Recrystallization of part of the latter yielded pure lactone of 2-(α-hydroxy-α-methylbenzyl)-7-fluoro-1-naphthoic acid, VII, m.p. 193.0–194.0°.

Anal. Calcd. for $C_{19}H_{13}FO_2$: C, 78.0; H, 4.5. Found: C, 77.7; H, 4.8.

Hydrogenation of 4.0 g. of VII, m.p. 178–182° in alcohol in the presence of 0.4 g. of palladium chloride and 4.0 g. of charcoal (Darco G-60) for 18 hr. at 40 p.s.i. and at 20° gave 3.0 g. (75%) of pure 2-(α-methylbenzyl)-7-fluoro-1-naphthoic acid (IX), m.p. 172.0–173.0°, on recrystallization from aqueous-ethanol.[15]

Anal. Calcd. for $C_{19}H_{15}FO_2$: C, 77.6; H, 5.1. Found: C, 77.5; H, 5.3.

When 1.0, g. of IX, m.p. 165–168°, was treated as described[16] VI, m.p. 102.0–103.0°, was obtained in 40% yield after purification as above. A mixed m.p. with the sample of VI prepared from II showed no depression.

Lactone of 2-(α-hydroxy-α-phenylbenzyl)-7-fluoro-1-naphthoic acid (VIII). To a Grignard reagent prepared from 1 g. of magnesium and 6.3 g. of bromobenzene in 50 ml. of ether was added a solution of 5.9 g. of III, m.p. 174–178°, in 100 ml. of benzene. After refluxing for 16 hr. the reaction mixture yielded 4.2 g. (60%) of VIII, m.p. 156–158°. Recrystallization from benzene-petroleum ether (b.p. 60–69°) afforded the analytical sample, m.p. 163.0–164.0°, which was not depressed by mixing with a sample of VIII obtained (see above) from the condensation of I with benzene.

Anal. Calcd. for $C_{24}H_{15}FO_2$: C, 81.4; H, 4.2. Found: C, 81.7; H, 4.3.

In addition to mixed melting point determinations, the identity of samples of supposedly identical compounds was checked by infrared analysis.

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(15) Catalytic hydrogenation was found to be superior to zinc and acid[9] or zinc and alkali reductions. The latter methods gave poor yields of reduced acid and considerable starting material was recovered unchanged. See forthcoming publication of M. S. Newman and E. H. Wiseman for further discussion.

(16) Compare to conversion of compound VIII to X in L. F. Fieser and M. S. Newman, *J. Am. Chem. Soc.*, **58**, 2376 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

Some New 9-Dimethylphenylanthracenes

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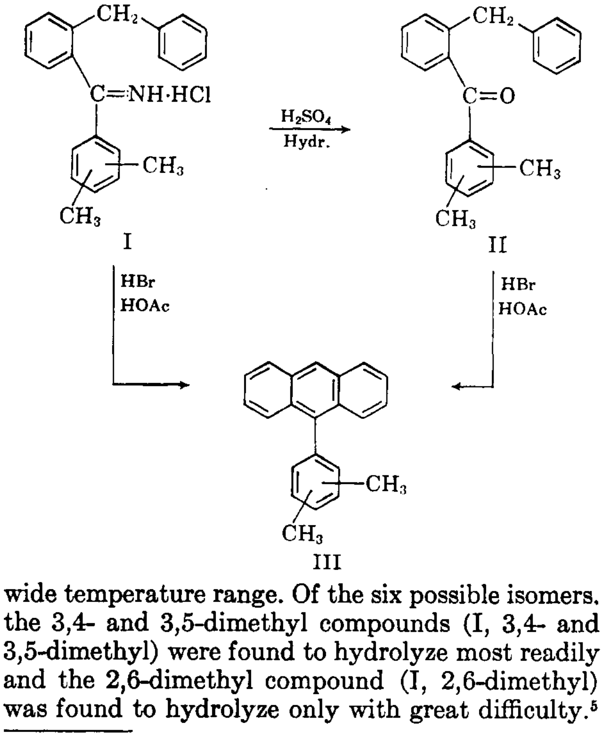
Using previously described methods of cyclization, a series of new 9-dimethylphenylanthracenes has been prepared. Six new ketimine hydrochlorides and six new ketones which are intermediates in the syntheses were isolated. Three additional new ketimine hydrochlorides were also prepared to complete previously reported work.

