Oximination of Benzylacetomesitylene (XII).—To a solution of 4.6 g. of sodium in 100 cc. of methyl alcohol was added 23.5 g. of amyl nitrite. Slowly and with shaking 25 g. of benzylacetomesitylene was added to the solution. It was tightly stoppered and allowed to stand in the refrigerator for several days. No solid separated out. The solution was poured into water and extracted with ether. The ether was evaporated off and the oil crystallized from dilute alcohol. There resulted 25 g. of a pale yellow solid, whose melting point and mixed melting point with the oxime of mesityl benzyl glyoxal was 87°.

The Oxime Benzoate (XIV).—A chilled solution of 5.62 g. of the oxime in 10 cc. of pyridine was added to a chilled mixture of 4.3 g. of benzoyl chloride and 25 cc. of pyridine and allowed to stand at room temperature for four hours. The reaction mixture was decomposed by pouring into ice and hydrochloric acid. It was extracted with ether, washed with water, dried over calcium chloride and concentrated. Addition of petroleum ether caused an almost quantitative precipitation of a colorless crystalline product.

Anal. Calcd. for $C_{25}H_{23}O_3N$: C, 77.9; H, 6.0. Found: C, 77.6; H, 6.0.

The oxime benzoate of mesitylbenzylglyoxal melts at 95°; insoluble in 5% sodium hydroxide. When 1 g. of the substance is heated above its melting point it decomposes violently, turning reddish-brown. The decomposition products are taken up in ether, and washed with sodium carbonate solution. The alkaline solution yields benzoic and trimethylbenzoic acids, separated by sublimation and identified by their melting points and mixed melting points. The ethereal solution yields benzyl cyanide, identified as benzalbenzyl cyanide.

The Semicarbazone (XV).—A solution of 3 g. of the alpha diketone in 25 cc. of alcohol was warmed with an aqueous solution of 3 g. of semicarbazide hydrochloride and 3 g. of anhydrous sodium acetate. Upon dilution with water there was precipitated a pale yellow solid, which after crystallization from alcohol melted at 227°.

Anal. Calcd. for $C_{19}H_{21}O_2N_3$: C, 70.6; H, 6.5. Found: C, 70.2; H, 6.6.

Summary

The results of the study of mesitylbenzylglyoxal show that di-ortho substituents in the mesityl group offer steric hindrance to all addition reactions to the carbonyl groups except in the case of reduction.

The di-ortho substituents seem to stabilize the enol and do not hinder addition to oxygen of the carbonyl groups.

WASHINGTON, D. C. RECEIVED MARCH 23, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 119]

The Preparation of Substituted *o*-Aroylbenzoic Acids in the Identification of Aromatic Hydrocarbons[1]

BY H. W. UNDERWOOD, JR., AND WILLIAM L. WALSH

At present there exists no satisfactory general method for the identification of aromatic hydrocarbons. Nitration and oxidation to quinones, while satisfactory procedures in certain cases, do not constitute methods applicable to all compounds of this class. Likewise, oxidation of side chains is not only limited in scope, but difficult to carry out on a small scale and valueless in distinguishing aromatic hydrocarbons containing different groups in the side chain such as methyl, ethyl, propyl, etc.

The present method has been applied, with minor modifications in individual cases, to a large number of aromatic hydrocarbons. It consists in the formation of crystalline acids which, for more positive identification, may be titrated and in certain cases dehydrated to the corresponding substituted anthraquinones. The melting points of the derivatives are for the most part scattered over a wide range, thereby facilitating identification. In the case of ethylbenzene, *m*- and *p*-xylenes (b. p. 136, 139, 138°, respectively) the melting points of the *o*-aroylbenzoic acids resulting from their condensation with phthalic anhydride lie too close together to make identification positive (m. p. 122, 126, 132°, respectively). Accordingly, tetrachlorophthalic anhydride has been substituted for phthalic anhydride, yielding *o*-aroyltetrachlorobenzoic acids (m. p. 173, 224, 246°, respectively) which possess the additional advantages of increased molecular weight and superior crystallizing properties.

A summary of the results is given in Table I, in which A represents the aromatic hydrocarbon used; B, the procedure described in the experimental part for the preparation of the derivative; C, the melting point of the corresponding *o*-aroylbenzoic acid; D and E, the theoretical and actual neutralization equivalents of each acid; F, the percentage by volume of alcohol in the dilute

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[1] Due to the death of Professor Underwood the present paper has been prepared by the junior author.

aqueous alcohol solution used in the recrystallization; and G, the volume in cc. of such a solution.

The neutralization equivalents included in the following table were calculated by titrating 0.1-g. samples of the acids dissolved or suspended in 10 cc. of neutral alcohol with 0.1 *N* sodium hydroxide using phenolphthalein as the indicator. The corresponding *o*-aroylbenzoic acid derivatives of anthracene and phenanthrene have been excluded from the above table due to the extreme difficulty involved in their purification. However this omission should constitute no serious objection since these hydrocarbons may be readily identified by oxidation to the corresponding quinone or by the preparation of their picrates.

