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Title: ACETYLENIC AND ALLENIC REARRANGEMENTS. I. ACTION OF ESTERS OF PHOSPHOROUS ACID

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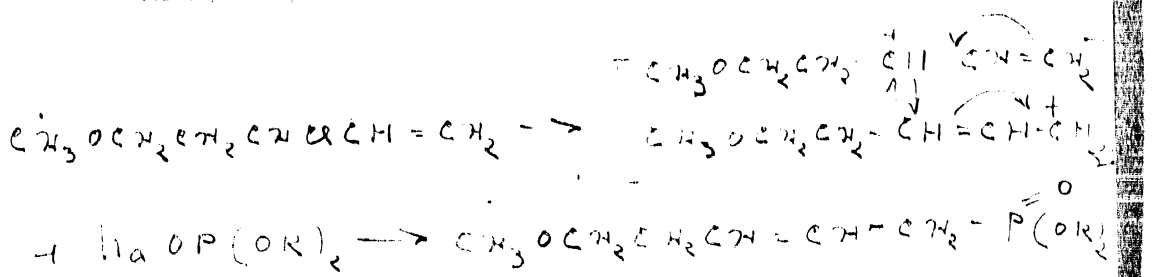
ACETYLENIC AND ALLENIC [illegible]. I.

[illegible] OF PHOSPHOROUS ACID [illegible]-2-METHYL-2-C[illegible]UTYNE-3

By A. N. Pudovik (Laboratory of Organic Chemistry, Kazan State University)

Introduction

A preceding report [1] by Pudovik and B. A. Arbuzov on allenic rearrangements was devoted to an investigation of the action of salts of dialkylphosphorous acids and esters of phosphorous acid on isomeric methoxychloropentenes, showing that the reactions between 1-methoxy-5-chloropentene-3 and sodium salts of dialkylphosphorous acids proceed normally without allyl rearrangement to form the corresponding 1-methoxy-5-dialkylphosphono-3-pentenes. An analogous reaction with 1-methoxy-3-chloropentene-4 in the presence of free dialkylphosphorous acids proceeds in an ionic fashion with a complete allyl regrouping, and leads to the formation of the corresponding 1-methoxy-5-dialkylphosphono-3-pentenes:



When free dialkylphosphorous acids are not present in the reaction medium, the corresponding methoxy-di[dialkylphosphono]-pentanes are formed as a result of further interaction of methoxyphosphonopentenes with a salt of a dialkylphosphorous acid.

As shown in T. A. Favorskiy's [2] investigation, 2-methyl-2-chlorobutyne-3 and other chloro-substituted acetylenic hydrocarbons which are analagous in structure, in the presence of cuprous chloride and an acid salt, are isomerized into a chloro-substituted allenic hydrocarbon and then into a chloro-substituted dienic hydrocarbon. Saponification of the allenic

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hydrocarbon proceeds with a rearrangement; Dimethylethinylcarbinol is formed.

A. I. Zakharova investigated the reaction of chloro-substituted acetylenic hydrocarbons with silver acetate [3], and with methyl magnesium iodide and phenyl magnesium bromide [4]. The reaction between silver acetate and 2-chloro-2-methylbutyne-3 leads to the formation of a mixture of isomeric acetates; but with 2-chloro-2-methylpentyne-3, only an acetate with an allenic structure is formed. The chief result of the reaction of 2-chloro-2-methylpentyne-3 and magnesium-organic compounds was the formation of allenic hydrocarbons.

Definite assumptions have not yet been made regarding these reactions, but certain analogies have been drawn: The reactions between 2-chloro-2-methylbutyne-3 and esters of phosphorous acid were carried out in this particular investigation according to the method of Academician A. Ye. Arbuzov [5], by heating the reagents in sealed tubes. The conclusion of the reaction was ascertained by noting the point at which the volume change in the reaction mixture was terminated.

