CHEMISTRY OF POLYENIC AND POLYACETYLENIC COMPOUNDS

COMMUNICATION 5. GENERAL METHOD FOR THE SYNTHESIS OF DIACETYLENIC ALCOHOLS

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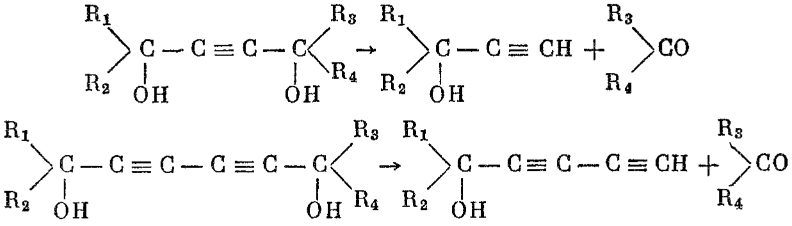
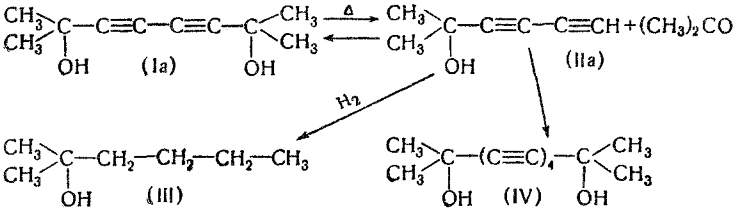
In a study of the chemical transformations of acetylene derivatives it was shown [1, 2] that ditertiary and secondary-tertiary acetylenic diols readily break down when heated in presence of alkaline reagents with formation of acetylenic alcohols. There are indications [3, 4] that diacetylenic diols (I) are able to break down in a similar way, but the diacetylenic alcohols (II) then formed have been isolated only in low yield.



This last reaction is of undoubted interest for the chemistry of unsaturated compounds, in as much as the diacetylenic alcohols (II) then obtained may serve, in their turn, as important starting materials for the synthesis of various polyacetylenic substances, including some found in nature. The development of a convenient method for the pyrolysis of diacetylenic diols (I) to diacetylenic alcohols (II) is therefore an important problem in synthesis, whose successful solution may open up new ways of building up various polyacetylenic systems.

With this object we made a detailed study of the conditions for the thermal cleavage of various diacetylenic diols (I), which are readily prepared by the oxidative condensation of acetylenic alcohols [5]. For the case of 2,7-dimethyl-3,5-octadiyne-2,7-diol (Ia) it was shown that this reaction goes best of all when a melt of the diol is heated in presence of potassium carbonate (about 5% on the weight of the diol); also, the yield and purity of the 2-methyl-3,5-hexadiyn-2-ol (IIa) formed depend on the rate of its removal from the reaction medium. The removal is effected by rapid vacuum distillation of the products into a receiver cooled with solid carbon dioxide; the decomposition temperature must be maintained in such a range (180-190° in the bath) that much sublimation of the original diol is avoided. Under these conditions the yield of pure 2-methyl-3-5-hexadiyn-2-ol (II) is 55-65%.



The resulting diacetylenic alcohol (IIa) is a mobile low-boiling liquid, and, according to the results of elementary analysis and gas-liquid chromatography, is an individual compound. In catalytic hydrogenation it absorbs four molecular proportions of hydrogen with formation of the known 2-methyl-2-hexanol (III) [3, 6], and under the conditions of oxidative condensation in presence of cuprous chloride it gives the known tetraacetylenic diol (IV) in quantitative yield [7]. On reaction of the organomagnesium complex of the diacetylenic alcohol (IIa) with acetone the original diacetylenic diol (Ia) is formed, and this can be obtained also in the reaction of the diacetylenic alcohol itself with acetone in presence of potassium hydroxide in ether.

