REACTION OF 2-PHENYL-3-ACETYL-4,5-BENZO-1,3,2-OXAZAPHOSPHOLANE WITH DIENES

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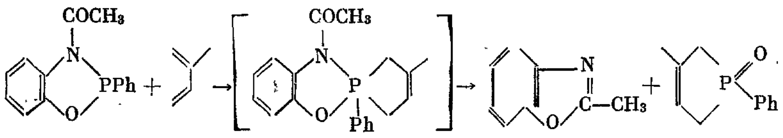
As is known, conjugated systems react with trivalent phosphorus derivatives to give adducts or their transformation products. The ease and direction of the reaction depend mainly on the character of the substituents on the phosphorus atom. It seemed of interest to study reactions of this type with trivalent phosphorus derivatives that contain the P–N fragment, with which satisfactory results could not be obtained up to now [1].

When 2-phenyl-3-acetyl-4,5-benzo-1,3,2-oxazaphospholane (I) is reacted with isoprene at 120-140° for 5 h the signal at δ –136 ppm, which corresponds to (I), is absent in the ^{31}P NMR spectrum of the reaction mass, and an intense peak with δ –54 ppm is present. Two products were isolated on fractional distillation. The low-boiling product with bp 77-78° (10 mm) is devoid of phosphorus and, based on the elemental analysis, IR, NMR, and mass spectral data, is 2-methylbenzoxazole (IV). Its IR spectrum has intense absorption bands at 1620, 1585, and 930 cm^{-1}, which are characteristic for the benzoxazole ring [2]. In the NMR spectrum the singlet line with δ 2.53 ppm belongs to the methyl protons, while the multiplet in the 7-7.60 ppm region belongs to the protons of a substituted benzene ring. Based on the IR and NMR spectral data, the second product is 1-phenyl-1-oxo-3-methyl-3-phospholene (III). In the IR spectrum of (III) a weak absorption band in the 1650 cm^{-1} region corresponds to the absorption of the double bond. In the NMR spectrum the protons of the CH_3 group give a singlet with δ 1.88 ppm, while the doublet with δ 5.41 ppm corresponds to the methine proton. $^3J_{PH}$ = 31 Hz. Apparently the reaction proceeds by the following scheme:



(I) (II) (IV) (III)

However, we were unable to either isolate or to detect (II) in the reaction mass. Even under mild conditions, on long standing at 20°, the ^{31}P NMR spectra contain only a weak signal with δ –54 ppm, which corresponds to (III). Apparently, adduct (II), in contrast to the adduct of 2-phenyl-4,5-benzo-1,3,2-dioxaphospholane with isoprene [3], is unstable and rapidly decomposes to the end products. The reaction with the butadiene is also similar to that with isoprene.

EXPERIMENTAL METHOD

Reaction of 2-Phenyl-3-acetyl-4,5-benzo-1,3,2-oxazaphospholane (I) with Isoprene. A mixture of 14 g of (I) and 3.74 of isoprene was heated in a sealed tube at 120-140° for 5 h. Fractional distillation gave 6.52 g (90%) of 2-methylbenzoxazole (II) with bp 77-78° (10 mm); d_4^{20} 1.1128; n_D^{20} 1.5468 [4], and 9.2 g (87.8%) of 1-phenyl-1-oxo-3-methyl-3-phospholene (III), bp 114-116° (0.002 mm); d_4^{20} 1.1462; n_D^{20} 1.5764. Found: C 68.36; H 6.64; P 15.86%. $C_{11}H_{13}OP$. Calculated: C 68.73; H 6.81; P 16.17%.

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CONCLUSIONS

2-Phenyl-3-acetyl-4,5-benzo-1,3,2-oxazaphospholane reacts with conjugated dienic hydrocarbons to give phospholenes and 2-methylbenzoxazole.

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