

duced hydroxyanthraquinone weighed 1.7 g. Oxidation of this material with sodium dichromate in acetic acid solution yielded an impure hydroxyanthraquinone. It seems probable, however, that a suitable oxidation process might be found whereby pure 2-hydroxyanthraquinone could be obtained from the reduction product.

### Summary

The benzoate of 4-hydroxydiphenyl, when heated with aluminum chloride, yields 4-(*p*-hydroxy-phenyl)-benzophenone. Diphenyl phthalate, treated in a similar manner, is converted into phenolphthalein and 1-hydroxyanthraquinone. Phenyl 2-(methoxybenzoyl)-benzoate is changed quantitatively by aluminum chloride into phenolphthalein.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 678]

## SOME ALPHA-ALKYLCINNAMIC ACIDS AND THEIR DERIVATIVES

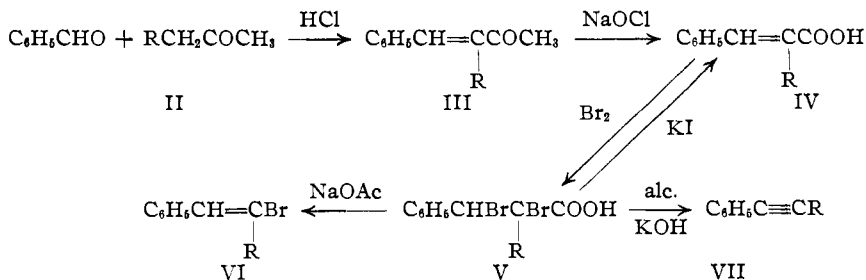
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### Introduction

The phenomenal success of  $\alpha$ -amylcinnamic aldehyde and other  $\alpha$ -alkylcinnamic aldehydes as perfume bases, led us to prepare several of the corresponding methyl ketones (methyl-( $\alpha$ -alkyl-)-styryl ketones) (III). These were synthesized by condensing benzaldehyde with alkyl acetones (II) by means of hydrogen chloride. The methyl ( $\alpha$ -alkyl-)-styryl ketones are readily converted to the  $\alpha$ -alkylcinnamic acids (IV) by means of sodium hypochlorite. The acids, in turn, are of interest, since, through their dibromides (V), they may be transformed into the  $\beta$ -alkyl- $\beta$ -bromostyrenes (VI), or into the alkylphenylacetylenes (VII).

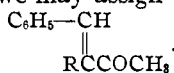


The dibromides are also readily reconverted to the  $\alpha$ -alkylcinnamic acids by means of potassium iodide.

Since the  $\alpha$ -alkyl cinnamic acids obtained were of the *trans* configuration

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(absence of indone formation with sulfuric acid),<sup>2</sup> we may assign the *trans* configuration (VIII) to the corresponding ketones<sup>3</sup>



Ethyl, *n*-propyl, *n*-butyl and *n*-amyl derivatives are reported in this paper. The attempt to prepare the isopropyl derivatives by starting with isopropyl acetone,  $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$ , gave an anomalous result, since it was not found possible to prepare a solid oxime from the supposed methyl ( $\alpha$ -isopropyl)-styryl ketone, nor to oxidize it to  $\alpha$ -isopropylcinnamic acid.<sup>4</sup> In this connection it is interesting to note that the application of the Perkin synthesis to the preparation of  $\alpha$ -isopropylcinnamic acid gives only a very small yield of that acid besides considerable  $\beta$ -isopropylstyrene.<sup>5</sup>

## Experimental

TABLE I  
METHYL ( $\alpha$ -ALKYL)-STYRYL KETONES

R	Reference	B. p., °C. (Mm.)	Analysis				M. p. of oxime, <sup>a</sup> °C.	Nitrogen in oxime Calcd. Found	
			Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found			
H	<i>Ann.</i> , 294, 275 (1897)	151-153 (25)					115-116		
CH <sub>3</sub>	<i>Ber.</i> , 35, 970 (1902)	127-130 (12)					103-104		
C <sub>2</sub> H <sub>5</sub>	<i>Ber.</i> , 35, 3090 (1902)	120-130 <sup>b</sup> (18)					85		
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	This paper	142-143 (14)	83.0	82.3	8.5	8.7	70	6.9	6.3
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	This paper	155-156 (15)	83.2	82.7	8.9	9.1	61	6.5	6.2
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	This paper	161-162 (14)	83.3	82.7	9.3	9.3	71	6.1	5.8

<sup>a</sup> Prepared by the method of Harries and deOsa, *Ber.*, 36, 2998 (1903). <sup>b</sup> This paper, 144-145° (22 mm.).