The thermal cleavage of diacetylenic diols was studied by us also for the cases of 3,8-dimethyl-4,6-decadiyne-3,8-diol [(I) $R_1 = R_3 = CH_3$; $R_2 = R_4 = C_2H_5$], 3,8-diethyl-4,6-decadiyne-3,8-diol [(I) $R_1 = R_2 = R_3 = R_4 = C_2H_5$], and 1,4-bis-1-hydroxycyclopentyl-1,3-butadiyne [(I) $R_1R_2 = -(CH_2)_4-$; $R_3R_4 = -(CH_2)_4-$]. In all these cases pyrolysis of the diol proceeded readily at 160-180° with formation of the corresponding diacetylenic alcohols in yields of up to 60%: 3-methyl-4,6-heptadiyn-3-ol [(II) $R_1 = CH_3$; $R_2 = C_2H_5$], 3-ethyl-4,6-heptadiyn-3-ol [(II) $R_1 = R_2 = C_2H_5$] and 1-(1-hydroxycyclopentyl)-1,3-butadiyne [(II) $R_1R_2 = -(CH_2)_4-$]. The pyrolysis of 1,4-bis-1-hydroxycyclohexyl-1,3-butadiyne went much as in the case of the other diols, but on distillation of the diacetylenic alcohol formed there was much decomposition, probably due to dehydration to an unstable vinyl diacetylenic compound. All the diacetylenic alcohols that we obtained rapidly darkened at room temperature and in a few hours were converted into solid polymers, which decomposed vigorously when heated. However, in ether solution they could be preserved for several days. When cooled with solid carbon dioxide, these diacetylenic alcohols generally crystallized out, and they could be preserved for a long time under such conditions. The ability of the diacetylenic alcohols (II) to give Grignard complexes was made use of by us for the synthesis of unsymmetrical diacetylenic diols, which are difficult to prepare in other ways in a sufficiently pure state. By this method, starting with 2-methyl-3,5-hexadiyn-2-ol (IIa) and a ketone or aldehyde, we prepared a series of diacetylenic diols, the yields and constants of which are given in the table.

All these diols were obtained in the first place as thick sirupy products, which slowly crystallized out when allowed to stand and for purification could be crystallized from benzene. In some cases the liquid diols can be distilled without appreciable decomposition. We showed that the thermal decomposition of the above-described secondary-tertiary diacetylenic diols in presence of potassium carbonate proceeds at a lower temperature (130-150°) and that the pyrolysis proceeds mainly at the carbon atom carrying the tertiary hydroxy group (elimination of acetone). In this way, from 2-methyl-3,5-octadiyne-2,7-diol [(I) $R_1 = H$; $R_2 = R_3 = R_4 = CH_3$] and 2-methyl-3,5-decadiyne-2,7-diol [(I) $R_1 = H$; $R_2 = n\text{-}C_3H_7$; $R_3 = R_4 = CH_3$] we obtained, respectively, 3,5-hexadiyn-2-ol [(II) $R_1 = H$; $R_2 = CH_3$] and 5,7-octadiyn-4-ol [(II) $R_1 = H$; $R_2 = n\text{-}C_3H_7$], the structures of which were confirmed by the reverse synthesis into the original diacetylenic diols. It was shown by gas-liquid chromatography that these compounds were not pure, but contained 5-10% of 2-methyl-3,5-hexadiyn-2-ol (IIa). This result shows that the pyrolysis of secondary-tertiary diacetylenic diols is accompanied by the partial elimination of an aldehyde group.

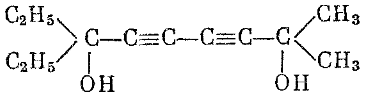
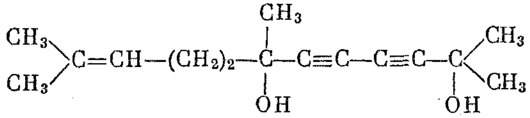
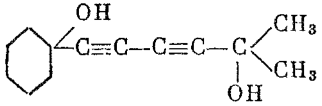
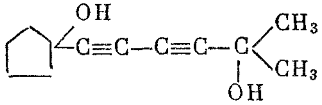
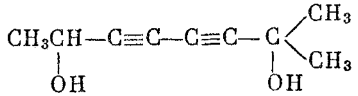
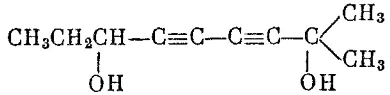
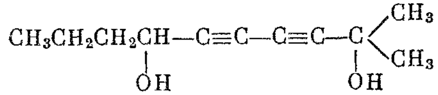
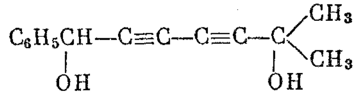
EXPERIMENTAL