As a result of the action of triethylphosphite on 2-chloro-2-methylbutyne-3, a basic product with b_{3} 183-185°; n_D^{20} 1.4508; d_4^{20} 1.1171, was formed along with low-boiling fractions. Analysis of the product, a thick, light-yellow liquid, according to the relative quantities of C, H, and P gave an empirical formula close to $C_5H_{32}O_6P_2$. The product was dissolved in water and then separated from solution in a stable form. Heating with water in a sealed tube at 140° for 3 hours did not change it, nor did it react with a cuprous halide [illegible] ethyl iodide during heating. On the basis of the above data, it was concluded that the product does not contain a trivalent atom of phosphorous. As a result of saponification with concentrated HCl, a thick liquid acid was formed; this liquid did not crystallize upon standing. [illegible] saponification also resulted in the formation of ethyl chloride (half as many molecules as the number of diethylphosphone groups in the basic product).

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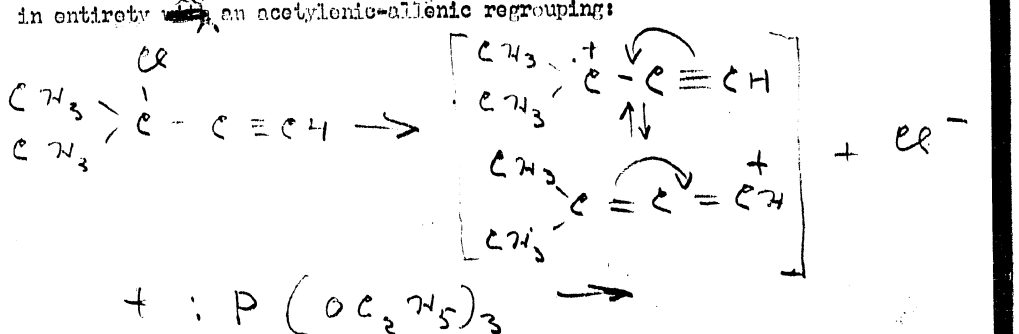
Elementary analysis of the products, results of acid titration and analysis of its barium salt, as well as examination of the properties of the product led to the conclusion that the substance is, apparently, a hydrocarbon chloro-substituted in the secondary position and resulting from the reaction of a chloro-substituted acetylenic hydrocarbon and triethylphosphite. For the purpose of obtaining a hydrocarbon chloro-substituted in the primary position, a reaction was conducted between the chloro-substituted acetylenic hydrocarbon and triethylphosphite under less rigid conditions: at lower temperatures and with an excess of the hydrocarbon in the presence of an inert solvent.

Decreasing the temperature from 150-160° to 120° caused the reaction to result principally in the formation of the product described above with b_{7} 135°; however, at 100°, there was scarcely any reaction noted. As a result of carrying out the reaction in a solution of benzene at 130°, in addition to the product already described, it was possible also to separate a substance with b_{10} 120-122°; n_D^{20} 1.4555; d_4^{20} 1.0237.

Elementary analysis of this latter product as to the relative amounts of C, H, and P led to the empirical formula $C_9H_{17}O_3P$, corresponding to methyl-(diethylphosphono)-butyne or its isomer. Because this latter product did not give a precipitate with an ammonia solution of silver oxide and cupric oxide, the conclusion was drawn to the effect that it has an allenic structure; and therefore, that the reaction between a chloro-substituted acetylenic hydrocarbon and triethylphosphite proceeds in entirety to an acetylenic-allenic regrouping:



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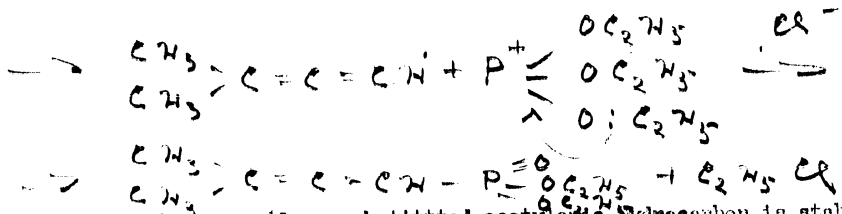
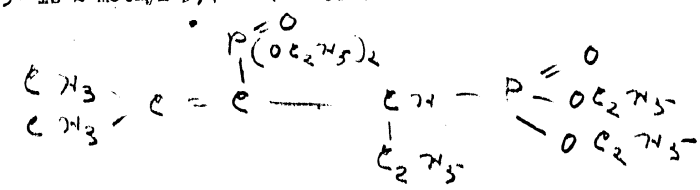


