tube with liquid nitrogen, 0.7 cc. of concd. hydrochloric acid was then poured in and the mixture was degassed by melting, freezing and pumping on a vacuum line. 10–15 cc. of acetylene-d_2 was admitted to the evacuated tube which was then sealed off. After one hour at room temperature, the tube was frozen, broken open on a vacuum line and the products trapped for analysis.

Magnesium–Hydrochloric Acid Reduction of Acetylene-d_2.—The procedure here was similar to that for zinc reducing agent; however, the reaction was run at 0° for 10 min. The amount of reduction was considerably smaller than for zinc.

Zinc–Acetic Acid Reduction of Tolane.—Three grams of tolane was dissolved in 50 cc. of 95% acetic acid, 6 g. of zinc dust was added and the mixture was heated on a steam cone for two hours, in the absence of light. Two more successive 6-g. additions of zinc, with alternate heating on the steam cone, were made. Heating was then continued for 24 hours. When diluted with water, the solution became cloudy and some oil collected on the surface. The oil was removed with a medicine dropper, weighed and dissolved in acetonitrile. Unreacted tolane precipitated from the aqueous solution.

Zinc (Copper)–Acetic Acid Reduction of Tolane.—Three grams of tolane was dissolved in 50 cc. of 95% acetic acid and 1 g. of zinc dust, previously washed with 25 cc. of 10% $CuSO_4$ solution, was added. The mixture was heated on a steam cone for 2 hours when an additional 2 g. of zinc–copper dust was added and heating was continued. A third addition of catalyst, with subsequent heating for two hours, was made. The reaction mixture was cooled, diluted with water and the oil which collected on the surface of the solution was collected and dissolved in acetonitrile. The system was protected from light.

Zinc (Copper)–Water Reduction of Acetylene-d_2.—The copper-activated reducing agent was prepared according to Straus.[7] One gram of zinc–copper, 5 cc. of water and 15 cc. of acetylene-d_2 gas were frozen into a Pyrex tube, degassed by freezing and pumping several times and the tube was then sealed off. The tube was heated to 75° with occasional shaking for 1 hour, frozen, broken open on a vacuum line and the products pumped out and analyzed.

Zinc (Palladium)–Alcohol Reduction of Acetylene-d_2.—The reducing agent was prepared by washing 5 g. of powdered zinc with 20 cc. of a 1% aqueous solution of $PdCl_2$. The solid was filtered and washed three times with 10-cc. portions of absolute alcohol. The catalyst was sucked dry. 2–5 g. of activated zinc, approximately 5 cc. of alcohol and 15 cc. of acetylene-d_2 gas were frozen into a Pyrex tube, degassed by freezing and pumping several times and the tube was then sealed off. The tube was heated to 50° with occasional shaking for 30 minutes. The remaining procedure was similar to that for the zinc (copper) runs.

Zinc (Copper)–Hydrochloric Acid Reduction of Acetylene-d_2 and Propyne-1-d_1.—0.4 g. of copper activated zinc, approximately 15 cc. of 1 N HCl and 15 cc. of acetylene-d_2 were employed in a manner similar to that described for zinc (copper)–water, except that a reaction temp. of 25° and reaction time of 1–10 hours were employed.

The procedure for propyne-1-d_1 was similar except that the experiment was scaled up fifteen-fold. The yield (percentage reduction) of propene-1-d_1 was very low and the product (12 cc.) was isolated by distillation on a low temperature column.

Magnesium (Copper)–Hydrochloric Acid Reduction of Acetylene-d_2.—The procedure employed was similar to that for zinc (copper) except that the reaction time was 30 min.

Sodium–Ammonium Reduction of Acetylene-d_2.—Ten cc. of 1–3 N sodium–ammonia solution was placed in a Pyrex tube and the mixture was degassed by freezing in liquid nitrogen and pumping several times. Approximately 15 cc. of acetylene-d_2 gas was then admitted, the tube was sealed off and heated to −35° where it was kept for 30 minutes, with occasional shaking. The sample tube was then frozen, opened and the ammonia removed by passage of the gases through 1 N sulfuric acid; the acetylene was trapped in liquid nitrogen and subsequently analyzed.