Synthesis of Tertiary Diacetylenic Alcohols

Preparation of 2-Methyl-3,5-hexadiyn-2-ol (IIa), and Some of its Reactions. A carefully stirred mixture of 83 g (0.5 mole) of 2,7-dimethyl-3,5-octadiyne-2,7-diol (Ia) and 5 g of potassium carbonate was heated rapidly until melting occurred (bath temperature 180-190°), and after the start of the vigorous elimination of acetone the pyrolysis products were distilled off in a vacuum of 20-30 mm with collection of the mixture of acetone and the diacetylenic alcohol in a receiver cooled with solid carbon dioxide. The liquid mixture of reaction products was shaked with anhydrous potassium carbonate, acetone was distilled off, and the residue was vacuum-distilled. We obtained 30.6 g (56.6%) of 2-methyl-3,5-hexadiyn-2-ol (IIa); b.p. 36-37° (0.4 mm); n_4^{20} 1.4936; m.p. 9-10° [9]. Found: C 77.53 78.03; H 7.49; 7.54%. C_7H_8O. Calculated: C 77.75; H 7.46%. From the residue remaining after the distillation 3.7 g of the original diol (IIa) can be isolated.

Reaction of 2-methyl-3,5-hexadiyn-ol (IIa) with acetone: To a suspension of 3 g (0.04 mole) of potassium hydroxide in 50 ml of dry ether at 0-2° we added 2.16 g (0.02 mole) of the diacetylenic alcohol (IIa). The mixture was stirred carefully for 90 minutes, and 1.16 g (0.02 mole) of acetone was then added at this temperature. Stirring was continued further for two hours, and the mixture was then left overnight. The reaction product was diluted with 20 ml of water, the ether layer was separated, and the aqueous part was carefully extracted with ether. After neutralization with carbon dioxide the solution was dried with anhydrous potassium carbonate, and ether was distilled off. We obtained 3.25 g of the diol (Ia), m.p. 124-126°, which after crystallization from benzene (yield 92%) had m.p. 131-132°, undepressed by admixture of a known sample [5].

Unsymmetrical Diacetylenic Diols Prepared from 2-Methyl-3,5-hexadiyn-2-ol*

Formula	Yield,(%)	B.p., °C (p, mm)	M.p. (°C)	Found, %		Calculated, %		Literature ref.
				C	H	C	H	
 $(C_2H_5)_2C(OH)-C\equiv C-C\equiv C-C(OH)(CH_3)_2$	63,4	—	73—74	74,06 74,17	9,25 9,47	74,19	9,34	—
 $(CH_3)_2C=CH-(CH_2)_2-C(CH_3)(OH)-C\equiv C-C\equiv C-C(OH)(CH_3)_2$	67,3	130—132 (0,4)	60—61	76,81 77,01	9,54 9,53	76,88	9,46	—
	62,0	—	120—121	75,73 75,61	8,78 8,56	75,69	8,80	—
	69,8	—	118—119	75,33 75,43	8,48 8,49	74,97	8,39	[8]
 $CH_3CH(OH)-C\equiv C-C\equiv C-C(OH)(CH_3)_2$	71	—	76—77	70,61 70,78	8,08 7,89	71,02	7,95	[4]
 $CH_3CH_2CH(OH)-C\equiv C-C\equiv C-C(OH)(CH_3)_2$	87	108—111 (0,5)**	43—44	71,95 71,95	8,69 8,49	72,26	8,49	—
 $CH_3CH_2CH_2CH(OH)-C\equiv C-C\equiv C-C(OH)(CH_3)_2$	63,4	118—120 (0,5)***	—	78,45 78,58	8,47 8,37	78,65	8,25	—
 $C_6H_5CH(OH)-C\equiv C-C\equiv C-C(OH)(CH_3)_2$	55	—	86—87	78,31 78,59	6,45 6,34	78,48	6,59	—

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*Carried out with the participation of Z. A. Navrezova.

