ORGANOPHOSPHOROUS MONOMERS

COMMUNICATION 2. α-CHLORO- AND α-BROMOVINYLPHOSPHINIC ACIDS AND THEIR DERIVATIVES

T. Ya. Medved' and M. I. Kabachnik

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

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In a previous communication in this series [1] we showed that the di-acid chloride of vinylphosphinic acid, $CH_2=CHPOCl_2$, can be readily prepared by catalytic dehydrochlorination of the di-acid chloride of β-chloroethylphosphinic acid. There also was given the information that the di-acid chloride of vinylphosphinic acid can be widely used in synthesis of organophosphorus monomers and polymers. In the present article are given results obtained in bromination and chlorination of the di-acid chloride of vinylphosphinic acid.

Addition of bromine to the di-acid chloride of vinylphosphinic acid is carried out as simply as to its ethyl ester [1, 2]. The reaction is complete after standing for 24 hr at room temperature a mixture of equimolecular amounts of the acid chloride and bromine in solution in chloroform

$$CH_2=CHPOCl_2 + Br_2 \rightarrow BrCH_2CHBrPOCl_2$$

The di-acid chloride of α, β-dibromoethylphosphinic acid (I) obtained in this manner was hydrolyzed to the free acid (II), the aniline salt of which (III) melted at 194-195°. During an attempt to prepare the anilide of this acid, dehydrobromination of the substance took place and the dianilide of α-bromovinylphosphinic acid (VIII) was obtained.

$BrCH_2CHBrPOX_2$
(I) $X=Cl$
(II) $X=OH$
(III) $X=OH$ (aniline salt)

$CH_2=CBrPOX_2$
(IV) $X=Cl$
(V) $X=OH$
(VI) $X=OH$ (aniline salt)
(VII) $X=OC_2H_5$
(VIII) $X=NHC_6H_5$

Under conditions similar to those previously found necessary by us for dehydrochlorination of the di-acid chloride of β-chloroethylphosphinic acid, dehydrobromination of the di-acid chloride of α,β-dibromoethylphosphinic acid was achieved:

$$BrCH_2CHBrPOCl_2 \xrightarrow[-HBr]{BaCl_2} CH_2=CBrPOCl_2$$

At the same time, the acid chloride of α-bromovinylphosphinic acid (IV) was formed in ~80% yield. By hydrolysis of the acid chloride, acid (V) was obtained as a syrup; the aniline salt of the acid, (VI), melts at 187-188°.

By reacting this acid chloride with alcohol, the ethyl ester of α-bromovinylphosphinic acid (VII) was obtained, synthesized previously by another method [1]. Its structure was demonstrated by ozonization; on ozonization, the dimedon derivative of formaldehyde was obtained.

Reaction of the di-acid chloride of vinylphosphinic acid with chlorine proceeds with considerably greater difficulty than with bromine. At room temperature, chlorine is added to the acid chloride very slowly; the reaction is accelerated somewhat by the action of sunlight. On heating the reaction mixture in a sealed tube at 125-130° for 5 hr, yield of reaction products reaches about 80%. In this case, besides chlorine addition at the double bond and formation of the di-acid chloride of α, β-dichloroethylphosphinic acid (IX), hydrogen chloride is split off from the latter, the di-acid chloride of α-chlorovinylphosphinic acid (X) being formed simultaneously. Both acid chlorides were obtained in pure form. It is noticed that the experiment to obtain the acid chloride of α, β-dichloroethylphosphinic acid by oxidative phosphorylation of vinyl chloride described in the literature [3] led to a mixture of isomers, separation of which was not achieved.

(IX) $ClCH_2CHClPOCl_2$ $CH_2{=}CClPOX_2$

(X) $X{=}Cl$; (XI) $X{=}OH$

(XII) $X{=}OH$ (aniline salt)   (XIII) $X{=}OCH_3$

(XIV) $X{=}OC_2H_5$; (XV) $X{=}NHC_6H_5$

The di-acid chloride of α, β-dichloroethylphosphinic acid was converted by catalytic dehydrochlorination over barium chloride into the acid chloride of α-chlorovinylphosphinic acid. As shown in further experiments, dehydrochlorination of the acid chloride of α, β-dichloroethylphosphinic acid can be achieved both in the absence of catalyst and at a lower temperature. Thus, if the reaction mixture formed by chlorination of the di-acid chloride of vinylphosphinic acid is maintained prior to the onset of distillation at 150-155° until hydrogen chloride evolution ceases, then distillation results mainly in formation of the di-acid chloride of α-chlorovinylphosphinic acid and only a small amount of the di-acid chloride of α, β-dichloroethylphosphinic acid. Much the same result is obtained on heating the reaction mixture in a sealed tube at 140-150°.