Bradsher's method of aromatic cyclodehydration[2] for the preparation of hydrocarbons was introduced in 1940. Later publications extended the usefulness of this synthesis. So for example, Bradsher and Vingiello[3] prepared a series of 9-(monosubstituted phenyl)anthracenes and Vingiello and Bořkovec[4] prepared a series of 9- and 10-(monosubstituted phenyl)-1,2-benzanthracenes. We have now extended Bradsher's aromatic cyclodehydration reaction to the preparation of 9-dimethylphenylanthracenes.



The reaction between 2-cyanodiphenylmethane and the appropriate Grignard reagent led to good yields of the ketimines, isolated as the hydrochlorides I. Although these compounds could be prepared in good yields in a fair state of purity, the preparation of analytical samples proved quite difficult. This was due in part to the tendency of the compounds (I) to hydrolyze and in part to the fact that the compounds melted with decomposition over a wide temperature range. Of the six possible isomers, the 3,4- and 3,5-dimethyl compounds (I, 3,4- and 3,5-dimethyl) were found to hydrolyze most readily and the 2,6-dimethyl compound (I, 2,6-dimethyl) was found to hydrolyze only with great difficulty.[5]

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(1) This paper has been abstracted in part from the Master's thesis of Edward Kramer and the Doctorate thesis of Sih-gwan Quo presented to the Virginia Polytechnic Institute in 1954 and 1959 respectively.

(2) C. K. Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940).

(3) C. K. Bradsher and F. A. Vingiello, *J. Am. Chem, Soc.*, **71**, 1434 (1949).

(4) F. A. Vingiello and A. Bořkovec, *J. Am. Chem. Soc.*, **77**, 4823 (1955) and references listed there.

(5) J. B. Culbertson's results in a study of the factors affecting the rates of hydrolysis of substituted diphenylketimines, *J. Am. Chem. Soc.*, **73**, 4818 (1951), clearly imply that the difficulty is due to steric hindrance.

Using various hydrolysis conditions, it was possible to prepare all six isomeric ketones of the type II.

The hydrocarbons (III) were prepared by cyclizing either the corresponding ketimine hydrochloride or the ketone using the usual[3] acid mixture but at about 170° in a sealed tube. It was thus possible to prepare five of the six possible isomeric hydrocarbons of the type III. The 2,6-dimethyl compound (III, 2,6-dimethyl) could not be prepared by the methods tried. These attempts included reactions on the ketone II, 2,6-dimethyl, as well as the ketimine hydrochloride I, 2,6-dimethyl. Relatively mild reaction conditions gave only recovery of starting material while stronger reaction conditions resulted in cleavage and gave anthracene and tars. A rather detailed study of the cleavage of *meso*-substituted polynuclear aromatic hydrocarbons currently in press[6] elucidates this latter observation.

EXPERIMENTAL[7,8]

2-Benzyl-2',3'-dimethyl diphenylketimine hydrochloride (I, *2,3-dimethyl*). A Grignard reagent was prepared from 4.0 g. (0.16 mole) of magnesium, 30 g. (0.16 mole) of 1-bromo-2,3-dimethylbenzene, 150 ml. of dry ether and a crystal of iodine. The reaction started slowly, but once started, it went on to completion very smoothly. A solution of 17 g. (0.088 mole) of 2-cyanodiphenylmethane in 200 ml. of dry toluene was added. During the addition the mixture was heated gently, and the ether was slowly distilled. When the vapor temperature reached approximately 105°, the solvent was allowed to reflux for 20 hr. The reaction mixture was then cooled and decomposed with 25 ml. of 20% ammonium chloride solution. The organic layer was decanted and the solid residue was washed with benzene. The toluene and benzene solutions were combined and 20 ml. of concentrated hydrochloric acid was added. After the walls of the flask were scratched with a glass rod, the crude ketimine hydrochloride crystallized; yield 29 g. (quant.), m.p. 195–200° dec. The analytical sample was prepared by recrystallization from 2*N* hydrochloric acid. The resulting white crystals melted at 195–200° with decomposition.

Anal. Calcd. for $C_{22}H_{22}NCl$: C, 78.67; H, 6.60; Cl, 10.55; N, 4.18. Found: C, 78.19; H, 6.67; Cl, 10.17; N, 4.29.

The other ketimine hydrochlorides were prepared in a similar way and are listed in Table I together with their respective melting points and analytical data.

