

TABLE I  
 CHARACTERISTICS AND ANALYSES OF THE DIOXOLES

Compound	Reactant + butyl- or monovinyl-acetylene	°C.	B. p., mm.	n <sub>D</sub>	°C.	d	MR		Carbon, %		Hydrogen, %	
							Calcd.	Found	Calcd.	Found	Calcd.	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	$\alpha$ -Hydroxyisobutyric acid	104	25	1.4225	25	0.953	49.48	49.69	64.47	64.91	9.75	9.95
2-[ $\beta$ -(2-Methyl-1,3-dioxolan-2-yl)-ethoxy]-ethanol, IV	Ethylene glycol <sup>a</sup>	140-142	20	1.4430	22	1.094	43.40	42.63	54.54	53.51	9.09	8.73
1,2-Bis-[ $\beta$ -(2-methyl-1,3-dioxolan-2-yl)-ethoxy]-ethane, V	Ethylene glycol <sup>a</sup>	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

<sup>a</sup> 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<sup>18</sup> 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

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

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  $\alpha$ -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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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

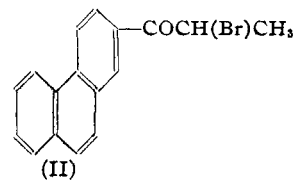
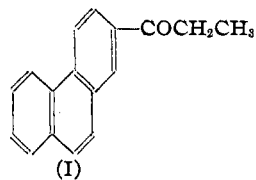
## Synthesis of Phenanthrene Derivatives. IV. Propionylphenanthrenes

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,<sup>1</sup> benzoyl chloride<sup>2</sup> and *o*-toluyl chloride.<sup>3</sup>

The structures of the propionylphenanthrenes were established by their oxidation to 2- and 3-phenanthroic acid by sodium hypochlorite solu-

tion 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.



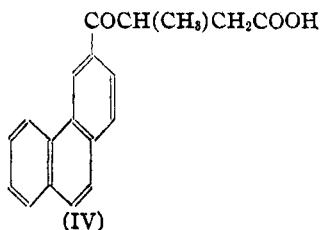
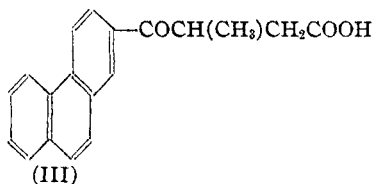
By interaction of bromine and 2- and 3-propionylphenanthrene  $\alpha$ -bromo-2-propionylphen-

(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).

anthrene (II) and  $\alpha$ -bromo-3-propionylphenanthrene are formed. By condensation of the bromopropionylphenanthrenes with sodiomalonic ester, followed by decarboxylation of the malonic acids obtained on hydrolysis of the esters,  $\beta$ -(2-phenanthroyl)-butyric acid (III) and  $\beta$ -(3-phenanthroyl)-butyric acid (IV) were obtained.



### Experimental

#### Reaction of Propionyl Chloride with Phenanthrene.—

To an ice-cold solution of 320 g. of aluminum chloride and 200 g. of phenanthrene in 1750 cc. of nitrobenzene was added 140 g. of propionyl chloride at one time. After being kept cold for half an hour, the mixture was allowed to stand at room temperature for twelve hours. After hydrolysis by ice and dilute hydrochloric acid, followed by removal of the nitrobenzene by steam distillation, the product was dissolved in a hot mixture of acetone and alcohol. On cooling 20 g. of 2-propionylphenanthrene crystallized out. By recrystallization from alcohol the 2-propionylphenanthrene was obtained in the form of colorless needles; m. p. 104–105°.

*Anal.* Calcd. for  $C_{17}H_{14}O$ : C, 87.2; H, 6.0. Found: C, 87.1; H, 6.2.

After standing in a refrigerator for three weeks the filtrate from which the 2-isomer had been removed deposited 60 g. of 3-propionylphenanthrene. By recrystallization from alcohol the 3-propionylphenanthrene was obtained as colorless needles; m. p. 55–57°.

*Anal.* Calcd. for  $C_{17}H_{14}O$ : C, 87.2; H, 6.0. Found: C, 87.3; H, 6.1.

A further quantity of the two ketones was obtained from the filtrate through their picrates.

