REACTION OF 2,5-DIPHENYL-3,4-DIAZACYCLOPENTADIEN-1-ONE 3,4-DIOXIDE WITH TRIALKYL PHOSPHITES

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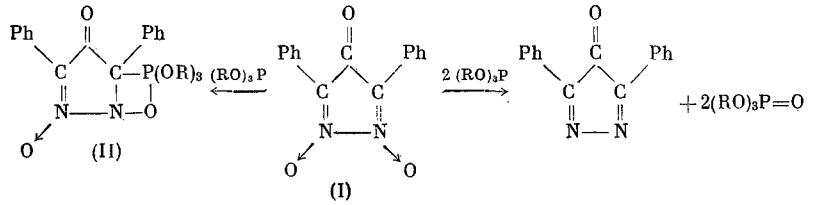
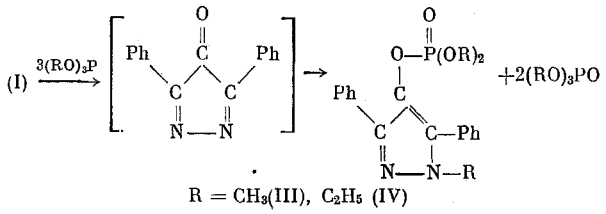
As a continuation of studying the reaction of dialkyl and trialkyl phosphites with heterocyclic α,β-unsaturated carbonyl compounds [1], we selected 2,5-diphenyl-3,4-diazacyclopentadien-1-one 3,4-dioxide (I) as a study object.

The reaction of (I) with $(RO)_3P$ can proceed with a transfer of oxygen from (I) to the trialkyl phosphite, with the formation of the trialkyl phosphate. A similar type of reaction was observed earlier [2]. Not excluded is the possibility of 1,3-dipolar cycloaddition [3, 4] with the formation of phosphorane (II), but this reaction path is less probable:



We found that the reaction of (I) with the trimethyl and triethyl phosphite proceeds when the reactants are taken in a 1:3 ratio. Oxygen is cleaved from both nitrogen atoms with the formation of 2 moles of the trialkyl phosphate. Then the $(RO)_3P$ adds to the $-\overset{O}{\overset{\|}{C}}-C=N$ conjugated system with the formation of the 1-alkyl-3,5-diphenyl-4-pyrazolyl dialkyl phosphates (III) and (IV):

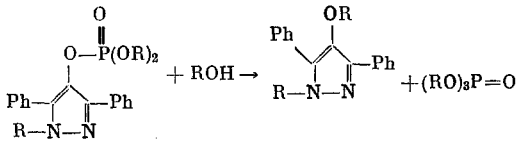


R = CH_3(III), C_2H_5 (IV)

Compounds (III) and (IV) are thermally unstable. Compound (IV) has bp 165-166° ($2 \cdot 10^{-4}$ mm) (with decompn.). The structure of the compounds was proved by the analysis data, the IR and NMR spectra, and a study of the chemical properties.

Reliable proof for the structure of 1-methyl-3,5-diphenyl-4-pyrazolyl dimethyl phosphate (III) is the liberation of 4-methoxy-1-methyl-3,5-diphenylpyrazole (V) [5] when (III) is distilled in a high vacuum.

The transesterification of (III) and (IV) gave the trialkyl phosphates, 4-methoxy-1-methyl-3,5-diphenylpyrazole (V) and 4-ethoxy-1-ethyl-3,5-diphenylpyrazole (VI):



R = CH_3 (III), C_2H_5 (IV) R = CH_3 (V), C_2H_5 (VI)

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Compound (I) does not react with dimethylphosphorus acid even in the presence of sodium alcoholate.

EXPERIMENTAL METHOD

The IR spectra were taken on a UR-10 spectrophotometer.

Reaction of 2,5-Diphenyl-3,4-diazacyclopentadien-1-one 3,4-Dioxide (I) [6] with Trimethyl Phosphite. With stirring, to a solution of 5 g of (I) in 70 ml of absolute benzene in a dry nitrogen atmosphere was added 7 g of $(CH_3O)_3P$. The mixture was heated for 6 h and then allowed to stand overnight at ~20°C. The benzene was removed in vacuo. When the mixture was heated to 120° in a high vacuum we isolated 5 g of trimethyl phosphate with bp 30-31° ($2 \cdot 10^{-4}$ mm); n_D^{20} 1.3967; d_4^{20} 1.2061. The residue represented 1-methyl-3,5-diphenyl-4-pyrazolyl dimethyl phosphate (III) as a viscous liquid with n_D^{20} 1.5880; δ_{31P} + 1.5 ppm. Found: C 60.26; H 5.39; N 7.99; P 8.79%. $C_{18}H_{19}N_2O_4P$. Calculated: C 60.32; H 5.34; N 7.82; P 8.65%. Infrared spectrum (ν, cm^{-1}): 705 s, 730 w, 782, 830, 860, 932 m, 1055 v.s, 1080 s (P–O–C), 1192 m (P–O–CH_3), 1300 v.s. (P=O), 1375 w, 1460 m, 1540, 1572, 1590, 1615 v.w., 2860, 2965, 3040, 3070. The distillation of (III) in a high vacuum gave 4-methoxy-1-methyl-3,5-diphenylpyrazole (V) with bp 168-170° ($2 \cdot 10^{-4}$ mm); bp 88-89° (from petroleum ether). The IR spectrum of (V) [5] corresponds to its structure.