By reacting the acid chloride of α-chlorovinylphosphinic acid with the alcohols, the methyl (XIII) and ethyl (XIV) esters of α-chlorovinylphosphinic acid are obtained. On reacting with aniline, the dianilide of the same acid is obtained (XV).

EXPERIMENTAL

Di-acid chloride of α, β-dibromoethylphosphinic acid (I). 10.8 g (0.075 M) of the di-acid chloride of vinylphosphinic acid and 11.12 g (0.07 M) of bromine in 50 ml of chloroform were left overnight at room temperature. After distillation in a stream of carbon dioxide, a substance was obtained with b. p. 120-122° (5 mm); yield 14.3 g (62.5%); $n^{20}D$ 1.5698; d^{20}_4 2.2155; MR found 45.07; MR calculated 45.02. On standing, the substance crystallized; m. p. 33-34°. Found: C 7.6; 7.4; H 1.1, 1.2; P 10.2, 9.6; Hal 76.1, 76.1%. $C_2H_3PCl_2Br_2$. Calculated: C 7.9; H 1.0; P 10.2; Hal 75.7%.

α, β-Dibromoethylphosphinic acid (II). To 6 ml of water was gradually added 2 g of the di-acid chloride of α, β-dibromoethylphosphinic acid. After distillation of water the residue was dried over phosphorus pentoxide and alkali. 1.6 g (90.8%) of colorless crystals was obtained with m. p. 115-116°. The substance was readily soluble in water and alcohol, insoluble in organic solvents. Found: C 8.8, 8.8; H 1.9, 2.0; P 11.2, 11.4%. $C_2H_5PO_3Br_2$. Calculated: C 9.0; H 1.9; P 11.6%.

Aniline salt of α, β-dibromoethylphosphinic acid (III). To 2.7 g (0.01 M) of α, β-dibromoethylphosphinic acid in 3 ml of alcohol was added 0.93 g (0.01 M) of aniline; the precipitate settling out was washed with ether and recrystallized from alcohol. 2.5 g (69.5%) of a substance was obtained with m. p. 194-195°. Found: C 26.6, 26.8; H 3.4, 3.3; P 8.6, 8.7; N 4.2, 4.0; Br 44.1, 44.2%. $C_8H_{12}PO_3NBr_2$. Calculated: C 26.6; H 3.3; P 8.6; N 3.9; Br 44.3%.

Dianilide of α-bromovinylphosphinic acid (VIII). 1.35 g (0.0044 M) of the di-acid chloride of α, β-dibromoethylphosphinic acid and 1.64 g (0.0176 M) of aniline in 10 ml of benzene were heated for 1.5 hr on a boiling water bath. After removal of the precipitate, benzene was distilled off, and the residue recrystallized from alcohol. 0.4 g (26.6%) of a substance was obtained with m. p. 156-157°. Found: C 49.6, 49.9; H 4.3, 4.4; P 9.3, 9.1; N 8.3, 8.3%. $C_{14}H_{14}POBrN_2$. Calculated: C 49.9; H 4.2; P 9.2; N 8.3%.

Di-acid chloride of α-bromovinylphosphinic acid (IV). 20 g (0.066 M) of the di-acid chloride of α, β-dibromoethylphosphinic acid was passed through a quartz tube filled with barium chloride and heated to 330-340°. After distillation of the condensate, 11.4 g (77.5%) of a liquid was obtained with b. p. 194-197° at atmospheric pressure; $n^{20}D$ 1.5273; d^{20}_4 1.8393; MR found 37.44; MR calculated 36.79. On standing, the substance crystallized; m. p. 36-39°. Found: C 10.9, 11.0; H 1.2, 1.0; P 14.1, 13.9%. $C_2H_2POCl_2Br$. Calculated: C 10.7; H 0.9; P 13.8%.

Soborovskii with co-workers [4] obtained the di-acid chloride of β-bromovinylphosphinic acid, the constants of which [b. p. 81-82° (3 mm); $n^{20}D$ 1.7415; d^{20}_4 1.4884] differed markedly from the constants of the α-derivative.