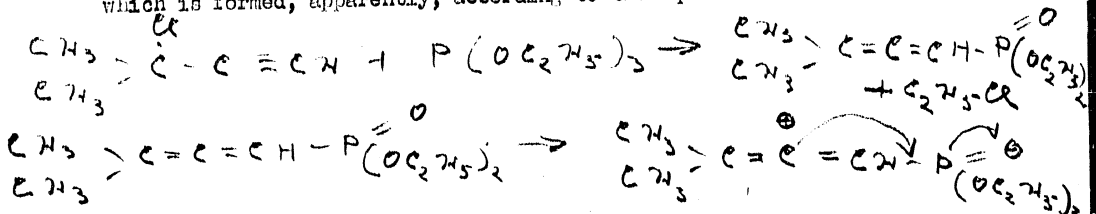
The same chloro-substituted acetylenic hydrocarbon is stable at 130°; no indication of it being changed or isomerized by 6 hours of heating was noted. Heating 2-methyl-4-diethylphosphonobutadiene-2,3 at 150-160° converted it into a [illegible] with b[illegible]; n_D^{20} 1.4[illegible]; d_4^{20} 1.[illegible], which served to confirm the structural formula characterizing it as an allenic derivative.

For conclusive determination of the structure of the product with b7135°, a reaction between 2-methyl-4-diethylphosphonobutadiene-2,3 and triethylphosphite was conducted at 150°. From this reaction there was obtained a product with b[illegible]137-138°; n_D^{20} 1.4580; d_4^{20} 1.1166; that is, one the constants of which are identical with the product prepared as a result of the direct action of triethylphosphite on the chloro-substituted acetylenic hydrocarbon. Through the oxidation of this product with potassium permanganate in an aqueous solution, acetone in the form of its dinitrophenylhydrazone was identified.

On the basis of the data thus derived it was concluded that the product with b7135° is 2-methyl-3,4-di-(diethylphosphono)-hexene-2:



which is formed, apparently, according to the equations:



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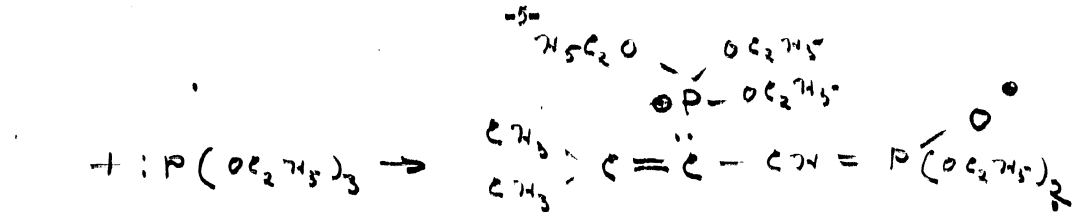
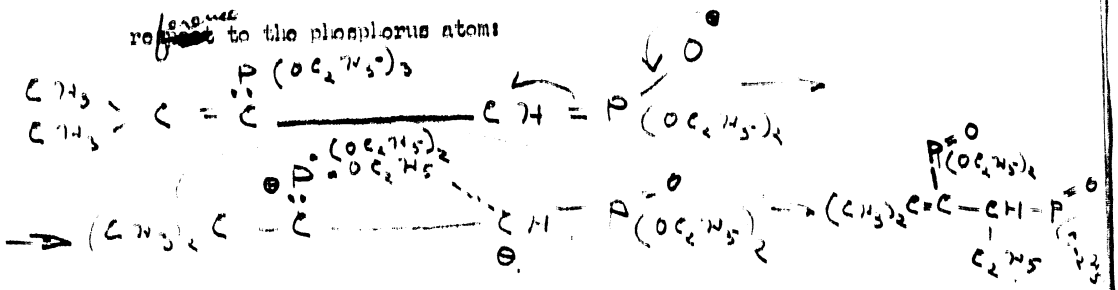


