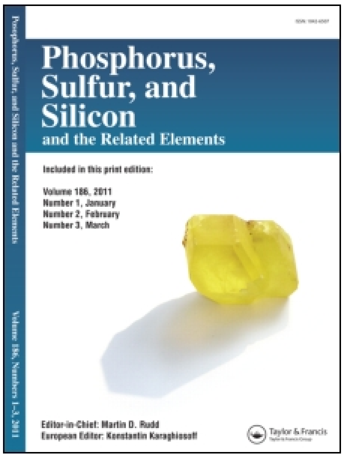

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Communication

FURTHER STUDIES ON THE BEHAVIOR OF 3,5-DI-TERT-BUTYL-1,2-BENZOQUINONE TOWARD PHOSPHORUS YLIDES†

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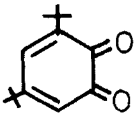
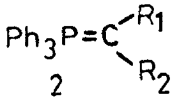
Key words: o-Quinones; 3,5-di-tert-butyl-1,2-benzoquinone; Wittig reactions.

It has been previously reported[1] that the titled quinone, 3,5-di-tert-butyl-1,2-benzoquinone (**1**) reacts with Wittig reagents in different interesting courses depending on the electronic nature of the substituents (R) in the ylides **2**. However, we have now extended our study on the potentiality of various ylides **2a**, **b** and **3** in the preparation of heterocyclic compounds derived from the same species **1**.

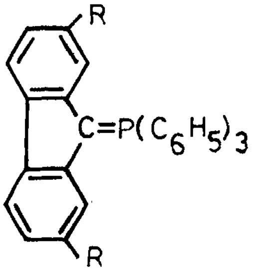


1

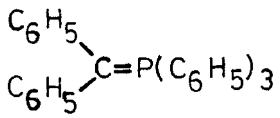


$Ph_3P=C(R_1)(R_2)$

2



2a, R = H
b, R = Br



$(C_6H_5)_2C=P(C_6H_5)_3$

3

Thus, when quinone **1** was treated with one equivalent of fluorenylidene-(**2a**)[2] or 2,7-dibromofluorenylidenetriphenyl-phosphorane (**2b**)[2] in dry benzene at ambient temperature for 3 hr, it gave colorless compounds assigned the corresponding 1,3-dioxole structures **4a** and **4b**, respectively. Triphenylphosphine was also isolated in both reactions in a quantitative yield. The new dioxides **4a** (mp. 178°C, 82%), and **4b** (mp 222°C, 90%) are crystalline solids, crystallized directly from the reaction mixture and purified by recrystallization from benzene.

The identity of **4** was verified by mixed m.p. determination and superimposable IR spectra with 9,9′(3,5-di-tert-butyl-o-phenylenedioxyl) fluorenes, prepared according to Schönberg et al.,[4,5] by the reaction of 9-diazofluorene or 9-diazo-2,7-dibromofluorene with the o-quinone (**1**).

Similarly, diphenylmethylenetriphenylphosphorane[6] has also been found to react with 3,5-di-tert-1,2-benzoquinone (**1**), yielding the corresponding 1,3-dioxole derivative **5** (mp. 128°C, 90%). Compound **5** was equally obtained and identified

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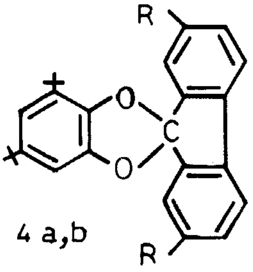
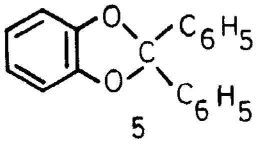
† Dedicated to Prof. M. Sidky on the occasion of his 62*nd* birthday.



4 a,b



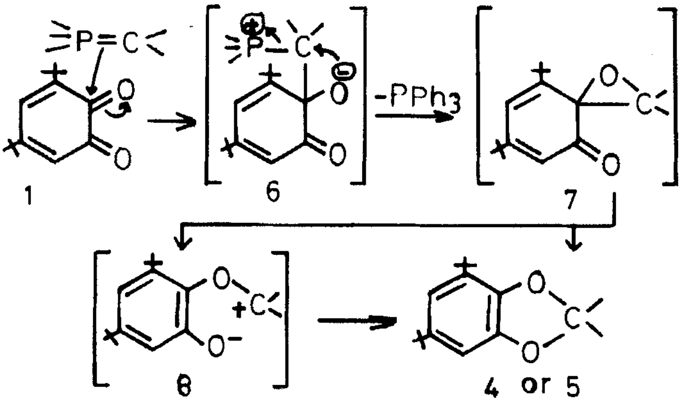
5

(mp., mixed mps. and comparative IR spectra) by allowing quinone **1** to react with diphenyldiazomethane.

Structural assignment for **4** and **5** comes from: a) Elemental and mass spectral analyses (by Field Ionization Method) which agree with the assigned structures **4** and **5**. b) The infrared spectra of the adducts revealed the absence of the aryl-carbonyl absorption in the region 1700–1650 cm^{-1}. They exhibit characteristic absorption spectra maxima at ca 1610 cm^{-1} (vinyl ether)[7] and ca 1600–1580 cm^{-1} (C—H, Ar). These absorptions are associated with out of plane deformation.[7] c) The PMR(DMSO, δ ppm) spectra of **4** and **5** have tert-butyl signals at ~1.24, 1.28 (25) and a multiplet at ~7.23–8.86 indicating the aromatic ring hydrogens.

Mechanistically, formation of compounds **4a**, **4b**, and **5** may be considered to proceed via **7** (Scheme I). It is reasonable to assume that the initial betaine **6** formed from **1** and the Wittig reagent can eliminate triphenylphosphine[8] which results in the formation of the intermediate epoxide (**7**)[9] which isomerizes[10] to the stable 1,3-dioxole derivatives **4** or **5**. This isomerization is probably effected through the dipolar form (**8**) which undergoes ring closure to yield the stable 1,3-dioxoles **4** or **5**. It is also possible that dioxoles **4** and **5** are formed directly from epoxide (**7**) by an orbital symmetry-allowed conversion.

In short, the reaction of **1** with phosphorus ylides of types **2a,b** and **3** yields products different from its reaction with normal alkylidene phosphoranes (e.g., **2**, $R_1 = R_2 = Br$; $R_1 = H$, $R_2 = COOMe$; $R_1 = H$, $R_2 = COOEt$ and $R_1 = H$, $R_2 = COPh$) previously described.[1] However, the anomalous behavior of **1** toward **2a,b** and **3** should be linked with its behavior toward diazoalkanes, whereby 1,3-dioxoles are likewise formed.[4,5,11]



SCHEME I

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