served in oxidized cyclohexylamine, di-n-butylamine [6], and benzylamine [9]. Also in cyclohexanol, whose α -hydroxy peroxide radicals possess oxidation-reduction properties, the k_7 values for the Cu and Mn stearates are close [4]. In absolute value, these constants differ by two orders of magnitude in substrates of different structure [4, 6, 9], and decrease strongly when the metal is bonded in the complex [4, 10]. Consequently, the ligand environment mainly determines the reaction rate of the metal salt with the peroxide radical, which was discussed previously in [3, 4].

CONCLUSIONS

1. Negative catalysis by transition metal salts is realized in radical-chain reactions for the oxidation of dimethylaminoethyl methacrylate, dimethylaminoethyl propionate, and dimethylbutylamine.

2. The rate constants for the reaction of the peroxide radicals of these tertiary amines. with manganese and copper acetates at 50° were measured.

LITERATURE CITED

- 1. E. M. Pliss, A. L. Aleksandrov, and M. M. Mogilevich, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 1441.
- 2. G. A. Kovtun and A. L. Aleksandrov, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 1274.
- 3. A. L. Aleksandrov and E. T. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1969, 1652.
- 4. A. L. Aleksandrov, G. I. Solov'ev, and E. T. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 1527.
- 5. A. V. Oberemko, A. A. Perchenko, E. T. Denisov, and A. L. Aleksandrov, Neftekhimiya, <u>11</u>, 229 (1971).
- G. A. Kovtun, A. L. Aleksandrov, and E. T. Denisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1973, 2611.
- 7. E. M. Pliss, A. L. Aleksandrov, and M. M. Mogilevich, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 2823.
- 8. G. A. Kovtun, Dissertation, Chernogolovka (1975).
- 9. G. A. Kovtun and A. L. Aleksandrov, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 38.
- 10. G. A. Kovtun, G. V. Ponomarev, and A. L. Aleksandrov, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 320.

REACTION OF 2-PHENYLAMINO-1,3,2-DIOXAPHOSPHOLANE WITH PHENYL ISOCYANATE

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The amides of P(III) acids, which contain a labile H atom on the N atom of the amide group, react with isocyanates to give phosphorylated ureas and 0,0-dialkyl amidinophosphonates [1, 2]. In the present paper it was found that 2-phenylamino-1,3,2-dioxaphospholane (I), in contrast to this, reacts with phenyl isocyanate in a 2:1 ratio to give the crystalline N,Nbis(1,3,2-dioxaphospholanyl)phenylamine (II) and N,N'-diphenylurea:

$$2 \boxed[]{}^{O}_{O} P-NHPh + PhNCO \rightarrow \boxed[]{}^{O}_{O} P-N-P \\ []{}^{O}_{O} P-N-P \\ []{}^{O}_{Ph} O + PhNHCNHPh \\ []{}^{O}_{O} P-N-P \\ []{}^{$$

The structure of (II) was confirmed by the IR and ³¹P NMR spectral data, and also by counter synthesis. The IR spectrum of (II) has absorption bands that are characteristic for the phospholane ring (725, 780 cm⁻¹), the P-N-P (920 cm⁻¹) and P-O-C (1030 cm⁻¹) groupings,

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 216-218, January, 1978. Original article submitted May 23, 1977. and the phenyl ring (1500, 1600 cm⁻¹). The chemical shift of the phosphorus atom in (II) is -134 ppm, which is characteristic for P(III) derivatives. The counter synthesis of (II) was accomplished by reacting 2-chloro-1,3,2-dioxaphospholane with either aniline or N+phenyl-hexamethyldisilazane:



The obtained phenylamine (II) is hydrolyzed with exceeding ease in the air. A more stable product of analogous structure is formed from the 4-methyl derivative of 2-chloro-1,3,2-dioxaphospholane and aniline:



Apparently, compounds with a P-N-P bond are formed by the disproportionation of dioxaphospholane (I) into compound (II) and aniline [3], in which connection the aniline reacts with phenyl isocyanate. The disproportionation reaction is reversible. Based on the ³¹P NMR data, diphosphorylated phenylamine (II) reacts easily with aniline to give an equilibrium mixture of (I) and (II). The addition of an isocyanate leads to a shift of this equilibrium toward the formation of (II) due to tying up the aniline as the urea.

Dioxaphospholane (I) when stored slowly disproportionates to the crystalline product (II) and aniline. In harmony with our concepts [4], the process proceeds due to the presence of the amine hydrochloride in the starting amidophosphite (based on the elemental analysis for chlorine the amount of hydrochloride is 3-5%).



