CHEMISTRY OF POLYENIC AND POLYACETYLENIC COMPOUNDS

COMMUNICATION 7. STUDY OF THE HYDRATION OF ETHYLENIC ACETYLENIC ALCOHOLS

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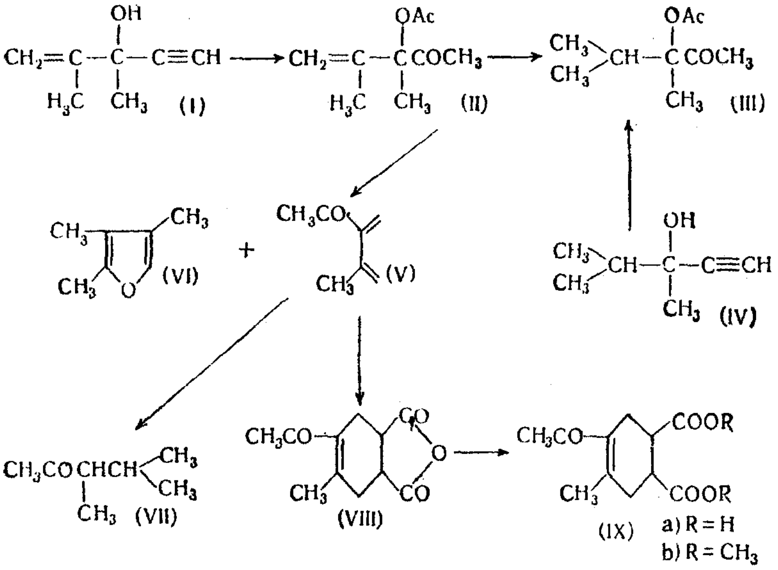
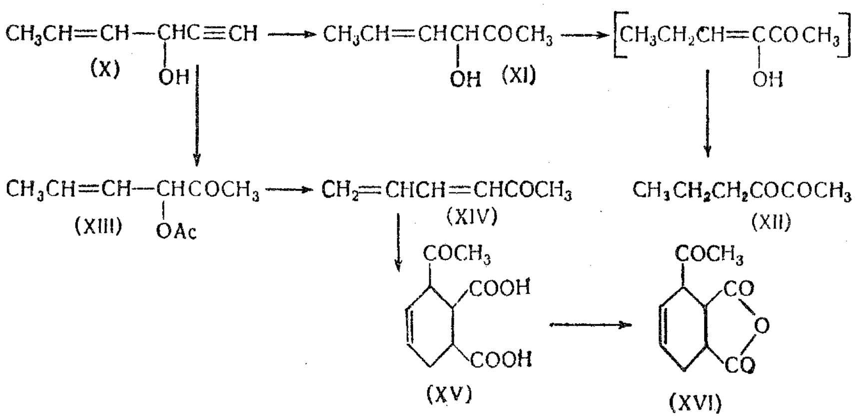
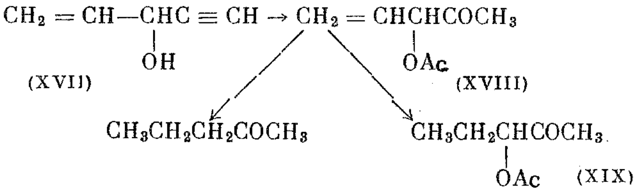
Continuing investigations based on the synthesis of oxygen-containing polyenic compounds from acetylenic alcohols [1, 2], we have studied the hydration of some ethylenic acetylenic alcohols. It was shown that, when 2,3-dimethyl-1-penten-4-yn-3-ol (I) is heated with a solution of mercuric oxide in acetic acid, 3-hydroxy-3,4-dimethyl-4-penten-2-one acetic ester (II) is formed in a yield of more than 75%. The structure of this product was proved by its infrared spectrum and by its catalytic hydrogenation into 3-hydroxy-3,4-dimethyl-2-pentanone acetic ester (III), which was shown by gas-liquid chromatography to be identical with the acetic ester of the product of the hydration of 3,4-dimethyl-1-pentyn-3-ol (IV):



