LITERATURE CITED

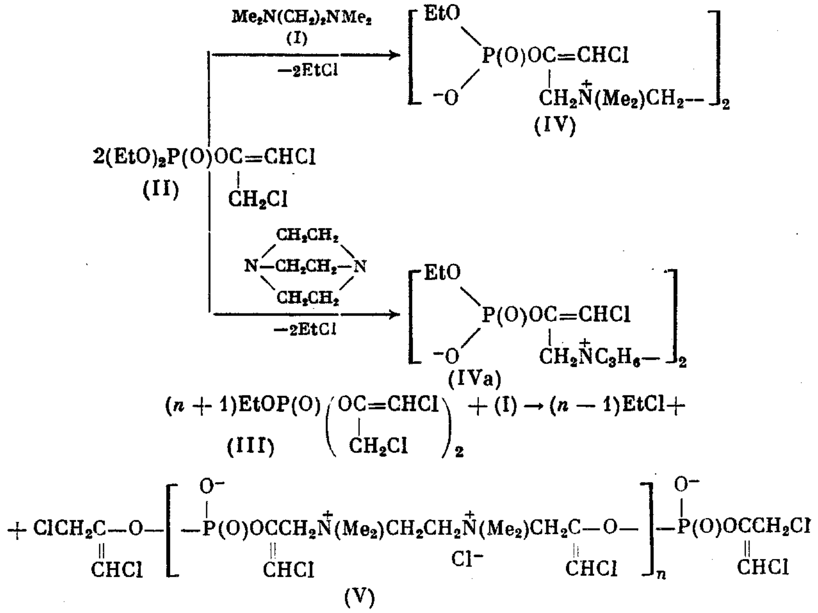
1. T. Zincke and R. Suhl, Ber., 39, 4148 (1906); M. S. Newman and A. G. Pinkus, J. Org. Chem., 19, 978 (1954).
2. J. R. Merchant and V. B. Jadhav, J. Indian Chem. Soc., 51, 95 (1974).
3. V. A. Nikanorov, V. I. Rozenberg, A. I. Yanovskii (Yanovsky), et al., J. Organomet. Chem., 307, 351, 363 (1986).
4. V. A. Nikanorov, G. V. Gavrilova, V. I. Rozenberg, and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., 2345 (1987).
5. E. R. Krajniak, E. Ritchie, and W. C. Taylor, Austr. J. Chem., 26, 1337 (1973).
6. B. F. Filimonov, G. S. Litvinenko, G. F. Dvorko, and S. A. Mramornova, Zh. Obshch. Khim., 49, 1098 (1979); 55, 1828 (1985).
7. J. W. Cook, J. Chem. Soc., 2160 (1926); 58 (1928); N. F. Salakhutdinov, A. N. Detsina, I. K. Korobeinicheva, and V. A. Koptyug, Zh. Org. Khim., 15, 1468 (1979).
8. J. R. Merchant and V. B. Jadhav, J. Chem. Soc., C, 499 (1968).
9. V. A. Nikanorov, G. V. Gavrilova, V. I. Rozenberg, and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., 2647 (1984); V. I. Bakhmutov, M. V. Galakhov, V. A. Nikanorov, et al., Dokl. Akad. Nauk SSSR, 295, 1376 (1987).
10. V. P. Vitullo, J. Org. Chem., 34, 224 (1969).

BIS- AND POLYBETAINES OF PHOSPHORUS-CONTAINING VINYLCHOLINES

A. S. Oganesyan, P. V. Petrovskii,
and Yu. G. Gololobov

UDC 66.095.253:547.415.1:547.26'118:547.466.1

In a search of new types of physiologically active phosphorus compounds soluble in water and resistant to hydrolysis, we developed a method for the preparation of phosphorus-containing betaines with an ammonium group in the substituted vinyl ester group [1]. This method is applicable for the synthesis of previously unknown bis- and polybetaines. This reaction is based on the alkylation of bisamines such as tetramethylethylenediamine (I) and triethylenediamine by O-phosphorylated allyl chlorides (II) and (III). The initially obtained trialkyl esters are dealkylated upon heating to betaines (IV) and (V).

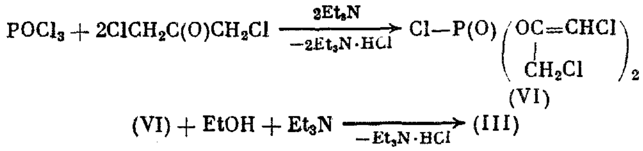


A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 913-915, April, 1988. Original article submitted June 25, 1987.

0568-5230/88/3704-0792$12.50

The composition and structure of these compounds were demonstrated by elemental analysis, IR and NMR spectroscopies, and molecular mass determination.

