[Contribution from the Department of Chemistry, University of Notre Dame]

The Synthesis of Some Dioxole Derivatives from Alkylacetylenes[1]

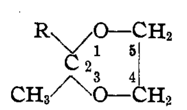
By D. B. Killian, G. F. Hennion and J. A. Nieuwland

Glycol ethylidene oxide, or 2-methyl-1,3-dioxolane, was first prepared by Wurtz[2] by heating glycol and acetaldehyde in sealed tubes for eight days on a water-bath. Later work[3,4,5] showed that aldehydes could be condensed with polyhydric alcohols with greater ease when phosphoric or sulfuric acid was used as a catalyst. Acetylene reacts with polyhydroxy compounds, in the presence of mercuric sulfate and sulfuric acid, to yield dioxolanes and dioxolones.[6,7] Nieuwland, Vogt and Foohey[8] have shown that cyclic acetals result in high yields from acetylene and polyhydroxy compounds when mercuric oxide and a solution of boron fluoride in methanol are used as catalysts.

The 2,2-dialkyl-1,3-dioxolanes have been reported in the literature in a limited number only. Acetone or other ketones of low molecular weight may be condensed with polyhydroxy compounds in the presence of mineral acids to yield cyclic ketals. Various methods[9,10,11] have been proposed for the synthesis of these compounds, but none of them is generally applicable. The number of references to this field is so large that an exhaustive literature survey of the subject cannot be made here.

Staedler[12] first described chloralide, 2,5-bis-trichloromethyl-1,3-dioxol-4-one, prepared by the action of sulfuric acid on chloral. Other 1,3-dioxol-4-ones have been described from time to time by various investigators.[13–15] Many techniques have been described for the preparation of such compounds by condensing an α-hydroxy acid with a ketone, an aldehyde or acetylene.

The authors have previously shown[16] that amylacetylene reacts with ethylene glycol, in the presence of mercuric oxide and boron fluoride, to yield 2-amyl-2-methyl-1,3-dioxolane. The addition of polyhydroxy alcohols and α-hydroxy acids to an alkylacetylene furnishes a convenient method for the synthesis of many dioxole derivatives. Dihydric alcohols, such as ethylene glycol, yield with alkylacetylenes compounds of type I; α-hydroxy acids, for example α-hydroxyisobutyric acid, give rise to compounds of type II; and polyhydric alcohols, such as mannitol, produce compounds of type III.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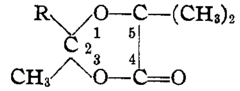
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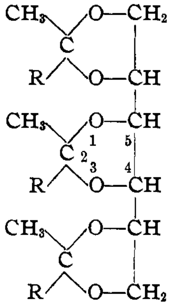
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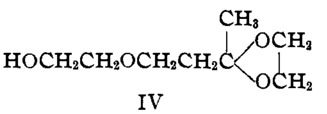
The addition of polyhydroxy alcohols to monovinylacetylene is of some interest since it has been shown that methanol reacts with monovinylacetylene in the ratio of three molecules of the alcohol to one of the acetylene to produce 1,3,3-trimethoxybutane.[17] We have found that ethylene glycol and monovinylacetylene yield two addition compounds, one formed from two molecules of glycol and one of the acetylene (IV); and the other from three molecules of glycol and two of the acetylene (V).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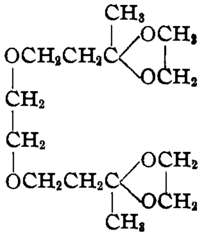
V

Experimental

General Procedure.—The catalyst was prepared by heating together momentarily, 5 g. of red mercuric oxide, 2 ml. of $(C_2H_5)_2O{\cdot}BF_3$, and 2 ml. of anhydrous methanol. To this was added 1–2 g. of trichloroacetic acid, and the

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(1) Paper XIV on the chemistry of the alkylacetylenes and their addition products; previous paper, *J. Org. Chem.*, **1**, 159 (1936).

(2) Wurtz, *Compt. rend.*, **53**, 378 (1861).

(3) Verley, *Bull. soc. chim.*, [3] **21**, 276 (1899).

(4) Clarke, *J. Chem. Soc.*, **101**, 1804 (1912).

(5) Read, Lathrop and Chandler, This Journal, **49**, 3116 (1927).

(6) Reichert, Bailey and Nieuwland, *ibid.*, **45**, 1552 (1923).

(7) Hill and Hibbert, *ibid.*, **45**, 3108 (1923).

(8) Nieuwland, Vogt and Foohey, *ibid.*, **52**, 1018 (1930).

(9) E. Fischer and Rund, *Ber.*, **49**, 88 (1916).

(10) Böeseken, *Rec. trav. chim.*, **48**, 931 (1929).

(11) Bogert and Roblin, This Journal, **55**, 3741 (1933).

(12) Staedler, *Ann.*, **61**, 104 (1847).

(13) Van Ekenstein and Blanksma, *Rec. trav. chim.*, **25**, 162 (1906).

(14) Blaise, *Bull. soc. chim.*, [4] **15**, 661 (1914).

(15) H. O. L. Fischer and Taube, *Ber.*, **60B**, 485 (1927).