Pyrolysis of the acetic ester (II) at 470° in a stream of nitrogen gives mainly (yield of up to 50%) 4-methyl-3-methylene-4-penten-2-one (V) with a little (about 10%) admixture of 1,2,3-trimethylfuran (VI), which we could not separate by the usual vacuum distillation. The presence of this impurity was shown by gas-liquid chromatography by comparison with a known sample of 1,2,3-trimethylfuran, prepared as described below. The structure of the diene (V) was proved by catalytic hydrogenation over platinum oxide into a mixture of products, from which 3,4-dimethyl-2-pentanone (VII) was isolated as its 2,4-dinitrophenylhydrazone [3]. 4-Methyl-3-methylene-4-penten-2-one (V) has interesting spectrographic peculiarities. Instead of the absorption maximum at 220-230 mμ that is characteristic for diene systems [4] it gives a broad absorption band only in the vacuum ultraviolet in the region of 206-215 mμ (ε 9800) and gives a red 2,4-dinitrophenylhydrazone showing absorption at 345.5 mμ (in isooctane), which is not normal for hydrazones of unsaturated ketones [4]. These spectrographic data permit us to suppose that, as a result of the effect of geometric factors, the conjugated double bonds in the diene (V) are not strictly coplanar. However, it enters fairly readily into diene synthesis with maleic anhydride with formation of the crystalline adduct (VIII), which has an absorption maximum characteristic for such unsaturated ketones [5]. When boiled with water, the anhydride (VIII) is converted quantitatively into the crystalline dicarboxylic (IXa), from which, after treatment with diazomethane and chromatography on alumina, we isolated the liquid diester (IXb). Both of these compounds have ultraviolet and infrared spectra that are in accord with the structure proposed for them. All this forms a reliable confirmation of the structure of the diene (V) and so of the original unsaturated ketol acetic ester (II). It was thus proved that, as a result of the acetylation of the hydroxy group, the hydration of an ethylenic acetylenic alcohol under the conditions that we have proposed proceeds normally and is not accompanied by side reactions. In this connection it was of interest to study this reaction for the case of 4-hexen-1-yn-3-ol (X), which under the usual hydration conditions gives instead of the expected ketol (XI), the α-diketone (XII) as a result of a secondary prototropic rearrangement [6]. It was found that 4-hexen-1-yn-3-ol (X), heated with mercuric acetate in acetic acid, gives up to 70% of 3-hydroxy-4-hexen-2-one acetic ester (XIII), the structure of which was proved by the following transformations:



In the pyrolysis of the acetic ester (XIII) up to 40% of the unstable 3,5-hexadien-2-one (XIV) was formed, and this has an absorption maximum at 259.5 mμ (ε 24250), which corresponds to the presence of conjugation between a 1,3-diene system and a carbonyl group. Since contradictory constants are given for 3,5-dexadien-2-one in the literature [7-9], we carried out its diene condensation with maleic anhydride. The dicarboxylic acid (XV) formed on hydrolysis of the adduct was treated with acetyl chloride to give the crystalline anhydride (XVI), whose melting point had the value given in the literature [9]. The hydration of 1-penten-4-yn-3-ol (XVII) was more sluggish and led to the corresponding 3-hydroxy-4-penten-2-one acetic ester (XVIII) in about 50% yield. In the course of the reaction most of the original acetylenic alcohol was resinified.