** n_D^{20} 1.5208.

*** n_D^{20} 1.5096.

Hydrogenation of 2-methyl-3,5-hexadiyn-2-ol (IIa). 5.4 g (0.05 mole) of the diacetylenic alcohol was hydrogenated as a solution in 25 ml of ethyl acetate in presence of a palladium catalyst. 4660 ml (17°, 758 mm) of hydrogen was absorbed, which corresponds to 3.84 moles of hydrogen per mole of the substance. After distillation we obtained 4.56 g (80%) of 2-methyl-2-hexanol (III); b.p. 140-142° (758 mm); n_D^{20} 1.4182 [3, 6].

Preparation of 2,11-Dimethyl-3,5,7,9-dodecatetrayne-2,11-diol (IV). A solution of 10.8 g (0.1 mole) of 2-methyl-3,5-hexadiyn-2-ol (IIa) in 25 ml of alcohol was added to a mixture of 20 g of cuprous chloride, 35 g of ammonium chloride, 0.5 ml of concentrated hydrochloric acid, and 100 ml of water, and the whole was stirred in an oxygen atmosphere for five hours. The reaction product was extracted with ether and washed with dilute (1: 1) hydrochloric acid. After removal of ether we obtained 10.5 g (98%) of the tetraacetylenic diol (IV), m.p. 150-152° (decomp.), which is in accord with the literature [7]. Found: C 78.28; 78.39; H 6.60; 6.70%. $C_{14}H_{14}O_2$. Calculated: C 78.48; H 6.59%.

Preparation of 3-Methyl-4,5-heptadiyn-3-ol [(II) $R_1 = CH_3$; $R_2 = C_2H_5$]. A carefully stirred mixture of 19.8 g (0.1 mole) of 3,8-dimethyl-4,5-decadiyne-3,8-diol [(I) $R_1 = R_3 = CH_3$; $R_2 = R_4 = C_2H_5$] and 1 g of potassium carbonate was heated to 145-150° (bath temperature 160°). Vigorous liberation of butanone set in. A vacuum of 20-25 mm residual pressure was then established, and volatile reaction products were distilled off into a receiver cooled with solid carbon dioxide. The mixture was shaken with anhydrous potassium carbonate, butanone was distilled off, and the residue was vacuum-distilled. We obtained 8.1 g (64%) of 3-methyl-4,6-heptadiyn-3-ol; b.p. 42-43° (0.4 mm); m.p. 11-12°; n_D^{20} 1.4956 [2]. Found: C 78.28; 78.28; H 8.17; 8.12%. $C_8H_{10}O$. Calculated: C 78.65%; H 8.25%.

Preparation of 3-Ethyl-4,6-heptadiyn-3-ol [(II) $R_1 = R_2 = C_2H_5$]. A mixture of 44 g (0.2 mole) of 3,8-diethyl-4,6-decadiyne-3,8-diol [(I) $R_1 = R_2 = R_3 = R_4 = C_2H_5$] and 2 g of potassium carbonate was heated at 180-190° (in bath) until the vigorous liberation of 3-pentanone began. A mixture of reaction products were distilled off at a residual pressure of 15-20 mm. The mixture was dried with potassium carbonate, 3-pentanone was distilled off, and the residue was vacuum-distilled. We obtained 15.2 g (56%) of 3-ethyl-4,6-heptadiyn-3-ol; b.p. 44-45° (0.3 mm); m.p. 19-20°; n_D^{20} 1.4964. Found: C 79.25; 78.98; H 8.92; 8.83%. $C_9H_{12}O$. Calculated: C 79.37; H 8.88%.

Preparation of 1-(1-Hydroxycyclopentyl)-1,3-butadiyne [(II) $R_1R_2 = -(CH_2)_4-$]. A carefully stirred mixture of 10.8 g (0.05 mole) of 1,4-bis-1-hydroxycyclopentyl-1,3-butadiyne and 0.5 g of potassium carbonate was heated to 180-190° (in the bath). Vigorous elimination of cyclopentanone occurred, and the pyrolysis products formed were distilled off at about 10 mm residual pressure. The mixture was dried with potassium carbonate and vacuum-distilled. We obtained 4.2 g (62.6%) of 1-(1-hydroxycyclopentyl)-1,3-butadiyne; b.p. 55-56° (0.45 mm); m.p. 30.5-31°; n_D^{20} 1.5248 [4]. Found: C 80.51; 80.62; H 7.78; 7.67%. $C_9H_{10}O$. Calculated: C 80.56; H 7.51%.