2',3'-Dimethyl-2-benzylbenzophenone (II, 2,3-dimethyl). A mixture of 13.0 g. (0.04 mole) of the ketimine hydrochloride, I, 2,3-dimethyl, 40 ml. of benzene and 150 ml. of 25% sulfuric acid was heated under reflux for 9 hr. The mixture was then cooled and the benzene layer separated, washed with dilute sodium hydroxide solution, then water and finally dried over calcium chloride and concentrated. The residual oil was distilled, b.p. 237–240° (1.5 mm.); 5.5 g. (48%).

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.80; H, 6.69.

The other ketones were prepared in a similar way and are listed in Table II together with their respective boiling and/or melting points and anaytical data.

TABLE I

New Ketimine Hydrochlorides

Methyl groups at	Yield, %	M.P.	Nitrogen Calcd.	Nitrogen Found
2,3	Quant.	195–200[a]	4.18[b]	4.29
2,4	70	134–140	4.18[b]	4.25
2,5	75	180–185	4.18[b]	4.04
2,6	Quant.	180–184	4.18[b]	4.35
3,4	70	193–194	4.18[b]	4.18
3,5	50	200–205	4.18[b]	4.24
2,[d]	70	182–185	4.35[c]	4.27
3,[d]	65	185–190	4.35[c]	4.43
4,[d]	55	186–190	4.35[c]	4.40

[a] All melted with decomposition. [b] Calculated for $C_{22}H_{22}NCl$. [c] Calculated for $C_{21}H_{20}NCl$. [d] The three monomethyl compounds represent previously unisolated intermediates in former work (See C. K. Bradsher and F. A. Vingiello *J. Am. Chem. Soc.*, **71**, 1434 (1949); F. A. Vingiello, J. G. Van Oot, and H. H. Hannabass, *J. Am. Chem. Soc.*, **74**, 4546 (1952); and F. A. Vingiello, M. O. L. Spangler and J. E. Bondurant, *J. Org. Chem.*, in press) and are being reported for the sake of completeness. They were prepared as were the dimethyl compounds (I).

TABLE II

New Ketones[a]

Methyl groups at	Yield, %	B.P.	Mm.	Carbon Found	Hydrogen Found
2,3	48	237–240[b]	1.5	87.80	6.69
2,4	61	216–218	2.0	87.69	6.84
2,5	98	[c]		87.57	7.07
2,6[e]	68	207–210[d]	2.0	87.86	6.74
3,4	52	240–241	5.0	87.59	6.71
3,5	83	213–215	1.5	88.19	6.93

[a] Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. [b] Crystallization from ethanol gave white crystals, m.p. 105–106°. [c] Crystals formed when the hydrolysis mixture was allowed to cool. These were recrystallized from ethanol and gave white crystals, m.p. 71.5–72.0°. [d] Crystallization from ethanol gave white crystals, m.p. 62–63°. [e] This ketone was prepared by heating the corresponding ketimine hydrochloride (I, 2, 6-dimethyl) with 42% sulfuric acid in a Carius tube for 12 hr. at 180°.

9-(2,3-Dimethylphenyl)anthracene (III, *2,3-dimethyl*). A mixture of 3 g. of the corresponding ketimine hydrochloride (I, 2,3-dimethyl), 20 ml. of 48% hydrobromic acid, and 40 ml. of glacial acetic acid was sealed in a Carius tube and heated for 9 hr. at 170°. After cooling, the tube was opened, and the acid mixture was neutralized with sodium hydroxide and extracted with benzene. The benzene extract was washed with water, dried over calcium chloride and concentrated. The concentrate was then chromatographed on a column (12 mm. × 300 mm.) packed with Fisher's Alumina (80–200 mesh) using petroleum ether (b.p. 30–60°) as the eluent.[9] On evaporation of the solvent from the percolate the hydrocarbon was obtained as white crystals; yield, 0.5 g. (20%). The analytical sample was prepared by recrystallizing this material from ethanol, m.p. 179–180°.

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(6) F. A. Vingiello and T. J. Delia, *J. Org. Chem.*, in press.

(7) All melting points are corrected.

(8) All analyses were carried out by Geller Microanalytical Laboratories, Bardonia, N. Y.

(9) Since the hydrocarbons are sensitive towards light, the chromatography is best performed in the absence of strong light. The progress of the hydrocarbon down the column is observed easily by illuminating the column with ultraviolet light from time to time.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.68; H, 6.60.

