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Abstract

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INTERACTION OF DIACETYLENE WITH CERTAIN HYDROXYL-CONTAINING COMPOUNDS

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Owing to its high reactivity, diacetylene is of interest for synthetic organic chemistry. However, its use is limited by its low availability. Three methods for obtaining diacetylene are known. The multistage and complicated Bauser method ([1]) can hardly be recommended even for laboratory practice. In Germany, diacetylene is obtained as a by-product in the arc method of acetylene production ([2]). Quite acceptable is the method described by Herbertz ([3,4]), which consists in the chlorination of butyn-(2)-diol-(1,4) and subsequent dehydrochlorination of dichlorobutyne. The data available in the literature ([5–7]) on the interaction of diacetylene with alcohols are preliminary in character and do not contain a detailed description of the conditions of this reaction or of the properties of the products isolated. The thorough investigations are the works of Herbertz ([3]) and Franke ([8]), in which the preparation of 1-methoxy-buten-1-yne-3, its interaction with methanol and carbonyl compounds, and certain transformations of the products of these additions are described.

The aim of the present investigation is to study the conditions of the interaction of diacetylene with butanol, cyclohexanol, and β-decalol, to isolate the products of this interaction, and to compare some of their properties. The interaction of diacetylene with alcohols proceeds under the influence of caustic alkalis on heating and is accompanied by the formation of ethynylvinyl ethers (equation (1)), which in an excess of alcohol pass into acetals of butyn-2-al-4 (equation (2)).

$$CH \equiv C—C \equiv CH + ROH \rightarrow CH \equiv C—CH{=}CH—OR, \qquad (1)$$

where R = C_4H_9 (I); C_6H_{11} (II); $C_{10}H_{17}$ (III).

$$CH \equiv C—CH{=}CH—OR \rightarrow CH \equiv C—CH_2—CH(OR)_2 \rightarrow \qquad (2)$$

$$\rightarrow CH_3—C \equiv C—CH(OR)_2,$$

where R = C_4H_9 (IV); C_6H_{11} (V); $C_{10}H_{17}$ (VI).

The reaction proceeds stepwise, which is demonstrated by the synthesis of butynal acetals from ethynylvinyl ethers and alcohols in alkaline and acidic media. In contrast to alkylacetylenes, the first molecule of alcohol adds to diacetylene against Markovnikov' s rule, which is a consequence of the influence of the second ethynyl group. The next molecule of alcohol adds to the ethynylvinyl ethers according to Markovnikov' s rule, with the subsequent isomerization discovered by Favorskii for hydrocarbons ([9]). In the interaction of diacetylene with hydroxyl-containing compounds, the rate of diacetylene absorption depends on the starting compound and the temperature. On heating to 100°, the formation only of ethynylvinyl ethers was observed. Acetals are formed in appreciable amounts at temperatures

above 130°, and also when the amount of the starting alcohol is increased. The interaction of diacetylene with β-decalol begins at 90° and is accompanied by the formation only of the ethynylvinyl ether; at elevated temperatures decalol was obtained; apparently the reaction proceeds as far as the formation of the acetal (VI), which decomposes during treatment of the mixture. The supposition concerning the instability of didecalyl acetal-butynal is quite probable, since even acetaldehyde didecalyl acetal is an extremely unstable compound, decomposing on vacuum distillation with liberation of β-decalol. To prove the structure of the ethers and acetals isolated, bromination, hydrolysis (2), and hydrogenation (partial and exhaustive) were used. In partial hydrogenation, 1-alkoxybutadienes are obtained (equation (3)).

$$CH \equiv C—CH = CH(OR) + H_2 \rightarrow CH_2 = CH—CH = CH(OR), \qquad (3)$$

where $R = C_{10}H_{17}$ (VII).

On exhaustive hydrogenation, saturated ethers of the series C_4H_9OR were obtained, where R = C_4H_9 (VIII); C_6H_{11} (IX); $C_{10}H_{17}$ (X). From the acetals of butynal the corresponding acetals of butyral were obtained: $C_4H_8(OR)_2$, where $R = C_4H_9$ (XI); C_6H_{11} (XII). Ethynylvinyl ethers are readily brominated. Thus, on saturation of ethynylvinyl butyl ether with bromine, two molecules of bromine were absorbed per molecule of ether. Addition of the first molecule of bromine probably takes place at the double bond and is accompanied by isomerization. The second molecule of bromine adds at the triple bond with formation of 1-butoxy-1,2,3,4-tetrabromobutene-2 (XIII):

$$CH \equiv C—CH = CH—OC_4H_9 \rightarrow CH_2Br—C \equiv C—CHBr—OC_4H_9 \rightarrow$$

$$\rightarrow CH_2Br—CBr = CBr—CHBr—OC_4H_9. \qquad (4)$$

(XIII)

