

Comparative Behaviour of 2,6-Di-*tert*-butyl- and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone with Some Phosphorus Reagents

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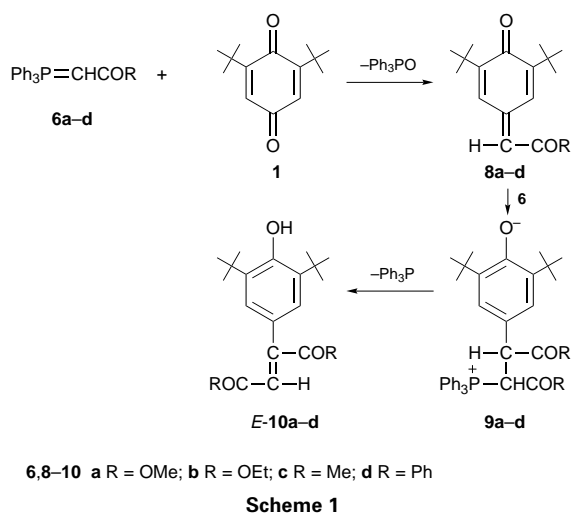
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2,6-Di-*tert*-butyl-1,4-benzoquinone (**1**) reacts with phosphorus ylides to give alkyl 1-*p*-hydroxyarylfumarates (ca. 75%); triethyl/methyl phosphites react with **1** and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **4**) on oxygen but triisopropyl phosphite reacts with **1** on oxygen and with **4** on carbon.

In connection with previous investigations,^{1,3} we are continuing our study of the interaction of the *p*-quinones 2,6-di-*tert*-butyl-1,4-benzoquinone (**1**) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **4**) with some penta- and tri-valent phosphorus reagents.

1. *Reactions of 2,6-Di-tert-butyl-1,4-benzoquinone (1) with Phosphorus Ylides 6a–d.*—Treatment of the quinone **1** with 2 mol. equiv. of alkoxy- (**6a,b**) or β -oxo-alkylidene phosphoranes (**6c,d**) in dry toluene solution followed by chromatography of the product mixture afforded the corresponding substituted phenols **10a–d** in ca. 75% yield (Scheme 1). The reaction of **6c,d** with **1** requires a protonating reagent (benzoic acid). The phenols **10a–d** were only obtained in the *E*-configuration and assigned the alkyl 1-*p*-hydroxyarylfumarate structure. Points in favour of this conclusion are (a) compounds **10** have sharp melting points and did not show any spectral evidence for isomerism; (b) it is generally accepted^{7–9} that the geometry of the double bond in intramolecular Wittig

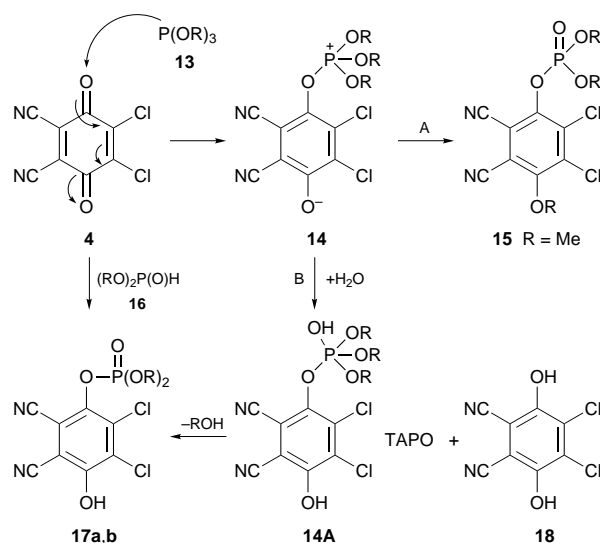


ig reaction is usually *E*; (c) other related examples^{3,4} of stabilized ylide reactions with *p*-quinones lead to either *E*-stereoselectivity or complete *E*-stereospecificity in these condensations. Mechanistically, the initially formed *p*-quinone methane intermediates **8a–d** give, by Michael addition of a second ylide species **6**, the betaines **9** which eliminate triphenylphosphine to give *E*-**10a–d**.

