromatographed on silica gel; system: cyclohexane, then cyclohexane containing increasing amounts of diethyl ether. Fraction (100% cyclohexane) gave 0.91 g, (70%) of a colorless product, m.p. 80°C (petroleum ether, b.r. 40–60°C) which proved to be triphenylphosphine. Characterization by comparison with an authentic specimen. Fraction (up to 9:1, 500 ml) provided a yellow substance, recrystallized from suitable solvent to give **8a** or **8b**.

Compound **8a**, 2.0 g (65%), m.p. 94°C (cyclohexane). $C_{19}H_{24}O_4$ (316.401). Calcd. C 72.12, H 7.64; found C 72.07, H 7.62. IR (KBr): 1765 $\left(\rangle C{=}O\text{, coumarin}\right)$, 1740 $\left(\rangle C{=}O\text{, ester}\right)$ and at 1235 cm^{-1} $\left(\rangle C—O—\right)$. ^{1}H-NMR: δ 1.23, 1.29 (18 H, tert-butyl, 2s); 3.9 (3H, OCH_3, s); 6.65 (1H, coumarin-H, s) and at 6.23, 6.99 ppm (2H, Ar-H, 2d). MS: m/z 316 (M^+).

Compound **8b**, 2.0 g, (62%), m.p. 88°C (pentane), $C_{20}H_{26}O_4$ (330.428). Calcd. C 72.69, H 7.93; found C 72.66, H 7.87. IR (KBr) cm^{-1}: 1765 (C=O, lactone), 1740 (C=O, ester. ^{1}H-NMR: 1.33, 1.48 (18H, tert-butyl, 2s); 1.35 (3H, OCH_2CH_3, t), 4.4 (2H, OCH_2, q); 6.95 (1H, —CH, at C-3, s), 7.42, 8.2 (2H, Ar-H, 2d). MS: m/z 330 (M^+).

Fraction (up to 8:2, 300 ml) afforded another yellow crystalline material (17%), and identified as the mono-substituted α,β-unsaturated ester **6a** or **6b**, respectively, with no depression upon admixture melting points.

Fraction (up to 6:4) gave 0.97 g (69%) of a colorless crystalline product, recrystallized from petroleum ether (b.p. 80–110°C) and proved to be triphenylphosphine oxide. Characterization by comparison with authentic specimen.

When the reaction was performed using equimolar amounts from the ylide **5a** and the monosubstituted product **6a**, the coumarin derivative **8a** and triphenylphosphine were obtained together with some unchanged **6a**.

Action of phosphonium ylides **5c,d** *on quinone* **1**.

General procedure. A solution of quinone **1** (2.2 g, 0.01 mol) in 20 ml benzene, was added dropwise under stirring to a solution of the ylide **5c**[17] or **5d**[18] (0.022 mol) in 20 ml benzene. The reaction mixture was refluxed for 8 h during which the color changed to orange. After the solvent was distilled off, the residue was chromatographed by the usual manner. The column was developed with pet. ether containing increasing amounts of chloroform. Fraction (up to 8:2 v/v) eluted a yellow substance, recrystallized from suitable solvent to give **9a,b**.

Compound **9a**, yellow crystals (1.86 g, 62% yield), m.p. 142°C (acetonitrile). $C_{20}H_{28}O_2$ (300.444). Calcd. C 79.95, H 9.39; found C 79.90, H 9.35. IR (KBr): 1725 cm^{-1} (—C(O)CH$_3$). ^{1}H-NMR: δ 1.29, 1.28 (18H, tert-butyl, 2s); 2.2, 2.3 (6H, C(O)CH$_3$, 2s); 5.9, 6.1 (2H, =CH, 2s) and at 7.45, 8.10 ppm (2H, Ar-H, 2d).

Compound **9b**, yellow crystals (3.3 g, 82% yield), m.p. 186°C (chloroform). $C_{30}H_{32}O_2$ (424.586). Calcd. C 84.86, H 7.59; found C 84.81, H 7.57, IR (KBr) cm^{-1}: 1690 (br. COPh). ^{1}H-NMR (δ ppm): 1.40, 1.56 (18H, —C(CH$_3$)$_3$, 2s), 7.35, 8.02 (2H, =CH, 2s) and 7.6, 7.88 (2H, Ar-H, 2d). MS m/z 424 (M$^+$).

Fraction (up to 6:4) gave 4.2 g (85%) of triphenylphosphine oxide m.p. and mixed m.p. 155°C.

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