Formation of the product by addition confirms the intermolecular rearrangement with transfer of an ethyl group to the carbon atom in the beta-position with reference to the phosphorus atom:



[redacted] the action of triethylphosphite on 2-methyl-4-chlorobutadiene-2,3 did not result in the separation of any definable products. The reaction between tributylphosphite [redacted] or trimethylphosphite and chloro-substituted acetylenic hydrocarbons proceeds analagously to their reaction with triethylphosphite, although less smoothly.

2-Methyl-4-dibutylphosphonobutadiene-2,3 with b_4 131-132°; n_D^{20} 1.4310; d_4^{20} 0.9594, and 2-methyl-4-dimethylphosphonobutadiene-2,3 were prepared, respectively, as a result of the above reactions. In addition, the high-boiling products 2-methyl-3,4-di-[dibutylphosphono]-hexene-2 with b_3 207-210°; n_D^{20} 1.4612; d_4^{20} 1.0505, and 2-methyl-3,4-di-[dimethylphosphono]-hexene-2 with b_6 180-182°; n_D^{20} 1.4782; d_4^{20} 1.2218, respectively, were formed along with [redacted] a certain quantity of low and other high-boiling fractions, [redacted]

The reaction between sodium diethylphosphide and [redacted] a chloro-substituted acetylenic hydrocarbon proceeds in a complicated manner, forming a mixture of products which boil in the range of 115-186° at 7 mm, which mixture, however, [redacted] does not yield a stable product.

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(6) $Me_2CClC:CH$ (10 g) and 16 g $(EtO)_3P$ after 10 hrs in a sealed tube at 150° gave 7.5 g $Me_2C:C(PO(OEt)_2)CHEtPO(OEt)_2$, $b_6$183-5°, $b_4$177-8°, n_D^{20}1.4598, d_4^{20}1.1171, about 1 g unidentified substances, b_{13}185-235°, and 8.7 g tar. The diphosphonate (above) is sol in H_2O and may be recovered unchanged even after 3 hrs at 140°; its hydrolysis with concd HCl gave a sirupy free acid contg 2 PO_3H_2 groups (confirmed by analysis of Ba salt which is not described). The results are similar when the reaction is run at 130-40° or even 120°, although it is less complete; no reaction took place at 90° after 10 hours. However, when the chloride (9 g) and the phosphite (14 g) were heated in 17 ml dry C_6H_6 6 hrs to 130° there was obtained 3.1 g $Me_2C:C:CHPO(OEt)_2$, b_{10}120-2°, n_D^{20}1.4555, d_4^{20}1.0237, 5.9 g diphosphonate identical with above described, and 6 g residue. The allene deriv does not yield ppts with ammoniacal Ag or Cu. The initial chloride is unchanged after 6 hrs at 130°. Oxidation of the diphosphonate with $EMnO_4$ gave Me_2CO confirming its structure, while heating the allene deriv (1.5 g) 7 hrs to 150-60° gave 0.4 g liquid, $b_5$97-120°, n_D^{20}1.4490, and 0.7 g dimer of the allene deriv, $b_5$205-6°, n_D^{20}1.4795, d_4^{20}1.0992. Heating the allene deriv (3 g) with 5 g $(EtO)_3P$ 10 hrs to 140° gave 2 g $(EtO)_3P$, 3 g crude products, $b_9$45-190°, and 1.3 g diphosphonate, identical with above described ($b_8$187-8°, n_D^{20}1.4580, d_4^{20}1.1166). Heating 16 g $(EtO)_3P$ with 10 g $Me_2C:C:CHCl$ 10 hrs to 150° gave much EtCl, 8.5 g crude $(EtO)_3P$ and unidentified other products. $(BuO)_3P$ (50 g) and 20 g $Me_2CClC:CH$ after 10 hrs at 150° gave 12 g BuCl, 2.3 g $(BuO)_3P$ and 4.3 g $Me_2C:C:CHPO(OBu)_2$, $b_4$131-2°, n_D^{20}1.4310, d_4^{20}0.9594, 4.3 g $Me_2C:C(PO(OBu)_2)$-$CHEtPO(OBu)_2$, $b_3$207-10°, n_D^{20}1.4612, d_4^{20}1.0505, and 3 g unidentified product, $b_3$210-227°, n_D^{20}1.4652. Repetition, using 15 g chloride, 20 g $(MeO)_3P$ and 20 g C_6H_6 after 8 hrs at 120° gave 9.8 g $MePO(OMe)_2$, b_{10}70°, n_D^{20}1.4112, 3.1 g $Me_2C:C:CHPO(OMe)_2$, b_{10}117°, n_D^{20}1.4682, and 9.6 g $Me_2C:C(PO(OMe)_2)$-$CHEtPO(OMe)_2$, $b_6$180-2°, n_D^{20}1.4782, d_4^{20}1.2218. Reaction of 20 g $Me_2CClC:CH$ with $(EtO)_2PONa$ (from 27 g $(EtO)_2POH$) in Et_2O gave, after refluxing 2 hrs a mixt of unidentified products, which $b_7$115-86°.

