

**Betaine of 1,2-Dimethyl-3,4-dihydroxy-5-hydroxymethylpyridine (VI).**—A solution of 1.32 g. of 2-methyl-3,4-dihydroxy-5-hydroxymethylpyridine (IV) in 10 ml. of 6 *N* sodium hydroxide was cooled in ice and then shaken with 1.8 ml. of redistilled dimethyl sulfate until the solution was clear. About 15 minutes were required. The solution, which had become warm spontaneously, was cooled in ice and acidified (to pH 5) with 6 *N* sulfuric acid. The solution was extracted continuously with chloroform for five hours. The betaine of 1,2-dimethyl-3,4-dihydroxy-5-hydroxymethylpyridine (0.47 g., 33%) suspended in the chloroform was collected on a filter and recrystallized from alcohol; m.p. 228–229°. Further extraction of the aqueous acid solution with chloroform did not increase the yield.

*Anal.* Calcd. for  $C_8H_{11}NO_3$ : C, 56.79; H, 6.56; N, 8.28. Found: C, 56.65; H, 6.59; N, 8.56.

**Treatment of 2-Methyl-3,4-dihydroxy-5-hydroxymethylpyridine (IV) with *p*-Toluenesulfonyl Chloride.**—To a suspension of 300 mg. of 2-methyl-3,4-dihydroxy-5-hydroxymethylpyridine in 2.5 ml. of pyridine cooled in an ice-bath, 924 mg. of *p*-toluenesulfonyl chloride was added in several portions. The solution became clear. After five minutes standing at room temperature, the mixture was added to an

excess of ice-water. An oil appeared, which crystallized after ether had been added to the mixture. The mixture was cooled, and the solid material collected on a filter and washed well successively with water, alcohol and ether. The crude 2-methyl-3-*p*-toluenesulfonyloxy-4-hydroxy-5-hydroxymethylpyridine (VII) weighing 160 mg. (27%) was recrystallized three times from alcohol, the final product melting at 228–229° (dec.).

*Anal.* Calcd. for  $C_{14}H_{15}NO_5S$ : C, 54.36; H, 4.89; N, 4.53. Found: C, 54.66; H, 5.09; N, 4.70.

The ether was distilled from the filtrate from which the crude material in the above preparation had been separated, and the aqueous solution was diluted with water and cooled in an ice-bath. The resulting crystals (530 mg., 59%) of 2-methyl-3-*p*-toluenesulfonyloxy-4-hydroxy-5-*p*-toluenesulfonyloxymethylpyridine (VIII) were filtered and washed successively with water, alcohol and ether. After two recrystallizations from alcohol, the melting point was constant at 140–141°.

*Anal.* Calcd. for  $C_{21}H_{21}NO_7S_2$ : C, 54.41; H, 4.57; N, 3.02; S, 13.83. Found: C, 54.53; H, 4.27; N, 3.25; S, 13.71.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