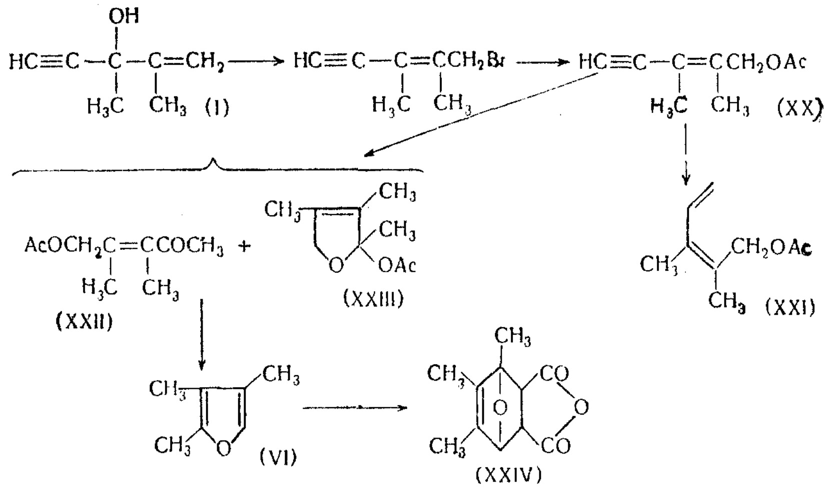


The acetic ester (XVIII) has an absorption band at 1647 cm^{-1} in the infrared spectrum, which is characteristic for the methylene group, and on hydrogenation over a palladium catalyst it readily absorbs one molecular proportion of hydrogen with formation of 3-hydroxy-2-pentanone acetic ester (XIX). On hydrogenation over platinum oxide in alcohol partial hydrogenolysis occurs, and, as well as the saturated acetic ester (XIX), 2-pentanone may be isolated (as its 2,4-dinitrophenylhydrazone) from the reaction products.

We studied also the hydration of 2,3-dimethyl-2-penten-4-yn-1-ol (XX). This was prepared in an over-all yield of up to 55% by the isomerization of the acetylenic alcohol (I) under the action of phosphorus tribromide with subsequent heating of the primary bromide formed with potassium acetate in N,N-dimethylformamide solution. In the infrared spectrum of the acetic ester (XX) these is an absorption band at 3305 cm^{-1}, which corresponds to the presence of hydrogen at a triple bond.

In accordance with its structure, the acetic ester (XX) may be selectively hydrogenated in presence of a palladium catalyst. There is then formed 2,3-dimethyl-2,4-pentadien-1-ol (XXI), whose ultraviolet spectrum

(λ_{max} 236 mμ, ε 19470) confirms the presence of a conjugated system of double bonds. On hydration of the acetic ester (XX) in presence of mercuric acetate in acetic acid a complex mixture of products is formed; we were unable to resolve this mixture by fractional distillation. The ultraviolet and infrared spectra of this mixture contained intense absorption bands at 223 mμ (ε 5220) and 1648 cm^{-1}, which indicate the presence of an α, β-unsaturated ketone grouping in the main product:



Also, the infrared spectrum was found to contain an intense band at 1748 cm^{-1}, which corresponds to the presence of an ester grouping. These data permit us to consider that the main product of the hydration of the ethylenic acetylenic acetic ester (XX) is 5-hydroxy-3,4-dimethyl-3-penten-2-one acetic ester (XXII). It is known from the literature that such systems are characterized by a high tendency to cyclization into dihydrofuran derivatives [10]. On this basis we may suppose that the mixture formed contains not only the acetic ester (XXII), but also the cyclic acetal (XXIII), which may quite probably be formed under these conditions [11]. The presence of such an acetal grouping probably accounts for the intense absorption band at 1762 cm^{-1} found in the mixture of hydration products. To confirm our conclusions about the composition of the hydration products obtained from 2,3-dimethyl-2-penten-4-yn-1-ol acetic ester (XX), the mixture of products was subjected to alkaline hydrolysis. The reaction product then obtained corresponded in analysis to 1,2,3-trimethylfuran (VI) and absorbed at 220 mμ (ε 6800), which is characteristic for a substituted furan system [6]; it readily gave a crystalline adduct with maleic anhydride (XXIV), and when heated with water this decomposed with formation of fumaric acid. This last reaction is characteristic only for the 7-oxabicyclo[2,2,1]heptene system, and it provides a fairly reliable confirmation of the structure of the 1,2,3-trimethylfuran (VI) obtained.