One-half mole of benzaldehyde was mixed with one mole of the alkyl acetone<sup>6</sup> and one-fourth mole of hydrogen chloride gas passed into the cooled mixture. The mixture, which soon became red, was then shaken for sixteen to twenty hours. At the end of this time the water formed in the reaction had separated as aqueous hydrochloric acid and was removed. Without further treatment, the oil was distilled under diminished pressure (about 20 mm.). Somewhat more than half of the alkyl acetone was recovered and a small residue, probably consisting of dibenzal-alkyl acetone (styryl- $\alpha$ -alkyl)-styryl ketone), remained in the flask. The principal fraction, consisting of crude methyl ( $\alpha$ -alkyl)-styryl ketone, was obtained in a yield of about 90% based on the alkyl acetone consumed, or about 75% based on the benzaldehyde employed. The crude

<sup>2</sup> Stoermer and Voht, *Ann.*, 409, 55 (1915).

<sup>3</sup> See Bogert and Davidson, *This Journal*, 53, 3122 (1931), for a discussion of the configuration of  $\alpha$ -amylcinnamic aldehyde.

<sup>4</sup> According to Gheorghiu and Arwentiew, *J. prakt. Chem.*, [2] 118, 295 (1928), the condensation product obtained by the action of hydrogen chloride on a mixture of benzaldehyde and isopropyl acetone has the constitution  $\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_2\text{CH}(\text{CH}_3)_2$  rather than  $\text{C}_6\text{H}_5\text{CH}=\text{CCOCH}_3$ .



<sup>5</sup> Schaarschmidt, Georgeacopol and Herzenberg, *Ber.*, 51, 1059 (1918).

<sup>6</sup> Ethyl acetone was prepared by the oxidation of methyl propyl carbinol. Propyl and amyl acetones were purchased from Akatos, Inc. Butyl acetone was synthesized according to "Organic Syntheses," 7, 60 (1927).

alkyl acetone fraction was treated with one-half mole of benzaldehyde and sufficient alkyl acetone to replace that consumed in the first reaction. Hydrogen chloride was then added and the reaction carried out as before. The process was repeated three times but could probably be carried on indefinitely. By using two moles of alkyl acetone to one of benzaldehyde and reworking the recovered alkyl acetone in this way, the amount of dibenzal derivative formed was greatly reduced, with consequent improvement in the yield of the desired product. The crude methyl ( $\alpha$ -alkyl)-styryl ketone may be used directly for the preparation of the  $\alpha$ -alkylcinnamic acids. To purify it, the crude product was washed with saturated sodium bisulfite, followed by water and then treated with alcoholic potassium hydroxide, thrown into water, acidified with acetic acid, extracted with benzene, dried over sodium sulfate and distilled. A middle fraction was taken for analysis. The methyl ( $\alpha$ -alkyl)-styryl ketones are liquids having a greenish-yellow tinge, with a floral odor which resembles, but is much weaker than, that of the  $\alpha$ -alkylcinnamic aldehydes.