## The Synthesis of 6-, 7- and 8-Methyl-1,2-benzfluorenes

BY MALCOLM E. GROSS<sup>1</sup> AND HERMAN P. LANKELMA

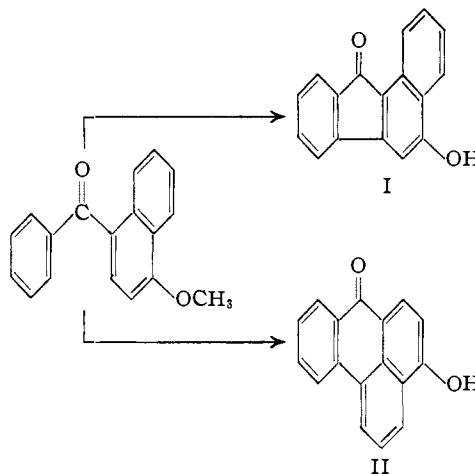
6-, 7- and 8-methyl-1,2-benzfluorenes have been synthesized from 4-methoxy-1-naphthyl *p*-, *m*- and *o*-tolyl ketones, respectively, by ring closure through the Scholl reaction to the 6, 7, and 8-methyl-3-hydroxy-1,2-benzfluorenones followed by stepwise reduction to the 3-hydroxy-1,2-benzfluorenols, the 3-hydroxy-1,2-benzfluorenones and the 1,2-benzfluorenes. The parent hydrocarbon, 1,2-benzfluorene, was prepared for comparison purposes by the same procedure. The fact that the three isomeric ketones gave three isomeric methyl-3-hydroxy-1,2-benzfluorenones is of interest since several cases have been reported where ring closure by the Scholl reaction gave, as a result of migration of the methyl group from the ortho to the meta position, only two products from three isomeric tolyl ketones.<sup>1a</sup> The three methyl-1,2-benzfluorenones have been further characterized by their ultraviolet absorption spectra. Ring closure of the 4-methoxy-1-naphthyl *m*-tolyl ketone could give 5-methyl-3-hydroxy-1,2-benzfluorenone by condensing ortho to the methyl group, although steric hindrance would make this improbable. An attempt was made to synthesize the 7-methyl-1,2-benzfluorene by a method which would leave no doubt as to its structure, but was unsuccessful. A method for the reduction of a phenol to an aromatic hydrocarbon with zinc dust which gives greatly improved yields, is described.

Only one of the eleven possible mono-methyl-1,2-benzfluorenes, the 9-methyl derivative,<sup>2</sup> has been reported. The present work describes the synthesis of three additional methyl-1,2-benzfluorenes, namely, the 6-, 7- and 8-methyl derivatives.

Scholl<sup>3</sup> in 1912 and Fierz-David<sup>4</sup> in 1928 reported that 4-hydroxy-1-benzoylnaphthalene, or its ethers would undergo a cyclodehydrogenation in the presence of aluminum chloride to give principally 3-hydroxy-1,2-benzfluorenone (I) with minor amounts of 2-hydroxy-1,9-benz-10-anthrone (II).

In the present work this reaction was employed with the three isomeric 4-methoxy-1-(*p*-, *m*- and *o*-tolyl)-naphthalenes to give the desired 6-, 7- and 8-methyl-3-hydroxy-1,2-benzfluorenones which were reduced stepwise to the 6-, 7- and 8-methyl-1,2-benzfluorenes. This may be illustrated by the synthesis of 6-methyl-1,2-benzfluorene from 4-methoxy-1-(*p*-tolyl)-naphthalene (III to VII).

After numerous trials it was found that the best method for preparing the 1-naphthyl tolyl ketones



(III) was the addition of slightly more than one mole of aluminum chloride to a solution of the tolyl chloride and methyl 1-naphthyl ether in a mixture of nitrobenzene and tetrachloroethane at 0–5°. The products were very clean and easy to purify and were consistently obtained in yields of about 95%.

The ring closure of the ketones to the 3-hydroxy-1,2-benzfluorenone was done by the Scholl reaction using a mixture of sodium chloride–aluminum

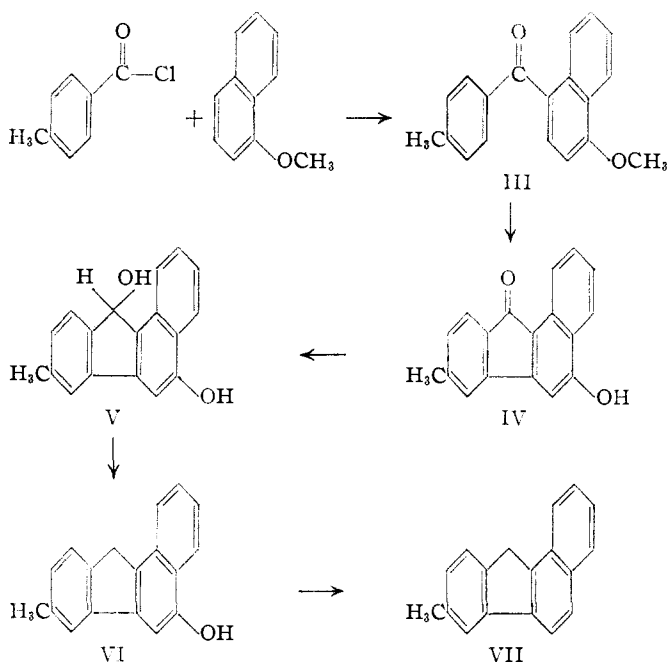
(1) B. F. Goodrich Co. Research Center, Brecksville, Ohio.