EXPERIMENTAL

3-Methyl-3-buten-2-one (b.p. 96-98°; n_D^{20} 1.4228) was synthesized by the pyrolysis of 3-hydroxy-3-methyl-2-butanone acetic ester [12], which was prepared in 80-87% yield by the direct addition of 2-methyl-3-butyn-2-ol to a stirred solution of mercuric acetate in acetic acid at 90-95° with subsequent heating at this temperature for 5-7 hours. 2,3-Dimethyl-1-penten-4-yn-3-ol (I) [b.p. 82-84° (86 mm); n_D^{20} 1.4542] was prepared in 62-67% yield by the condensation of 3-methyl-3-buten-2-one with a small excess of lithium acetylide in liquid ammonia [13]. The use of a 2–3-fold excess of lithium acetylide increased the yield of the acetylenic alcohol (I) only slightly (by 5-8%). 2,4-Dinitrophenylhydrazones were prepared by treating the carbonyl compounds with a solution of 2,4-dinitrophenylhydrazine in 2 N HCl at room temperature with subsequent chromatography on alumina and recrystallization.

3-Hydroxy-3,4-dimethyl-4-penten-2-one Acetic Ester (II). 30 g of 2,3-dimethyl-1-penten-4-yn-3-ol (I) was added with stirring over a period of 15 minutes to 6 g of mercuric oxide dissolved by heat in 125 ml of acetic acid. The reaction mixture was heated gradually to 90-95° and kept at this temperature for six hours. The solution was filtered and neutralized with iced sodium carbonate solution; the hydration product was extracted with ether (three 100-ml portions) and dried with magnesium sulfate. After two vacuum distillations we obtained 36 g (76%) of the acetic ester (II); b.p. 75-77° (5 mm); m.p. 6°; n_D^{20} 1.4432. Found: C 63.73; 63.82; H 8.38; 8.47%. $C_9H_{14}O_3$. Calculated: C 63.51; H 8.29%. The infrared spectrum of the acetic ester (II) in CCl_4 solution had absorption bands at 1637 cm^{-1} (= CH_2), 1728 cm^{-1} (–C = O), and 1744 cm^{-1} (–$OCOCH_3$).

The 2,4-dinitrophenylhydrazone formed red crystals, m.p. 169-170° (from a mixture of ethanol and ethyl acetate); λ_{max} 358 mμ (alcohol). Found: C 51.44; 51.68; H 5.15; 5.23; N 16.11; 16.11%. $C_{15}H_{18}N_4O_6$. Calculated: C 51.42; H 5.18; N 15.99%.

3-Hydroxy-3,4-dimethyl-2-pentanone Acetic Ester (III). 1. 11.9 g of the acetic ester (II) was hydrogenated as a solution in 42 ml of absolute alcohol in presence of 5% of palladium on calcium carbonate. In the course of 2 h 40 min 1732 ml of hydrogen was absorbed (for one double bond 1720 ml of hydrogen at 19° and 743 mm is required). Catalyst was filtered off, and the residue was vacuum-distilled. We obtained 10.5 g of 3-hydroxy-3,4-dimethyl-2-pentanone acetic ester (III); b.p. 94-95° (18 mm); n_D^{20} 1.4317. Found: C 62.81; 62.53; H 9.26; 9.17%. $C_9H_{16}O_3$. Calculated: C 62.76; H 9.36%.

2. 15 g of 3,4-dimethyl-1-pentyn-3-ol (IV) (b.p. 134-135°; n_D^{20} 1.4370), prepared by the condensation of 3-methyl-2-butanone with acetylene under pressure [14], was added to a solution of mercuric acetate (from 3 g of mercuric oxide) in 65 ml of acetic acid at 95°, and the mixture was kept at this temperature for five hours. After the usual treatment and vacuum distillation we obtained 17.2 g (75%) of the acetic ester (III), b.p. 89-90° (16 mm) and n_D^{20} 1.4318. The two samples were found to be identical when analyzed by the method of gas-liquid chromatography.