Magnesium–Ammonia Reduction of Acetylene-d_2.—Large excess of magnesium powder in 10 cc. of liquid ammonia with 15 cc. of acetylene-d_2 failed to give reduction during 2 hours at 0°.

Magnesium–Ammonia (Ammonium Chloride) Reduction of Acetylene-d_2.—0.5 g. of magnesium powder and 0.6 g. of ammonium chloride were placed in a Pyrex tube and evacuated. Ten cc. of liquid ammonia was condensed in, followed by 10 cc. of acetylene-d_2 gas. The tube was sealed off and kept for one hour at −35°. The tube was then frozen, cracked open and the same procedure for product recovery followed as for sodium–ammonia.

Chromous Chloride Reduction of Acetylene-d_2 and Propyne-1-d_1.—The reduction of acetylene-d_2 was carried out in the manner described elsewhere.[6] The same procedure was followed for propyne-1-d_1; however, in this case the percentage reduction was relatively very small and the product was purified and isolated by distillation on a low temperature column.

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[CONTRIBUTION NO. 115 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Preparation of Substituted Benzilic Acids

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The preparations of thirty-two methyl-, methoxy- and phenyl-substituted benzilic acids are described. The characteristics of these as well as of certain intermediate aldehydes, benzoins and benzils are tabulated.

In connection with work on the kinetics of hydrogenation of phenyl groups, it became desirable to synthesize certain substituted benzilic acids. A number of these acids as well as some of the intermediates used in their preparation are previously unreported compounds. The purpose of this paper is to describe the synthesis of these substances and to record certain of their physical constants.

Experimental Part

A. Preparation *via* the Benzilic Acid Rearrangement.—The substituted benzaldehydes listed in Table I were prepared by the Sommelet reaction of the corresponding chloromethyl- or bromomethyl-hydrocarbon with an aqueous alcoholic solution of hexamethylenetetramine. The details of this method are illustrated by the following example.

Four moles of *o*-methylbenzyl chloride (562 g.) was added to a solution of 4.4 moles of hexamethylenetetramine (612 g.) in two liters of 60% aqueous ethanol containing 400 ml. of 37% formalin and the mixture was heated under reflux overnight. Most of the ethanol was removed by steam distillation, one liter of water was added, and steam distillation was continued until the distillate was free of oily droplets. The total steam distillate was diluted with twice its volume of water and extracted with ether. The ether extract was washed successively with dilute sulfuric acid, dilute sodium hydroxide and water, and then distilled. There was obtained 336–384 g. of *o*-tolualdehyde (70–80% yield), which boiled at 197–199°.

TABLE I

PREPARATION OF METHYL-SUBSTITUTED BENZALDEHYDES

Benzaldehyde	Prepared from	Yield, %	Method of prep. or source of intermediate
2-Methyl	2-Methylbenzyl chloride	70–80	1
3-Methyl	3-Methylbenzyl bromide	70	2
4-Methyl	4-Methylbenzyl chloride	70–80	3
2,3-Dimethyl[a]	2,3-Dimethylbenzyl chloride	75	1
2,4-Dimethyl	2,4-Dimethylbenzyl chloride[b]	60–65	4
2,5-Dimethyl	2,5-Dimethylbenzyl chloride	75–80	4
3,5-Dimethyl	3,5-Dimethylbenzyl bromide	75	5
2,4,5-Trimethyl	2,4,5-Trimethylbenzyl chloride[b]	55–60	4

[a] A previously unreported compound which boils at 97–101° at 5–10 mm. pressure. The semicarbazone, m.p. 221.0–221.5°, was prepared in the usual way. *Anal.* Calcd. for $C_{10}H_{13}N_3O$: N, 21.97. Found: N, 21.73. The 2,4-dinitrophenylhydrazone, m.p. 235.4–236.0°, was prepared as usual. *Anal.* Calcd. for $C_{15}H_{14}N_4O_4$: N, 17.83. Found: N, 17.76. [b] It was shown[4] that chloromethyl-*m*-xylene and chloromethylpseudocumene contain appreciable quantities of 2,6-dimethylbenzyl chloride and 2,3,6-trimethylbenzyl chloride, respectively. However, it was also shown[6] that benzyl chlorides with both ortho positions occupied do not give aldehydes by the Sommelet method. Therefore, the present preparation of 2,4-dimethyl- and 2,4,5-trimethylbenzaldehydes gives isomerically pure products. The yields in these two cases are, however, somewhat lower than normal.

