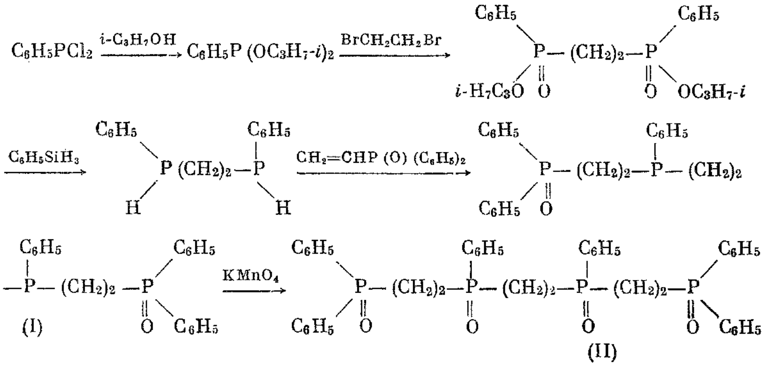
PREPARATION OF HEXAPHENYLTRIETHYLENETETRAPHOSPHINE TETRAOXIDE

T. Ya. Medved', S. A. Pisareva,
Yu. M. Polikarpov, and M. I. Kabachnik

UDC 542.91:547.1'118

Previously we had synthesized some nitrogen-free organophosphorus complexons [1]; in the molecules of these complexons the role of the acid function is fulfilled by either phosphonic or phosphinic groups, while phosphine oxide groups fulfill the function of the basic group. The synthesis of such compounds was accomplished by the condensation of the esters of trivalent phosphorus acids with either the oxides of tertiary bis- and tris-chloromethylphosphines or the esters of bis(chloromethyl)phosphinic acid [2].

In the present communication is described the synthesis of the first member of a group of polyalkylenepolyphosphinic compounds, which contain four phosphoryl groups, connected by ethylene bridges. The synthesis was accomplished according to the scheme:



The intermediate diphenylethylenediphosphine was obtained by the reduction of the diisopropyl ester of diphenylethylenediphosphinic acid with phenylsilane. This method of reduction proved to be simpler and more reliable than the previously described method [3].

EXPERIMENTAL METHOD

The diisopropyl ester of diphenylethylenediphosphinic acid was obtained as described in [4, 5], phenylsilane was obtained as described in [6], and vinyldiphenylphosphine oxide was obtained as described in [7].

Diphenylethylenephosphine. With good stirring, to 20.5 g of the diisopropyl ester of diphenylethylenediphosphinic acid was added 34.5 g of phenylsilane. The reaction was run in a dry nitrogen stream at 65-70° for 5 h. Distillation gave 6 g (46.8%) of substance with bp 170-173° (1 mm). From [3]: bp 161-162° (0.8 mm).

Bis-(2-diphenylphosphinylethyl)diphenylethylenediphosphine (I). A mixture of 1.1 g of diphenylethylenediphosphine and 2 g of vinyldiphenylphosphine oxide in 10 ml of benzene was heated in a sealed ampul on the steam bath for 30 h. At the end of reaction the precipitate was filtered and then recrystallized from benzene. We obtained 1.7 g (55%) of substance with mp 246-247°. The substance is soluble in chloroform, hot alcohol, benzene, and nitromethane. Found: C 71.4, 71.3; H 6.1, 6.2; P 17.3, 17.3%. $C_{42}H_{42}P_4O_2$. Calculated: C 71.8; H 6.0; P 17.7%.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2839-2840, December, 1971. Original article submitted November 13, 1970.

Hexaphenyltriethylenetetraphosphine Tetraoxide (II). To an alcohol solution of 1 g of diphosphine (I) was added in portions of 0.2-0.5 ml a solution of $KMnO_4$ in acetone until the color ceased to change. The obtained precipitate of MnO_2 was filtered and then washed twice with 50 ml portions of boiling alcohol. The filtrate was concentrated in vacuo. The obtained precipitate was recrystallized from alcohol. We obtained 0.52 g (50%) of substance, which failed to melt below 400°. The substance is stable in the air; when refluxed it dissolved in a large volume of alcohol or nitrobenzene. Found: C 68.2, 68.3; H 5.9, 5.9; P 16.3, 16.3%. $C_{42}H_{42}P_4O_4$. Calculated: C 68.7; H 5.7; P 16.9%.

CONCLUSIONS

Bis-(2-diphenylphosphinylethyl)diphenylethylenediphosphine and hexaphenyltriethylenetetraphosphine tetraoxide were synthesized.

LITERATURE CITED

1. T. Ya. Medved', Yu. M. Polikarpov, S. A. Pisareva, E. I. Matrosov, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 2062 (1968).
2. M. I. Kabachnik and T. Ya. Medved', Izv. Akad. Nauk SSSR, Otd. Khim. Nauk., 2103 (1962).
3. K. Issleib and H. Weichmann, Chem. Ber., 101, 2197 (1968).
4. P. Mastalerz, Roczn. Chem. (Ann. Soc. Chem. Polonarum), 38, 61 (1964).
5. P. Mastalerz, Roczn. Chem. (Ann. Soc. Chem. Polonarum), 39, 1129 (1965).
6. H. Schlesinger, J. Amer. Chem. Soc., 78, 2278 (1956).
7. M. I. Kabachnik, T. Ya. Medved', Yu. M. Polikarpov, and K. S. Yudina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1584 (1962).