Initial divinyl phosphate (III) was obtained from $POCl_3$, 1,3-dichloroacetone, and ethanol according to our previous procedure [2].



$$POCl_3 + 2ClCH_2C(O)CH_2Cl \xrightarrow[-2Et_3N\cdot HCl]{2Et_3N} Cl{-}P(O)\left(\begin{array}{l}OC{=}CHCl\\ \;|\\ CH_2Cl\end{array}\right)_2$$

(VI)

$$(VI) + EtOH + Et_3N \xrightarrow[-Et_3N\cdot HCl]{} (III)$$

EXPERIMENTAL

The NMR spectra were taken on a Bruker WP-200SY spectrometer. The PMR spectra were taken at 200 MHz with TMS as the external standard. The ^{31}P NMR spectra were obtained at 81 MHz with 85% H_3PO_4 as the external standard. The IR spectra were taken neat or in KBr pellets on a UR-20 spectrometer.

Di-N,N'-(β-O-ethoxyphosphoroyl-γ-chloro)-allyl-N,N,N',N'-tetramethylethylene-diammonium Disphosphate (IV). A mixture of 0.01 mole vinyl phosphate (II) [2] and 0.005 mole diamine (I) was maintained for 48 h in 5 ml benzene at 20°C and then heated in vacuum at 100°C. The solid residue was crystallized from ethanol to give (IV) in 63% yield, mp 220°C (dec.). IR spectrum (ν, cm^{-1}): 950, 1050, 1090 (POC), 1260,(P=O), 1640 (C=C), 3080 (=CH–). PMR spectrum in D_2O (δ, ppm, J, Hz): 1.26 t (6H, CH_3, $^3J_{HH}$ = 7.0), 3.28 s (12H, CH_3N), 4.07 m (8H, $CH_2O + CH_2CH_2$), 4.32 s (4H, CH_2C=), 6.56 d (2H, =CH–, $^4J_{HP}$ = 2.4), δ_P –4.95 ppm. Molecular mass 526, calculated 513. Found: Cl 13.38; N 5.80; P 11.79%. Calculated for $C_{16}H_{32}Cl_2N_2O_8P_2$: Cl 13.84; N 5.45; P 12.08%.

Di-N,N'-(β-O-ethoxyphosphoroyl-γ-chloro)allyltriethylenediammonium Diphosphate (IVa). A crystalline product was obtained by the above-mentioned method with mp 180°C (dec.). IR spectrum (ν, cm^{-1}): 950, 1060, 1090 (POC), 1265 (P=O), 1645 (C=C), 3010 (=CH–). PMR spectrum (D_2O, δ, ppm, J, Hz): 1.29 t (6H, CH_3, $^3J_{HH}$ = 7.1), 4.13 m (16H, $CH_2O + CH_2CH_2$), 4.51 s (4H, CH_2C=), 6.60 d (2H, =CH–, $^4J_{HP}$ = 2.3), δ_P –4.88 ppm. Found: Cl 13.39; N 5.95; P 11.78%. Calculated for $C_{16}H_{28}Cl_2N_2O_8P_2$: Cl 13.39; N 5.50; P 12.18%.

Bis-(α-chloromethyl-β-chlorovinyl)chlorophosphate (VI). A sample of 0.066 mole 1,3-dichloroacetone in 60 ml abs. ether was added to a mixture of 0.03 mole $POCl_3$ at 0°C and, then, a solution of 0.075 mole Et_3N in 30 ml ether was added with stirring. The reaction mass was stirred for 6 h at about 20°C. On the following day, the reaction mixture was filtered and evaporated. The residue was distilled in vacuum to give (VI) in 60% yield, bp 135-140°C (0.1 mm). ^{31}P NMR spectrum: δ_P –6.32 ppm. PMR spectrum (δ, ppm, J, Hz): 4.27 m (4H, CH_2Cl), 6.20 d (2H, =CH–, $^4J_{HP}$ = 2.2).

O-Ethyl-bis-(α-chloromethyl-β-chlorovinyl)phosphate (III). A mixture of 0.017 mole Et_3N and 0.017 mole abs. ethanol was added with stirring to 0.016 mole (VI) in 20 ml ether at 20°C, On the following day, the residue was filtered off. The residue was maintained in vacuum at 40-50°C. ^1H and ^{31}P NMR spectroscopy indicated that the reaction product is a single compound. This product decomposes upon distillation at high vacuum. PMR spectrum (δ, ppm): 1.3 d. t (3H, CH_3), 4.2 s (4H, CH_2Cl), 4.3 m (2H, CH_2O), 6.1 s (1H, =CH–), δ_P –14.52 ppm.