(1a) L. F. Fieser and E. B. Hershberg, *THIS JOURNAL*, **60**, 1658 (1938); F. Mayer, E. Fleckenstein and H. Gunther, *Ber.*, **63**, 1464 (1930); ref. 5.

(2) G. M. Badger, *J. Chem. Soc.*, 535 (1941).

(3) R. Scholl and C. Seer, *Ann.*, **394**, 111 (1912).

(4) H. E. Fierz-David and G. Jaccond, *Helv. Chim. Acta*, **11**, 1042 (1928).



chloride as the condensing agent.<sup>5</sup> The best results were obtained by fusing the ketone at 100–120° for 2–3 hours with NaCl–AlCl<sub>3</sub> (1:4 parts by weight). The molar ratio of aluminum chloride to ketone was about 10:1. The products were invariably difficult to purify, and the yields of pure product were low (7 to 14%).

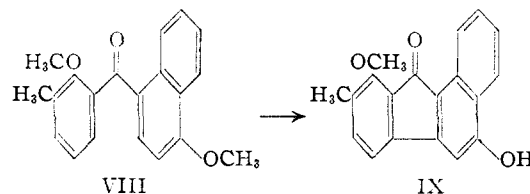
The most satisfactory method of reducing the 3-hydroxy-1,2-benzfluorenone to the 1,2-benzfluorene proved to be reduction to the 3-hydroxy-1,2-benzfluorenenol (V) with zinc dust and glacial acetic acid followed by the action of fuming hydriodic acid to give the 3-hydroxy-1,2-benzfluorene (VI). Since the benzfluorenenols are very sensitive to air oxidation, the hydroxybenzfluorenenones were reduced in the form of their acetates, and the intermediate benzfluorenenols were not isolated. The yields of 3-hydroxy-1,2-benzfluorenes were 75–85%. For purposes of identification the hydroxy benzfluorenenols were isolated as the diacetates.

The conversion of the 3-hydroxy-1,2-benzfluorenes to the 1,2-benzfluorenes by the conventional distillation with zinc dust gave extremely small yields. Heating with zinc dust suspended in a melt of zinc chloride–sodium chloride<sup>6</sup> similarly gave very poor results. It appeared probable that the reduction would be favored by keeping the phenol in contact with the zinc at a high temperature for a longer time. This was done by heating the phenol with zinc dust in a sealed Pyrex tube to dull red heat (540°) for 15 minutes. Yields of from 24 to 69% of hydrocarbon were obtained.

The parent hydrocarbon, 1,2-benzfluorene, was synthesized from 4-methoxy-1-naphthyl phenyl ketone by the same method employed for the methyl derivatives. The 6- and 8-methyl-1,2-benzfluorenes formed complexes with symmetrical trinitrobenzene containing 1 mole of hydrocarbon and 2 moles of trinitrobenzene; the complex of the 7-

methyl-1,2-benzfluorene contained 1 mole of each. All three complexes are easily dissociated, the 7-methyl being quite difficult to isolate. The 2,4,7-trinitrofluorenone complexes all formed in a 1:1 mole ratio and were definitely more stable than the corresponding T.N.B. complexes.

An attempt was made to synthesize the 7-methyl-1,2-benzfluorene from 2-methoxy-3-methyl phenyl-1-(4-methoxynaphthyl) ketone. Ring closure of this ketone could only occur para to the methyl group.