**Oxidation of 2- and 3-Propionylphenanthrenes.**—A suspension of 1 g. of propionylphenanthrene in 100 cc. of 3% sodium hypochlorite solution containing 1 g. of potassium hydroxide was refluxed for four hours. The solution was filtered and the filtrate was acidified; the phenanthroic acid which precipitated was filtered off and recrystallized from chlorobenzene. From the 2-propionylphenanthrene 2-phenanthroic acid (m. p. 258–260°) was obtained; it gave a methyl ester whose melting point was not depressed when the compound was mixed with authentic 2-phenanthroic acid methyl ester. Similarly 3-propionylphenanthrene gave 3-phenanthroic acid (m. p. 265–270°) whose identity was likewise established through the methyl ester.

onylphenanthrene gave 3-phenanthroic acid (m. p. 265–270°) whose identity was likewise established through the methyl ester.

**Synthesis of Propionylphenanthrenes.**—To the Grignard reagent which had been prepared from 10 g. of ethyl bromide in 30 cc. of ether was added 30 cc. of benzene and 10 g. of cyanophenanthrene (2-, 3- or 9-isomer). After the mixture had been refluxed for four hours, it was cooled and hydrolyzed with ice-cold ammonium chloride solution. The aqueous solution was removed and the ether-benzene solution was shaken with dilute hydrochloric acid; from the aqueous solution of the ketone-imine hydrochloride the ketone was obtained by hydrolysis. The 2- and 3-propionylphenanthrenes were identical with those obtained by reaction of propionyl chloride with phenanthrene. The yields were: 2-propionylphenanthrene, 77%; 3-propionylphenanthrene, 22%; 9-propionylphenanthrene, 86%. The 9-propionylphenanthrene was purified by distillation under reduced pressure followed by recrystallization from alcohol; from this solvent it was obtained in the form of colorless, heavy hexagonal plates; m. p. 55–57°.

*Anal.* Calcd. for  $C_{17}H_{14}O$ : C, 87.2; H, 6.0. Found: C, 87.6; H, 6.3.

**Picrates of Propionylphenanthrenes.**—On cooling hot saturated alcoholic solutions of equal parts of propionylphenanthrene (2-, 3- and 9-isomer) and picric acid the picrates crystallized in the form of yellow needles composed of ketone and picric acid in a 1:1 ratio.

TABLE I  
PROPIONYLPHENANTHRENE PICRATES

Picrate of	M. p., °C.	Anal. for N	
		Calcd.	Found
2-Propionylphenanthrene	104.5–107	9.05	9.01
3-Propionylphenanthrene	111–113	9.05	9.05
9-Propionylphenanthrene	105.5–107	9.05	9.01

**Bromopropionylphenanthrenes.**—A solution of 21.6 g. of 3-propionylphenanthrene in 500 cc. of absolute ether was treated at 0° with a solution of 4.6 cc. of bromine in 125 cc. of ether. After forty minutes the precipitate of  $\alpha$ -bromo-3-propionylphenanthrene was filtered off; an additional quantity of the compound was obtained by evaporation of the filtrate after the latter had been treated with anhydrous sodium carbonate in order to neutralize the hydrogen bromide.  $\alpha$ -Bromo-3-propionylphenanthrene crystallizes from methyl alcohol and benzene in the form of long colorless needles; m. p. 117–118°; yield, 20 g. (70%).

*Anal.* Calcd. for  $C_{17}H_{13}OBr$ : Br, 25.6. Found: Br, 26.3.

For the preparation of the 2-isomer 10 g. of 2-propionylphenanthrene was treated with 2.2 cc. of bromine in 800 cc. of ether; after two hours the mixture was worked up in the manner described for the 3-isomer.  $\alpha$ -Bromo-2-propionylphenanthrene crystallizes from benzene-alcohol in colorless plates; m. p. 131.5–133°; yield 11 g. (82%).

*Anal.* Calcd. for  $C_{17}H_{13}OBr$ : Br, 25.6. Found: Br, 25.5.

**$\beta$ -Phenanthroylbutyric Acids.**—Five grams of  $\alpha$ -bromo-3-propionylphenanthrene was added to a solution of sodio-

malonic ester which had been prepared from 5 g. of malonic ester and 0.5 g. of sodium in 20 cc. of benzene. After being refluxed for four hours the mixture was hydrolyzed and the substituted malonic ester was heated with 40 cc. of 5% sodium hydroxide solution. From the aqueous solution the phenanthrolyl-isoglutaric acid was obtained by acidification. The acid was decarboxylated by heating a suspension of the acid in water for three hours. The  $\beta$ -(3-phenanthrolyl)-butyric acid which was formed was purified through its ammonium salt followed by recrystallization of the acid from acetic acid.  $\beta$ -(3-Phenanthrolyl)-butyric acid crystallizes from acetic acid in colorless prisms; m. p. 144–146°; yield 1.5 g. (32%).

