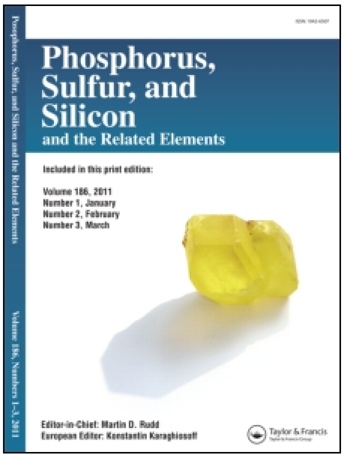

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PHOSPHONIUM YLIDS, IV.[1]
The Reaction of Tetrahalo-*o*-benzoquinones with Diphenylmethylenetriphenylphosphorane and Fluorenylidenetriphenylphosphoranes. An Anomalous Behavior of the Wittig Reagent

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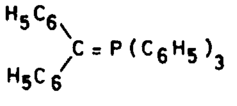
A novel synthesis of 1,3-dioxoles (**6a**), (**6b**) and (**7a–d**) by the action of diphenylmethylenetriphenylphosphorane (**1**) and fluorenylidenetriphenylphosphoranes (**2**) on tetrahalo-*o*-benzoquinones (**5**) is reported. A possible reaction mechanism is considered and the structural assignments are supported by chemical and physical evidence.

INTRODUCTION

Although diphenylmethylenetriphenylphosphorane (**1**) and fluorenylidenetriphenylphosphoranes (**2**) are known to undergo the Wittig reaction with *o*-quinones,[2] e.g. phenanthrenequinone, and vicinal triketones,[3] e.g. 1,2,3-indantrione, to yield the corresponding ethylenes (**3**) and (**4**), formation of 1,3-dioxoles using the same phosphorane reagents has not yet been reported.



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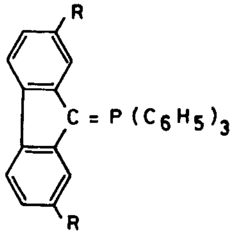
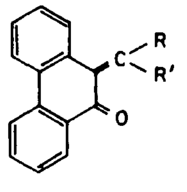
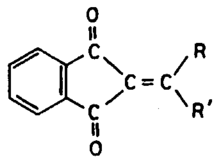


2a, R = H
b, R = Br



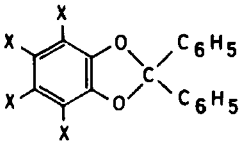
3a, R = R' = C_6H_5
b, R + R' = 9-fluorenylidene



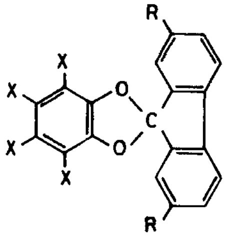
4a, R = R' = C_6H_5
b, R + R' = 9-fluorenylidene

RESULTS AND DISCUSSION

We have found that tetrachloro- and tetrabromo-*o*-benzoquinones (**5a, b**), highly reactive *o*-quinones,[4] react readily with diphenylmethylenetriphenylphosphorane (**1**) in dry benzene at room temperature to yield colorless compounds proved to be 2-diphenylmethylene 4,5,6,7-tetrahalogeno-1,3-benzodioxoles (**6a**) and (**6b**), respectively. Their identity was established by direct comparison (mixture m.p., TLC, IR analyses and MS spectra) with authentic samples prepared by the action of diphenyldiazomethane on tetrachloro- and tetrabromo-*o*-benzoquinones.[5] In the same vein, fluorenylidenetriphenylphosphorane (**2a**) and 2,7-dibromofluorenylidenetriphenylphosphorane (**2b**) react with tetrachloro- and tetrabromobenzoquinones (**5a, b**) to give the corresponding 1,3-dioxole derivatives (**7a–d**) in high yields. Compounds (**7a**) and (**7b**) were found identical (mixture m.p. and superimposable IR spectra) with (9: 9-tetrahalo-*o*-phenylenedioxy)fluorenes[6] obtained by the reaction of 9-diazofluorene with tetrachloro-*o*-benzoquinone (**5a**) and tetrabromo-*o*-benzoquinone (**5b**). In each case, triphenylphosphine was isolated as a minor reaction product.



