

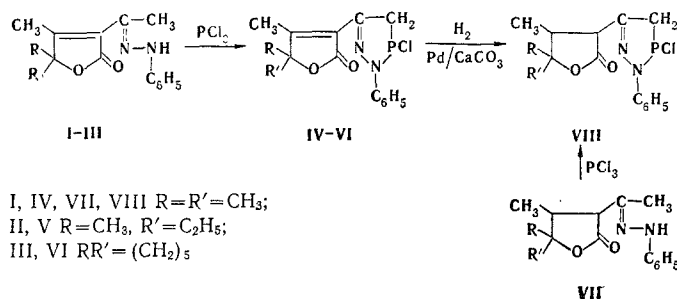
RESEARCH ON UNSATURATED LACTONES

XXIX.* SYNTHESIS OF 1,2,3-PHOSPHODIAZOLE DERIVATIVES
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UDC 547.722.3'724'778.07

The phenylhydrazones of 2-acetyl-2-buten-4-olides react with phosphorus trichloride to give 1,2,3-phosphodiazole derivatives. The reaction proceeds similarly if the double bond in the butenolide is hydrogenated. However, if there is a benzoyl group rather than an acetyl group present, only N-dichlorophospho derivatives of the phenylhydrazones are formed.

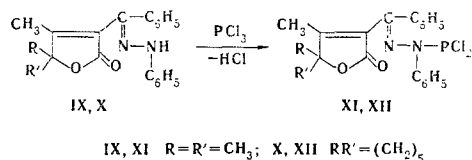
We have studied the reaction of phenylhydrazones of 2-acetyl-2-buten-4-olides with phosphorus trichloride. 1,2,3-phosphodiazole derivatives, which are crystalline substances with unpleasant odors, are obtained when the components (1:1.5) are heated in the presence of triethylamine. A similar reaction occurs in the methyl ketone series [2].



The characteristic frequencies of the absorption of the carbonyl group of a five-membered lactone ring ($1755-1761\text{ cm}^{-1}$), of the C = N group ($1658-1666\text{ cm}^{-1}$), and of the phenyl ring ($1580-1600\text{ cm}^{-1}$) are found in the IR spectra of the compounds obtained.

Under similar conditions, the reaction of 2-acetyl-3,4,4-trimethylbutane-4-olide phenylhydrazone (VII) with phosphorus trichloride gives a 1,2,3-phosphodiazole (VIII) that contains a saturated lactone ring in the 5 position. This same compound (VIII) is formed by hydrogenation of the phosphodiazole over Pd/CaCO₃ in ethanol.

2-Benzoyl-2-buten-4-olides (IX, X) that do not have CH groups in the α position relative to the hydrazone grouping undergo substitution of the hydrogen of the NH group of the phenylhydrazone to give dichlorophospho derivatives (XI, XII).



* See [1] for communication XXVIII.

The dichlorophospho derivatives of 2-benzoyl-2-buten-4-olide phenylhydrazones also are crystalline substances with a disagreeable odor.

EXPERIMENTAL

The IR spectra of mineral-oil suspensions of the compounds were recorded with an IKS-14 spectrometer. The 2-acetyl-3,4,4-trialkyl-2-buten-4-olide phenylhydrazones (I-III) were obtained by the method in [3].

1-Chloro-2-phenyl-4-(3,4,4-trimethyl-2-buten-4-olide-2-yl)-5H-1,2,3-phosphodiazole (IV). A mixture of 3.9 (0.015 mole) of 2-acetyl-3,4,4-trimethyl-2-buten-4-olide (I), 2.32 g (0.023 mole) of triethylamine, and 16 ml of methylene chloride was added dropwise to a cooled mixture of 3.2 g (0.023 mole) of PCl_3 and 8 ml of methylene chloride, after which the mixture was heated at 35° for 4 h and allowed to stand at room temperature until hydrogen chloride evolution ceased. The precipitate - triethylamine hydrochloride - was removed by filtration, the solvent was removed from the filtrate, and the residue was recrystallized to give 4.2 g (84%) of IV with mp 252° (from dioxane). Found: C 55.5; H 5.2; Cl 11.1; N 8.3%. $\text{C}_{15}\text{H}_{16}\text{ClN}_2\text{O}_2\text{P}$. Calculated: C 55.8; H 5.0; Cl 11.0; N 8.7%.

