

CONCLUSIONS

The five-membered heterocycle in the structure of 3-oxo-3-chloromethyl-2,3-dihydro-1,3-benzoxaphosphole is planar to within ± 0.03 Å with the greatest (CPC)_{endo} bond angle equal to $91.33(7)^\circ$.

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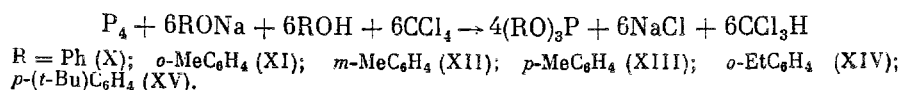
REACTION OF ELEMENTAL PHOSPHORUS WITH PHENOLS

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The reactions of elemental phosphorus (P_4) with phenols to give triaryl phosphites hold both practical and theoretical interest. However, the available data on this reaction does not indicate their general features [1-3]. In the present work, we studied the reactions of P_4 with various phenols in order to clarify the effect of the pK_a value of the phenol and the nature and position of the ring substituent on the course of the reaction and yield of triaryl phosphites.

The PhO^- anions do not react with P_4 , while $AlkO^-$ and $AlkS^-$ anions undergo quantitative reaction [2, 4]. This discrepancy results both from the reduced nucleophilicity of PhO^- anions and the strong association of these ions in solution in comparison with $AlkO^-$ and $AlkS^-$ ions [5]. In order to increase the actual concentration of free PhO^- in solution, the reactions of P_4 with phenols were studied with the addition of crown ethers or in DMF. The reactions were carried out in the presence of corresponding phenolates and CCl_4 . The following phenols were selected for study: phenol (I), *o*-, *m*-, and *p*-cresols (II)-(IV), *o*-ethylphenol (V), *p*-tert-butylphenol (VI), *p*-chlorophenol (VII), *p*-fluorophenol (VIII), and *p*-nitrophenol (IX):



The reactions were carried out in an argon atmosphere at 50-90°C over 1-5 h depending on the phenol taken in DMF or in the presence of 15-crown-5 or 18-crown-6. The reactions in the presence of cation-solvating agents proceed rather selectively and rapidly to give triaryl phosphites with an impurity of triaryl phosphates or only phosphates depending on the nature of the phenol. The separation of the reaction mixtures containing crown ethers is difficult due to the high solubility of the complexes of the crown ethers and reaction products in same solvents. The range of phenol pK_a values, in which reaction with P_4 is possible, is 9-11. The reaction of P_4 with phenols (I)-(IV) proceeds with the complete conversion of P_4 and the greatest triaryl phosphite yields. The yield of triaryl phosphites (X)-(XIII) is 85, 73, 66, and 56%, respectively. The conversion of P_4 and the triaryl phosphite yield drop with increasing size of the alkyl substituent [phenols (V) and (VI)]: (XIV) was obtained in 25% yield, while (XV) was detected only spectrally. The corresponding phosphates, (*p*-ClC₆H₄O)₃PO (XVI) and (*p*-FC₆H₄O)₃PO (XVII) were obtained in 11 and 14% yields in the case of halophenols (VII) and (VIII). The reaction of *p*-nitrophenol (IX) (pK_a 7.15) with P_4 does not proceed.

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Thus, the composition and yield of the products formed in the reaction of P_4 with phenols depend on the acidity of the phenol and the nature of the ring substituent.

EXPERIMENTAL

The reactions were carried out in a glass reactor equipped with a stirrer, bubbler, thermometer, and condenser in a dry argon atmosphere in absolute solvents. The sodium phenolates were obtained according to Williams and Donahue [6]. The ^{31}P NMR spectra were taken on a KGU-4 spectrometer at 10.2 MHz relative to 85% H_3PO_4 . The IR spectra were taken on a Specord 75IR spectrophotometer. The gas-liquid chromatographic analysis was carried out on a Tsvet 5 chromatograph using a column packed with 15% FM-16 on Chromosorb and helium as the gas carrier.

Triphenyl Phosphite (X). A sample of 10.6 g (0.048 mole) 15-crown-5 was added to a mixture of 1 g (0.032 g-atom) P_4 , 4.5 g (0.048 mole) (I), and 5.6 g (0.048 mole) PhONa in 40 ml CCl_4 at 50°C and heated for 3 h at 50-70°C until P_4 was entirely consumed. The reaction mixture was evaporated at 10 mm and the residue was extracted with ether. After removal of the ether, the residue was subjected to molecular distillation at 170°C and 10 mm to give 8.5 g (85%) (X), n_D^{25} 1.5890. Found: P, 9.42%. Calculated for $C_{18}H_{15}O_3P$: P, 9.5% [7].

Tri(o-methylphenyl) Phosphite (XI). A sample of 18.7 g (0.14 mole) o-MeC₆H₄ONa was added in portions to a mixture of 15.5 g (0.14 mole) (II), 22 g (0.14 mole) CCl_4 , 2.8 g (0.09 g-atom) P_4 , and 26 g (0.35 mole) DMF at 20°C. The reaction mixture was warmed to 40-50°C and a finely dispersed precipitate formed. The mixture was heated at 70°C until P_4 was completely consumed. The NaCl precipitate was separated by centrifugation and the supernatant was evaporated at 10 mm. Gas-liquid chromatography indicated that the volatile fraction contained $CHCl_3$, CCl_4 , and DMF. The ^{31}P NMR spectrum of the residue gave signals at δ 131 and -18 ppm. Fractionation gave 23 g (73%) (XI), bp 183°C (0.8 mm), n_D^{25} 1.5758. Found: P, 8.25%. Calculated for $C_{21}H_{21}PO_3$: P, 8.8%. δ P 131 ppm [7].