In favor of such a structure for the tetrabromo ether is the fact that in aqueous medium it is quantitatively titrated with 0.1 N NaOH, which confirms the presence in it of an α-Br atom, and from the hydrolysate tribromocrotonaldehyde was isolated (equation (5))

$$CH_2Br—CBr = CBr—CHBr—OC_4H_9 + H_2O \rightarrow$$

$$\rightarrow C_4H_9OH + HBr + CH_2Br—CBr = CBr—CHO. \quad (5)$$

The reactions listed testify to the considerable reactivity of ethynylvinyl ethers in ionic transformations, revealing certain peculiarities of the double bond in them. On the basis of diacetylene, 16 compounds were synthesized, of which 10 have not been described in the literature.

Experimental Part

Preparation of diacetylene*. Butyne-(2)-diol-(1,4) was chlorinated with thionyl chloride at a temperature from −15° to +10° for 12 hours and heated to 60° until SO_2 disappeared from the reaction mixture. Dichlorobutyne was distilled off in vacuo at a mixture temperature not above 110°. Yield 70% of theory. A mixture of 24 g of dichlorobutyne, 3 g of ethanolamine, and 50 g of ethyl alcohol, with stirring, was heated to 70–75° in a stream of nitrogen; 80 ml of 40% NaOH was added dropwise to the same place. Diacetylene was passed through a concentrated NaOH solution and dry $CaCl_2$ and condensed in a coil trap at −70°. 6.35 g (50% of theory) of diacetylene was collected.

Interaction of diacetylene with butanol, cyclohexanol, and β-decalol. Into a cylindrical reaction vessel equipped with a stirrer and reflux condenser was placed a 2% solution of caustic potash in alcohol. After flushing the system with dry nitrogen,

* By the method of Herbertz, improved in our laboratory with the participation of E. V. Dubrova.

Table 1

Conditions for obtaining and characteristics of the isolated ethers and acetals

Compound formula	Molar ratio alcohol : diacetylene	Reaction temperature, °C	Yield, % of theory	B.p., °C/mm	n_D^{20}	d_4^{20}	MR, found	MR, calc.	M, found	M, calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H	B.p., °C/mm
$CH_3CH(OC_4H_9)C\equiv CH$ (I)	3 : 1	100	60.0*	60	1.4702	0.8664	40.02	38.26	122.0	124.2	77.66	13.39	77.36	13.85	176
$CH_3CH(OC_4H_9)CH{=}CH_2$	1	110		60.5/11 p.	1.4144	°/a.									178 (2)
$CH_3CH(OC_4H_9)C\equiv CH$ (IV)	4 : 1	120	25.6**	105/11	1.4398	0.8755	39.71	39.97	195.0	198.2	72.53	12.07	72.73	11.17	178
$CH_3CH(OC_4H_9)CH{=}CH_2$	1	125													85/3 (5)
$CH_3CH(OC_4H_9)_2$ (II)	5 : 1	95	40.0*	85.8/1	1.4035	0.8946	46.96	45.29	146.3	150.1	79.61	13.46	79.89	9.39	100
$CH_3CH(OC_4H_9)CH{=}CH_2$	1	98													105 (5,6)
$CH_3CH(OC_6H_{11})C\equiv CH$ (V)	5 : 1	130	30.5**	125.5	1.4890	0.9857	53.36	74.04	248.0	250.4	76.66	10.32	76.26	10.47	165
$CH_3CH(OC_6H_{11})CH{=}CH_2$	1	137		126/3											167 (5,6)
$CH_3CH(OC_6H_{11})_2$ (III)	3 : 1	90	60.0*	130.5	1.4568	0.9946	63.13	61.56	199.0	201.3	82.39	12.61	82.29	9.86	—
$CH_3CH(OC_6H_{11})CH{=}CH_2$	1	95													

* In addition, butynal acetal was isolated.
** In addition, ethynylvinyl ether was isolated.