Table I

Melting Points, Neutralization Equivalents, etc., of Aroylbenzoic Acids

All melting points given in this paper are uncorrected

A	B	C	D	E	F	G
Benzene	I	127–128	226	225	30	10
Toluene	I	137–138	240	239	30	10
Mesitylene	I	211–212	268	270	80	10
m-Diethylbenzene	I	114–116	282	280	30	10
1,3,5-Triethylbenzene	I	129.5–130.5	310	312	50	10
Tetralin	I	153–155	280	278	30	10
Naphthalene	I	172–173	276	279	30	20
Acenaphthene	I	198–200	302	300	50	30
Diphenyl	I	224–225	302	301	80	20
Fluorene	I	227–229	314	313	50	30
Durene	I	263–265	282	278	40	30
n-Propylbenzene	II	125–126	268	270	30	10
n-Butylbenzene	II	97–98	282	283	30	10
Cumene	II	133–134	268	266	30	10
Cymene	II	123–124	282	284	30	10
Ethylbenzene	III	172–173	392	394	70	20
o-Xylene	III	177.5–178.5	392	391	70	20
m-Xylene	III	222–224	392	394	80	20
p-Xylene	III	244–246	392	393	40	20

Experimental

Procedure I.—To an intimate mixture of 0.4 g. of phthalic anhydride and 0.8 g. of anhydrous aluminum chloride in a dry 15-cm. test-tube are added 10 cc. of carbon bisulfide and about 0.4 g. of the hydrocarbon to be identified. The mixture is heated under reflux on a water-bath until no more hydrogen chloride is evolved, then the test-tube is removed and cooled under the tap. If the mixture separates into two layers the upper carbon bisulfide layer is decanted; if it does not, 10 cc. of 6 *N* hydrochloric acid is added, drop by drop at first, and later in 1-cc. portions with frequent stirring. The resulting product, if solid, is separated by filtration and washed with two 5-cc. portions of cold water. If a viscous liquid separates, the mixture is cooled in an ice-bath until it solidifies; the aqueous layer is decanted and the residue is washed in the test-tube with two 5-cc. portions of cold water. The product in either case is transferred to a small beaker and boiled for one minute with a mixture of 10 cc. of 6 *N* ammonium hydroxide, 20 cc. of water and about 0.1 g. of decolorizing carbon. (In the case of the acid resulting from the condensation of durene an additional 80 cc. of water must be used in order to dissolve the difficultly soluble ammonium salt.) The solution is filtered by suction while hot and the filtrate is poured onto about 25 g. of crushed ice contained in a small beaker, then acidified with 6 *N* hydrochloric acid with stirring. After standing for ten minutes the precipitate of aroyl benzoic acid is brought upon a filter, washed with small portions of water until free from acid and dried in air. The product is recrystallized to constant melting point in the volume of dilute alcohol specified in Table I.

Procedure II.—In this case the same general method is employed except that 2.4 g. of anhydrous aluminum chloride, 1.2 g. of phthalic anhydride, 1 cc. of hydrocarbon and 10 cc. of carbon bisulfide are used. At the end of the reaction the test-tube is cooled under the tap, the carbon bisulfide layer is decanted and 15 cc. of 6 *N* hydrochloric acid is added with the precautions previously mentioned. After cooling the mixture in an ice-bath the aqueous layer is decanted and the oily product is washed with two 5-cc. portions of cold water. To remove the unconverted hydrocarbon, a current of steam is passed through this mixture until the odor of the former is no longer perceptible. The aqueous layer is then decanted and the residue extracted under reflux with three 20-cc. portions of ligroin (b. p. 90–120°). The combined ligroin extractions are cooled in an ice-bath and the gummy precipitate of aroylbenzoic acid which appears is allowed to stand with occasional stirring until it becomes granular. The solid is collected on a filter, dried in air and finally recrystallized as specified in Table I.

A further modification of Procedure II is necessary for the preparation of the derivative of cymene. After acidification of the reaction mixture with 6 *N* hydrochloric acid the aqueous layer is decanted and the product is dissolved in 5 cc. of 6 *N* sodium carbonate solution in a small beaker. The solution is evaporated to dryness over a small flame with constant shaking to prevent spattering. To the resulting solid is added 20 cc. of boiling benzene, after which it is brought on a filter and extracted with 5-cc. of boiling alcohol. It is then dissolved in 20 cc. of cold water and the solution is acidified with 6 *N* hydrochloric acid. The precipitate is collected on a filter, washed well with water, dried in air and recrystallized from 30% aqueous alcohol.

