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Donald B. Denneya; Anil D. Pendsea

^a Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey

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SHORT COMMUNICATION

Reactions of Tris(diethylamino)phosphine with Some Quinones

DONALD B. DENNEY and ANIL D. PENDSE

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

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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. 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

$$(C_{6}H_{5})_{3}P + O \longrightarrow O \longrightarrow P(C_{6}H_{5})_{3}$$

$$(O \longrightarrow OH)$$

$$(O \longrightarrow$$

by a complex pathway to give the ion pair 7.4 Triethyl phosphite and 6 react to give tetrachloro 5.5

$$(1) + CI \longrightarrow CI \longrightarrow CI \longrightarrow CI \longrightarrow CI \longrightarrow CI$$

$$O \longrightarrow CI \longrightarrow CI \longrightarrow CI \longrightarrow CI$$

$$O \longrightarrow CI \longrightarrow CI \longrightarrow CI$$

$$OP(C_6H_5)_3 \longrightarrow O$$

$$OP(C_6H_5)_3 \longrightarrow O$$

$$OP(C_7)$$

On the other hand 6, and triisopropyl phosphite 8, react to give the product 9.6

Compounds 10 and 11, have been shown to possess activity in the Leukemia P388 test system.⁷ They were prepared by addition of tri(diethyl-

amino)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-dicyano-quinone 13 react with 12 to give adducts 14 and 15.

$$X \xrightarrow{O} P[N(C_2H_5)_2]_3 + Cl^-$$

$$(14)X = C1; (15)X = CN$$

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 ³¹P nmr spectra of the reaction mixtures.

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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 $\delta + 36.15$ downfield from 85% phosphoric acid. The ^{1}H 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 ($J_{\text{HCCH}} = 7 \text{ Hz}$) for the hydrogens of the methyl groups. The ³¹P 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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