4-Methyl-3-methylene-4-penten-2-one (V). 13 g of the acetic ester (II) was passed through a quartz tube (diameter 12 mm; length of heated part 30 cm) at 470-480° in a stream of nitrogen in the course of 18 minutes. The pyrolysis product was neutralized with saturated sodium carbonate solution and extracted with three 60-ml portions of ether. The ether layer was dried with magnesium sulfate. After two distillations we obtained 4.2 g (about 50%) of product of b.p. 64-66° (75 mm) and n_D^{20} 1.4576, which contained mainly 4-methyl-3-methylene-4-penten-2-one (V). Found: C 76.30; 76.26; H 9.15; 9.10%. $C_7H_{10}O$. Calculated: C 76.32; H 9.15%.

According to gas-liquid chromatography this product contained 5-10% of the isomeric 2,3,4-trimethylfuran (VI). In the vacuum ultraviolet spectrum 4-methyl-3-methylene-4-penten-2-one (V) had a very broad absorption band in the range 206.5-214.8 mμ with a uniform intensity of 9800 (alcohol). In the infrared spectrum of the diene (in CCl_4) we found an absorption band at 1688 cm^{-1} (weak) and 1702 cm^{-1} (conjugated C = O). After treatment with a solution of 2,4-dinitrophenylhydrazine we isolated the hydrazone in low yield as bright-red rhombic crystals, m.p. 122° (from petroleum ether); λ_{max} 224.5 mμ (ε 36300) and 360.3 mμ (ε 24500) (alcohol); λ_{max} 345.5 mμ (isooctane). Found: C 53.79; 53.71; H 4.94; 4.99; N 19.36; 19.22%. $C_{13}H_{14}N_4O_4$. Calculated: C 53.79; H 4.86; N 19.30%.

Condensation of the Diene (V) with Maleic Anhydride. A mixture of 1.5 g of the diene (V), 1.5 g of maleic anhydride, and 15 ml of benzene was boiled in presence of hydroquinone for four hours. After removal of solvent and recrystallization we obtained 0.5 g of the crystalline adduct (VIII); m.p. 97-98° (isooctane); λ_{max} 240 mμ; ε 6250 (alcohol). Found: C 63.22; 63.17; H 5.91; 5.83%. $C_{11}H_{12}O_4$. Calculated: C 63.45; H 5.81%.

The residue remaining after the isolation of the anhydride (VIII) was hydrolyzed with water, and we then obtained 75 mg of fumaric acid, formed as a result of the cleavage of the adduct formed by maleic anhydride with the 2,3,4-trimethylfuran (VI) present in the mixture. The anhydride (VIII) was boiled with water for 30 minutes, and recrystallization from water then gave the corresponding dicarboxylic acid (IXa); m.p. 159-160°; λ_{max} 246 mμ; ε 5900 (alcohol). Infrared spectrum: 1632 cm^{-1} (double bond conjugated with C = O), 1674 cm^{-1} (conjugated $-C=O$), 1700 cm^{-1} ($-COOH$). Found: C 58.62; 58.73; H 6.38; 6.47%; titration equivalent 111; 112. $C_{11}H_{14}O_5$. Calculated: C 58.40; H 6.24%; titration equivalent 113.

On treatment of the acid (IXa) with diazomethane with subsequent purification by chromatography on alumina we isolated the liquid diester (IXb); λ_{max} 244 mμ; ε 6110 (alcohol). Infrared spectrum: 1690 cm^{-1} (conjugated $-C=O$), 1742 cm^{-1} ($-COOCH_3$). Found: 61.53; 61.34; H 7.17; 7.07%. $C_{13}H_{18}O_5$. Calculated: C 61.40; H 7.14%.