Procedure III.—The same general procedure is likewise followed in this case except that 0.8 g. of tetrachlorophthalic anhydride,[2] 1.0 g. of anhydrous aluminum chloride, 0.4 g. of hydrocarbon and 10 cc. of carbon bisulfide are used. The solid product left after treatment with hydrochloric acid is collected on a filter and extracted with two 10-cc. portions of boiling water to remove traces of tetrachlorophthalic acid. It is then transferred to a small beaker and boiled for one minute with a mixture of 20 cc. of 6 *N* ammonium hydroxide, 50 cc. of water, and about 0.1 g. of decolorizing carbon. The hot solution is filtered

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(2) Prepared by heating tetrachlorophthalic acid for eight hours at 110°.

TABLE II

ANALYSES

	Calcd.		Found			
	Cl, %		Cl, %			
o-(2,3-Dimethylbenzoyl)-tetrachlorobenzoic acid	36.18		36.24	36.37		
o-(2,4-Dimethylbenzoyl)-tetrachlorobenzoic acid	36.18		36.08	36.23		
o-(2,5-Dimethylbenzoyl)-tetrachlorobenzoic acid	36.18		36.25	36.13		
o-(4-Ethylbenzoyl)-tetrachlorobenzoic acid	36.18		36.03	36.14		
2,3-Dimethyl-5,6,7,8-tetrachloroanthraquinone	37.94		37.86	37.83		
	C, %	H, %	C, %		H, %	
o-(4-*n*-Butylbenzoyl)-benzoic acid	76.61	6.38	76.57	76.67	6.45	6.49
o-(2,4-Diethylbenzoyl)-benzoic acid	76.61	6.38	76.54	76.58	6.31	6.51
o-(2,4,6-Triethylbenzoyl)-benzoic acid	77.41	7.10	77.52	77.48	7.04	7.16

by suction; the filtrate is acidified with 6 *N* hydrochloric acid. After cooling in an ice-bath the precipitate is brought upon a filter, washed free from acid with small portions of cold water and dried at 105°. It is recrystallized as specified in Table I.

In the case of *o*-xylene and ethylbenzene the melting points of their respective derivatives with tetrachlorophthalic anhydride lie within a range that might conceivably make identification difficult. The following procedure therefore serves as a further means of differentiation by converting the *o*-(2,3-dimethylbenzoyl)-tetrachlorobenzoic acid to the corresponding anthraquinone derivative under conditions in which the ethylbenzoyl derivative gives no quinone.

One-tenth g. of acid in a 15-cm. test-tube is boiled for one minute with 4 cc. of 50% sulfuric acid. The test-tube is cooled under the tap and its contents are poured into 20 cc. of cold water. The yellow solid which separates is collected on a filter, washed with three 2-cc. portions of 6 *N* ammonium hydroxide and then with small portions of cold water until free from alkali. The product is dried in air and recrystallized from 10 cc. of 80% aqueous alcohol in the form of bright yellow needles.

The above procedure might profitably be applied to the dehydration of other acids, *e. g.*, *o*-benzoyl, toluyl and xyloyl benzoic acids. Its general application, however, is impossible due to sulfonation which results in the case of acids with long chain substituents.[3]

In the course of this investigation several new compounds have been obtained, the analyses of which are given in Table II.

In a future paper the applicability of the present method to aromatic chloro compounds will be demonstrated.

Summary

1. A general method for the identification of aromatic hydrocarbons is described.

2. The *o*-aroyl benzoic acid derivatives of nineteen of the more common aromatic hydrocarbons have been obtained.

3. Tetrachlorophthalic anhydride has been substituted for phthalic anhydride with decided advantage, in some cases.

4. The practicability of dehydrating some of the derivatives to the corresponding quinones has been demonstrated.

[3] Scholl, Potschiwauscheg and Lenko, *Monatsh.*, **32**, 687 (1911).

CAMBRIDGE, MASS. RECEIVED MARCH 29, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Methylcholanthrene

BY LOUIS F. FIESER AND ARNOLD M. SELIGMAN

The purpose and the main results of this work have been discussed in a preliminary communication,[1] and the present paper contains the experimental details.

The essential feature of the synthesis (I ⟶ II) is a modification of the Elbs condensation in which one of the meso carbon atoms of the reaction product is originally a part of an alicyclic ring in the diaryl ketone.

The ordinary Elbs reaction often is complicated by the elimination or degradation of alkyl groups[2] and by the migration of an aroyl group in the naphthalene nucleus,[3] and even in a favorable case, as in the synthesis of 1,2,5,6-dibenzanthracene[4] the yields seldom exceed 20–30%. The ketones I and III, however, lose water rapidly at a temperature of 400–410° and, although some low-boiling hydrocarbons result from the hydrolytic

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[1] Fieser and Seligman, THIS JOURNAL, **57**, 228 (1935).

[2] Cook, *J. Chem. Soc.*, 456 (1932).

[3] Cook, *ibid.*, 487 (1931).

[4] Clar, *Ber.*, **62**, 350 (1929); Fieser and Dietz, *ibid.*, **62**, 1827 (1929).