Transesterification of 1-Methyl-3,5-diphenyl-4-pyrazolyl Dimethyl Phosphate (III) with Methanol. Phosphate (III) was heated in excess absolute methanol in the presence of Na for 8 h. After neutralization of the reaction mixture with CH_3COOH and removal of the excess methanol in vacuo we isolated 4-methoxy-1-methyl-3,5-diphenylpyrazole (V) with mp 88-89° (from petroleum ether). The compound was identified by the mixed melting point. After the separation of (V), filtration, and distillation of the residue we obtained trimethyl phosphate with bp 40° (1 mm); n_D^{20} 1.4000; d_4^{20} 1.2058. The compound was also identified by the IR spectrum.

Reaction of 2,5-Diphenyl-3,4-diazacyclopentadien-1-one 3,4-Dioxide (I) with Triethyl Phosphite. With stirring, to a solution of 1.9 g of (I) in 50 ml of absolute benzene in a dry nitrogen atmosphere was added 6 g of $(C_2H_5O)_3P$. The mixture was heated for 2.5 h and then allowed to stand overnight at ~20°. After removal of the benzene, the excess $(C_2H_5O)_3P$ and 2.6 g of triethyl phosphate, we obtained 1-ethyl-3,5-diphenyl-4-pyrazolyl diethyl phosphate (IV) as a viscous yellowish liquid with n_D^{20} 1.5535; δ_{31P} + 5 ppm. Found: N 6.74; P 7.74%. $C_{21}H_{25}N_2O_4P$. Calculated: N 6.99; P 7.74%. Phosphate (IV) was isolated by chromatographing the reaction mixture on silica gel and elution with a 3 : 2 benzene–ether mixture; n_D^{20} 1.5620; d_D^{20} 1.1410; δ_{31P} + 5 ppm. Found: C 63.00; H 6.20; N 7.03; P 7.41%. $C_{21}H_{25}N_2O_4P$. Calculated: C 62.98; H 6.29; N 6.99; P 7.74%. Infrared spectrum of (IV) (ν, cm^{-1}): 692 s, 728, 758 m, 780, 800, 810, 925, 970, 990 s, 1055 v.s., 1070 s (P–O–C), 1105, 1170 m (P–O–C_2H_5), 1085, 1200 w, 1290 v. s. (P=O), 1320 s, 1380 m, 1395 s, 1453 s, 1480 m, 1500 w, 1535, 1570, 1590, 1612 v. w. 2880, 2920, 2942, 2990, 3040, 3070.

Transesterification of 1-Ethyl-3,5-diphenyl-4-pyrazolyl Diethyl Phosphate (IV) with Ethanol. Phosphate (IV) was heated in excess absolute ethanol in the presence of Na for 2 h. Here we obtained: triethyl phosphate with bp 70-72° (3 mm); n_D^{20} 1.4070; d_0^{20} 1.0690, and 4-ethoxy-1-ethyl-3,5-diphenylpyrazole (VI) with mp 146-147° (from CCl_4). Found: N 9.46%. $C_{19}H_{20}N_2O$. Calculated: N 9.58%. Infrared spectrum of (VI) in Nujol (ν, cm^{-1}): 705 s, 725, 742 w, 762, 783 m, 832, 930 w, 970 m, 1021 w, 1035 m, 1068 s, 1080 m, 1113 w. 1177 s, 1095 w, 1272 s, 1295 m, 1330 v.s., 1382, 1455, 1470 v.s., 1565, 1590, 1610 v.s., 3030, 3070.

CONCLUSIONS

The trimethyl and triethyl phosphite react with 2,5-diphenyl-3,4-diazacyclopentadien-1-one 3,4-dioxide to give 1-alkyl-3,5-diphenyl-4-pyrazolyl dialkyl phosphates.

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