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Experimental Part

1. Action of Triethylphosphite on 2-Methyl-2-chlorobutyne-3

Experiment I: 10 g of the second reagent, prepared according to Favorskiy's method, and 16 g of the first were heated together in a sealed tube at 150° for 10 hours. There was hardly any decrease in volume during this time. A slight pressure was noted when the tube was opened, because of the ethyl chloride formed during the reaction. After the ethyl chloride was distilled off by slight heating, the mixture was itself distilled in vacuum from a small flask with a Widmer dephlegmator. Several distillations yielded 2.6 g of a fraction boiling in the range 80-185° at 13 mm, and also 7.5 g of 2-methyl-3,4-di-(diethyl hosphono)-hexene-2:

b_6 183-5°; b_4 177-80°; n_D^{20} 1.4598; d_4^{20} 1.1171

0.1060 g of substance weighed in; 0.1871 g CO_2; 0.0783 g H_2O

0. 1676 g of substance weighed in; 48.4 ml NaOH (T 0.02136)

Found % of C: 47.87; of H: 8.21; of P: 17.00

Calculated % of C: 48.64; of H: 8.64; of P: 16.80

$C_{15}H_{32}O_6P_2$.

About 1 g of a fraction with b. p. 185-235° and 8.7 g of a resinous residue were also obtained.

This experiment was repeated with larger quantities of the reagents to derive analagous results.

Experiment II: The reaction was conducted with a double excess of the hydrocarbon at 130-140°, using 20 g to 16 g of triethylphosphite and heating them again for 10 hours. Distillation of the reaction mixture in vacuum (after distilling off the ethyl chloride) resulted in the separation of 11.2 g of the original hydrocarbon with b. p. 74-78°, 3.1 g of a fraction boiling in the range 81-125° at 7 mm, 9 g of 2-methyl-3,4-di-(diethylphosphono)-hexene-2 with b. p. 185° at 7 mm; n_D^{20} 1.4610, and about 8 g of residue.

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Experiment III: A reaction with equimolecular quantities of the reagents was conducted at 90° for 10 hours. Distillation of the reaction mixture gave the original reaction products.

Experiment IV: 9 g of the hydrocarbon and 14 g of the phosphite were heated in 17 g of absolute benzene in a sealed tube at 130° for 6 hours. The benzene was then distilled off, and subsequent distillations of the reaction mixture yielded 3.1 g of 2-methyl-4-diethylphosphonobutadiene-1,3: (Analysis during intense and prolonged heating of the tube in a combustion boat showed that the fused black-colored material did not decompose.)