3,4-Dimethylbenzaldehyde was prepared in 59–67% yield by a modification of the method of Smith and Nichols[7] from 3,4-dimethylmagnesium bromide and ethoxymethyleneaniline.[8] This modification involved the addition of the Grignard reagent to the ethoxymethyleneaniline.

These and the following aldehydes were used to prepare benzoins which were oxidized to benzils by the method of Clarke and Dreger[9]: 4-isopropylbenzaldehyde, 2-methoxybenzaldehyde, 4-methoxybenzaldehyde, 2,3-dimethoxybenzaldehyde, 3,4-dimethoxybenzaldehyde and 3,4-methylenedioxybenzaldehyde. Of these latter compounds, which were obtained from the Eastman Kodak Company, the first was purified through its sodium bisulfite addition compound and the remaining five were purified by washing with 10% sodium hydroxide solution, drying and distilling *in vacuo*.

The method used for the preparation of benzoins from the methyl-substituted benzaldehydes was based on those of Stierlin[10] for the preparation of *p*-toluoin and Weiler[11] for the preparation of 3,5,3′,5′-tetramethylbenzoin. The details of the method used are illustrated by the following example.

In a two-liter all-glass flask equipped with reflux condenser, there were placed 300 g. of ethanol, 300 g. of distilled water, 40 g. of reagent grade potassium cyanide and 212 g. of *o*-tolualdehyde. The mixture was heated under reflux for 1.5 hours and a small portion was removed, diluted with water, extracted with ether, and steam distilled to remove unchanged aldehyde. The non-volatile residue was taken up in ether, washed with sodium bicarbonate solution and the ether removed on the steam plate. A small amount of 95% ethanol was added and the solution was cooled by the addition of small lumps of Dry Ice. The crystals of *o*-toluoin thus formed were added to the main batch, which was allowed to stand in the refrigerator overnight. The resulting crystals were removed by filtration and washed with cold, dilute ethanol and water, and dried. The filtrate, to which was added sixty additional grams of potassium cyanide, was again refluxed for 1.5 hours, cooled and seeded, and allowed to stand overnight. The second crop of crystals was treated like the first. The filtrate was steam distilled to remove unchanged aldehyde and the oily residue was dissolved in ethanol and seeded. After standing overnight a third crop of crystals was deposited. The three portions of crystals weighed 50, 58 and 25 g., respectively, a total of 133 g. or 63% yield. The combined portions were recrystallized from dilute ethanol after which treatment the melting point was 78–79°.

In the case of several of the benzoins it was impossible to obtain crystalline products. When this was true, the reaction mixture was steam distilled to remove unchanged aldehyde and the remaining oil was oxidized to the benzil by the method of Clarke and Dreger.[9]

A summary of the benzoins prepared by this method is given in Table II.

TABLE II

PREPARATION OF METHYL-SUBSTITUTED BENZOINS

Benzoin	Yield, %	M.p., °C. Obsd.	Lit.
2,2′-Dimethyl	63	78–79	79[12]
3,3′-Dimethyl	Oil only	....	....[12]
4,4′-Dimethyl	72	88–89	88–89[10]
3,5,3′,5′-Tetramethyl	75	93–94	93–94[11]
2,3,2′,3′-Tetramethyl	Oil only	....	.....[a]
2,4,2′,4′-Tetramethyl	Oil only	....	.....[a]
2,5,2′,5′-Tetramethyl	33	76.6–77.2	...[a,b]
3,4,3′,4′-Tetramethyl	Oil only	....	.....[a]
2,4,5,2′,4′,5′-Hexamethyl	5	250 (dec.)	...[a,c]
4,4′-Diisopropyl[d]	53	99–100	99–100[12] 98[12] 101[14]

[a] Previously unreported. [b] *Anal.* Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.30; H, 7.44. [c] *Anal.* Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.71; H, 7.54. [d] Prepared by the method of Boesler.[13]

Table III summarizes the information concerning the alkoxybenzoins.