Oligomer (V). A mixture of 0.005 mole ester (III) and 0.005 mole diamine (I) was heated in 5 ml dry 2-butanone for 6 h at 80°C. The precipitate was washed with ether, maintained for 4 h in vacuum at 60-80°C, and reprecipitated from ethanol. The ^{31}P NMR spectrum has signals at δ_P –11.8 and –11.9 ppm in 1:3 ratio. The ratio of the =CH proton signals of the terminal and internal vinyl groups in the PMR spectrum is 1:6. δ_H 6.3 d, $^4J_{HP}$ = 2.0 Hz (terminal vinyl group), δ_H 6.7 d, $^4J_{HP}$ = 2.5 Hz (internal vinyl group). The latter is an approximate value since there is overlap of several signals from the vinyl protons of the polymer chain. In light of the above ratios, the molecular mass of the oligomer was estimated to be about 2500 (n = 6).

The authors thank G. I. Timofeeva for the determination of the molecular mass of (IV).

CONCLUSIONS

Phosphorus-containing vinylcholine bis- and polybetaines were obtained upon the alkylation of tetramethylethylenediamine and triethylenediamine by O-phosphorylated allyl chlorides with subsequent thermal dealkylation.

LITERATURE CITED

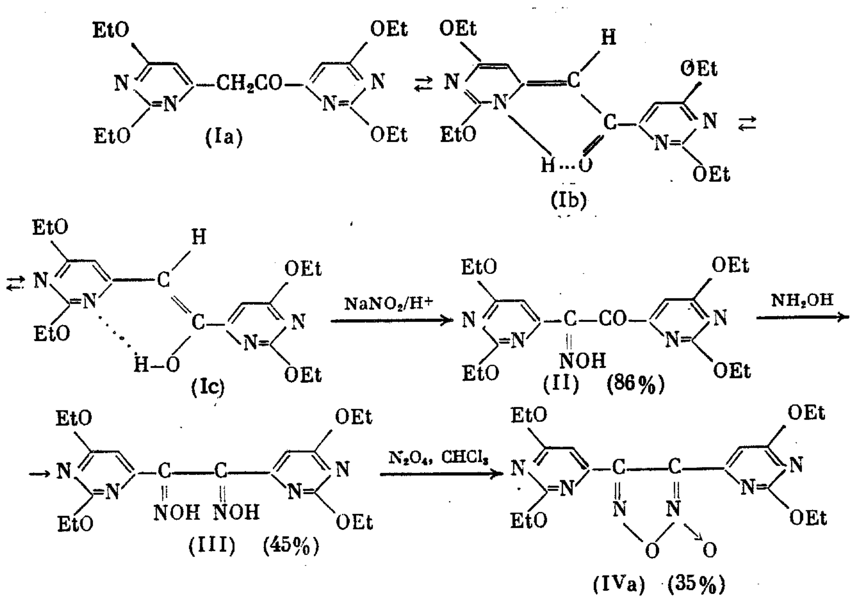
1. Yu. G. Gololobov and A. S. Oganesyan, Izv. Akad. Nauk SSSR, Ser. Khim., 2333 (1986).
2. Yu. G. Gololobov, T. V. Kim, and E. I. Kiseleva, Dokl. Akad. Nauk SSSR, 272, 1388 (1983).

SYNTHESIS OF BIS(PYRIMIDYL)FUROXANES BY THE OXIDATION OF BIS(PYRIMIDYL)GLYOXIMES

L. I. Khmel'nitskii, N. N. Makhova,
M. A. Epishina, Yu. A. Strelenko,
S. G. Baram, and V. P. Mamaev*

UDC 542.943:547.855.7

Bis(pyrimidyl)furoxanes (IV) have been obtained by the action of nitric acid [1] and a nitrating mixture [2] on the corresponding 4(6)-methylpyrimidines. These products are apparently obtained as the result of the dimerization of intermediate pyrimidylnitrile oxides formed through consecutive nitration steps of the methyl group, nitrosation of the nitromethyl fragment, and decomposition of the pyrimidinenitrolic acid generated by analogy with the work of Nakagoma and Castle [3]. In the present work, we propose a different approach to the synthesis of such compounds based on the oxidation of bis(pyrimidyl)glyoximes. The reaction was carried out in the case of 1,2-bis(2, 4-diethoxypyrimidin-6-yl)glyoxime (III) obtained from 1,2-bis(2,4-diethoxypyrimidin-6-yl)-1-oxoethane (I) through intermediate oximinoketone (II).



Starting (I) was synthesized by the condensation of 2,4-diethoxy-6-methylpyrimidine (V) and the ethyl ester of 2,4-diethoxypyrimidine-6-carboxylic acid (VI) in diemthylformamide in the presence of NaH.

---

*Deceased.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 915-917, April, 1988. Original article submitted July 2, 1987.

0568-5230/88/3704-0794$12.50