B. p. 120-122°C at 10 mm; n_D^{20} 1.4555; d_4^{20} 1.0237.

0.1283 g of substance weighed in; 0.2460 g CO_2; 0.0966 g H_2O.

0.1476 g of substance weighed in; 38.6 ml NaOH (T 0.02136)

Found % of C: 52.29; of H: 8.36; of P: 14.2

Calculated % of C: 52.94; of H: 8.33; of P: 15.2.

5.9 g of 2-methyl-3,4-di-(diethylphosphono)-hexene-2 with b. p. 132° at 10 mm; n_D^{20} 1.4590, and about 6 g of residue were formed.

2-Methyl-4-diethylphosphonobutadiene-1,3 does not give a residue when diluted with an ammonia solution of silver oxide and cupric oxide.

2. Experiments in heating 2-methyl-2-chlorobutyne-3

12 g of a chloro substitute of acetylene hydrocarbon with b. p. 74-79° and n_D^{20} 1.4210 were heated in a sealed tube at 130° for 6 hours. Upon opening the tube after cooling no pressure was observed. The refractive index of the liquid was 1.4210. Distillation of the liquid yielded 11.2 g of the original chloride.

3. Investigation of 2-Methyl-3,4-di-(diethylphosphono)-hexene-2

I. Action of water.

a) 10 g of the product were dissolved in water, and then the solution was distilled in vacuum. First the water was distilled off, and then the unchanged product.

b) 4 g of 2-methyl-3,4-di(diethylphosphono)-hexene-2 and 0.45 g of water were heated in a sealed tube for 3 hours at 140°. Distillation of the reaction mixture then gave 3.2 g of the original product.

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II. Action of ethyl iodide.

6 g of the subject compound and 6 g of ethyl iodide were heated for 3 hours at 140°. The original reagent in unchanged form was obtained then by distillation.

III. Action of cuprous iodide. Addition of this reagent to the subject compound did not change the temperature of the reaction mixture, and no interaction was observed as a result of heating. The iodide was not dissolved ~~in~~ by the product.

IV. Saponification of 2-Methyl-3,4-di-(diethylphosphono)-hexene-2.

6.2 g of the product were heated with 20 ml of concentrated HCl in a sealed tube for 6 hours at 160°. After cooling, ~~over~~ the surface of the water layer there ~~took place a considerable~~ was a noticeable layer of ethyl chloride. Comparison of ~~According to the difference in~~ the weights of the tube ~~when opening~~ before and after opening after ~~the~~ it had been subjected to slight heating ~~was found~~ showed that ~~the~~ 1.30 g of ethyl chloride was formed. ~~[illegible]~~. According to ~~the~~ theory, ~~the calculation in~~ saponification of two phosphono groups should ~~be~~ yield ~~liberated~~ 4.2 g of ethyl chloride. An ~~water~~ aqueous solution was repeatedly concentrated ~~as a result~~ by means of ~~the~~ periodic addition of ~~distilled~~ distilled water and boiling with animal charcoal. An aqueous solution of ~~the~~ the acid was titrated ~~with~~ with a solution of NaOH. During conversion on a hard alkali ~~in titration was consumed~~ actually was used up in titration, as compared with the theoretical value, ~~2.3 g, according to theory,~~ 2.6 g. As a result of ~~the dilution to a neutral solution~~ the addition of barium chloride to a neutral solution, ~~was~~ was precipitated the barium salt. This salt ~~which~~ was then carefully washed with distilled water.