Synthesis of Unsymmetrical Diacetylenic Diols

A solution of 5.4 g (0.05 mole) of 2-methyl-3,5-hexadiyn-2-ol (IIa) in 10 ml of dry ether was added over a period of ten minutes at 6-10° to a Grignard reagent prepared from 2.64 g (0.11 mole) of magnesium and 12 g(0.11 mole) of C_2H_5Br in 50 ml of dry ether, after which the reaction mixture was stirred at room temperature for three hours. A solution of the appropriate ketone or aldehyde (0.05 mole) in 10 ml of ether was then added at 7-10°. The mixture was stirred vigorously for one hour and then left overnight. On the next day the reaction complex was decomposed by dilution with saturated ammonium chloride solution. The reaction product was carefully extracted with ether, the extract was dried with potassium carbonate, and ether was distilled off. The thick residue of reaction product slowly crystallized out. For purification it may be crystallized from a little benzene. In the case of liquid diols, they may be distilled in a good vacuum without appreciable decomposition. The constants of the diols prepared by this general method are given in the table.

Synthesis of Secondary Diacetylenic Alcohols

Preparation of 3,5-Hexadiyn-2-ol [(II) $R_1 = H$; $R_2 = CH_3$]. A mixture of 30.4 g (0.2 mole) of 2-methyl-3,5-octadiyne-2,7-diol [(I) $R_1 = H$; $R_2 = R_3 = R_4 = CH_3$] and 2 g of potassium carbonate was heated to the start of melting and then the pyrolysis products were distilled off. The breakdown of the diol was finished completely at 140-150° (in the bath). The mixture was dried with potassium carbonate and vacuum-distilled. This gave 9.8 g (52.1%) of the diacetylenic alcohol [(II) $R_1 = H$; $R_2 = CH_3$]; b.p. 30-32° (0.55 mm); n_D^{20} 1.5026 [9]. Found: C76.90; 76.98; H 6.84; 6.69%. C_6H_6O. Calculated: C 76.57; H 6.43%. According to gas-liquid chromatography this product contained about 5% of 2-methyl-3,5-hexadiyn-2-ol (IIa). On treatment of the Grignard complex of this, 3,5-hexadiyn-2-ol with acetone by the method given above, a yield of up to 60% can be obtained of the original 2-methyl-3,5-octadiyne-2,7-diol, m.p. 75-76°, undepressed by admixture of a known sample.

Preparation of 5,7-Octadiyn-4-ol [(II) $R_1 = H$; $R_2 = n\text{-}C_3H_7$]. A mixture of 10 g of 2-methyl-3,5-decadiyne-2,-7-diol [(I) $R_1 = H$; $R_2 = n\text{-}C_3H_7$, $R_3 = R_4 = CH_3$] and 0.1 g of finely ground potassium carbonate was heated in a bath, and already at 110-120° the elimination of acetone began. At a vacuum of about 10 mm and a bath temperature of about 140° a yellowish-brown liquid was distilled off. After redistillation in a vacuum we isolated 4.3 g (63.2%) of 5,7-octadiyn-4-ol; b.p. 55-57° (0.45 mm); n_D^{20} 1.4970 [9]. Found: C 78.45; 78.58; H 8.47; 8.37%. $C_8H_{10}O$. Calculated: C 78.65; H 8.25%. According to gas-liquid chromatography this product contained about 7% of 2-methyl-3,5-hexadiyn-2-ol (IIa).

SUMMARY

1. A preparative method is proposed for the synthesis of tertiary and secondary diacetylenic alcohols; it is based on the pyrolysis of ditertiary and secondary-tertiary diacetylenic diols in presence of potassium carbonate.

2. Some unsymmetrical diacetylenic diols, difficultly accessible by other methods, were synthesized from 2-methyl-3,5-hexadiyn-2-ol.

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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.