TABLE II  
*Trans*- $\alpha$ -ALKYLCINNAMIC ACIDS

R	Reference	M. p., °C.	Equivalent Weight		Analysis			
			Calcd.	Found	Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found
H	Ger. Pat. 21,162 (1882)	133						
CH <sub>3</sub>	<i>Ber.</i> , 35, 3552 (1902)	81-2 (74 mm.)						
C <sub>2</sub> H <sub>5</sub>	<i>Ann.</i> , 409, 57 (1915)	104-105 (this paper, 107°)						
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	This paper	93	190	190	75.8	75.8	7.4	7.3
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>Ber.</i> , 34, 929 (1901)	83-84						
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	This paper	80	218	218	77.0	77.0	8.3	8.2

To one-tenth mole of crude methyl ( $\alpha$ -alkyl)-styryl ketone dissolved in 200 cc. of alcohol and chilled in a freezing mixture was added with stirring a solution of one mole of sodium hydroxide in 100 cc. of water into which *three-tenths mole of chlorine had been passed in the cold*. The temperature was kept below 20°, the addition requiring about fifteen minutes. The mixture was then stirred for an hour at room temperature. At this stage two layers were present as well as some solid salt. The mixture was distilled, chloroform coming over first, then alcohol and water and finally some oily material. About 250 cc. of distillate was collected. The residue separated into two layers, an aqueous layer and one consisting of the molten sodium  $\alpha$ -alkylcinnamate. On cooling, the latter solidified and was removed. This was dissolved in several hundred cc. of boiling water, the solution clarified with Norite and finally acidified with hydrochloric acid. Fine white needles of the  $\alpha$ -alkylcinnamic acid separated. Recrystallization from 75% acetic acid gave an odorless, colorless product; yield, about 80%. For analysis, the acids were recrystallized several times from 75% acetic acid and then several times from dilute alcohol.

TABLE III  
 $\alpha$ -ALKYLCINNAMIC ACID DIBROMIDES (HIGHER MELTING FORMS)

R	Reference	M. p., °C.	Analysis			
			Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
H	<i>J. Chem. Soc.</i> , 83, 669 (1903)	203-204				
CH <sub>3</sub>	<i>Ber.</i> , 21, 276 (1889)	137				
C <sub>2</sub> H <sub>5</sub>	This paper	99-100	39.3	39.4	3.6	3.6
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	This paper	149-150	41.3	40.7	4.0	4.0
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	This paper	109-110	42.9	43.1	4.4	4.3
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	This paper	143-144	44.5	43.7	4.8	4.6

According to the method of Sudborough and Thompson<sup>7</sup> one-tenth mole of finely pulverized  $\alpha$ -alkylcinnamic acid was placed in a wide-mouthed glass-stoppered bottle, into which was lowered a test-tube containing 0.11 mole of bromine. The bottle was sealed and allowed to stand for one to two weeks. During this time the solid was occasionally turned over to expose it more thoroughly to the action of the bromine vapor. The gain in weight of the acid was almost theoretical. The slightly sticky solid was triturated with petroleum ether, filtered and washed with petroleum ether. A pulverulent solid, melting about ten degrees below the pure dibromide was obtained in yields of from 75 to 90%. After several crystallizations from carbon tetrachloride + petroleum ether, it was obtained in dense sugar-like crystals of constant melting point.

**Reduction of the  $\alpha$ -Alkylcinnamic Acid Dibromides.**—0.01 Mole of the dibromide was refluxed for twenty minutes with 0.04 mole of potassium iodide in 25 cc. of alcohol. The mixture was thrown into dilute sodium bisulfite. The theoretical quantity of crude acid was obtained, which when recrystallized from 75% acetic acid gave the pure  $\alpha$ -alkylcinnamic acid; yield, 75%.

TABLE IV  
 $\beta$ -ALKYL  $\beta$ -BROMOSTYRENES

R	Reference	B. p., °C. (Mm.)	Analysis			
			Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
H	<i>Ber.</i> , 42, 2878 (1909)	218–220				
CH <sub>3</sub>	<i>Ber.</i> , 21, 276 (1889)	226				
C <sub>2</sub> H <sub>5</sub>	This paper	126–128 (23)	56.8	57.2	5.2	5.5
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	This paper	138–140 (22)	58.7	59.3	5.8	5.9
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	This paper	148–150 (20)	60.2	60.7	6.3	6.6
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	This paper	161–162 (18)	61.6	61.9	6.7	6.8