1.0824 g of substance weighed in; 1.049 g $BaSO_4$

Found % of Ba: 57.0

Calculated % of Ba: 56.7

C H O P BAa

$C_7H_{12}O_6P_2Ba_2$

V. Oxidation of 2-methyl-3,4-di-(diethylphosphono)-hexene-2.

To 5 g of the compound dissolved in 200 ml of water, during cooling with running water, were added 3 g of powered ~~per~~ potassium permanganate. After ~~completion of~~ the oxidation was completed, the manganese peroxide was filtered off. From the filtrate was then ~~filtered~~ distilled ~~2p ml~~

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20 ml of a distillate, which was added to an alcohol solution of dinitrophenylhydrazine. After being precipitated into a residue, the dinitrophenylhydrazine was fused at 124-126°. Dinitrophenylhydrazine prepared from acetone and dinitrophenylhydrazine has a b. p. of 125-127°. A mixed sample did not produce a depression in the temperature of fusion.

4. Heating 2-Methyl-4-diethylphosphonobutadiene-2,3

1.5 g of this substance was heated in a sealed tube for 7 hours at 150-160°. As a result of the distillation of the reaction mixture was obtained 0.4 g of a fraction with b. p. 97-120° at 5 mm; n_D^{20} 1.4490, and 0.7 g of the dimer 2-methyl-4-diethylphosphonobutadiene-2,3:

b. p. 205-206° at 5 mm; n_D^{20} 1.4795; d_4^{20} 1.0992

0.1104 g of substance weighed in; 32.3 ml NaOH (T 0.01848)

Found % of P: 15.0

Calculated % of P: 15.2

$C_{18}H_{34}O_6P_2$

5. Action of Triethylphosphite on 2-Methyl-5-diethylphosphonobutadiene-2,3

A mixture of 3 g of the latter compound and 5 g of the former were heated in a sealed tube at 140° for 10 hours. As a result of the distillation of the reaction mixture about 2 g of triethylphosphite were obtained along with 3 g of a fraction with b. p. 45-190° at 9 mm as well as 1.3 g of a product:

b. p. 187-188° at 8 mm; n_D^{20} 1.4580; d_4^{20} 1.1166

0.0996 g of substance weighed in; 33.1 ml NaOH (T 0.01848)

Found % of P: 17.0

Calculated % of P: 16.8

$C_{15}H_{32}O_6P_2$

6. Action of Triethylphosphite on 2-Methyl-4-chlorobutadiene-2,3

10 g of the hydrocarbon and 1.5 g of the phosphite were heated at 150° for 10 hours in a sealed tuve. Distillation of the reaction mixture drove off a considerable quantity of ethyl chloride which burns over water) and then 8.5 g of a fraction with b_{19} 22-78°; n_D^{20} 1.4176 and 7.5 g with b_{16} 78-85°; n_D^{20} 1.4320. There remained from the distillation 4.5 g of a residue. Distillation of the fraction with b. p. 22-78° at 19 mm gave the

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original tributylphosphite; distillation of the second fraction yielded a fraction with b_{11} 67-70°; n_D^{20} 1.4280, which was not investigated further.

7. Action of Tributylphosphite on 2-Methyl-3-chlorobutyne-3

50 g of the first and 20 g of the the second compound were heated for 10 hours in a sealed tube at 150°. The following fractions were obtained by distillation:

1st - b_{760} 75-80°; n_D^{20} 1.4060; 13.8 g;

2nd - b_{6} 110-130°; n_D^{20} 1.4372; 3.4 g;

3rd - b_{6} 133-140°; n_D^{20} 1.4374; 4.6 g;

4th - b_{7} 140-235°; n_D^{20} 1.4525; 2.3 g;

5th - b_{2} 205-221°; n_D^{20} 1.4593; 17.6 g;

6th - b_{2} 221-236°; n_D^{20} 1.4600; 4.2 g;

Residue - 16.4 g.