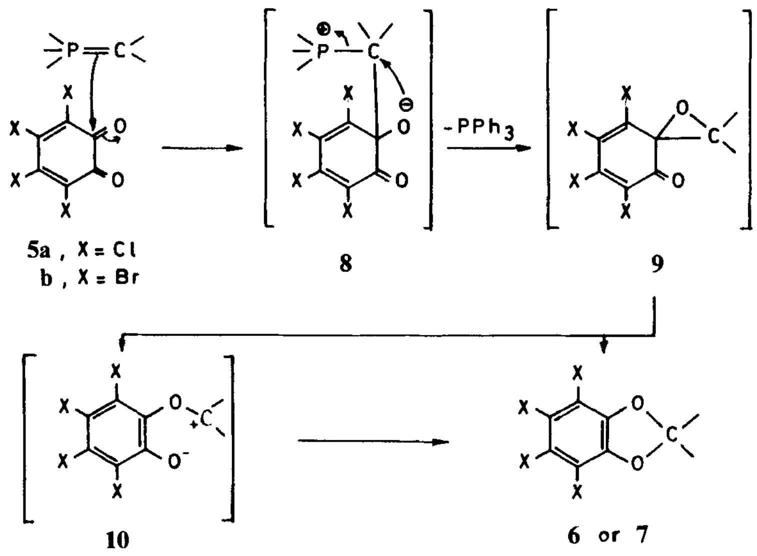
6a, X = Cl
b, X = Br



7a, X = Cl, R = H
b, X = Br, R = H
c, X = Cl, R = Br
d, X = Br, R = Br

The structure of the newly prepared 1,3-dioxole compounds (**7c**) and (**7d**) was inferred from their correct analytical values and the IR spectra which lack absorption bands in the carbonyl region. The band around 1610 cm^{-1} cannot be assigned unequivocally to carbonyl group,[7] since phenyl in plane-skeletal vibration can occur here.[8] Moreover the vinyl ether in 1,3-dioxoles is known to yield such a band.[9] We propose the reaction course depicted in Scheme 1 to account for this unexpected result. The reaction, which can be rationalized in terms of carbon-attack on the carbonyl carbon of quinone (**5**) by the phosphorane reagent, yields the betaine species (**8**). Subsequent elimination of triphenylphosphine[10] results in the formation of the intermediate epoxide (**9**)[11] which isomerizes[12] to the stable 1,3-dioxole derivatives (**6**) or (**7**). This isomerization is probably effected through the dipolar form (**10**) which undergoes ring-closure to yield the stable 1,3-dioxoles (**6**) or (**7**). It is also possible that dioxoles (**6**) or (**7**) are formed directly from epoxide (**9**) by an orbital symmetry-allowed conversion.

It is of interest to notice that phosphoranes of the present study are reminiscent of diazoalkanes in their reaction with tetrahalo-*o*-benzoquinones, whereby 1,3-dioxoles are likewise formed.[5,6,9,13–15]



The significance of this finding is not only the discovery of an anomalous behavior of a Wittig reagent but also the demonstration of a novel route for preparing the 1,3-dioxoles via phosphonium ylids.

EXPERIMENTAL

All melting points are uncorrected. Benzene (thiophene-free) was dried (Na). IR spectra were recorded in KBr with a Perkin-Elmer 137 Infracord. The mass spectra were recorded at 70 eV on Varian MAT 711 Spectrometer and/or Varian MAT 112 equipment.

