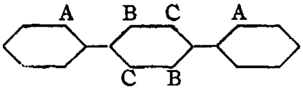
Summary

1. Two stereoisomeric 3,6-di-(2,4-dimethylphenyl)-2,5-dibromodihydroquinones and some derivatives have been prepared.

2. These substances are the racemic and the meso modifications of a molecule of the following type



3. It may be concluded that the same conditions which cause optical isomerism in the diphenyl series also exist in the terphenyl series.

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[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

MIXED BENZOINS. II

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In continuation of the work described in Part I,[1] six new benzoins, together with their benzils and desoxy compounds have been prepared. The work described cannot be said to support, or detract from, the theoretical conclusions advanced in Part I, as data on the reactivity of the aldehydes are lacking. The benzoins described in the present paper were all prepared in the usual manner, by mixing the reactants and refluxing, as it was found that the technique earlier described gave little, if any, better yields in the present cases. The results described in Part I and Part II represent the best that can be obtained by fractionation methods, and it is evident that further knowledge can only be attained by complete analysis of the reaction mixtures. It is hoped to carry this out in some cases.

Attention was given to the possibility of the occurrence of isomeric mixed benzoins, but no examples were found. Their occurrence, however, is not excluded, as in general only about one-half of the reactants was accounted for. The mixed benzoins described are very probably individuals and not mixtures or addition compounds, as in each case only one desoxy compound was obtained on reduction.

The mixed benzoins described are not specifically named, as it is not possible to assign either of the two alternative structures with any degree of probability.

Experimental

Benzoin from *p*-Dimethylaminobenzaldehyde and Anisaldehyde, (A).—Seven and one-half grams of *p*-dimethylaminobenzaldehyde, and 7.0 g. of anisaldehyde, dis-

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[1] Buck and Ide, THIS JOURNAL, 52, 220 (1930).

solved in 50 cc. of 50% alcohol, were refluxed for two and one-half hours with 4.0 g. of potassium cyanide. The product, recrystallized from alcohol, forms white flakes, moderately soluble in alcohol and very soluble in ether, benzene and ligroin; yield 52%. The product melts at 144° (uncorr.).

Anal. Calcd. for $C_{17}H_{19}O_3N$: N, 4.91. Found: N, 4.67.

Benzoin from *p*-Chlorobenzaldehyde and Piperonal, (B).—This benzoin was prepared by refluxing a solution of 3.5 g. of *p*-chlorobenzaldehyde, 3.8 g. of piperonal and 5.0 g. of potassium cyanide in 50 cc. of 50% alcohol for two hours. The yield was 40%. On recrystallization from alcohol the compound forms yellow needles melting at 110° (uncorr.). It is moderately soluble in alcohol, very soluble in ether and chloroform and slightly soluble in benzene and ligroin.

Anal. Calcd. for $C_{15}H_{11}O_4Cl$: C, 61.95; H, 3.79. Found: C, 61.81; H, 3.68.

Benzoin from *o*-Chlorobenzaldehyde and Anisaldehyde, (C).—Seven grams of *o*-chlorobenzaldehyde, 6.8 g. of anisaldehyde and 4.0 g. of potassium cyanide, dissolved in 75 cc. of 50% alcohol, were refluxed for two hours. On standing crystals separated. After recrystallization from alcohol, the compound forms colorless, hexagonal crystals, melting at 84° (uncorr.). It is moderately soluble in alcohol and ligroin and very soluble in benzene, ether and chloroform; yield 60%.

Anal. Calcd. for $C_{15}H_{13}O_3Cl$: Cl, 12.83. Found: Cl, 12.72.

Benzoin from *o*-Chlorobenzaldehyde and Veratric Aldehyde, (D).—A solution of 8.3 g. of veratric aldehyde, 7.0 g. of *o*-chlorobenzaldehyde and 4.0 g. of potassium cyanide in 75 cc. of 50% alcohol was refluxed for two and one-half hours. On cooling the product crystallized out. After recrystallization from alcohol the compound forms fine white needles, melting at 140° (uncorr.). It is moderately soluble in alcohol, ligroin and benzene and very soluble in ether and chloroform; yield 70%.

Anal. Calcd. for $C_{16}H_{15}O_4Cl$: Cl, 11.57. Found: Cl, 11.30.