Distillation of the first fraction yielded 12 g of butyl chloride with b. p. 76-78° at 760 mm; n_D^{20} 1.4052; the second and third fractions yielded 2.3 g of the original tributylphosphite and 4.3 g of 2-methyl-4-dibutylphosphonylbutadiene-2,3: (Analysis of the carbon and oxygen was not possible due to the fusion which took place.)

b. p. 131-132 at 4 mm; n_D^{20} 1.4310; d_4^{20} 0.9594

0.1272 g of substance weighed in; 27.6 ml of NaOH (T 0.01848)

Found % of P: 11.1

Calculated % of P: 11.8

$C_{13}H_{25}O_3P$

This product does not give a residue with an ammonia solution of silver oxide and cupric oxide. As a result of the distillation of the fifth and sixth fractions were obtained 4.3 g of a fraction with b_{3} 145-203°; n_D^{20} 1.4580, and 14.5 g of 2-methyl-3,4-di-(dibutylphosphonyl)-hexene-2: (Analysis of the carbon and oxgen was not possible because of the fusion.)

b. p. 207-210° at 3 mm; n_D^{20} 1.4612; d_4^{20} 1.0505

0.1142 g of substance weighed in; 24.2 ml NaOH (T 0.02145)

Found % of P: 12.6

Calculated % of P: 12.2

$C_{22}H_{48}O_6P_2$

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Besides, about 3 g of a fraction with b_3 210-227°; n_D^{20} 1.4652, were obtained.

8. Action of Trimethylphosphite on 2-Methyl-2-chlorobutyne-3

15 g of the second compound, 20 g of the first, and 20 g of benzene were heated in a sealed tube at 120° for 8 hours. Pressure was observed when the tube was opened. After elimination of methyl chloride (Burning over water) from the reaction mixture ~~and~~ the benzene residue was distilled in vacuum. ~~A fraction~~ 13.6 g of a fraction ~~was liberated~~ boiling in the range ~~of~~ 80-110° at 14 mm; n_D^{20} 1.4310 (was prepared in yields) 7.6 g with b_{14} 110-135°; n_D^{20} 1.4715 and 16.1 g with b_{14} 201-210°; n_D^{20} 1.4730. There was also 4.1 g of residue. As a result of the distillation of the first fraction ~~was separated~~ 9.8 g of methyl ester of ~~methy~~ methylphosphonic acid with b_{10} 70°; n_D^{20} 1.4112 was separated. Distillation of the second fraction ~~was~~ yielded 3.1 g of 2-methyl-4-dimethylphosphonbutadiene-2,3, which did not give a residue with ammonia solution of silver oxide:

b. p. 117° at 10 mm; n_D^{20} 1.4682; d_4^{20} 1.0852

0.1052 g of substance weighed in; 28.5 ml NaOH (T 0.02458)

Found % of P: 18.5

Calculated % of P: 17.6

$C_7H_{13}O_3P$

As a result of distillation of the third fraction was obtained 9.6 g of 2-methyl-3,4-di-(dimethylphosphon)-hexene-2:

b.p. 180-182° at 6 mm; n_D^{20} 1.4782; d_4^{20} 1.2218

0.1454 g of substance weighed in; 57.2 ml NaOH (T 0.01848)

Found % of P: 20.2

Calculated % of P: 20.6

$C_{10}H_{22}O_6P_2$

In addition, a small ~~quantity~~ quantity of low and high-boiling fractions were obtained.

9. Action of ~~Diethylphosphoru~~ Sodium ~~Diethylphosphoride~~ Diethylphosphide on 2-Methyl-2-chlorobutyne-3

An ether solution of the phosphide was prepared from 27 g of

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of diethylphosphorous acid and 4.5 g of sodium in 80 ml of absolute ether. To the solution was then gradually added 20 g of 2-methyl-2-chlorobutyne-3. This effected a noticeable heating of the reaction mixture, but no precipitate of sodium chloride was noticed. The mixture was heated 2 hours on a water bath and then was processed with water. After drying the ether layer and the residue was itself distilling off the ether was distilled in vacuum. As a result of this latter distillation yielded several fraction boiling in the range 115-186° at 7 mm. A repeated distillation liberated a fraction (3.4 g) boiling at 182-186° at 7 mm; n_D^{20} 1,4685 with a 14.8 % content of phosphorus, which, however, was not investigated further.

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