Hydrogenation of the Diene (V). 1.8 g of the diene (V) was hydrogenated in 40 ml of alcohol in presence of a platinum catalyst. In the course of 40 minutes 900 ml of hydrogen was absorbed (for two double bonds 775 ml of hydrogen at 22° and 750 mm is required). After fractionation we obtained 1.1 g of a mixture of hydrogenation products, from which, after suitable treatment, we isolated a 2,4-dinitrophenylhydrazone of m.p. 94-95°, which corresponds to the hydrazone of 3,4-dimethyl-2-pentanone (VII) [3]. Found: C 52.86; 52.83; H 6.04; 6.19; N 18.76; 18.69%. $C_{13}H_{18}N_4O_4$. Calculated: C 53.05; H 6.16; N 19.04%.

3-Hydroxy-4-hexen-2-one Acetic Ester (XIII). 11 g of 4-hexen-1-yn-3-ol (X) [b.p. 72-74° (29 mm); n^{20}_D 1.4632], prepared by the reaction of crotonaldehyde with sodium acetylide in liquid ammonia [15], was added at 80-85° to a solution of mercuric acetate (from 2 g of mercuric oxide) in 40 ml of acetic acid. The temperature of the mixture was raised to 95° and kept at this level, with stirring, for seven hours. After the treatment described above we obtained 12 g (67%) of the acetic ester (XIII); b.p. 91-93° (13 mm); b.p. 107-109° (28 mm); n^{20}_D 1.4412. In the infrared spectrum of this acetic ester there was only an intense frequency at 1738 cm^{-1} ($-OCOCH_3$). Found: C 61.21; 61.29; H 7.60; 7.53%. $C_8H_{12}O_3$. C 61.51; H 7.75%.

3,5-Hexadien-2-one (XIV). 7.6 g of the acetic ester (XIII) was passed through a quartz tube in a stream of nitrogen at 480-485° in the course of 18 minutes. The pyrolysis product was neutralized with sodium carbonate solution and extracted with three 35-ml portions of ether; the extract was dried with magnesium sulfate. Distillation gave 2.2 g (about 40%) of the unstable diene (XIV); b.p. 61-64° (30 mm); n^{24}_D 1.4872; λ_{max} 259.5 mμ; ε 24250 (alcohol). The literature gives greatly varying constants for 3,5-hexadien-2-one (XIV): b.p. 45-47° (15 mm); n^{20}_D 1.4789 [7]; b.p. 36-38° (8 mm); n^{20}_D 1.4875 [8]; b.p. 29° (1.5 mm); n^{20}_D 1.5019 [9]. The 2,4-dinitrophenylhydrazone prepared from (XIV), after chromatography (neutral alumina) and washing on the filter, had m.p. 175-175.5°; λ_{max} 379-389 mμ (alcohol). Found: C 51.88; 51.79; H 4.60; 4.71; N 19.82; 19.94%. $C_{12}H_{12}N_4O_4$. Calculated: C 52.17; H 4.38; N 20.28%.

1.2 g of the diene (XIV) was heated with 1 g of maleic anhydride in 15 ml of benzene in presence of hydroquinone, and the oily adduct was hydrolyzed with 2% potassium hydroxide solution to give the dicarboxylic acid (XV), m.p. 156-157° (ethyl acetate). Found: C 56.39; 56.29; H 5.61; 5.53%. $C_{10}H_{12}O_5$. Calculated: C 56.60; H 5.70%.

Boiling of 0.2 g of this acid with excess of acetyl chloride for five hours gave the anhydride (XVI), m.p. 83-84° (isooctane), which is in accord with the literature [9].