Reaction of diphenylmethylenetriphenylphosphorane (**1**) *with tetrachloro-o-benzoquinone* (**5a**). To a solution of diphenylmethylenetriphenylphosphorane (**1**)[16] (0.42 g, 0.001 mol) in dry benzene (25 ml) was added a solution of tetrachloro-*o*-benzoquinone (**5a**)[17] (0.24 g, 0.001 mol) in benzene (10 ml). The mixture was left at room temperature for 6 hr, during this time the mixture turned to a clear solution and a white precipitate appeared immediately, filtered, recrystallized from ethyl alcohol to give compound (**6a**) as colorless crystals m.p. 143° (0.38 g, 92%). Mixture melting point with authentic sample, prepared from the reaction of tetrachloro-*o*-benzoquinone and freshly prepared diphenyldiazomethane, gave no depression.[5] Benzene was evaporated from the filtrate and the residual substance (0.32 g, 75%) was recrystallized from benzene-pet. ether (b.r. 60–80) to yield colorless crystals proved to be triphenylphosphine (m.p. and mixed m.p.).[18]

Similarly, the reaction of tetrabromo-*o*-benzoquinone (**5b**)[19] (0.4 g, 0.001 mol) with diphenylmethylenetriphenylphosphorane (**1**) (0.001 mol) in benzene (30 ml) for 5 hr at room temperature, afforded (**6b**) as colorless crystals (95%), m.p. 173° (mixed m.p. and comparative IR spectrum with authentic sample).[5]

Reaction of fluorenylidenetriphenylphosphorane (*FTP*, **2a**) *with tetrachloro-o-benzoquinone* (**5a**). To a solution of FTP (**2a**)[20] (0.42 g, 0.001 mol) in dry benzene (25 ml) was added a solution of tetrachloro-*o*-benzoquinone (**5a**) (0.24 g, 0.001 mol) in benzene (10 ml). The mixture left at room temperature for 5 hr whereby the color of the solution faded gradually. The white precipitate that formed was filtered, recrystallized from benzene to give (**7a**) as colorless crystals m.p. 281° (0.36 g, 90%). Mixed melting point of (**7a**) with authentic sample, prepared from diazofluorene and tetrachloro-*o*-benzoquinone, gave no depression.[6] From the filtrate, triphenylphosphine (m.p. and mixed m.p.)[18] was isolated in an almost quantitative yield.

Similarly, the reaction of tetrabromo-*o*-benzoquinone (**5b**) (0.4 g, 0.001 mol) with FTP (**2a**) (0.001 mol), in benzene (25 ml) for 3 hr at room temperature, afforded compound (**7b**) as colorless crystals (93%), m.p. 310° (from xylene). Mixture melting point with authentic sample gave no depression.[6] Triphenylphosphine (85%) was also separated from the reaction mixture and identified (m.p. and mixed m.p.).[18]

Reaction of 2,7-dibromofluorenylidenetriphenylphosphorane (**2b**) *with tetrachloro-o-benzoquinone* (**5a**). A solution of compound (**2b**)[21] (0.6 g, 0.001 mol) in benzene (25 ml) was added to a solution of tetrachloro-*o*-benzoquinone (**5a**) (0.24 g, 0.001 mol) in the same solvent (25 ml) and the mixture left at room temperature for 5 hr. The colorless material that precipitated was filtered (0.51 g, 91%) and recrystallized from xylene to give (**7c**) as colorless crystals m.p. 325°. Anal. Calcd. for $C_{19}H_6O_2Cl_4Br_2$: C, 40.17; H, 1.06. Found: C, 40.1; H, 1.13%. Mol. Wt. Calcd.: 568.057. Found (MS): 568. After evaporation of benzene filtrate, triphenylphosphine (ca. 85%) was isolated and identified (m.p. and mixed m.p. with authentic sample gave no depression).[18]

Similarly, the reaction of tetrabromo-*o*-benzoquinone (**5b**) (0.4 g, 0.001 mol) with 2,7-dibromofluorenylidenetriphenylphosphorane (**2b**) (0.6 g, 0.001 mol), in benzene (25 ml) for 3 hr at room temperature, afforded (**7d**) as colorless crystals (95%), m.p. 335° from xylene. Anal. Calcd. for $C_{19}H_6O_2Br_6$: C, 30.6; H, 8.11. Found: C, 30.53; H, 8.2%. Mol. Wt. Calcd.: 746.659. Found (MS): 746. After evaporation of the filtrate, triphenylphosphine was isolated in 80% as colorless crystals (mixture m.p. with authentic sample gave no depression).[18]

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