The 7-methyl-3-hydroxy-8-methoxy-1,2-benzfluorenone (IX) was obtained in good yield, but all attempts to demethylate the ether were unsuccessful.

The ultraviolet absorption spectra of the three methyl benzfluorenes are presented in Table I. The ultraviolet absorption spectrum of 1,2-benzfluorene has been determined by Orchin and Friedel.<sup>7</sup>

TABLE I  
ULTRAVIOLET ABSORPTION MAXIMA FOR 6-, 7- AND 8-METHYL-1,2-BENZFLUORENE<sup>a,b</sup>

6-Methyl-1,2-benzfluorene		7-Methyl-1,2-benzfluorene		8-Methyl-1,2-benzfluorene	
$\lambda$ , m $\mu$	log $\epsilon$	$\lambda$ , m $\mu$	log $\epsilon$	$\lambda$ , m $\mu$	log $\epsilon$
344	3.05	345	2.92	343	2.97
328s	3.35	330s	3.25	330s	3.17
315	4.17	315	4.22	315	4.13
303	4.23	302	4.25	303	4.18
294	4.15	293	4.16	293	4.12
263	4.91	265	4.81	264	4.91
254	4.73	255	4.68	254	4.76
245s	4.45	246s	4.37	245s	4.42
226	4.45	222	4.37	218	4.50

<sup>a</sup> Beckman, spectrophotometer, model DU. <sup>b</sup> s = shoulder.

### Experimental

The aluminum chloride used in this work was a sublimed grade obtained from Ohio Apex, Inc., Nitro, West Virginia. Methyl 1-naphthyl ether was prepared in 50% yield from 1-naphthol and methanol<sup>8</sup> and in 89% yield from 1-naphthol and dimethyl sulfate.<sup>9</sup> *o*-, *m*- and *p*-toluyl chlorides were prepared by the action of phosphorus pentachloride on the corresponding acids. The yields were 91% in each case.

**4-Methoxy-1-naphthyl Phenyl Ketone and 4-Methoxy-1-naphthyl *o*-, *m*- and *p*-Tolyl Ketones.**—These ketones were prepared from the acid chloride and methyl 1-naphthyl ether by the Friedel–Crafts ketone synthesis. The reaction was carried out at low temperature (0–5°) in a mixed solvent of nitrobenzene and tetrachloroethane. This is essentially the method suggested by Fieser<sup>10</sup> for Friedel–Crafts ketone syntheses involving reactive aromatic hydrocarbons.

The following description for the preparation of 4-methoxy-1-naphthyl *p*-tolyl ketone is representative. *p*-Tolyl

(7) M. Orchin and R. A. Friedel, *THIS JOURNAL*, **71**, 3002 (1949).

(8) L. Gattermann, *Ann.*, **244**, 72 (1888).

(9) C. S. Hiers and F. D. Hager, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 59.

(10) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 413.

(5) L. F. Fieser and E. L. Martin, *THIS JOURNAL*, **58**, 1443 (1936).

(6) E. Clar, *Ber.*, **72**, 1645 (1939).

## SUMMARY OF THE RESULTS

Ketone	Yield, %	M.p., °C.	Formula	Analyses, %			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
4-Methoxy-1-naphthyl phenyl	88.5	83-84 <sup>11</sup>	.....	...	...	..	..
4-Methoxy-1-naphthyl <i>o</i> -tolyl	98	93.5-94.5	C <sub>19</sub> H <sub>16</sub> O <sub>2</sub>	82.58	82.46	5.84	5.66
4-Methoxy-1-naphthyl <i>m</i> -tolyl	93	77-78	C <sub>19</sub> H <sub>16</sub> O <sub>2</sub>	82.58	82.45	5.84	5.72
4-Methoxy-1-naphthyl <i>p</i> -tolyl	95	110-111	C <sub>19</sub> H <sub>16</sub> O <sub>2</sub>	82.58	82.39	5.84	5.67