3-Hydroxy-4-penten-2-one Acetic Ester (XVIII). 20 g of 1-penten-4-yn-3-ol (XVII) [b.p. 72-75° (105 mm); n^{22}_D 1.4492; prepared in 22% yield by the condensation of acrolein with a twofold excess of lithium acetylide in liquid ammonia] was added to a solution of mercuric acetate (from 4.5 g of mercuric oxide) in 75 ml of acetic acid at 85° over a period of 12 minutes. The reaction mixture was heated to 95° and kept at this temperature for four hours. The reaction product was neutralized with sodium carbonate solution and extracted with three 80-ml portions of ether; the extract was dried with magnesium sulfate. Vacuum distillation gave 16.8 g (48%) of the acetic ester (XVIII); b.p. 82-86° (20 mm); n^{20}_D 1.4342. Found: C 59.24; 59.47; H 7.06; 7.13%. $C_7H_{10}O_3$. Calculated: C 59.14; H 7.09%. In the infrared spectrum of this acetic ester absorption was observed at 1647 cm^{-1} ($=CH_2$) and 1739 cm^{-1} ($-OCOCH_3$).

3-Hydroxy-2-pentanone Acetic Ester (XIX). 1. 3.7 g of the above acetic ester (XVIII) was hydrogenated in 17 ml of absolute alcohol in presence of 5% of palladium on calcium carbonate. After 645 ml of hydrogen had been absorbed (for one double bond 584 ml of hydrogen at 18° and 739 mm is required) hydrogenation stopped completely. Distillation of the product gave 3.45 g of the acetic ester (XIX); b.p. 76-78° (18 mm); n^{18}_D 1.4180. Found: C 58.13; 57.93; H 8.22; 8.39%. $C_7H_{12}O_3$. Calculated: C 58.31; H 8.39%.

2. 6 g of the acetic ester (XVIII) was hydrogenated in 25 ml of absolute alcohol in presence of 0.15 g of platinum dioxide. In the course of 2.5 hours 1420 ml of hydrogen was absorbed (for one double bond 1040 ml of hydrogen at 19° and 739 mm is required). Catalyst was filtered off, and solvent was distilled off at ordinary pressure. On treatment of this distillate with 2,4-dinitrophenylhydrazine solution the 2,4-dinitrophenylhydrazone of 2-pentanone was isolated; m.p. 140-141° (from alcohol), undepressed by admixture of a known sample. Vacuum distillation of the residue gave 3.7 g of 3-hydroxy-2-pentanone acetic ester (XIX); b.p. 78-80° (20 mm); n^{22}_D 1.4164.

2,3-Dimethyl-2-penten-4-yn-1-ol Acetic Ester (XX). A solution of 55 g of 2,3-dimethyl-1-penten-4-yn-3-ol (I) in 250 ml of dry ether and 3 ml of dry puridine was cooled down to a temperature of from −10° to −14° and stirred while a solution of 18 ml of phosphorus tribromide in 100 ml of ether was added gradually. When the addition was complete, the temperature of the mixture was raised to 20° (two hours); the reaction mixture was poured onto ice, and the ether extract was washed with cold 2% bicarbonate solution and with saturated salt solution; it was dried with magnesium sulfate in presence of hydroquinone. On vacuum distillation in a stream of nitrogen we obtained 65 g of an extremely lachrymatory and very unstable bromo compound; b.p. 74-79° (20 mm); n^{20}_D 1.5324. On distillation, much of the bromo compound resinified, so that it was better to use the crude, undistilled bromo compound for further reaction. For the preparation of the acetic ester (XX) a mixture of 45 g of the bromo compound [b.p. 74-79° (20 mm)], 26 g of freshly roasted potassium acetate, and 150 ml of dry N,N-dimethylformamide was heated at 55-60° for five hours with stirring and then left overnight. The precipitate was filtered off, solvent was vacuum-evaporated (60°, 24 mm), and the residue was distilled in a stream of nitrogen with a full-condensation head. We obtained 26.2 g (69%) of the acetic ester (XX); b.p. 66-68° (5.5 mm); n_D^{20} 1.4742; λ_{max} 228 mμ; ε 13950 (alcohol). The infrared spectrum contains an absorption band at 3305 cm^{-1} (H – C ≡). Found: C 70.86; 70.70; H 7.95; 7.96%. $C_9H_{12}O_2$. Calculated: C 71.02; H 7.95%. When this reaction was carried out without distillation of the bromo compound, from 55 g of the acetylenic alcohol (I) we obtained 41.0 g of the acetic ester (XX); b.p. 58-61° (2 mm); n_D^{20} 1.4749. The over-all yield was 54%.