TABLE III

PREPARATION OF ALKOXYBENZOINS

Benzoin	Method of prepn.	Yield, %
4-Methoxy	15	23
2,2′-Dimethoxy	16	70
4,4′-Dimethoxy	17	40
2,3,2′,3′-Tetramethoxy	18	52
3,4,3′,4′-Tetramethoxy	[a]	Oil only
3,4-Methylenedioxy	19	30
3,4,3′,4′-Bis-(methylenedioxy)	20	84

[a] Prepared by the method used for 2,3,2′,3′-tetramethoxybenzoin and oxidized as an oil to the benzil.

Table IV summarizes the information concerning the benzils.

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TABLE IV

CHARACTERISTICS OF SUBSTITUTED BENZILS

Benzil	M.p., °C. Obsd.	M.p., °C. Lit.	Formula	Composition, % (for new cpds. only) Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2,2′-Dimethyl	92–93	92–94[21] 92[22]					
3,3′-Dimethyl	103–104	103[12]					
4,4′-Dimethyl	104–105	104–105[10]					
2,3,2′,3′-Tetramethyl	117.0–118.5	....	$C_{18}H_{18}O_2$	81.17	81.04	6.81	6.76
2,4,2′,4′-Tetramethyl	134.5–135.5	....	$C_{18}H_{18}O_2$	81.17	81.16	6.81	6.87
2,5,2′,5′-Tetramethyl	122.4–122.7	....	$C_{18}H_{18}O_2$	81.17	81.27	6.81	6.76
3,4,3′,4′-Tetramethyl	126.0–126.8	128.5[23]					
3,5,3′,5′-Tetramethyl	139.5–139.6	....	$C_{18}H_{18}O_2$	81.17	81.04	6.81	6.84
2,4,5,2′,4′,5′-Hexamethyl	143.2–143.6	....	$C_{20}H_{22}O_2$	81.60	81.83	7.53	7.42
4,4′-Diisopropyl	83–84	84[13]					
4-Methoxy	61–62	61.5–63.0[24]					
2,2′-Dimethoxy	127–128	127[16]					
4,4′-Dimethoxy	132–133	133[13]					
2,3,2′,3′-Tetramethoxy	142–143	140–142[25] 144.9–145.4[18]					
3,4,3′,4′-Tetramethoxy	225.2–225.8	220,[19] 223[26]					
3,4-Methylenedioxy	116.5–117.5	117–118[19]					
3,4,3′,4′-Bis-(methylenedioxy)	170–171	170–171[20]					

TABLE V

CHARACTERISTICS OF SUBSTITUTED BENZILIC ACIDS PREPARED *via* THE BENZILIC ACID REARRANGEMENT

Benzilic acid	M.p., °C. Obsd.[a]	M.p., °C. Lit.	Neutral equiv. Calcd.	Neutral equiv. Found	Formula	Composition, % (for new cpds. only) Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Color prod. by conc. H_2SO_4
2,2′-Dimethyl	154.0–156.0	162–163[21] 147–148[29]	256.3	255.7	$C_{16}H_{16}O_3$					Purple-red
3,3′-Dimethyl	134.0–135.0		256.3	256.6	$C_{16}H_{16}O_3$	74.98	74.68	6.29	6.18	Violet
4,4′-Dimethyl	132.0–133.8	131–132[30] 133–135[31]	256.3	255.7	$C_{16}H_{16}O_3$					Orange
3,5,3′,5′-Tetramethyl	189.2–191.0		284.3	283.5	$C_{18}H_{20}O_3$	76.03	76.16	7.09	7.00	Pale blue
4,4′-Diisopropyl	157.6–159.0	119–120[13]	312.4	313.8	$C_{20}H_{24}O_3$					Orange-red
4-Methoxy	147.0–147.5	147.5–149[24]	258.3	261.0	$C_{15}H_{14}O_4$					Red-orange
2,2′-Dimethoxy	161.2–163.6	160[27,28]	288.3	288.6	$C_{16}H_{16}O_5$					Blue-green
4,4′-Dimethoxy	165.0–167.0 (dec.)	164[13] 171[28] 175[27]	288.3	290.6	$C_{16}H_{16}O_5$					Purple[b]
2,3,2′,3′-Tetramethoxy	107.5–108.8		348.3	348.3	$C_{18}H_{20}O_7$	62.06	62.17	5.79	5.74	Blue-purple
3,4,3′,4′-Tetramethoxy	124.5–125.5	131[26,28]	384.1	348.3[c]	$C_{18}H_{20}O_7$					Blue-green
3,4-Methylenedioxy	139.0–140.0 (dec.)		272.3	274.8	$C_{15}H_{12}O_6$	66.17	66.25, 66.23	4.45	4.45, 4.41	Purple
3,4,3′,4′-Bis-(methylenedioxy)	Oil only	139[28]								Blue-green