chloride (50 g., 0.32 mole), methyl 1-naphthyl ether (47.5 g., 0.3 mole), purified nitrobenzene (100 ml.) and *sym*-tetrachloroethane (400 ml.) were placed in a flask and cooled to 0-5°. Sublimed aluminum chloride (44 g., 0.33 mole) was added slowly with stirring during a period of 90 minutes. Some of the complex precipitated out before all of the aluminum chloride had been added. The mixture was stirred at a temperature of 0-5° for an additional five hours and then allowed to warm to room temperature overnight. The complex was hydrolyzed by slowly adding pieces of ice

hydride and pyridine and purified by recrystallization from acetic acid. 2.75 g. melting at 199-202° and 0.46 g. melting at 193-197° from the mother liquor was obtained; a total yield of 14.5%. It was finally purified by sublimation, orange needles, m.p. 201.5-203.5°; 150 mg. of the acetate was hydrolyzed to the phenol by refluxing with a solution of 150 mg. of potassium hydroxide in 7.5 ml. of methanol. The phenol was obtained as a bright red solid which crystallized in small red plates from anisole. It slowly decomposed without melting, above 235°.

## SUMMARY OF RESULTS

The 1,2-benzfluorenone	Yield, %	M.p., °C.	Formula	Analyses, %			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
3-Acetoxy	2.8	183.5-184.5 <sup>13</sup>	.....	...	...	..	..
3-Hydroxy-6-methyl		Decomp. above 235	C <sub>19</sub> H <sub>12</sub> O <sub>2</sub>	83.06	83.04	4.65	4.67
3-Acetoxy-6-methyl	14.5	201.5-203.5	C <sub>20</sub> H <sub>14</sub> O <sub>2</sub>	79.46	79.54	4.67	4.71
3-Hydroxy-7-methyl		Decomp. above 225	C <sub>19</sub> H <sub>12</sub> O <sub>2</sub>	83.06	83.06	4.65	4.66
3-Acetoxy-7-methyl	7.0	195-197	C <sub>20</sub> H <sub>14</sub> O <sub>2</sub>	79.46	79.59	4.67	4.76
3-Hydroxy-8-methyl		Decomp. above 200	C <sub>19</sub> H <sub>12</sub> O <sub>2</sub>	83.06	83.09	4.65	4.70
3-Acetoxy-8-methyl	11.6	172-173.5	C <sub>20</sub> H <sub>14</sub> O <sub>2</sub>	79.46	79.49	4.67	4.75

with stirring and cooling. Three hundred ml. of 4 *N* hydrochloric acid was then added to dissolve basic aluminum salts. The solvents were removed by steam distillation; the oily residue was washed with water and allowed to stand until it solidified (about two days). The crude ketone was crystallized from ethanol.

**3-Hydroxy-1,2-benzfluorenone and 6-, 7-, and 8-Methyl-3-hydroxy-1,2-benzfluorenes.**—The Scholl condensation of ketones to 1,2-benzfluorenes was carried out by heating the ketone with a mixture of sodium chloride-aluminum chloride. After a large number of trials in which the variables NaCl:AlCl<sub>3</sub> ratio, temperature and time were investigated, the following conditions were found to be most suitable. The preparation of 6-methyl-3-hydroxy-1,2-benzfluorenone from 4-methoxy-1-naphthyl *p*-tolyl ketone is representative. A mixture of sodium chloride (20 g., 0.34 mole), sublimed aluminum chloride (80 g. 0.6 mole) and 4-methoxy-1-naphthyl *p*-tolyl ketone (20 g., 0.073 mole) was heated at 120-125° with slow stirring for three hours. Fusion of the solids started at 110° with rapid evolution of hydrogen chloride. The melt was poured onto a large quantity of ice and hydrochloric acid. The solid was recovered

**3,9-Diacetoxy-1,2-benzfluorene and 6-, 7- and 8-Methyl-3,9-diacetoxy-1,2-benzfluorenes.**—The 3-acetoxy-6-, 7- and 8-methyl-1,2-benzfluorenes were reduced to the fluorenols by the action of zinc dust and acetic acid. Because of the sensitivity of the benzfluorenols to oxygen, they were characterized as the acetates and reduced to the 3-hydroxy-1,2-fluorenes without isolation. The reduction of 3-acetoxy-6-methyl-1,2-benzfluorenone is representative.