Table 2

Hydrogenation of ethynylvinyl ethers and butynal acetals

No. of starting compound	Product obtained	Yield, % of theory	B.p., °C/mm	n_D^{20}	d_4^{20}	MR, found	MR, calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Literature data: b.p., °C	Literature data: n_D^{20}	Literature data: d_4^{20}	Literature data: source
I	C_4H_9 — O — C_4H_9 (VIII)	80.0	61 — 62/51	1.4002	0.7589	50.15	50.77					141.9 mm	1.4500	0.7525	(11)
IV	CH_3 — CH_2 — CH_2 — $CH(OC_4H_9)_2$ (XI)	75.0	138 — 9	1.4153	0.8432	69.99	70.90	70.93	12.80	71.22	12.95	—	1.4210	0.8575	(12) (17.5°)
II	C_4H_9 — O — C_6H_{11} (IX)	89.0	193 — 4/a. p.	1.4380	0.8654	47.41	47.82	—	—	—	—	193.5 (a. p.)	1.4436	0.8664	(13)
V	CH_3 — CH_2 — CH_2 — $CH(OC_6H_{11})_2$ (XII)	78.6	120 — 1/3.5	1.4666	0.9397	75.04	74.97					—	—	—	—
III	C_4H_9 — O — $C_{10}H_{17}$ (X)	82.0	133 — 134.5/10	1.4772	0.9266	64.19	64.09	79.72	11.56	79.90	11.96	112.45	—	—	—	—
III	CH_2=CH — CH=CH — $OC_{10}H_{17}$ (VII)	80.0	110.4 — 1/2.5	1.5040	0.9533	64.07	63.16	81.29	10.48	81.58	10.78	110.75	—	—	—	—

diacetylene was passed into the reaction vessel, heated on a Vaseline bath. After the reaction was complete, the mixture was washed with water, dried over potassium hydroxide, and distilled in vacuo. The products isolated were colorless liquids; they gave a positive test for a triple bond. The characteristics of

the compounds isolated are given in Table 1.

Reaction of butylethynylvinyl ether (I) with butyl alcohol (3) in an acidic medium. To a mixture of 4.1 g of butylethynylvinyl ether (I) and 4.6 g of butanol, with stirring, was added 1 drop of conc. H_2SO_4. After neutralization of the catalyst the mixture was distilled in vacuo. 3.5 g of a fraction, 92-96° (6 mm), was collected, which after redistillation had the constants of dibutyl acetal of butyn-2-al-4 (IV): b.p. 103-104°/9 mm; $n_D^{20} = 1.4400$; $d_4^{20} = 0.8764$ (Table 2). Yield 55% of theory.

Hydrolysis of β-decalylethynylvinyl ether (III) in an acidic medium. a) 5 g of (III) and 25 ml of 10% H_2SO_4 were heated to 80° for 1 hour. From the oily layer, by distillation, 2.8 g (85% of theory) of β-decalol was isolated, b.p. 142-143°/33 mm, $n_D^{20} = 1.5010$. From the aqueous layer, the semicarbazone of butyn-1-al-4 was obtained, m.p. 120°. The literature gives m.p. 122° ([3]).

In addition, 0.22 g of triacetylbenzene was isolated, m.p. 164° (in the literature 165° ([3])); its formation is explained by concomitant hydration and trimerization of the aldehyde.

Hydrogenation of ethynylvinyl ethers and acetals of butynal. Hydrogenation was carried out at room temperature in methanol solution: exhaustive hydrogenation over Pt, partial hydrogenation over Pd. The experimental results are shown in Table 2.

Bromination of ethynylvinyl butyl ether (I). 12.6 g of bromine, dissolved in 5 ml of CCl_4, was added dropwise to 3.65 g of (I), dissolved in 3 ml of CCl_4 at −10°. The reaction mixture was stirred at room temperature for 2 hours. 11.3 g of crystalline butyl ether of 1,2,3,4-tetrabromobutene-2 (XIII) was obtained; after recrystallization from petroleum ether it melted at 59-60°. Its yield was 88.2% of theory.

Hydrolysis of butyl ether of 1,2,3,4-tetrabromobutene-2 (XIII). a) 0.1476 g of (XIII) and 25 ml of water were shaken in a flask at room temperature for 1 hour. Titration of the hydrolysate required 2.89 ml of 0.01 NaOH, which corresponds to 99.8% of titratable H* ([10]). b) 5.4 g of the tetrabromo ether (XIII) was boiled with 20 ml of water for 1 hour. After drying of the oily layer over sodium sulfate, it was distilled in vacuo. 3.3 g (87.4%) of a fraction, 128-135°/2 mm, was collected; after redistillation it proved to be 1,2,3-tribromocrotonaldehyde (XIV). B.p. 137-138°/3 mm; $n_D^{20} = 1.6540$; $d_4^{20} = 2.6150$, $MR_D = 43.00$, calc. $C_4H_3OBr_3/MR = 43.42$.

Found, %: C 15.45; 15.54; H 1.04; 1.09; Br 78.59; 78.86
$C_4H_3OBr_3$. Calculated, %: C 15.66; H 0.99; Br 78.13

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Note: Figure translations are in progress. See original paper for figures.