*Anal.* Calcd. for  $C_{19}H_{16}O_3$ : C, 78.1; H, 5.5. Found: C, 78.0; H, 5.6.

In a similar manner  $\alpha$ -bromo-2-propionylphenanthrene was condensed with sodiomalonic ester. The substituted malonic acid which was obtained was heated at 180° for one hour in order to decarboxylate it to  $\beta$ -(2-phenanthrolyl)-butyric acid. The latter acid was obtained as fine colorless crystals from acetic acid; m. p. 173–174°; yield 32%.

*Anal.* Calcd. for  $C_{19}H_{16}O_3$ : C, 78.1; H, 5.5. Found: C, 78.0; H, 5.8.

### Summary

2- and 3-Propionylphenanthrene have been isolated from the reaction between propionyl chloride, phenanthrene and aluminum chloride in nitrobenzene. The same ketones in addition to 9-propionylphenanthrene have been synthesized from the corresponding cyanophenanthrenes through the Grignard reaction.

$\beta$ -(2-Phenanthrolyl)-butyric acid and  $\beta$ -(3-phenanthrolyl)-butyric acid have been synthesized.

ANN ARBOR, MICHIGAN

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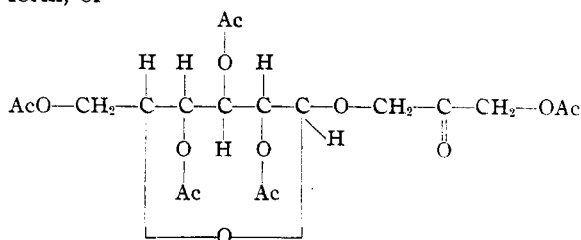
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## The Mechanism of Carbohydrate Oxidation. XX.<sup>1</sup> The Preparation of Oligosaccharide Acetates Containing Dihydroxyacetone Constituents

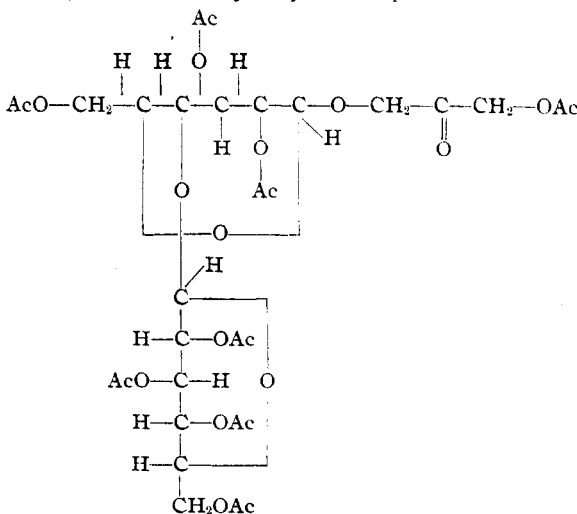
BY LEONARD C. KREIDER AND WM. LLOYD EVANS

When Evans and Hockett<sup>2</sup> advanced a mechanism to explain the action of potassium hydroxide on gentiobiose (6-glucosidoglucose) to produce lactic acid, they pointed out that 3-glucosidoglyceraldehyde was a theoretically possible intermediate in this degradation. In the alkaline environment of this reaction it is possible for this glyceraldehyde derivative to undergo the well-known Lobry de Bruyn and van Ekenstein rearrangement to give 3-glycosidodihydroxyacetone. In order to test the Evans and Hockett mechanism it was desirable to subject a 3-glucosidotriose, the postulated reaction intermediate, to the action of potassium hydroxide. At that time glucosidotrioses were unknown. We then succeeded in devising a general method for the synthesis of oligosaccharides that contain dihydroxyacetone as the reducing portion of the molecule. This synthesis has already been applied to the preparation of 3-glucosidodihydroxyacetone (described in a preliminary report<sup>3</sup>),  $\beta$ -*d*- and  $\beta$ -*l*-arabinosidodihydroxyacetone and  $\beta$ -*d*- and  $\beta$ -*l*-xylosidodihydroxyacetone, all as their acetates.<sup>1</sup> The present paper gives detailed direc-

tions for the preparation, in a pure crystalline form, of



$\beta$ -*d*-Glucosidodihydroxyacetone pentaacetate



$\beta$ -Cellobiosidodihydroxyacetone octaacetate

(1) Number XIX of this series: L. C. Kreider and W. L. Evans, *THIS JOURNAL*, **58**, 797 (1936).

(2) W. L. Evans and R. C. Hockett, *ibid.*, **53**, 4384 (1931).

(3) L. C. Kreider and W. L. Evans, *ibid.*, **57**, 229 (1935).