Zinc dust (0.3 g.) was added in small portions to a boiling solution of 0.3 g. of 3-acetoxy-6-methyl-1,2-benzfluorenone in 30 ml. of glacial acetic acid. The solution became colorless in about 20 minutes. It was necessary to maintain an atmosphere of nitrogen over the solution during the reduction to prevent the oxidation of the fluorenol by the air. The fluorenol was precipitated by pouring the solution into ice-water with stirring. Due to its sensitivity to oxygen, it was converted to the acetate, 6-methyl-3,9-diacetoxy-1,2-benzfluorene, by acetylation with acetic anhydride in the presence of pyridine. This derivative crystallized from ethanol as colorless needles; m.p. 141-143.5°; yield 0.22 g. (65%). Repeated crystallization from alcohol gave a melting point of 144.5-146°.

## SUMMARY OF RESULTS

The 1,2-benzfluorene	Yield, %	M.p., °C.	Formula	Analyses, %			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
6-Methyl,3,9-diacetoxy	65	144.5-146	C <sub>22</sub> H <sub>18</sub> O <sub>4</sub>	76.28	76.41	5.24	5.43
7-Methyl,3,9-diacetoxy	68	189-191	C <sub>22</sub> H <sub>18</sub> O <sub>4</sub>	76.28	76.25	5.24	5.40
8-Methyl,3,9-diacetoxy	58	146-147	C <sub>22</sub> H <sub>18</sub> O <sub>4</sub>	76.28	76.42	5.24	5.40

by filtration and washed free of acid. It was a very crude product which proved difficult to purify. It was extracted three times with hot 1% sodium hydroxide solution containing 0.1% sodium hydrosulfite. The extracts were acidified with acetic acid to precipitate the phenol. The brownish-red solid which was still very impure weighed 16.4 g. and represented 84% of the starting ketone. Due to the fact that the keto-phenol is much less soluble in acetic acid than the impurities,<sup>12</sup> the solid was extracted three times with 30 ml. of boiling glacial acetic acid. The residue was a bright red solid (4.4 g.) of semi-pure product. This phenol is high melting and very slightly soluble. It was found expedient to purify it in the form of the acetate. The acetate was prepared by heating the phenol with acetic an-

**3-Hydroxy-1,2-benzfluorene and 6-, 7- and 8-Methyl-3-hydroxy-1,2-benzfluorenes.**—Attempts to reduce the 3-hydroxy-1,2-benzfluorenes to the 3-hydroxybenzfluorenes with nickel-aluminum alloy by the method of Papa<sup>14</sup> and by a modification of the Clemmensen reduction<sup>15</sup> were unsuccessful. Similarly distillation of the hydroxy-1,2-benzfluorenes with zinc<sup>11</sup> failed to give the 1,2-benzfluorenes. The reduction of the 3-acetoxy-1,2-benzfluorenol-9 to the 3-hydroxy-1,2-benzfluorene with fuming hydriodic acid gave excellent yields. For this purpose the fluorenol need not be isolated but was reduced in the acetic acid solution in which it was prepared. The preparation of 6-methyl-3-

(13) J. W. Cook and R. W. G. Preston, ref. 11.

(11) J. W. Cook and R. W. G. Preston, *J. Chem. Soc.*, 553 (1944), report a melting point of 80-81° for this ketone.

(12) J. W. Cook, *ibid.*, 268 (1939).

(14) D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, **7**, 587 (1942).