Tri(m-methylphenyl) Phosphite (XII). a) Phosphite (XII) was obtained by analogy with (XI) from 22.3 g (0.2 mole) (III), 31.6 g (0.2 mole) CCl_4 , 4 g (0.13 g-atom) P_4 , 37.6 g (0.51 mole) DMF, and 26.8 g (0.2 mole) m-MeC₆H₄ONa. The yield of (XII) was 30 g (66%), bp 135°C (0.1 mm), n_D^{25} 1.5740. Found: P, 8.42%. Calculated for $C_{21}H_{21}PO_3$: P, 8.8%. δ P 130 ppm [7].

b) A sample of 5.66 g (0.025 mole) 15-crown-5 was added to a mixture of 0.5 g (0.016 g-atom) P_4 , 2.78 g (0.025 mole) (III), 3.35 g (0.025 mole) m-MeC₆H₄ONa, and 15 ml CCl_4 and heated for 3 h at 50-70°C until P_4 was completely consumed. The mixture was evaporated in vacuum and the residue was extracted with ether. After removal of the ether, the residue was subjected to molecular distillation at 170°C (10 mm) to give 3 g (53%) (XII) identical to the sample described above.

Tri(p-methylphenyl) Phosphite (XIII). This was obtained by analogy with (XI) from 22.3 g (0.2 mole) (IV), 31.6 g (0.2 mole) CCl_4 , 4 g (0.129 g-atom) P_4 , 37.6 g (0.51 mole) DMF, and 26.8 g (0.2 mole) p-MeC₆H₄ONa. At the end of the reaction, the mixture was treated with water and the lower layer was separated. The aqueous phase was extracted with two 100-ml portions of ether. The ethereal extracts were combined with the organic layer and dried over Na_2SO_4 . After removal of the solvent, the residue was distilled to give 25.5 g (56%) (XIII), bp 250°C (10 mm), n_D^{25} 1.5725. Found: P, 8.35%. Calculated for $C_{21}H_{21}PO_3$: P, 8.8%. δ P 128 ppm [7].

Tri(p-tert-butylphenyl) Phosphite (XV). This was obtained by analogy with (XI) from 2.3 g (0.074 g-atom) P_4 , 17.8 g (0.12 mole) (VI), 20.4 g (0.12 mole) p-(t-Bu)C₆H₄ONa, 18.2 g (0.12 mole) CCl_4 , and 16 g DMF. A total of 1.2 g (52%) unreacted P_4 was recovered from the reaction mixture. The ^{31}P NMR spectrum of the residue showed a signal for (XV) at δ P 132 ppm [8]. Phosphite (XV) could not be isolated in pure form.

Tri(o-ethylphenyl) Phosphite (XIV). A sample of 11.8 g (0.08 mole) o-EtC₆H₄ONa was added in portions to a mixture of 10 g (0.08 mole) (V), 12.67 g (0.08 mole) CCl_4 , 1.6 g (0.05 g-atom) P_4 and 15 g (0.2 mole) DMF at 70°C and heated for 3 h at 90°C. A portion of the solvent was evaporated. A precipitate of NaCl and unreacted P_4 was formed upon the addition of 200 ml acetone. The precipitate was filtered off and dissolved in water; 0.4 g (25%) P_4 was separated. The filtrate was evaporated and the residue was fractionated to give 6 g of a fraction with bp 144-160°C (0.1 mm), n_D^{25} 1.5591 consisting of a mixture of (XIV), δ P 132 ppm, and tri(o-ethylphenyl) phosphate, δ P 16 ppm [8] as indicated by ^{31}P NMR spectroscopy. The ratio of the integral intensities of these peaks was 4:1.

Tri(p-fluorophenyl) Phosphate (XVII). A sample of 17.3 g (0.13 mole) p-FC₆H₄ONa was added in portions to a mixture of 14.4 g (0.13 mole) VIII), 19.6 g (0.12 mole) CCl₄, 2.5 g (0.08 g-atom) P₄, and 23.5 g (0.32 mole) DMF and heated for 5 h at 70-90°C. The reaction mixture was treated consecutively with water and ether and 1.3 g (52%) unreacted P₄ was separated. After the removal of P₄, the filtrate was treated with 1:10 methanol-water. The lower layer containing (XVII) was separated. Water was removed by azeotropic distillation with benzene. The residue was subjected to molecular distillation at 140-150°C (10 mm). The heavy vat residue crystallized. These crystals were washed with hexane to give 2 g (14%) (XVII) relative to reacted P₄, mp 50-52°C. Found: C, 56.40; H, 3.20; P, 8.23%. Calculated for C₁₈H₁₂F₃PO₄: C, 56.80; H, 3.15; P, 8.15%. δ P 18 ppm, $\nu_{P=O}$ 1290 cm⁻¹ [8].

Tri(p-chlorophenyl) Phosphate (XVI). This was obtained by analogy with (XVII) from 2.8 g (0.09 g-atom) P₄, 18.57 g (0.14 mole) (VII), 22.1 g (0.14 mole) CCl₄, 26.4 g (0.36 mole) DMF, and 21.7 (0.14 mole) p-ClC₆H₄ONa. A total of 1.7 g (60.7%) unreacted P₄ was recovered from the reaction mixture. The yield of (XVI) was 1.6 g (10.5% relative to reacted P₄), mp 112°C. Found: P, 7.67%. Calculated for C₁₈H₁₂Cl₃PO₄: P, 7.22%, δ P 17 ppm, $\nu_{P=O}$ 1300 cm⁻¹ [8].

CONCLUSIONS

The composition and yield of the products formed upon the reaction of elemental phosphorus with phenols depends on the acidity of the phenol and the nature of the ring substituent. The phenol pK_a range, in which the reaction of elemental phosphorus with phenols is possible, is 9-11.

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