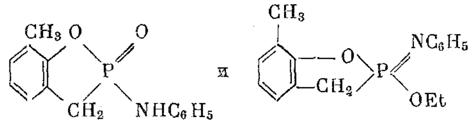
ON THE REACTION OF DIETHYLANILIDO PHOSPHITE WITH 2-DIETHYLAMINOMETHYL-6-METHYLPHENOL

B. E. Ivanov, A. B. Ageeva, and S. V. Pasmanyuk

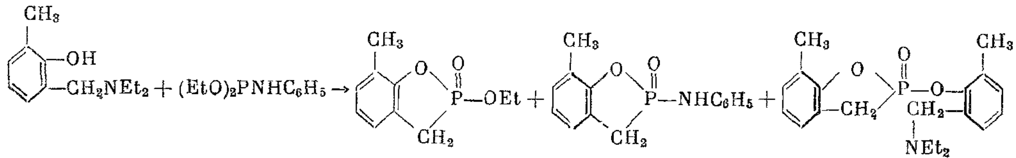
UDC 542.91+661.718.1+547.561

In our previous reports we discussed the reaction of esters and ester amides of phosphorous acid with Mannich phenol bases. These bases react with dialkyl phosphorous acids [1], trialkyl phosphites [2] and triamidophosphites to form products with various structures.

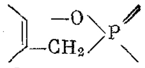
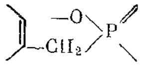
Starting from the possibility of the existence of two tautomeric forms of anilinophosphite [3], we can postulate that both forms will react with Mannich phenol bases, and thus expect two reaction products:



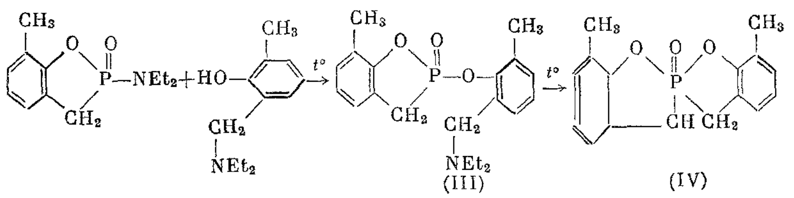
To verify this assumption, we studied the reaction of diethylanilidophosphite with 2-diethylaminomethyl-6-methylphenol. The reaction was performed by heating an equimolar mixture of the reagents for 5 h at 165 to 170°. We obtained three reaction products:



(I) (II) (III)

The constants and the IR spectra of (I) correspond to those of 2-oxo-2-ethoxy-7-methyl-1-oxa-2-phosphaindan, obtained in [1, 2]. The structure of 2-oxo-2-anilido-7-methyl-1-oxa-2-phosphaindan (II) is confirmed by ultimate analysis data and the IR spectra. The spectrum contains absorption bands characteristic of P=O (1265 cm^{-1}), $N\langle^{H}_{Ph}$ (3135 cm^{-1}) [4], and  (865 cm^{-1}) groups (Fig. 1). Our forformula for (III) is confirmed by the ultimate analysis and the presence in the IR spectrum of bands characteristic of the P=O (1260 cm^{-1}), P–O–Ph (1180 cm^{-1}) [4], and  (865 cm^{-1}) groups.

Additional confirmation of the structure of 2-oxo-2-(2'-methyl-6'-diethylaminomethyl)phenoxy-7-methyl-1-oxa-2-phosphaindan) is its alternative synthesis from 2-diethylaminomethyl-6-methylphenol and 2-oxo-2-diethylamido-7-methyl-1-oxa-2-phosphaindan. The product thus obtained is identical with (III). When heated for 4 h in tetralin at 210-220°, it formed 3',9''-dimethyl-2,3,5,6-dibenzo-7a-oxo-1,7-dioxa-7a-phosphatetrahydroindan (IV), previously described by the authors.



(III) (IV)

EXPERIMENTAL

Reaction of Diethylanilidophosphite with 2-Diethylaminomethyl-6-methylphenol. A solution of 19.3 g of 2-diethylaminomethyl-6-methylphenol and 21.2 g of diethylanilidophos-

---

Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1600-1602, July, 1967. Original article submitted January 10, 1967.