(15) H. F. Miller and G. B. Bachman, *THIS JOURNAL*, **57**, 2447 (1935).

hydroxy-1,2-benzfluorene is illustrative. 6-Methyl-3-acetoxy-1,2-benzfluorenone (1.2 g.) was reduced to the fluoranol with 1.6 g. of zinc dust and 80 ml. of glacial acetic acid as previously described. The cooled solution was filtered, and 9 g. of fuming hydriodic acid (density 1.99) in 8 ml. of glacial acetic acid was added. After refluxing for 3 hours, the solution was cooled and poured into 300 ml. of a saturated solution of sulfurous acid cooled with ice. The white precipitate was collected by filtration, washed, and dried at 50° *in vacuo*. It was recrystallized from benzene; yield 0.78 g. (80%) of fine colorless needles, m.p. 205–210°. Further purification by sublimation at 200° (1 mm.), gave a melting point of 207–210° (dec.).

zene, the hydrocarbon residue still had a slight yellow color. It was vacuum sublimed at 140° at less than 1 mm. pressure which gave a colorless sublimate. Recrystallization (twice) from ethanol gave fine plates, m.p. 184–184.5°. The following is a summary of the results. (T.N.B. represents the complexing agent *sym*-trinitrobenzene; T.N.F., the agent 2,4,7-trinitrofluorenone.)

**7-Methyl-3-hydroxy-8-methoxy-1,2-benzfluorenone.**—2-Methoxy-3-methylbenzoic acid was prepared by the method of Cohen and Dudley.<sup>16</sup> It was converted to the acid chloride by the action of oxalyl chloride. The excess oxalyl chloride was removed by distillation at atmospheric pressure. Methyl 1-naphthyl ether was acylated with the acid

## SUMMARY OF RESULTS

The 1,2-benzfluorene	Yield, %	M.p., °C.	Formula	Analyses: %			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
3-Hydroxy	71	219 <sup>b</sup>					
3-Acetoxy	..	155–156 <sup>b</sup>					
6-Methyl-3-hydroxy	80	207–210 dec.	C <sub>18</sub> H <sub>14</sub> O	87.78	87.75	5.73	5.75
6-Methyl-3-acetoxy		139–140 <sup>a</sup>	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub>	83.31	83.28	5.59	5.72
7-Methyl-3-hydroxy	75	210–212 dec.	C <sub>18</sub> H <sub>14</sub> O	87.78	87.71	5.73	5.79
7-Methyl-3-acetoxy		190–192	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub>	83.31	83.44	5.59	5.48
8-Methyl-3-hydroxy	87	212–215 dec.	C <sub>18</sub> H <sub>14</sub> O	87.78	87.70	5.73	5.74
8-Methyl-3-acetoxy		130–131	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub>	83.31	83.34	5.59	5.58

<sup>a</sup> Also 150°; a double melting point. <sup>b</sup> J. W. Cook and R. W. G. Preston, ref. 11.

**1,2-Benzfluorene and 6-, 7- and 8-Methyl-1,2-benzfluorenes.**—The ordinary zinc dust distillation of the 3-hydroxy-1,2-benzfluorenes gave extremely poor yields of the 1,2-benzfluorenes. By heating with zinc in a sealed tube, however, good yields were obtained. The following preparation of 6-methyl-1,2-benzfluorene is illustrative. 6-Methyl-3-hydroxy-1,2-benzfluorene (0.6 g.) was ground in a mortar with 24 g. of zinc dust. This was placed in a piece of 14 mm. Pyrex tubing sealed at one end. The tube was sealed, wrapped with heavy aluminum foil, and heated at 550° for 15 minutes in an electrically heated muffle furnace. The tube was cooled and cautiously opened at Dry Ice temperature by breaking the tip. There was always considerable pressure in the tube, probably due to hydrogen generated by the zinc and the moisture present. The pyrolyzed material was extracted with hot benzene, filtered, the filtrate re-

chloride (undistilled), as previously described. The ketone, m.p. 90–90.5°, was obtained in 76% yield. *Anal.* Calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>: C, 78.41; H, 5.92. Found: C, 78.43; H, 5.96.