One-tenth mole of  $\alpha$ -alkylcinnamic acid dibromide, 100 cc. of alcohol and 0.11 mole of sodium acetate trihydrate were heated by means of an air-bath in a bulb attached to an empty upright bulb condenser, which, in turn, was connected to a downward condenser. The reaction took place immediately with the evolution of carbon dioxide and the separation of sodium bromide. The heating was continued until 90 cc. of alcohol had been recovered. Brine was then added to the residue and the product steam distilled, the water in the condensate being returned to the boiler. The oil was separated and dried; yield of crude, about 85%. The bromostyrenes are greenish-tinted oils which are heavier than water, and possess a harsh floral odor.

TABLE V  
ALKYLPHENYLACETYLENES

R	Reference	B. p., °C. (Mm.)	Analysis			
			Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
H	THIS JOURNAL, 44, 425 (1922)	142–143				
CH <sub>3</sub>	<i>Ber.</i> , 21, 276 (1889)	185				
C <sub>2</sub> H <sub>5</sub>	<i>J. Chem. Soc.</i> , 29, 162 (1876)	201–203				
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	This paper	102–103 (18.5)	91.7	90.9	8.3	8.5
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	This paper	119–121 (18)	91.1	91.1	8.9	8.8
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	This paper	126–127 (15)	90.7	89.9	9.3	9.0

Earlier methods of preparation for this group involved the alkylation of phenylacetylene or the dehalogenation of a halostyrene. The following procedure yielded the alkylphenylacetylene directly from the cinnamic acid dibromide.

<sup>7</sup> Sudborough and Thompson, *J. Chem. Soc.*, 83, 669 (1903).

One-tenth mole of  $\alpha$ -alkylcinnamic acid dibromide (or the crude product obtained by adding one-tenth mole of bromine to one-tenth mole of  $\alpha$ -alkylcinnamic acid in carbon tetrachloride and then evaporating the carbon tetrachloride with a current of air) was gradually added to a solution of 0.7 mole of potassium hydroxide in 100 cc. of alcohol. Sufficient heat was evolved to cause the mixture to boil. Most of the alcohol was then removed with the aid of a column. Water was added to the residue and the product steam distilled, the water in the distillate being returned to the boiler. The oil was separated and dried; yield of crude, about 70%. These acetylenes are colorless oils, lighter than water, with a "green-leaf" odor resembling methyl heptene carbonate.

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### Summary

Condensation of benzaldehyde with ethyl, *n*-propyl, *n*-butyl and *n*-amyl acetone yielded the corresponding methyl ( $\alpha$ -alkyl-)-styryl ketones, which were converted into the  $\alpha$ -alkylcinnamic acids by means of sodium hypochlorite. These acids, through their dibromides, were converted into the  $\beta$ -alkyl- $\beta$ -bromostyrenes and the alkylphenylacetylenes.

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## THE OZONIDES OF ORTHO-XYLENE AND THE STRUCTURE OF THE BENZENE RING<sup>1</sup>

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### Introduction

The problem of the existence and the position of ethylenic linkages in benzene with the possibility of the existence of isomeric ortho-disubstitution products has been the subject of many interesting speculations ever since Kekulé<sup>3</sup> advanced his theory of the structure of the benzene nucleus. Some results have been published<sup>4</sup> which indicate the occurrence of such isomers.

Harries and his co-workers<sup>5</sup> have described osazone derivatives of the decomposition products of ozonides of benzene and mesitylene. It seemed

<sup>1</sup> Presented before the Organic Division of the American Chemical Society at its 80th meeting in Cincinnati, 1930.

<sup>2</sup> Abstract of a thesis presented to the Graduate Faculty by A. G. Cole in partial fulfillment of the requirements for the degree of Master of Science.

<sup>3</sup> Kekulé, *Ann.*, **137**, 158 (1866).

<sup>4</sup> Borsche and Bahr, *ibid.*, **402**, 81 (1913); Hodgson, *Chem. Abstracts*, **21**, 572 (1927).

<sup>5</sup> Harries, "Ozone and seine Einwirkung," Julius Springer, Berlin, 1916.