(16) Hennion, Killian *et al.*, This Journal, **56**, 1130 (1934).

(17) Killian, Hennion and Nieuwland, *ibid.*, **56**, 1786 (1934).

TABLE I

CHARACTERISTICS AND ANALYSES OF THE DIOXOLES

Compound	Reactant + butyl- or monovinyl-acetylene	B. p., °C.	B. p., Mm.	n_D	°C.	d	MR Calcd.	MR Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-Butyl-2-methyl-1,3-dioxolane	Ethylene glycol	62–63	20	1.4232	21	0.922	40.23	40.36	66.22	66.50	11.19	11.23
2-Butyl-4-chloromethyl-2-methyl-1,3-dioxolane	Glycerol monochlorohydrin	109	25	1.4420	25	1.032	49.72	49.45		Cl,	18.41	18.05
2-Butyl-2-methyl-5-phenyl-1,3-dioxol-4-one	Mandelic acid	136–138	19	M. p., 44–45					71.75	71.14	7.75	7.68
2-Butyl-2,5,5-trimethyl-1,3-dioxol-4-one, II	α-Hydroxyisobutyric acid	104	25	1.4225	25	0.953	49.48	49.69	64.47	64.91	9.75	9.95
2-[β-(2-Methyl-1,3-dioxolan-2-yl)-ethoxy]-ethanol, IV	Ethylene glycol[a]	140–142	20	1.4430	22	1.094	43.40	42.63	54.54	53.51	9.09	8.73
1,2-Bis-[β(2-methyl-1,3-dioxolan-2-yl)-ethoxy]-ethane, V	Ethylene glycol[a]	204–206	20	1.4572	21	1.098	72.31	72.01	57.89	58.21	9.03	9.13
Dimethyl 2-butyl-2-methyl-1,3-dioxolane-4,5-dicarboxylate	Dimethyl tartrate	141–142	9	1.4412	25	1.103	62.03	62.32	55.35	55.88	7.75	7.93
2-Butyl-2-methyl-4,5-bis-(2-butyl-2-methyl-1,3-dioxolan-4-yl)-dioxolane, III	Mannitol	210–212	9	1.4572	20	0.999	116.30	116.68	67.23	67.24	10.35	10.95

[a] Second reactant, monovinylacetylene.

resulting mixture placed in a three-necked flask equipped with a mercury-sealed motor-driven stirrer, a reflux condenser and a dropping funnel. The appropriate polyhydroxy compound was then added to the catalyst mixture and the alkylacetylene added dropwise, if liquid, and, if a gas, as is the case with monovinylacetylene, in a slow stream using a liquid ammonia condenser[18] on the reaction flask.

The reactions were spontaneous and occasionally required cooling by immersing the flask in a water-bath. After stirring for two hours the contents of the flask was mixed with a small amount of sodium methylate and fractionated *in vacuo*. The yields were in all cases good, namely, between 70 and 90% of the theoretical amounts. The characteristics and analyses of the dioxoles synthesized are given in Table I.

Acknowledgment.—The authors gratefully acknowledge the kind assistance of Dr. Austin M. Patterson for reading the manuscript of this article and suggesting the nomenclature used.

Summary

1. Various dioxolanes and dioxolones have been synthesized from polyhydric alcohols and α-hydroxy acids with butylacetylene and monovinylacetylene.

2. Monovinylacetylene reacted with ethylene glycol to yield two products. The first was formed by the condensation of two moles of glycol with one of monovinylacetylene; the second by the condensation of three moles of glycol with two of the vinylacetylene.

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[18] Vaughn and Pozzi, *J. Chem. Ed.*, **8**, 2433 (1931).

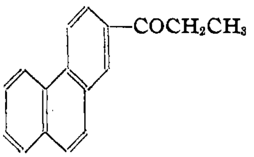
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Synthesis of Phenanthrene Derivatives. IV. Propionylphenanthrenes

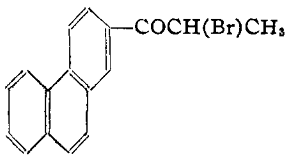
BY W. E. BACHMANN AND W. S. STRUVE

From the reaction between propionyl chloride, phenanthrene and aluminum chloride in nitrobenzene a mixture of propionylphenanthrenes is formed from which it is possible to isolate 2-propionylphenanthrene (I) and 3-propionylphenanthrene. This result is similar to those obtained with acetyl chloride,[1] benzoyl chloride[2] and *o*-toluyl chloride.[3]

The structures of the propionylphenanthrenes were established by their oxidation to 2- and 3-phenanthroic acid by sodium hypochlorite solution as well as by synthesis from the corresponding 2- and 3-cyanophenanthrenes by means of ethylmagnesium bromide. By the Grignard reaction we have also synthesized 9-propionylphenanthrene.



(I)



(II)

By interaction of bromine and 2- and 3-propionylphenanthrene α-bromo-2-propionylphen-

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[1] Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

[2] Bachmann, *ibid.*, **57**, 555 (1935).

[3] Bachmann and Pence, *ibid.*, **57**, 1130 (1935).