The chlorophosphite is formed during the reversible protonation of the amidophosphite by the amine hydrochloride, which then reacts with the starting amidophosphite to give (II) and aniline. The process is accompanied by regeneration of the amine hydrochloride. If the crystalline (II) is periodically removed by filtration, then the equilibrium is shifted completely toward the disproportionation products. The position of this equilibrium is quite dependent on the temperature. A study of the disproportionation of phosphite (I) at various temperatures employing the ³¹P NMR method disclosed that this process is facilitated by an increase in the temperature. The intensity of the signals of product (II), with $\delta_{31P} = 134$ ppm, relative to product (I), with δ_{31p} - 130 ppm, increases from a 1:1 ratio at 20°C to a 3:1 ratio at 40°. With further increase in the temperature up to 80° an increase in the solubility of the crystalline (II) in the reaction products leads to a shift of the equilibrium toward the starting amidophosphite up to a 5:4 ratio, and up to a 1:1 ratio at 130°. A further increase in the temperature leads to a destruction of the reaction products. The use of a double excess of aniline shifts the equilibrium toward the starting amidophosphite (I). The tying up of the aniline formed during reaction by the isocyanate leads to a shift of this equilibrium toward the product with the P-N-P bond. Such a reaction course is evidently realized due to the greater reactivity of the aniline toward the isocyanate than the starting amidophospite. This confirms our previously made conclusion that the formation of insertion products in the reactions of amidophosphites with isocyanates [4] is realized due to the isocyanate reacting with the amine and not with the starting amidophosphite.

EXPERIMENTAL

Reaction of 2-N-Phenylamino-1,3,2-dioxaphospholane (I) with Phenyl Isocyanate. With cooling and stirring, to a solution of 5 g of (I) in 30 ml of ether was added 3.3 g of phenyl isocyanate in drops. The obtained white precipitate was filtered and washed with ether. We

obtained 6.8 g (97%) of N,N°-diphenylurea with mp 235° (from ethanol). The ether was removed from the filtrate, and the residual viscous yellow oil was recrystallized from ether to give 3.8 g (84%) of N,N-bis(dioxaphospholanyl)phenylamine with mp 138-139°, δ_{31P} - 134 ppm. Found: P 22.09; N 5.13%. C10H13NO3P2. Calculated: P 22.70; N 5.15%.

<u>N,N-Bis(1,3,2-dioxaphospholanyl)phenylamine (II)</u>. a) To a solution of 3.2 g of N-phenylaminohexamethyldisilazane in 50 ml of hexane was added 4.3 g of 2-chloro-1,3,2-dioxaphospholane in drops. The obtained precipitate was filtered and then recrystallized from benzene to give 3.6 g (90%) of (II) with mp 138-140°. The mixed melting point with the product from the preceding experiment was 138-140°.

b) With stirring and cooling to 0 to -5° , to a mixture of 4.65 g of aniline and 10.1 g of triethylamine in 200 ml of ether, in a dry argon atmosphere, was added 12.6 g of 2-chloro-1,3,2-dioxaphospholane in drops. The mixture was stirred for 1 h at 0°, and for another 2 h at $\sim 20^{\circ}$. The precipitate of triethylamine hydrochloride was filtered. The ether was removed from the filtrate under reduced pressure, and the residue was recrystallized from ether to give 11 g (81%) of (II) with mp 138-140°.

<u>N,N-Bis(1,3,2-dioxa-4-methylphospholanyl)phenylamine</u>. With cooling and stirring, to a solution of 10.6 g of aniline and 20.2 g of triethylamine in 200 ml of ether, in a dry argon atmosphere, was added 28 g of 2-chloro-1,3,2-dioxa-4-methylphospholane in drops. The mixture was stirred for 30 min at 0°, and then for 2 h at 20°. The precipitate of triethylamine hydrochloride was filtered. The ether was removed from the filtrate under reduced pressure, and recrystallization of the residue from petroleum ether gave 15.3 g (51%) of N,N-bis(1,3,2-dioxa-4-methylphospholanyl)phenylamine with mp 81-83°. Found: P 19.93; N 4.62%. $C_{12}H_{17}NO_4P_2$. Calculated: P 20.60; N 4.65%.

CONCLUSION

The reaction of 2-N-phenylamino-1,3,2-dioxaphospholane with phenyl isocyanate proceeds to give N,N-bis(1,3,2-dioxaphospholanyl)phenylamine and diphenylurea due to the reversible disproportionation of the starting amidophosphite to N,N-bis(1,3,2-dioxaphospholanyl)phenyl-amine and aniline.

LITERATURE CITED

- 1. A. N. Pudovik and E. S. Batyeva, Zh. Obshch. Khim., 38, 285 (1968).
- 2. R. F. Hudson and R. J. Searley, Chimia, 4, 117 (1966).
- 3. É. E. Nifant'ev, G. F. Bebikh, and T. P. Sakodynskaya, Zh. Obshch. Khim., 41, 2011 (1971).
- E. S. Batyeva, E. N. Ofitserov, V. A. Al'fonsov, and A. N. Pudovik, Dokl. Akad. Nauk SSSR, <u>224</u>, 339 (1976).