[a] Benzilic acids tend to decompose by decarboxylation at temperatures near their melting points. Consequently, the observed melting points are not entirely reproducible, since the length of time the sample is at elevated temperatures affects its purity. [b] Ford–Moore[28] indicates that this compound gives a blue-green color. [c] The calculated neutral equivalent for the compound with two molecules of water of hydration is 384.3.

For the preparation of the benzilic acids from the benzils the method of Schoenberg and Keller[27] was used for the alkyl substituted compounds and that of Ford-Moore[28] was used for the alkoxy substituted compounds. Table V gives a summary of the benzilic acids prepared by these methods. The colors produced when the benzilic acids are dissolved in sulfuric acid are also given. Absorption spectra of many of these solutions were recorded but are not reproduced here since slow color changes take place as some of the solutions age.

B. Preparation *via* the Reaction of Ethyl Phenylglyoxalate with the Appropriate Grignard Reagent.—A number of unsymmetrical alkyl substituted benzilic acids were prepared by the reaction of the proper substituted phenylmagnesium halide (bromide or iodide) with ethyl phenylglyoxalate. The resulting esters were distilled *in vacuo* and saponified to yield the corresponding acids. This procedure is illustrated by the following example.

A Grignard solution was prepared from 43 g. of *p*-bromotoluene (0.25 mole) and 14 g. of ethyl bromide (0.125 mole) with 8.7 g. of magnesium (0.38 gram atom) in 300 ml. of ether. This solution was added slowly with vigorous stirring to a solution of 71 g. of ethyl phenylglyoxalate (0.4 mole) in 200 ml. of ether. The mixture was poured into ice and the gummy mass was dissolved by use of dilute hydrochloric acid. The ether layer was separated and washed successively with two portions of water, dilute sodium bicarbonate solution, and water, and the ether was evaporated. The oil was distilled *in vacuo* and there was obtained 35 g. of ethyl *p*-methylbenzilate (0.13 mole, 50% yield), which boiled at 175° at approximately 2 mm. pressure. At this pressure the introduction of additional methyl groups into the molecules of these esters produced an elevation in their boiling points of approximately 10° per additional methyl group. The ester was refluxed overnight with a solution of 10 g. of sodium hydroxide in a mixture of 50 ml. of water and 50 ml. of 95% ethanol. Next, 100 ml. of water was added and the ethanol was removed by distillation. The solution was diluted and cooled, made almost neutral with dilute hydrochloric acid, and extracted three

