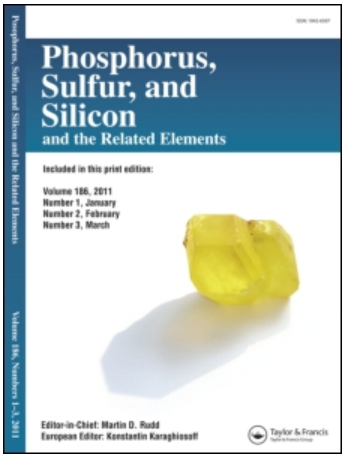

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SHORT COMMUNICATION

Reactions of Tris(diethylamino)phosphine with Some Quinones

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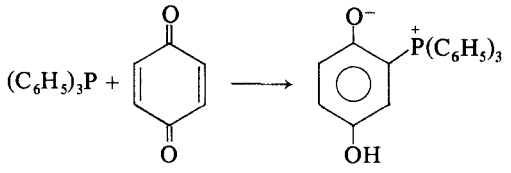
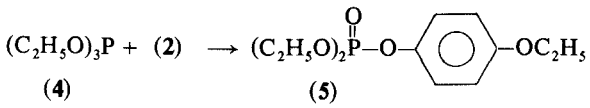
Tris(diethylamino)phosphine reacts with chloranil and 2,3-dichloro-4,5-dicyanoquinone to give products of addition to carbon with loss of chloride ion.

The reactions of trivalent phosphorus compounds with para quinones have been studied in considerable detail by Ramirez and his co-workers.[1] They take several interesting courses. For example, triphenylphosphine **1**, and benzoquinone **2**, react to give the betaine **3**.[2] Triethyl phosphite **4**, reacts with **2** to give the phosphate **5**,[3] Chloranil **6** and **1** react

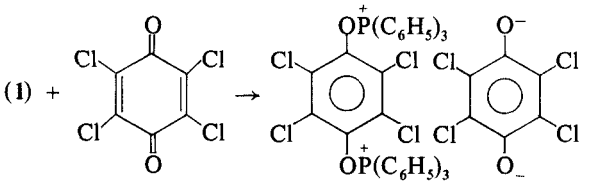


(1) (2) (3)



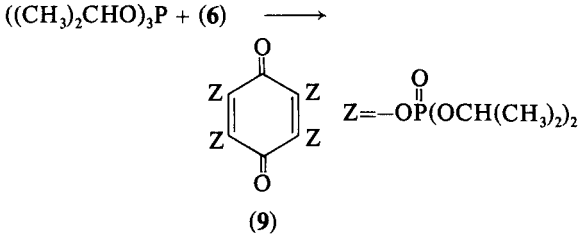
(4) (5)

by a complex pathway to give the ion pair **7**.[4] Triethyl phosphite and **6** react to give tetrachloro **5**.[5]



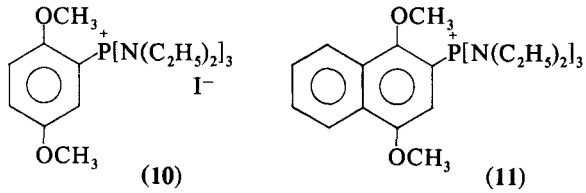
(6) (7)

On the other hand **6**, and triisopropyl phosphite **8**, react to give the product **9**.[6]

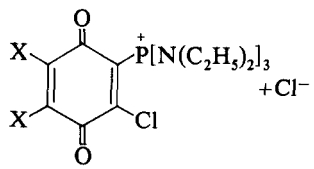


(9)

Compounds **10** and **11**, have been shown to possess activity in the Leukemia P388 test system.[7] They were prepared by addition of tri(diethylamino)phosphine **12** to the appropriate quinone followed by alkylation of the betaine, and analogue of **3**, with methyl iodide.[8] It seemed of interest to investigate the reactions of **12** with other quinones. Both chloranil **6** and 2,3-dichloro-4,5-dicyanoquinone **13** react with **12** to give adducts **14** and **15**.



(10) (11)



(**14**)X = Cl; (**15**)X = CN

The behaviour of **12** towards **6** is entirely different from that of triphenylphosphine **1**. This may be due in part to the greater nucleophilicity of **12** as compared to **1**.[9]

Other quinones which were allowed to react with **12** gave many products as evidenced by the ^{31}P nmr spectra of the reaction mixtures.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Preparation of **15** *and* **14**. Compound **12**, 3.6 g (0.014 mole) in 20 ml of ice cold benzene was treated dropwise with a solution of **13**, 2.2 g (0.009 mole) in 225 ml of benzene over a period of 1.5 h. The reaction mixture was evaporated to dryness *in vacuo* and the resulting brownish-yellow solid was washed with pentane to give 4 g of product. The product **15**, was crystallized from methanol, mp 210–215°C.

Anal. Calcd. for $C_{20}H_{30}Cl_2N_5O_2P$: C, 50.64; H, 6.30; N, 14.7. Found: C, 50.40; H, 6.45; N, 14.6.

The infrared spectrum showed characteristic absorptions for the cyano group 4.2 μ and the carbonyl group 5.6 μ.

The ^{31}P nmr spectrum had one resonance at δ + 36.15 downfield from 85% phosphoric acid. The ^1H nmr spectrum of the compound in deuterated chloroform had a broad resonance centered at δ 3.32 for hydrogens of the methylene groups and a triplet at δ 1.35 (J_{HCCH} = 7 Hz) for the hydrogens of the methyl groups.

Treatment of the compound with alcoholic silver nitrate gave a precipitate of silver chloride.

By an entirely analogous procedure **6** and **12** gave a material which was crystallized from methanol, mp 230–235°C.

Anal. Calcd. for $C_{18}H_{30}Cl_4N_3O_2P$: C, 43.83; H, 6.13; N, 8.51. Found: C, 43.45; H, 6.27; N, 8.45.

The infrared spectrum had a carbonyl absorption at 5.4 μ.

The ^1H nmr spectrum in chloroform shows a broad ill-defined absorption for hydrogens of the methylene groups between δ 3.0–3.8 and a poorly defined triplet at δ 1.3 (J_{HCCH} = 7 Hz) for the hydrogens of the methyl groups. The ^{31}P nmr spectrum had one resonance at δ + 35.13.

Treatment of **14** with alcoholic silver nitrate led to the formation of a precipitate of silver chloride.

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