α-Bromovinylphosphinic acid (V). Obtained similarly to substance (II) from 2.6 g of the di-acid chloride of α-bromovinylphosphinic acid; a colorless syrup; yield 2.1 g (96%). Found: C 13.0, 13.1; H 2.5, 2.5; P 17.0, 16.9. $C_2H_4PO_3Br$. Calculated: C 12.9; H 2.2; P 16.6%.

Aniline salt of α-bromovinylphosphinic acid (VI). Obtained from 1.3 g (0.007 M) of α-bromovinylphosphinic acid and 0.65 g (0.007 M) of aniline similarly to substance (III); yield 0.7 g (36%); m. p. 187-188°. Found: C 34.4, 34.7; H 4.2, 4.2; P 11.1, 11.2; N 5.5, 5.3%. $C_8H_{11}PO_3NBr$. Calculated: C 34.3; H 4.0; P 11.1; N 5.0%.

Ethyl ester of α-bromovinylphosphinic acid (VII). To 50 ml of absolute ethyl alcohol at 0 – 5° was gradually added with stirring 7 g (0.03 M) of the di-acid chloride of α-bromovinylphosphinic acid. The mixture was then left overnight. After elimination of alcohol, the residue was distilled in vacuo. 4.1 g (54%) of a substance was obtained with b. p. 78-78.5° (2 mm); $n^{20}D$ 1.4649; d^{20}_4 1.3778; MR found 48.74; MR calculated 48.07. Found: C 30.4, 30.3; H 5.2, 5.1; P 12.4, 12.8; Br 32.9, 33.0%. $C_6H_{12}PO_3Br$. Calculated: C 29.6; H 5.0; P 12.7; Br 32.9%.

Ozonization of ethyl ester of α-bromovinylphosphinic acid. Into a solution of 1 g of the ethyl ester of α-bromovinylphosphinic acid in 50 ml of carbon tetrachloride cooled in ice water was bubbled ozonized oxygen for 3 hr. To the solution was added 75 ml of water, and the mixture heated for 9 hr at 60°. From the distillate was obtained the condensation product with dimedon; m. p. 189-190°. Mixed sample: m. p. 189-190°.

Di-acid chloride of α,β-dichloroethylphosphinic acid (IX). A solution of 7.25 g (0.05 M) of the di-acid chloride of vinylphosphinic acid in 15 ml of carbon tetrachloride was saturated with chlorine until increase in weight was 4.1 g (0.058 M). The mixture was then allowed to stand for four days at room temperature. From the reaction mixture two fractions were obtained: I with b. p. 80-87° (8 mm); 3.1 g (34%), being the di-acid chloride of α-chlorovinylphosphinic acid; II with b. p. 84-85° (3 mm); 3.2 g (29.5%), being the di-acid chloride of α,β-dichloroethylphosphinic acid; $n^{20}D$ 1.5220; d^{20}_4 1.6616; MR found 39.62; MR calculated 39.22. Found: C 11.5, 11.5; H 1.3, 1.4; P 14.2, 14.3; Cl 65.8, 65.4%. $C_2H_3Cl_4PO$. Calculated: C 11.1; H 1.4; P 14.3, Cl 65.7%.

Di-acid chloride of α-chlorovinylphosphinic acid (X). 18.3 g (0.084 M) of the di-acid chloride of α,β-dichloroethylphosphinic acid was passed through a tube filled with barium chloride and heated to 330-340°. On distillation of the condensate a substance was obtained with b. p. 61-62° (11 mm) – 13.3 g (87.5%); $n^{20}D$ 1.5003; d^{20}_4 1.5453; MR found 33.89; MR calculated 34.17. On standing, the substance crystallized; m. p. 28-30°. Found: C 13.9, 13.8; H 1.3, 1.3; P 17.3, 17.2; Cl 59.1, 58.9%. $C_2H_2POCl_3$. Calculated: C 13.4; H 1.1; P 17.3; Cl 59.3%.

