PREPARATION OF SUBSTITUTED 4-(3-METHYL-3-HYDROXY-1-BUTYNYL)-2-ETHOXY-1,3-DIOXOLANES

I. Yu. Kibina, Sh. M. Musantaeva,
and A. V. Shchelkunov

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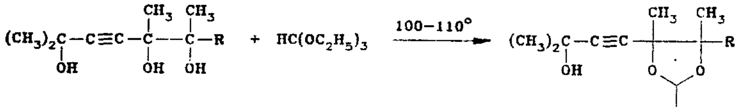
A method has been developed for the preparation of 4-(3-hydroxy-1-alkynyl)-substituted 2-ethoxy-1,3-dioxolanes (which are novel flotation reagents for coal) based on the reaction between acetylene 1,2,5-triols and orthoformic ester in the presence of catalytic quantities of benzoic acid.

The wide distribution of cyclic acetals in nature, the systematic use of acetal protective agents in the chemistry of carbohydrates and steroids [1, 2], and the physiological activity of some 1,3-dioxolanes makes the study of these compounds of considerable current interest.

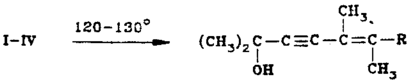
2-Ethoxy-1,3-dioxolanes are generally prepared by heating 1,2-diols with orthoformic ester in the presence of catalytic quantities of benzoic acid [3].

The absence of any reference in the literature to the preparation of alkynyl-substituted 2-ethoxy-1,3-dioxolanes of the acetal series prompted us to examine the possibility of preparing the latter from the appropriate acetylene 1,2,5-triols and to seek a variety of practical uses for them. This object was achieved by reacting acetylene 1,2,5-triols with orthoformic ester in the presence of benzoic acid, as a result of which 4-(3-methyl-3-hydroxy-1-butynyl)-2-ethoxy-1,3-dioxolanes (I-IV) were obtained as the sole product of the reaction in yields of 55-72% (see Table 1):



I R=CH_3; II R=C_2H_5; III R=C_3H_7; IV R=C_4H_9

It is known that 2-ethoxy-1,3-dioxolanes can be used for the synthesis of olefins [3]. Hence the structure of all the dioxolanes which we prepared was confirmed by breaking them down to known [4] vinylacetylene alcohols (V-VIII):



$$\text{I–IV} \xrightarrow{120-130^\circ} (CH_3)_2\underset{\substack{|\\OH}}{C}-C\equiv C-\overset{\substack{CH_3\\|}}{C}=\underset{\substack{|\\CH_3}}{C}-R$$

V-VIII

Additional confirmation of their structure was obtained by the alkaline thermolysis of 4,4,5-trimethyl-5-(3-methyl-3-hydroxy-1-butynyl)-2-ethoxy-1,3-dioxolane to acetone and 4,4,5-trimethyl-5-ethynyl-2-ethoxy-1,3-dioxolane (IX).

Further heating of the dioxolane IX in the presence of catalytic quantities of benzoic acid at 140-160°C led to a known vinylacetylene hydrocarbon [5].

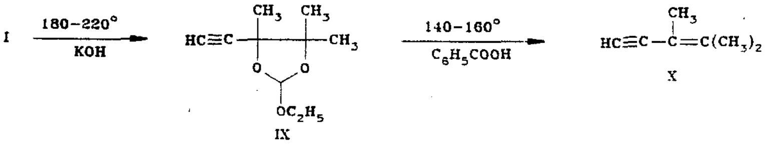


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TABLE 1. 2-Ethoxy-1,3-dioxolanes I-IV

Compound	bp, °C (mm Hg)	d_4^t	n_D^t	IR spectrum, ν, cm^{-1}	Found, %		Empirical formula	Calculated, %		Yield, %
					C	H		C	H	
I	113—116 (3)	$0,9789^{26}$	$1,4635^{26}$	2220 (C≡C), 3400 (OH), 1200—950*	64,2	9,4	$C_{13}H_{22}O_4$	64,5	9,1	72
II	125 (6)	$0,9654^{26}$	$1,4692^{26}$	2120 (C≡C), 3400 (OH), 1200—950*	65,3	9,1	$C_{14}H_{24}O_4$	65,6	9,4	60
III	140—142 (5)	$0,9904^{27}$	$1,4689^{27}$	2220 (C≡C), 3400 (OH), 1200—950*	66,5	9,5	$C_{15}H_{26}O_4$	66,7	9,6	67
IV	135 (4)	$0,9798^{24}$	$1,4650^{24}$	2270 (C≡C), 3450 (OH), 1200—950*	67,4	9,9	$C_{16}H_{28}O_4$	67,6	9,8	55

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*Orthoformate group.

2-Ethoxy-1,3-dioxolanes I-IV were found to be effective flotation agents for the recovery of coal from coal slurries.

EXPERIMENTAL

Infrared spectra were run as thin films on a UR-20 instrument. The purity of the dioxolanes was monitored by GLC using a Khrom-31 chromatograph with katharometer detector and a column 2400 × 6 mm packed with 5% PMS-100 on Polychrome-1; carrier gas was helium (80-85 ml/min), temperature 200°C.

Substituted 4-(3-Methyl-3-hydroxy-1-butynyl)-2-ethoxy-1,3-dioxolanes (Table 1). A mixture of 0.058 mole acetylene 1,2,5-triol, 0.058 mole orthoformic ester and 0.0024 mole benzoic acid was heated in a bath at 100°C, distilling off the ethanol as it formed. The reaction was stopped when evolution of carbon dioxide commenced (detected by cloudiness in baryta water The reaction mixture was cooled, diluted with ether and neutralized with potash. The deposit was removed by filtration and the product recovered from the filtrate by fractionation to yield the dioxolanes I-IV (Table 1).

4,4,5-Trimethyl-5-ethynyl-2-ethoxy-1,3-dioxolane (IX). A mixture of 4 g (0.015 mole) dioxolane I and 0.12 g KOH was quickly heated to 160°C until the appearance of vapors of the decomposition products. The mixture of products was then distilled, the distillate dried over magnesium sulfate, and redistillation yielded 2.2 g (80%) dioxolane IX, bp 110-112°C at 40 mm, n_D^{20} 1.4420; d_4^{20} 0.9910. IR spectrum (cm^{-1}): 2100, 3320 (C≡C), 1200-950 (orthoformic group). Found, %: C 59.8, H 9.0. $C_{10}H_{16}O_3$. Calculated, %: C 60.0, H 8.6.

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