1-Chloro-2-phenyl-4-(3,4-dimethyl-4-ethyl-2-buten-4-olide-2-yl)-5H-1,2,3-phosphodiazole (V). Similarly, 4.1 g (0.015 mole) of phenylhydrazone II gave 5 g (50%) of V with mp $253-254^\circ$ (from dioxane). Found: C 57.1; H 5.3; Cl 10.9; N 8.1%. $\text{C}_{16}\text{H}_{18}\text{ClN}_2\text{O}_2\text{P}$. Calculated: C 57.1; H 5.4; Cl 10.6; N 8.3%.

1-Chloro-2-phenyl-4-(3-methyl-4,4-pentamethylene-2-buten-4-olide-2-yl)-5H-1,2,3-phosphodiazole (VI). Similarly, 3.6 g (49.3%) of VI, with mp 260° (from dioxane), was obtained by reaction of 6 g (0.025 mole) of phenylhydrazone III and 3.8 g (0.038 mole) of triethylamine in 30 ml of methylene chloride with a mixture of 5.23 g (0.038 mole) of PCl_3 and 10 ml of methylene chloride. Found: C 59.4, H 5.9; Cl 9.5; N 8.0%. $\text{C}_{18}\text{H}_{20}\text{ClN}_2\text{O}_2\text{P}$. Calculated: C 59.6; H 5.5; Cl 9.8; N 7.7%.

2-Acetyl-3,4,4-trimethylbutan-4-olide Phenylhydrazone (VII). A mixture of 13.6 g (0.08 mole) of 2-acetyl-3,4,4-trimethylbutan-4-olide and 8.61 g (0.08 mole) of phenylhydrazine was allowed to stand at room temperature for 24 h. The precipitated crystals were recrystallized to give 13.8 g (68%) of VII with mp $102-104^\circ$ (from alcohol). Found: N 10.9%. $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2$. Calculated: N 10.8%.

1-Chloro-2-phenyl-4-(3,4,4-trimethylbutan-4-olide-2-yl)-5H-1,2,3-phosphodiazole (VIII). A) As in the method described above, 2 g (40%) of VIII, with mp 244° (from chloroform-hexane), was obtained from 4.8 g (0.034 mole) of PCl_3 in 8 ml of CH_2Cl_2 , 3.9 g (0.015 mole) of phenylhydrazone VII, and 3.13 g (0.03 mole) of triethylamine in 16 ml of CH_2Cl_2 . Found: Cl 10.7%. $\text{C}_{15}\text{H}_{18}\text{ClN}_2\text{O}_2\text{P}$. Calculated: Cl 10.9%.

B) A solution of 0.5 g (0.0016 mole) of phosphodiazole IV in 20 ml of absolute ethanol was hydrogenated over Pd/CaCO_3 (5% Pd). The alcohol was removed by distillation at the end of the hydrogenation to give 0.4 g (80%) of VIII with mp $244-246^\circ$ (from chloroform-hexane). No melting-point depression was observed for a mixture of this product with the product described above. IR spectrum: 1765 cm^{-1} (lactone ring $\text{C}=\text{O}$), $1658-1666\text{ cm}^{-1}$ ($\text{C}=\text{N}$), and 1603 cm^{-1} (phenyl group).

2-Benzoyl-3,4,4-trialkyl-2-buten-4-olide Phenylhydrazones (IX, X). These compounds were obtained by the method in [1].

Dichlorophospho Derivative (XI) of 2-Benzoyl-3,4,4-trimethyl-2-buten-4-olide. A 2.5-g (0.008 mole) sample of phenylhydrazone IX and 1.57 g (0.015 mole) of triethylamine in 10 ml of CH_2Cl_2 were heated with 2.36 g (0.016 mole) of PCl_3 at 40° for 12 h. Workup gave 0.8 g (24.3%) of XI with mp $215-216^\circ$ (from toluene). Found: C 57.3; H 5.2; Cl 16.3; N 7.0%. $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{N}_2\text{O}_2\text{P}$. Calculated: C 57.0; H 4.5; Cl 16.9; N 6.7%.

Dichlorophospho Derivative (XII) of 2-Benzoyl-3-methyl-4,4-pentamethylene-2-buten-4-olide. As in the preceding experiment, 0.2 g (16.6%) of XII with mp 225° (from toluene) was obtained from a mixture of 1 g (2.7 mmole) of phenylhydrazone X, 0.6 g (6 mmole) of triethylamine, 5 ml of CH_2Cl_2 , and 0.87 g (5.9 mmole) of PCl_3 . Found: Cl 16.0; N 6.3%. $\text{C}_{23}\text{H}_{23}\text{Cl}_2\text{N}_2\text{O}_2\text{P}$. Calculated: Cl 15.4; N 6.1%.

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