A mixture of 43.5 g (0.3 M) of the di-acid chloride of vinylphosphinic acid and 120 ml of carbon tetrachloride was saturated with chlorine until increase in weight was 23.3 g (0.33 M), and was heated in sealed glass tubes for 5 hr at 125-130°. After elimination of carbon tetrachloride, the residue was distilled at bath temperature 155-160° and 120 mm, and then fractionated. 1.7 g of a substance was obtained with b. p. 88-96° (9 mm); $n^{20}D$ 1.5173 (contaminated di-acid chloride of α,β-dichloroethylphosphinic acid) and 39.7 g (73.5%) of the di-acid chloride of α-chloroethylphosphinic acid with b. p. 59-61° (14 mm); $n^{20}D$ 1.4993; d^{20}_4 1.5418. The substance crystallized; m. p. 29-30°.

α-Chlorovinylphosphinic acid (XI). Obtained similarly to substance (II), from 4.5 g (0.025 M) of the di-acid chloride of α-chlorovinylphosphinic acid; colorless crystals with m. p. 33-34°; 3.5 g (97%). Found: C 16.8, 16.6; H 3.2, 2.9; P 21.5, 21.5; Cl 24.7, 24.5%. $C_2H_4PO_3Cl$. Calculated: C 16.9; H 2.8; P 21.7; Cl 24.9%.

Aniline salt of α-chlorovinylphosphinic acid (XII). Obtained similarly to substance (III), from 1.5 g (0.105 M) of α-chlorovinylphosphinic acid and 0.98 g (0.105 M) of aniline; yield 1.5 g (71%); m. p. 209-210°. Found: C 41.3, 41.0; H 4.8, 4.8; P 13.4, 13.5; N 6.4, 6.2%. $C_8H_{11}PO_3NCl$. Calculated: C 40.8; H 4.7; P 13.2; N 5.9%.

Methyl ester of α-chlorovinylphosphinic acid (XIII). Obtained in the usual manner from 8.95 g (0.05 M) of the di-acid chloride of α-chlorovinylphosphinic acid, 3.2 g (0.1 M) of methyl alcohol, and 10.1 g (0.01 M) of triethylamine in 180 ml of ether; b. p. 60-61° (3 mm); yield 5.7 g (62%); $n^{20}D$ 1.4506; d^{20}_4 1.2715; MR found 36.08; MR calculated 35.94. Found: C 28.7, 28.5; H 5.0, 4.9; P 17.4, 17.5; Cl 20.4, 20.4%. $C_4H_8PO_3Cl$. Calculated: C 28.2; H 4.7; P 18.2; Cl 20.8%.

Ethyl ester of α-chlorovinylphosphinic acid (XIV). Obtained from 8.95 g (0.05 M) of the di-acid chloride of α-chlorovinylphosphinic acid, 4.6 g (0.1 M) of ethyl alcohol, and 10.1 g (0.1 M) of triethylamine in 180 ml of ether; b. p. 77° (3 mm); yield 5.6 g (56.5%); $n^{20}D$ 1.4462; d^{20}_4 1.1622; MR found 45.59; MR calculated 45.18. Found: C 36.4, 36.6; H 6.4, 6.1; P 15.5, 15.6; Cl 17.5, 17.4%. $C_6H_{12}PO_3Cl$. Calculated: C 36.6; H 6.1; P 15.6; Cl 17.8%.

Ozonization of ethyl ester of α-chlorovinylphosphinic acid. The experiment was carried out as in the case of ozonization of the ethyl ester of α-bromovinylphosphinic acid. The condensation product with dimedon melted at 189-190°; the mixed sample had m. p. 189-190°.

Dianilide of α-chlorovinylphosphinic acid (XV). A mixture of 5.37 g (0.03 M) of the di-acid chloride of α-chlorovinylphosphinic acid and 11.16 g (0.12 M) of aniline in 25 ml of benzene was heated for 1.5 hr on a boiling water bath. The precipitate settling out was separated, washed with water to remove aniline hydrochloride and recrystallized from aqueous alcohol. 5.45 g (62%) of acicular crystals was obtained with m. p. 167-169°. Found: C 57.4, 57.3; H 5.1, 5.2; P 10.5, 10.6; Cl 12.3, 12.6%. $C_{14}H_{14}POClN_2$. Calculated: C 57.4; H 4.8; P 10.6; Cl 12.1%.

SUMMARY

By addition of bromine or chlorine to the di-acid chloride of vinylphosphinic acid with subsequent dehydrohalogenation of the reaction products, the di-acid chlorides of α-bromo or α-chlorovinylphosphinic acid can be readily obtained. Several derivatives of these acids were prepared.

LITERATURE CITED

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