SYNTHESIS AND PROPERTIES OF bis[N-ALKYL(aryl)-AMINOMETHYL]PHOSPHINIC ACIDS

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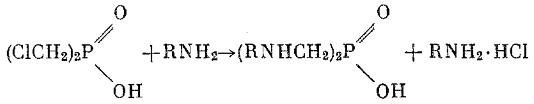
We have already reported [1] the synthesis of bis(N,N-dialkylaminomethyl)phosphinic acid derivatives. bis[N-Alkyl (aryl)aminomethyl]phosphinic acids and their derivatives, which can be used as monomers for synthesis of phosphorous-containing polymers, are of definite interest.

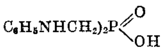
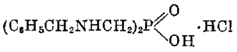
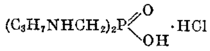
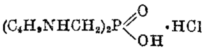
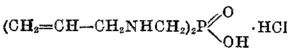
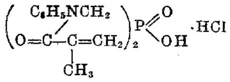
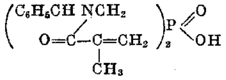
In this communication is described the preparation of bis[N-Alkyl (aryl)aminomethyl]phosphinic acids by the reaction of primary aliphatic and aromatic amines with bischloromethylphosphinic acid by the following scheme:



To prevent formation of tarry condensation products, a large excess of the corresponding amines is used in the reaction. The products separate either as internal salts or as hydrochlorides, depending on the properties of the compounds being prepared. The properties of the products are presented in Table 1. The structure was confirmed by IR spectra.

Bis[N-Alkyl (aryl)aminomethyl]phosphinic acids are capable of different types of transformations determined by the presence of a labile hydrogen atom on the amino group. Thus, treatment of bis(N-phenylaminomethyl)phosphinic acid and bis(N-benzylaminomethyl)phosphinic acid with methacroyl chloride under heterophase amidation conditions yields the corresponding methacroyl derivatives (VI) and (VII). For bis-(N-phenyl-N-methacroylaminomethyl)phosphinic acid, formation of a complex with the sodium salt of methacrylic acid in the ratio 2 : 1, which is decomposed by hydrochloric acid, is characteristic.

TABLE 1

Compound	Yield, %	mp °C	Found/Calculated, % P	Found/Calculated, % N	Empirical formula
	63,5	180—181	11,20 / 11,21	10,40 / 10,14	$C_{14}H_{17}N_2PO_2$
	72	220—222	9,09 / 9,09	8,21 / 8,22	$C_{16}H_{22}N_2PO_2$
	47,6	238—239	12,90 / 12,65	11,26 / 11,44	$C_8H_{22}N_2PO_2$
	37	240—242	11,28 / 11,35	10,34 / 10,30	$C_{10}H_{26}N_2PO_2Cl$
	33,85	200—202	12,56 / 12,86	11,64 / 11,63	$C_8H_{18}N_2PO_2Cl$
	69	70—71	7,80 / 7,47	6,34 / 6,76	$C_{22}H_{25}N_2PO_4$
	64	146—147	7,09 / 7,00	6,50 / 6,35	$C_{24}H_{29}N_2PO_4$

A. E. Arbuzov Institute of Organic and Physical Chemistry of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1860-1862, August, 1968. Original article submitted December 12, 1967. Additions submitted March 14, 1968.

EXPERIMENTAL

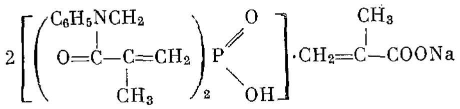
bis(N-Phenylaminomethyl)phosphinic Acid. A mixture of 50 g of bischloromethylphosphinic acid and 284 g of aniline was heated for 10 h at a temperature of 110-120°C in a stream of nitrogen. The crystals which precipitated from the reaction mass upon cooling were filtered, washed, and then extracted with hot benzene to separate the traces of aniline. The remaining residue was washed with water to a negative reaction for chloride ions in the washing waters (upon acidification, an additional amount of product precipitated from the washing waters). After recrystallization from ethyl alcohol, 53 g (63%) of bis(N-phenylaminomethyl)phosphinic acid was obtained as an internal salt having mp 180-181°.