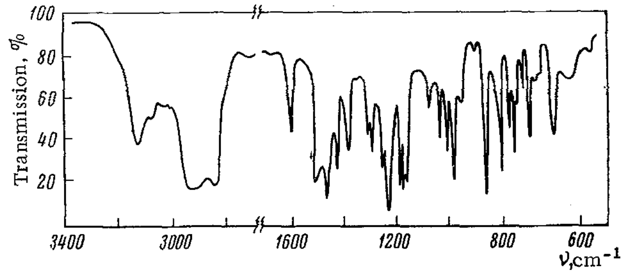


Fig. 1

phite in 20 ml of n-nonane was heated for 5 h at 165-170°. 7.5 ml of diethylamine distilled during this process. After removal of the solvent and the precipitated aniline (6.5 g), crystals were precipitated in the reaction mixture. These were filtered and washed with petroleum ether. The yield of (II) was 7.1 g (30%), the mp was 182-184°. Found %: C 65.25; H 5.73; P 11.32; N 5.28. $C_{14}H_{14}NPO_2$. Calculated %: C 64.96; H 5.40; P 11.96; N 5.40.

After separation of the crystals, the reaction mixture was fractionated. We isolated the fraction with bp 104.5° ($2 \cdot 10^{-2}$ mm), which crystallized completely; the crystals were washed with petroleum ether. The yield of (I) was 6.9 g (33%), the mp was 88-90°. Found %: P 14.63. $C_{10}H_{13}PO_3$. Calculated %: P 14.62.

Further distillation gave 8 g of a fraction with bp 125-160° ($2 \cdot 10^{-2}$ mm). From this fraction we obtained 5.9 g (17%) of (III); the bp was 127-130° ($2 \cdot 10^{-2}$ mm); n_D^{20} 1.5835; d_4^{20} 1.2015. Found %: C 66.86; H 6.60; P 9.13; N 3.91. MR 99.91. $C_{20}H_{26}NPO_3$. Calculated %: C 66.90; H 7.20; P 8.64; N 3.90. MR 99.62. 5.8 g of tar remained.

Reaction of 2-Diethylaminomethyl-6-methylphenol with 2-Oxo-2-diethylamido-7-methyl-1-oxa-2-phosphaindan. A solution of 9.89 g of 2-diethylaminomethyl-6-methylphenol and 12.25 g of phosphaindan in 15 ml of tetrahydronaphthalene was heated for 8 h at 215-225°. 5.2 ml of diethylamine distilled during this process. After removal of the solvent the reaction mixture was distilled. We obtained 5 g of unreacted substance and 3.5 g of tar, 10 g of the fraction with bp 140-160° ($2.5 \cdot 10^{-2}$ mm); fractionation of this gave 8 g (50%) of (III) with bp 145-150° ($3 \cdot 10^{-2}$) and n_D^{20} 1.5835. The substance crystallized completely when left to stand. The crystals were washed with petroleum ether; the mp was 64-65°. Found %: N 3.50; P 8.96. $C_{20}H_{26}NPO_3$. Calculated %: N 3.90; P 8.64.

Conversion of 2-Oxo-2-(2'-methyl-6'-diethylaminomethyl)phenoxy-7-methyl-1-oxa-2-phosphaindan (III) in 3',9"-Dimethyl-2,3,5,6-dibenzo-7a-oxo-1,7-dioxa-7a-phosphatetrahydroindan. A solution of 5 g of (III) in 20 ml of tetralin was heated for 4 h at 220-225°. After removal of the solvent the tar (4.32 g) was dissolved in acetone. The crystals of (IV) thus obtained were washed with acetone and petroleum ether; the mp was 226-228°. A mixed melt with previously prepared (IV) showed no depression of the melting point. The yield of (IV) was 1.4 g (35%). Found %: P 10.50. $C_{15}PO_3$. Calculated %: P 10.83.

CONCLUSIONS

1. The reaction of diethylanilidophosphite with 2-diethylaminomethyl-6-methylphenol gives 2-oxo-2-ethoxy-7-methyl-1-oxa-2-phosphaindan (I), 2-oxo-2-anilido-7-methyl-1-oxa-2-phosphaindan (II), and 2-oxo-2-(2'-methyl-6'-diethylaminomethyl)phenoxy-7-methyl-1-oxa-2-phosphaindan (III).

2. The reaction of 2-diethylaminomethyl-6-methylphenol with 2-oxo-2-diethylamido-7-methyl-1-oxa-2-phosphaindan gives 2-oxo-2-(2'-methyl-6'-diethylaminomethyl)phenoxy-7-methyl-1-oxa-2-phosphaindan, which is converted by heat to 3',9"-dimethyl-2,3,5,6-dibenzo-7a-oxo-1,7-dioxa-7a-phosphatetrahydroindan.

LITERATURE CITED

1. B. E. Ivanov and L. A. Valitova, Authors' certificate No. 183747 (1966); Byull. izobr., No. 14 (1966).
2. B. E. Ivanov and L. A. Valitova, Izv. AN SSSR, Ser. khim., 1967, 1087.
3. M. I. Kabachnik and V. A. Gilyarov, DAN SSSR, 96, 991 (1954).
4. L. Bellamy, The Infrared Spectra of Complex Molecules [Russian translation], IL (1963).