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TABLE VI

CHARACTERISTICS OF BENZILIC ACIDS PREPARED BY THE GRIGNARD SYNTHESIS

Benzilic acid	M.p., °C. Obsd.[a]	M.p., °C. Lit.	Neutral equiv. Calcd.	Neutral equiv. Found	Formula	Composition, % (for new cpds. only) Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Color prod. by concd. H_2SO_4
2-Methyl	114.0–115.4		242.3	242.3	$C_{15}H_{14}O_3$	74.36	74.38	5.82	5.80	Orange-red
3-Methyl	118.0–119.0		242.3	243.3	$C_{15}H_{14}O_3$	74.36	74.24	5.82	5.89	Red
4-Methyl	132.0–133.2	133–134[32] 132[28]	242.3	243.9	$C_{15}H_{14}O_3$					Orange
2,3-Dimethyl	128.0–129.0		256.3	259.3	$C_{16}H_{16}O_3$	74.98	74.83	6.29	6.20	Yellow-orange
2,4-Dimethyl	129.5–131.5		256.3	256.4	$C_{16}H_{16}O_3$	74.98	74.89	6.29	6.20	Purple
2,5-Dimethyl	Uncrystallizable oil									Red
2,6-Dimethyl	121.8–122.6		256.3	255.8	$C_{16}H_{16}O_3$	74.98	74.81	6.29	6.37	Purple
3,4-Dimethyl	122.4–124.2		256.3	255.9	$C_{16}H_{16}O_3$	74.98	74.53	6.29	6.34	Red-violet
3,5-Dimethyl	108.0–109.0		256.3	255.9	$C_{16}H_{16}O_3$	74.98	74.53	6.29	6.38	Purple-red
2,3,4-Trimethyl	139.0–140.0 (dec.)		270.3	275.2	$C_{17}H_{18}O_3$	75.53	75.75	6.71	6.82	Red-purple
2,3,5-Trimethyl	149.6–151.8		270.3	271.0	$C_{17}H_{18}O_3$	75.53	75.59	6.71	6.73	Yellow-gray
2,3,6-Trimethyl	Uncrystallizable oil									Blue-purple
2,4,5-Trimethyl	Uncrystallizable oil									Intense blue
2,4,6-Trimethyl	87–89[b]	87–89[33]	270.3[c]	304.7	$C_{17}H_{18}O_3$					Red-purple
3,4,5-Trimethyl	137.8–140.2		270.3	271.4	$C_{17}H_{18}O_3$	75.53	75.57	6.71	6.70	Purple-pink
2,3,4,5-Tetraethyl	153.8–155.8		284.3	289.5	$C_{18}H_{20}O_3$	76.03	76.16	7.09	7.00	Pink
2,3,4,6-Tetraethyl	123–124 (dec.)[34]		284.3	287.6	$C_{18}H_{20}O_3$					Purple-red
2,3,5,6-Tetramethyl	138–139		284.3	287.3	$C_{18}H_{20}O_3$	76.03	76.00	7.09	7.04	Salmon-pink
2,3,4,5,6-Pentamethyl	146–147 (dec.)		298.4	302.5	$C_{19}H_{22}O_3$	76.47	76.54	7.43	7.40	Red
4-Phenyl	167.2–168.6[d]	168–170[35] 164–167[36]	304.3	305.6	$C_{20}H_{15}O_3$					Intense blue

[a] Note (*a*) of Table V applies here also. [b] Recrystallized from methanol. [c] Calculated neutral equivalent for the compound with one molecule of methanol of solvation is 302.4. [d] Recrystallized from 50% aqueous acetic acid.

times with benzene. The aqueous layer was then acidified completely and the resulting gummy precipitate was allowed to stand until it crystallized. The crystals were removed by filtration, dried and recrystallized four times from thiophene-free benzene. The yield was approximately 10 g. (35% yield). It melted at 132.0–133.2° (uncor.).

Table VI gives a summary of the benzilic acids which were prepared by this method.

The halides used for the preparation of the Grignard reagents discussed above were either purchased from the Eastman Kodak Company or prepared as indicated in Table VII.