2,3-Dimethyl-2,4-pentadien-1-ol Acetic Ester (XXI). 11.4 g of the acetic ester (XX) was hydrogenated as a solution in 40 ml of ethyl acetate over 5% palladium catalyst on calcium carbonate. In the course of 3.5 hours 1750 ml was absorbed, which corresponds to one molecular proportion of hydrogen. A test for the triple bond with an ammoniacal solution of silver oxide was negative. After vacuum distillation of the product we obtained 8.7 g of the diene (XXI); b.p. 64-65° (2.5 mm); n_D^{20} 1.4788; λ_{max} 236 mμ; ε 19470 (alcohol). Found: C 69.73; 69.85; H 8.90; 8.72%. $C_9H_{14}O_2$. Calculated: C 70.10; H 8.95%.

Hydration of 2,3-Dimethyl-2-penten-4-yn-1-ol Acetic Ester (XX). 10 g of the acetic ester (XX) was heated at 95° with a solution of 2 g of mercuric oxide in 50 ml of acetic acid for six hours. The reaction product was filtered off, neutralized with sodium carbonate solution, and extracted with three 60 ml portions of ether; the extract was dried with magnesium sulfate. On distillation we obtained 8.2 g (73%) of a mixture of hydration products, b.p. 88-92° (1.8 mm) and n_D^{20} 1.4462, which had a geraniumlike odor. In the ultraviolet spectrum this mixture had an absorption band at 223 mμ (ε 5220); and in the infrared spectrum there were bands at 1648 cm^{-1} (–C = C conjugated with C = O), 1748 cm^{-1} (–OCOCH$_3$), and 1762 cm^{-1}.

For the purpose of hydrolysis, 4.8 g of the mixture of hydration products was added to a suspension of 7.5 g of potassium carbonate in 40 ml of methanol (much heat was evolved), and the mixture was boiled for two hours. The reaction mixture was diluted with an equal amount of water and carefully extracted with ether. After distillation we obtained 2.05 g of 2,3,4-trimethylfuran (VI); b.p. 126-128°; n_D^{20} 1.4518; λ_{max} 220 mμ; ε 6800 (heptane). Found: C 76.21; 76.18; H 9.02; 8.97%. $C_7H_{10}O$. Calculated: C 76.32; H 9.15%. For 2,3,4-trimethylfuran the literature [16] gives only b.p. 54-55° (57 mm).

When boiled in benzene with maleic anhydride, 2,3,4-trimethylfuran (VI) gave the adduct (XXIV), m.p. 87-87.5° (from a 1 : 8 mixture of benzene and petroleum ether). Found: C 63.49; 63.51; H 5.60; 5.82%. $C_{11}H_{12}O_4$. Calculated: C 63.45; H 5.81%. When this adduct was boiled with water, only fumaric acid was isolated; m.p. 282-284°, undepressed by admixture of a known sample.

SUMMARY

1. The hydration of ethylenic acetylenic alcohols in presence of mercuric acetate in acetic acid is not accompanied by secondary isomerization processes and gives the corresponding unsaturated α-ketol acetic esters in high yields.

2. The pyrolysis of the acetic esters of 3-hydroxy-3,4-dimethyl-4-penten-2-one (II) and 3-hydroxy-4-hexen-2-one (XIII) was studied, and the dienes (V) and (XIV) were obtained in satisfactory yields.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.