The Scholl condensation of this ketone to 3-hydroxy-7-methyl-8-methoxy-1,2-benzfluorenone was carried out as previously described. 6.4 g. of the ketone gave 2.1 g. of the fluorenone, a yield of 35%. The acetate melted at 210–215° with decomposition. It was hydrolyzed with alcoholic potash and the phenol recrystallized from anisole; red crystals which decomposed without completely melting, above 200°. *Anal.* Calcd. for C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>: C, 78.58; H, 4.86. Found: C, 78.54; H, 4.89.

All attempts to demethylate the ether were unsuccessful; aluminum chloride under various conditions, refluxing with fuming hydriodic acid in glacial acetic acid, and refluxing with a sodium pyridine complex,<sup>17</sup> all failed.

Hydrocarbon or hydrocarbon complex	Yield, %	M.p., °C.	Formula	Analyses, %			
				Carbon		Hydrogen	
				Calcd.	Found	Calcd.	Found
1,2-Benzfluorene	62	188–189 <sup>a</sup>					
1,2-Benzfluorene T.N.B. complex		144–145 <sup>b</sup>					
1,2-Benzfluorene T.N.F. complex		213–215 <sup>b</sup>					
6-Methyl-1,2-benzfluorene	24	184–184.5	C <sub>18</sub> H <sub>14</sub>	93.87	93.77	6.13	6.13
6-Methyl-1,2-benzfluorene, T.N.B. comp.		135–135.5	C <sub>30</sub> H <sub>20</sub> N <sub>6</sub> O <sub>12</sub>	54.90	54.86	3.07	3.03
6-Methyl-1,2-benzfluorene, T.N.F. comp.		190–191	C <sub>31</sub> H <sub>19</sub> N <sub>3</sub> O <sub>7</sub>	68.25	68.54	3.51	3.52
7-Methyl-1,2-benzfluorene	54	175–176	C <sub>18</sub> H <sub>14</sub>	93.87	93.78	6.13	6.21
7-Methyl-1,2-benzfluorene-T.N.B. comp.		125–127	C <sub>24</sub> H <sub>17</sub> N <sub>3</sub> O <sub>6</sub>	65.01	65.41	3.87	3.91
7-Methyl-1,2-benzfluorene-T.N.F. comp.		192–193	C <sub>31</sub> H <sub>19</sub> N <sub>3</sub> O <sub>7</sub>	68.25	68.61	3.51	3.62
8-Methyl-1,2-benzfluorene	69	121–122.5	C <sub>18</sub> H <sub>14</sub>	93.87	93.85	6.13	6.14
8-Methyl-1,2-benzfluorene-T.N.B. comp.		149–149.5	C <sub>30</sub> H <sub>20</sub> N <sub>6</sub> O <sub>12</sub>	54.90	55.09	3.07	3.11
8-Methyl-1,2-benzfluorene-T.N.F. comp.		202–204	C <sub>31</sub> H <sub>19</sub> N <sub>3</sub> O <sub>7</sub>	68.25	68.53	3.51	3.59

<sup>a</sup> O. Kruber, *Ber.*, 70, 1556 (1937) reports m.p. 189–190°. <sup>b</sup> M. Orchin and R. A. Friedel, *THIS JOURNAL*, 71, 3002 (1949).

duced to a volume of 10 ml. and passed through a column of activated alumina with thorough flushing by 200 ml. of anhydrous benzene. The filtrate on evaporation gave a crystalline solid which was complexed with *sym*-trinitrobenzene to give 388 mg. of orange plates from alcohol, m.p. 133–135°. This corresponds to 136 mg. of hydrocarbon, a yield of 24%. The complex was dissolved in 10 ml. of dry benzene and dissociated by passing through a tower of activated alumina with thorough washing. After removing the ben-

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