bis(N-Benzylaminomethyl)phosphinic Acid. A mixture of 35 g of bischloromethylphosphinic acid and 250 ml of benzylamine was heated with intense stirring for 10 h at a temperature of 110-120°. The excess benzylamine was distilled from the reaction mass in vacuum. The remaining crystalline mass was dissolved in water and acidified with conc. HCl to an acid reaction. Upon acidification, the precipitated crystals of bis(N-benzylaminomethyl)phosphinic acid monohydrochloride have mp 220-222° after recrystallization from water, yield 52.5 g (72%).

bis(N-Allylaminomethyl)phosphinic Acid. A mixture of 10 g of bischloromethylphosphinic acid and 50 g of allylamine was heated in a sealed tube for 10-12 h at a temperature of 95-110°. The excess allylamine was distilled from the reaction mixture. The remaining viscous mass was dissolved in ethyl alcohol and treated with 7.74 g of NaOH dissolved in alcohol. The precipitated NaCl was filtered and the filtrate was evaporated to dryness. The dry residue was dissolved in alcohll and acidified with 12 ml of 37% HCl. The solution was filtered while hot. Upon cooling, 5 g (34%) of bis(N-allylaminomethyl)phosphinic acid crystallized from the filtrate as the monohydrochloride having mp 200-202°.

bis(N-Allylaminomethyl)phosphinic Acid. A mixture of 10g of bischloromethylphosphinic acid and 50g of allylamine was heated in a sealed tube for 10-12 h at a temperature of 95-110°. The excess mixture was the same as in the case of bis(N-allylaminomethyl)phosphinic acid. Properties of the obtained acids are presented in Table 1.

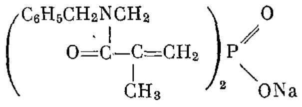
Dimethacroylamide of bis(N-Phenylaminomethyl)phosphinic Acid. To a basic solution (15.2 g of NaOH in 100 ml of H_2O) and 15 g of bis(N-phenylaminomethyl)phosphinic acid was poured a solution of 22.7 g (0.218 mole) of the acid chloride of methacrylic acid in $CHCl_3$. The mixture was stirred for 1 h at 0°. The reaction mixture was acidified with 5 ml of 37% HCl and the layers were separated. From the organic layer after removal of the solvent and treatment with ethyl ether precipitated 20.6 g of a crystalline product, which after recrystallization from an alcohol–ether mixture had mp 239-241° and corresponds to a compound of the composition:



Found %: P 6.63; N 6.33. $C_{48}H_{55}N_4P_2O_{10}Na$. Calculated %: P 6.50; N 5.90.

The same product is obtained upon treatment of a solution of bis(N-phenyl-N-methacroylaminomethyl)-phosphinic acid in chloroform with an aqueous solution of sodium methacrylate. Free bis(N-phenyl-N-methacroylaminomethyl)phosphinic acid is obtained upon acidification of a solution of the complex in $CHCl_3$ with dilute HCl. After recrystallization from alcohol, the product has mp 70-71°, yield 15.5 g (69%).

Dimethacroylamide of bis(N-Benzoylaminomethyl)phosphinic Acid. Obtained under analogous conditions. Initially separates from the reaction in the form



having mp 272.5-273.5°. Found %: P 6.85; N 6.42. $C_{24}H_{28}N_2PO_4Na$. Calculated %: P 6.70; N 6.10.

The free acid separates upon acidification with dilute HCl, and after recrystallization from an alcohol–ether mixture has mp 145-146°.

CONCLUSIONS

Reaction of primary aliphatic and aromatic amines with bischloromethylphosphinic acid yielded a series of bis(N-alkyl(aryl)aminomethyl)phosphinic acids and the methacroylamides of several of them were obtained.

LITERATURE CITED

1. M. K. Il'ina and I. M. Shermergorn, Izv. Akad. Nauk SSSR, Ser. Khim., 1967, 1346.