THE CONDENSATION PRODUCTIONS OF CHLORAL AND THE AMIDES OF ORGANOPHOSPHORIC ACIDS

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Recently the attention of investigators has been turned to synthetic products fromed by the reaction of chloral with dialkyl- and trialkylphosphites, since many of these compounds possess insecticidal properties. It was therefore of interest to obtain the condensation products of chloral with the amides of organophosphoric acids. In this paper we present the results of studies of the reaction of chloral with some amides of dialkylphosphoric acids.

Our experiments showed that this reaction leads to the formation of N-α-hydroxy-β-trichlorethylamides of dialkylphosphoric acids according to the following scheme

$$(RO)_2P(O)NH_2 + CCl_3CHO \rightarrow (RO)_2P(O)NHCH(OH)CCl_3$$

In order to confirm the structure of the compounds described, one of them ($R = C_3H_7$) was reacted with the chloroanhydride of diethylphosphoric acid. In the case of the structure indicated, the hydrogens of the amide and hydroxyl groups must be replaced in the organophosphoric residues.

$$(C_3H_7O)_2P(O)NHCH(OH)CCl_3 + 2\,ClP(OC_2H_5)_2 + 2\,(C_2H_5)_3N \rightarrow$$
$$\rightarrow (C_3H_7O)_2P(O)\underset{\displaystyle P(OC_2H_5)_2}{\underset{|}{N}}CH[(OP(OC_2H_5)_2]CCl_3 + 2(2_2N_5)_3NHCl$$

As indicated, the exchange reaction takes place easily and completely in an ether solution. The reaction of chloral with the amides of dialkylphosphoric acids takes place on heating equimolecular quantities of the reagents for from one to one and a half hours at a temperature of 60-90°. In this way we obtained quantitative yields of N-α-hydroxy-β-trichloroethylamides of dialkylphosphoric acids $(RO)_2P(O)NHCH(OH)CCl_3$, where the alkyl groups were methyl, ethyl, propyl, isopropyl, and butyl. The formulas of the compounds, their melting points and analytical data are shown in the following table.

Compound No.	Formula	M. p., °C	Phosphorus content, % found	Phosphorus content, % calculated
I	$(CH_3O)_2P(O)NHCH(OH)CCl_3$	103—104	11,78; 11,70	11,38
II	$(C_2H_5O)_2P(O)NHCH(OH)CCl_3$	96—97	10,38; 10,49	10,32
III	$(C_3H_7O)_2P(O)NHCH(OH)CCl_3$	81—82	9,47; 9,45	9,44
IV	$(i\text{-}C_3H_7O)_2P(O)NHCH(OH)CCl_3$	138—139	9,43; 9,64	9,44
V	$(C_4H_9O)P(O)NHCH(OH)CCl_3$	79—80	8,7; 8,77	8,69
VI	$C_2H_5OP(O)[NHCH(OH)CCl_3]_2$	Thick, viscous liquid		
VII	$(C_2H_5)_2P(O)NHCH(OH)CCl_3$	Thick liquid		

Most of the substances shown in the table are crystalline and are soluble in the ordinary organic solvents. The substances that have one of the lower hydrocarbon radicals adjacent to the phosphorus are also soluble in water. The melting points of the crystalline products did not show the regularity which is usually observed in compounds of a homologous series. For example, N-α-hydroxy-β-trichloroethylamide of diisopropylphosphoric acid (IV) melts considerably higher than the corresponding compound, which has a complex hydrocarbon chain in the ester group next to the phosphorus (III). Similar departures from normal occur in connection with other compounds. Preliminary study of the insecticidal properties of compounds (I) and (II) showed that their aqueous solutions caused the death of house flies.

EXPERIMENTAL

Unsubstituted amides of organophosphoric acids were obtained by the action of dry gaseous ammonia on ether solutions of alkylchlorophosphates.

$$(RO)_2POCl + 2NH_3 \rightarrow (RO)_2P(O)NH_2 + NH_4Cl$$

The ammonium chloride precipitate was filtered off and the amide, after removal of the solvent, was condensed with chloral. In those cases where the amides obtained were not soluble in ether and separated out with the ammonium chloride, the mixture was not separated but was used for the subsequent reaction. The quantity of amide was calculated in accordance with the theoretical composition of the mixture. Such mixtures of an amide with ammonium chloride were formed in the production of the amide of dimethylphosphoric acid and the diamide of ethylphosphoric acid.

N-α-hydroxy-β-trichloroethylamide of dimethylphosphoric acid (I). For the reaction the amide of dimethylphosphoric acid $(CH_3O)_2P(O)NH_2$ mixed with ammonium chloride was used (see the preparation of the amides of organophosphoric acids). The theoretical content of amide in the mixture was 70%. For the reaction 6.26 g of a mixture containing 4.38 g (0.035 M) of the amide $(CH_3O)_2P(O)NH_2$ and 5.16 g (0.035 M) of chloral were used. The reaction mixture was stirred and heated on a water bath at a temperature of 90-95° for one and a half hours. After cooling, the thick mass was dissolved in 10 ml of ether. The precipitate of ammonium chloride was filtered off. After removing the solvent from the filtrate, 7.9 g (82.9%) of a thick liquid was obtained. On the following day the reaction product became a dense, white mass of crystals. The substance on recrystallization from petroleum ether (b. p. 70-120°) formed small needles with a m. p. 103-104°. Found: P 11.78, 11.70%. $C_4H_9O_4PNCl_3$. Calculated: P 11.38%. The substance dissolves easily in water, benzene and dioxane (on heating), is relatively insoluble in ether, and is almost completely insoluble in boiling petroleum ether.