Benzoin from *m*-Chlorobenzaldehyde and *p*-Dimethylaminobenzaldehyde, (E).—The compound was prepared by refluxing, for two hours, a solution of 7.0 g. of *m*-chlorobenzaldehyde, 7.5 g. of *p*-dimethylaminobenzaldehyde and 4.0 g. of potassium cyanide in 75 cc. of 50% alcohol. After recrystallization from alcohol, the benzoin forms either large dark brown rhombs, or small yellow rhombs, both forms melting at 140° (uncorr.) and showing no depression when mixed. On reduction both gave the same desoxy compound. The compound is moderately soluble in benzene, alcohol and ether, slightly soluble in ligroin and very soluble in chloroform: yield 45%.

Anal. Calcd. for $C_{16}H_{16}O_2NCl$: Cl, 12.24. Found: Cl, 11.98.

Benzoin from *m*-Bromobenzaldehyde and Anisaldehyde, (F).—Seven grams of anisaldehyde, 9.3 g. of *m*-bromobenzaldehyde and 4.0 g. of potassium cyanide, dissolved in 50 cc. of 50% alcohol, were refluxed for two and one-half hours. The oil which separated was crystallized from alcohol. After recrystallization the compound forms yellow cubes, melting at 88° (uncorr.). It is moderately soluble in alcohol, benzene, ether and ligroin and very soluble in chloroform: yield 20%.

Anal. Calcd. for $C_{15}H_{13}O_3Br$: C, 56.04; H, 4.08. Found: C, 55.79; H, 3.91.

It should be pointed out that in the preparation of some mixed benzoins considerable patience is necessary to induce crystallization of the crude products, prolonged exposure of the solutions to temperatures around 0° sometimes being required. The authors have obtained clear indications of the formation of a number of other mixed benzoins but as yet have not succeeded in isolating sufficient crystalline material to justify descriptions of the experiments.

Benzil Derivatives.—The mixed benzoin (usually 2.0 g. was taken) dissolved in alcohol was oxidized with a slight excess of Fehling's solution and recrystallized from alcohol until pure. There is, of course, no ambiguity in the structure. The benzils are tabulated in Table I.

TABLE I

BENZIL DERIVATIVES

Formula	Benzoin	M. p., °C.	Yield, %	Appearance	Analysis, %		
						Calcd.	Found
$Me_2NC_6H_4COCOC_6H_4OMe$	A	128	85	Yellow hexagons	N	4.94	4.79
p-$ClC_6H_4COCOC_6H_3O_2H_2C$	B	132	78	Fine yellow needles	C	62.38	62.24
					H	3.12	2.99
o-$ClC_6H_4COCOC_6H_4OMe$	C	104	70	Yellow rhombs	Cl	12.92	13.02
o-$ClC_6H_4COCOC_6H_3(OMe)_2$	D	117	85	Yellow rhombs	C	63.04	63.00
					H	4.31	4.40
m-$ClC_6H_4COCOC_6H_4NMe_2$	E	130	90	Slender amber plates	C	66.77	66.53
					H	4.91	5.21
m-$BrC_6H_4COCOC_6H_4OMe$	F	94	88	Fine yellow needles	C	56.42	56.22
					H	3.48	3.62

TABLE II

DESOXY COMPOUNDS

Formula	Benzoin	M. p., °C.	Yield, %	Appearance	Analysis, %			
					Calcd.		Found	
					C	H	C	H
$C_{17}H_{19}O_2N$	A	130	88	White flakes	75.79	7.06	75.50	7.33
$C_{15}H_{11}O_3Cl$	B	113	80	White needles	65.56	4.01	65.72	4.09
$C_{15}H_{13}O_2Cl$	C	96	85	White prisms	69.08	5.03	69.00	4.91
$C_{16}H_{15}O_3Cl$	D	110	80	White needles	66.07	5.20	66.44	5.26
$C_{16}H_{16}ONCl$	E	125	80	White needles	70.18	5.89	69.90	5.99
$C_{15}H_{13}O_2Br$	F	54	86	Fine white flakes	59.01	4.30	58.82	4.24

Desoxy Compounds.—These were prepared in general by refluxing 2.0 g. of mixed benzoin, 3 cc. of concentrated hydrochloric acid, 10 cc. of alcohol and 2.0 g. of tin with a trace of copper sulfate for five to six hours. The product was then crystallized from alcohol. The structure naturally depends on that of the parent benzoin and at present it is not possible to decide between the two alternative structures. Only one desoxy compound was obtained from each benzoin, indicating that the latter was a definite compound, not a mixture of two isomers (see Table II).

Summary

In continuation of previous work, six new mixed benzoins have been isolated and their benzils and desoxy compounds prepared.

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