2. *Reactions of Quinones 1 and 4 with Trialkyl Phosphites.*—In dichloromethane solution, the products of the reaction of **4** with trimethyl phosphite **13a** were the *p*-alkoxyaryl dialkyl phosphate **15a** (18%), the *p*-hydroxyaryl dialkyl phosphate **17a** (20%) and the hydroquinone **18** (45%) (Scheme 2). No methyl chloride or acetonitrile could be

detected. The results with triethyl phosphite (**13b**) were similar, except that the parallel *p*-ethoxyaryl diethyl phosphate (**15**; R = Et) was not observed. However the phosphate **17b** (28%) and **18** (55%) were isolated by fractional crystallization of the product mixture. These results can be explained *via* initial attack by phosphorus on oxygen in **4** to yield the phosphonium species **14** which in the case of **13a** (R = Me) would allow group translocation, giving the alkyl ether of dialkyl *p*-hydroxyaryl phosphate **15** (Path A, Scheme 2). Conversely, partial hydrolysis of **14** (adsorption water) results in the formation of **17a,b** *via* with intermediate **14A** (Path B). On the other hand, the formation of **18** can be explained in terms of the high redox potential of DDQ^{15a} together with the strong reducing character of the tertiary phosphite reagents¹⁴ which would facilitate the reduction of **4** with water (unavoidable moisture) to give **18** along with trialkyl phosphate. That **17b** and **18** are only formed from the reaction of **13b** with **4** can be attributed to the high reduction potential of **13b** as compared to its methyl analogue,^{2,16} which facilitates the other competing reaction (reduction of DDQ) with formation of **18** in a high yield (55%).

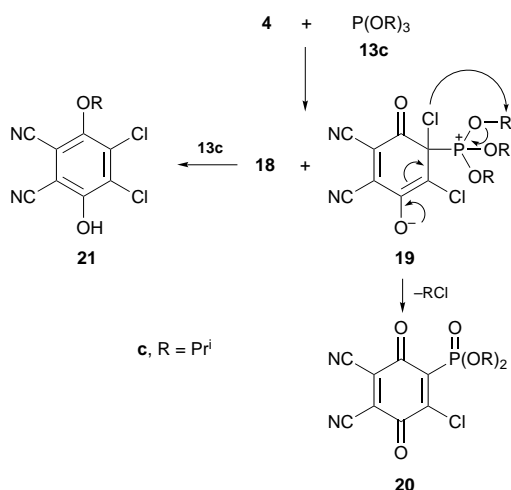
Conversely, when **4** was allowed to react with triisopropyl phosphite (**13c**) under the same reaction conditions as used with **13a,b**, the reaction went *via* a different pathway to give the benzoquinone-diisopropyl phosphoante derivative **20** and the hydroquinone monoisopropyl ether **21** in nearly equal amounts (~35%) (Scheme 3). It is obvious that carbon attack takes place in the latter reaction to give the alkoxyphosphonium salt **19**, which is then dealkylated by the displaced chloride ion (Michaelis–Arbuzov reaction) to give **20**. Meanwhile, initial reduction of DDQ **4** to **18** (see above) and



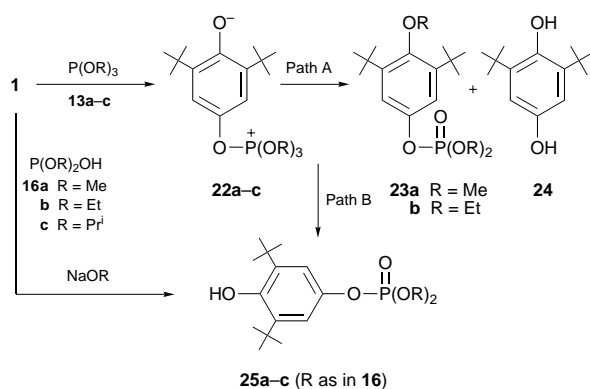
13–17 a R = Me; b R = Et

Scheme 2

*To receive any correspondence.



Scheme 3



Scheme 4

further alkylation of the product with a second molecule of **13c** affords the respective monoisopropyl ether **21**.

Next, the reaction of the trialkyl phosphites **13a-c** with 2,6-di-*tert*-butyl-1,4-benzoquinone (**1**) was also investigated. The reaction of **1** with trimethyl and triethyl phosphites (**13a,b**) proceeded smoothly in boiling toluene (3 h) to give

the corresponding ether phosphates **23a** (72%) and **23b** (80%), respectively. With **13c**, the same reaction conditions afforded **25c** (80%).

Hydroquinone **24** was, however, formed in the three reactions (<8%) (Scheme 4). The formation of **25c** instead of the parallel **23c** is not unexpected in view of the bulky isopropyl group which would impede the Arbuzov reaction. The structures of **23a** and **23b** were assigned through elemental analysis and by IR, ¹H and ³¹P NMR and mass spectroscopy, but the identity of the known¹⁸ compound **25c** was established by mp, mixed mp and comparative IR and mass spectra with an authentic sample prepared by the action of diisopropyl phosphite on **1** in the presence of sodium alkoxide.¹⁸

Techniques used: Elemental analysis, mass spectrometry, IR, ¹H and ³¹P NMR

References: 24

Equations: 6

Schemes: 4

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