TABLE VII

SOURCE OF HALIDES USED FOR GRIGNARD REAGENTS

Halides	Source
o-Bromotoluene	E. K. Co.
m-Iodotoluene	Prepared from E. K. Co. *m*-toluidine[37]
p-Bromotoluene	E. K. Co.
3-Iodo-*o*-xylene	Prepared from E. K. Co. 3-nitro-*o*-xylene[38]
4-Bromo-*o*-xylene	Prepared from E. K. Co. *o*-xylene[39]
2-Iodo-*m*-xylene	Prepared from E. K. Co. 2-amino-*m*-xylene[40]
4-Iodo-*m*-xylene	Prepared from E. K. Co. 4-amino-*m*-xylene[37]
5-Bromo-*m*-xylene	Prepared from E. K. Co. 4-amino-*m*-xylene[41]
2-Bromo-*p*-xylene	Prepared from E. K. Co. *p*-xylene[39]
4-Bromohemimellitene	Prepared from hemimellitene[4,42]
5-Bromohemimellitene	Prepared from hemimellitene[4,43]
5-Bromopseudocumene	Prepared from pseudocumene[4,44]
3-Bromopseudocumene	Prepared by the method of Smith[45]
6-Bromopseudocumene	Prepared from 5-aminopseudocumene[46]
2-Bromomesitylene	E. K. Co.

Bromoprehnitene, bromoisodurene and bromodurene were prepared from the hydrocarbons[4] by direct bromination[42] in yields of 93–95%. Bromopentamethylbenzene was prepared from pentamethylbenzene[4] by direct bromination by the method of Smith and Nichols[7] in 97% yield.

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(32) A. McKenzie and E. W. Christie, *Biochem. Z.*, **277**, 426 (1935).

(33) H. H. Weinstock and R. C. Fuson, THIS JOURNAL, **58**, 1233 (1936).

(34) J. C. Essner and E. Gossin, *Bull. soc. chim.*, [2] **42**, 172 (1884), indicate the preparation of the compound but do not give its melting point.

(35) F. F. Blicke and N. Grier, THIS JOURNAL, **65**, 1725 (1943).

(36) S. I. Burmistrov and E. A. Shilov, *Zhur. Obshchei Khim.*, **16**, 295 (1946).

(37) By the method of H. J. Lucas and E. R. Kennedy, ref. 9, p. 351, for making iodobenzene from aniline.

(38) By the reduction of 3-amino-*o*-xylene by the method of S. A. Mahood and P. V. L. Schaffner, ref. 9, p. 160, for reducing dinitrotoluene, followed by diazotization by the method of Lucas and Kennedy.[37]

(39) By the method of W. A. Wisansky and S. Ansbacher, *Org. Syntheses*, **28**, 22 (1948).

(40) By a method similar to that of Lucas and Kennedy,[37] but with sulfuric acid instead of hydrochloric acid in the diazotization solution.

(41) By the method of L. Fieser and H. Heymann, THIS JOURNAL **64**, 380 (1942).

(42) By the method of L. I. Smith, ref. 9, p. 95, for making bromomesitylene (yield of 4-bromohemimellitene, 96%).

(43) By nitration (52% yield) by the method of G. Powell and F. R. Johnson, ref. 9, p. 449, for making nitromesitylene, followed by reduction (88% yield) by the method of Mahood and Schaffner,[38] bromination, diazotization by a method similar to that of Fieser and Heymann,[41] followed by deamination with 20 moles of hypophosphorous acid per mole of diazotized amine. The resulting bromohemimellitene (64% yield based on 4-aminohemimellitene) consisted of about 5% 4-bromohemimellitene and 95% 5-bromohemimellitene which was separated by repeated recrystallization from 95% ethanol to give 90% of pure 5-bromohemimellitene, a previously unreported compound, which melts at 27.1–27.4° and boils at 98° at about 2 mm. pressure, *Anal.* Calcd. for $C_9H_{11}Br$: C, 54.29; H, 5.57; Br, 40.14. Found: C, 54.33; H, 5.68; Br, 40.40.

(44) By the method of Smith,[42] followed by repeated recrystallization from 95% ethanol until the melting point was 73° (yield about 80%).

(45) By the Jacobsen reaction on the mixture of 5-bromo- and 3-bromopseudocumene obtained from the mother liquors from the recrystallization of 5-bromopseudocumene by the method of L. I. Smith, "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 384, in about 75% yield.

(46) By a method similar to that used by L. I. Smith and C. L. Moyle, THIS JOURNAL, **58**, 9 (1936), but with deamination with ten moles of hypophosphorus acid per mole of diazotized amine, in 55–60% yields.