N-α-hydroxy-β-trichloroethylamide of diethylphosphoric acid (II). To a suspension of 5.4 g (0.035 M) of the amide of diethylphosphoric acid $(C_2H_5O)_2P(O)NH_2$ in ether 5.16 g (0.035 M) of chloral was added immediately. The temperature rose from 21 to 36°. The reaction mixture was stirred and heated on a water bath at 90-100° for 2 hr. On the following day the mass crystallized. After recrystallization from petroleum ether small needles with a melting point of 96-97° were obtained. Found: P 10.38, 10.49%. $C_6H_{13}O_4PNCl_3$. Calculated: P 10.32%. The substance is soluble in ether, benzene, dioxane, petroleum ether (on heating), and also in water.

N-α-hydroxy-β-trichloroethylamide of dipropylphosphoric acid (III). In order to produce the N-monosubstituted amide, 6.34 g (0.035 M) of the amide of dipropylphosphoric acid $(C_3H_7O)_2P(O)NH_2$ was allowed to react with 5.16 g (0.035 M) of chloral. After the addition of the chloral to the amide, the temperature of the mixture decreased from 21 to 16°. The reaction mixture was stirred and heated on a water bath at 90-96° for one hour. On cooling, the contents of the flask became a dense, white, crystalline mass. The product was crystallized from petroleum ether and yielded fine, white needles with a melting point of 81-82°. Found: P 9.47, 9.45%. $C_8H_{17}O_4PNCl_3$. Calculated: P 9.44%. The substance is soluble in ether, alcohol, and water (after prolonged contact), and it is soluble in petroleum ether on heating.

N-α-hydroxy-β-trichloroethylamide of diisopropylphosphoric acid (IV). The N-monosubstituted amide of diisopropylphosphoric acid was obtained in a similar manner by the action of chloral (0.035 M) on the amide of diisopropylphosphoric acid $(i\text{-}C_3H_7O)_2P(O)NH_2$ (0.035 M). Within 50 min after heating the mixture (bath temperature 90-96°), the reaction product crystallized completely while still hot. The N-monosubstituted amide, after recrystallization from a mixture of benzene and petroleum ether (1:1; b. p. petroleum ether 70-120°), formed small needles, m. p. 138-139°. The yield of pure product was 7.3 g (63.5%). Found: P 9.43, 9.64%. $C_8H_{17}O_4PNCl_3$. Calculated: P 9.44%. The substance is soluble in ether, in benzene on heating, and almost completely insoluble in hot petroleum ether.

N-α-hydroxy-β-trichloroethylamide of dibutylphosphoric acid (V). The N-monosubstituted amide of dibutylphosphoric acid was obtained in a similar manner to the preceding substituted amides. The product was recrystallized from petroleum ether (b. p. 70-120°). On drying, the substance does not crumble but forms a dense mass which must be cut and crushed with a spatula; m. p. 79-80°. Found: P 8.7, 8.77%. $C_{10}H_{21}O_4PNCl_3$. Calculated: P 8.69%. The substance dissolves easily in ether, and in petroleum ether on heating; it is insoluble in water.

Di-N-α-hydroxy-β-trichloroethylamide of ethylphosphoric acid (VI). The diamide of ethylphosphoric acid $(C_2H_5O)P(O)(NH_2)_2$ in a mixture of ammonium chloride (see the production of the amides of organophosphoric acids)

with a theoretical content of 53.7% of the diamide was used for the reaction. To a suspension of 6.14 g of the mixture of diamide and ammonium chloride containing 3.3 g (0.0266 M) of the diamide in ether was added 7.83 g (0.0532 M) of chloral. Since the diamide is hygroscopic, measures were taken to prevent moisture from the air from entering the reaction vessel. The reaction mixture was heated with stirring on a water bath at 50-60° for one and a half hours. After cooling, the reaction product was dissolved in ether and the ammonium chloride filtered off. After removing the solvent 11 g (98.7%) of a very thick, viscous liquid was obtained which did not crystallize even after prolonged standing. The substance was not soluble in ether, benzene or water.

N-α-hydroxy-β-trichloroethylamide of diethylphosphoric acid (VII). 4.35 g (0.036 M) of the amide of diethylphosphoric acid $(C_2H_5)_2P(O)NH_2$ was allowed to react with 5.3 g (0.036 M) of chloral. On mixing these substances together the temperature of the mixture, despite cooling of the flask by a stream of water, rose from 21 to 65°. The reaction mixture was stirred and heated for 1 hr on a water bath at a temperature of 60-65°. The product obtained was a very thick liquid which did not crystallize even after prolonged standing. The substance was only slightly soluble in ether, benzene (with heating), and water.

The action of the chloroanhydride of diethylphosphoric acid on N-α-hydroxy-β-trichloroethylamide of dipropylphosphoric acid. To a solution of 3.94 g (0.12 M) of the amide $(C_3H_7O)_2P(O)NHCH(OH)CCl_3$ (m. p. 81-82°) in 60 ml of ether was added 3.75 g (0.024 M) of an ether solution of diethylchlorophosphite $(C_2H_5O)_2PCl$ (b. p. 72-73° [60 mm]) through a dropping funnel, with stirring, in a flask cooled by water. After the addition of the chloride the thick mass was stirred for 2 hr while the solvent was allowed to boil lightly. 3.22 g (97.1%) of the salt of the amide $(C_2H_5)_3N \cdot HCl$ and a residue of 6.43 g (94.3%) after removal of the solvent were obtained.

The reaction product was a fairly mobile liquid with an ether-like odor. On distillation in vacuo (1 mm), the substance decomposed (bath temperature 175-200°).

SUMMARY

A number of monosubstituted amides $(RO)_2P(O)NHCH(OH)CCl_3$ were obtained by the reaction of chloral with dialkylphosphoric acids, and subsequently characterized.