the ionization potential of (II) permits the reliable demonstration of the presence of (II) in various reaction systems.

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C-ADDITION OF DIMETHYL PHOSPHITE TO

p-BENZOQUINONE

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It is well known that in contrast to aldehydes and ketones which, in the presence of basic catalysts, add dialkyl phosphites at the carbonyl group carbon atom, p-benzoquinone under these conditions gave the products of O-P addition, namely, dialkyl-p-hydroxyphenyl phosphates. We have discovered that in the absence of base, dimethyl phosphite adds mainly at the terminal carbon atom of p-benzoquinone and a C-phosphorylated hydroquinone (I) is formed in 55% yield. Isomeric dimethyl-p-hydroxyphenyl phosphate (~10% yield relative to the ³¹P NMR spectral data, δ 5 ppm) and hydroquinone (III) (8% yield) which is C,C-diphosphorylated in the ring, are also found

(III)



Maintenance of a solution of p-benzoquinone in a fivefold molar excess of dimethyl phosphite at 20°C for three weeks leads to the complete disappearance of quinone, as indicated by thin layer chromatography. The excess phosphite was removed in vacuum and tetramethyl-2,5-dihydroxy-1,4-phenylene diphosphonate (III) was crystallized at 0°C over 3 h from the residue as colorless needles with mp 126°C (reprecipitated from ether by high-boiling petro-leum ether), $\delta^{31}P$ 24 ppm. PMR spectrum (CCl₄, δ , ppm): 3.70 m (4CH₃), 6.97 t (J_{HPa} + J_{HPb} = 7 Hz, 2H in Ar), 11.56 s (2HO). IR spectrum (vaseline suspension, v, cm⁻¹): 1210 (P=O), 1270 (POC) UV spectrum (methanol, λ_{max} , nm(ε_{max})): 220.5 (11,000), 337 (6500). Dimethyl-2,5-dihydroxyphenyl phosphonate (I) slowly crystallized from the filtrate at 0° as colorless needles with mp 136.5°C (from benzene), $\delta^{31}P$ 22 ppm. PMR spectrum ((Me₂N)₃PO, δ , ppm): 3.70 m (2CH₃, J_{HP} = 11 Hz), 7 m (3H in Ar), 9.86 s and 10.67 s (···H=OAr + ···HOAr). IR spectrum (vaseline suspension, v, cm⁻¹): 1210 (P=O), 1275 (POC), 3000-3500 (···H=OAr).

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UV spectrum (methanol, λ_{max} , nm (ε_{max}): 224.5 (5800), 313 (5100). The elemental analyses were in accord with the formula of (I) and (III).

An unidentified product with δ 8 ppm was detected in the reaction mixture by ³¹P NMR spectroscopy.

SELECTIVITY OF THE ACYLATION OF N-PHENYLMALEIMIDE

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We have observed that in the reaction of N-phenylmaleimide with acetyl chloride in the presence of lewis acids the acylation has a selective nature depending on the solvent. In nitrobenzene a hydrogen atom on the ring is replaced [1], with the formation of,4-acetyl-N-phenylmaleimide (III), and in pyridine, acetyl chloride is added at the carbon-carbon double bond [2]. In the latter case, the resulting α -acetyl- β -chloro-N-phenylsuccinimide (IV) easily releases HCl, being converted to α -acetyl-N-phenylmaleimide (V)



Compound (III) was synthesized by the reaction of 3.28 g of (I), 1.42 g of (II), and 2.66 g of AlCl₃ in 20 ml of nitrobenzene at 0°C for 3 h, 52.6% yield, mp 163-164°C. IR spectrum (ν , cm⁻¹): 1720, 1780 (C=0), 830 (n-C₆H₄), 2950 (CH₃). Found: C 65.42; H 5.36; N 6.98%. C₁₂H₉NO₃. Calculated: C 66.04; H 5.54; N 6.42%.

Compound (V) was obtained similarly in 50 ml of pyridine, 83.1% yield, mp 233-235°. IR spectrum (ν , cm⁻¹): 1710, 1780 (C=0), 700, 760 (C₆ H₅), 2930 (CH₃). Found: C 65.31; H 5.28; N 6.87%. C₁₂H₉NO₃. Calculated: C 66.04; H 5.54; N 6.42%.

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