The 2,5-dimethyl compound (III, 2,5-dimethyl) was prepared in a similar way and is listed in Table III together with its melting point and analytical data.

9-(2,4-Dimethylphenyl)anthracene (III, *2,4-dimethyl*). A mixture of 5 g. of the corresponding ketone (II, 2,4-dimethyl), 15 ml. of 48% hydrobromic acid, and 30 ml. of glacial acetic acid was sealed in a Caruis tube and heated for 48 hr. at 170°. The mixture was worked-up in a manner similar to that described above for the 2,3-dimethyl compound (III, 2,3-dimethyl) and gave 0.6 g. (13%) of white needle-like crystals, m.p. 102–104°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.66; H, 6.50. The remaining hydrocarbons were prepared in a similar way and are listed in Table III together with their respective melting points and analytical data.

TABLE III

NEW HYDROCARBONS[a]

Methyl groups at	Yield, %	M.P.	Carbon Found	Hydrogen Found
2,3	20	179–180	93.68	6.60
2,4	18	102–104	93.66	6.50
2,5	12	118–119	93.50	6.71
3,4	58	139–140	93.46	6.50
3,5	74	159–160	93.60	6.46

[a] Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43.

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BLACKSBURG, VA.

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., PLASTICS DIVISION]

Chloromethylation of β-Chloroethylbenzene and the Preparation of *p*-Vinylbenzyl Alcohol[1]

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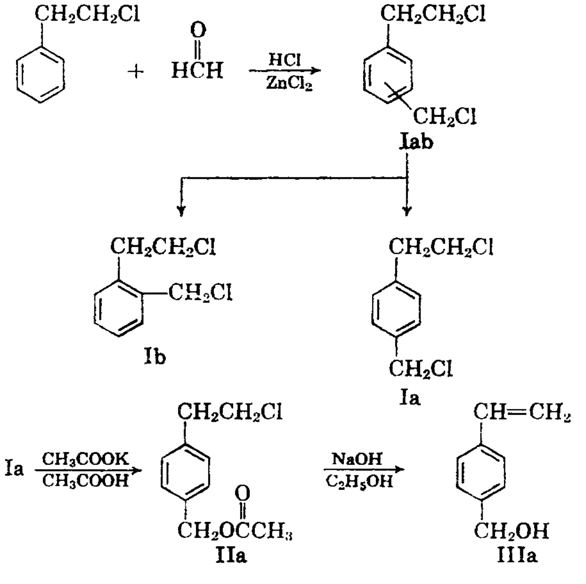
Received November 21, 1960

Chloromethylation of β-chloroethylbenzene gave a mixture of β-chloroethylbenzyl chlorides having an isomer distribution of 74 ± 3% *para* and 26 ± 3% *ortho*. No serious attempt was made to detect the *meta* isomer, although it could have been present only in small amount. Crystallization of this mixture gave the pure *para* isomer and fractional distillation afforded a sample of the *ortho* isomer. Higher boiling products obtained were identified as bis(chloromethyl)-β-chloroethylbenzene and bis(β-chloroethyl)diphenylmethane. The *ortho* and *para* isomers were converted to *ortho*- and *para*-β-chloroethylbenzyl acetate. Alcoholic base converted *p*-(β-chloroethyl)benzyl acetate to *p*-vinylbenzyl alcohol while similar treatment converted the *ortho* isomer to isochroman. The formation of isochroman is explained on the basis of a rapid saponification of the benzyl acetate portion of the molecule followed by nucleophilic displacement of the chlorine atom.

The preparation of vinylbenzyl alcohol first reported by Emerson *et al.*[3] utilized a series of steps starting with the chloromethylation of ethyl benzene. This work reports the synthesis of *p*-vinylbenzyl alcohol and the attempted synthesis of the *ortho* isomer.

The route used involved (a) the chloromethylation of β-chloroethylbenzene to yield a mixture of the *ortho* and *para* isomers of β-chloroethylbenzyl chloride, (Iab), which were separated into their pure components, (Ia and Ib); (b) conversion of the *p*-(β-chloroethyl)benzyl chloride (Ia) to *p*-(β-chloroethyl)benzyl acetate (IIa); and (c) the simultaneous hydrolysis and dehydrohalogenation of (IIa) to *p*-vinylbenzyl alcohol (III).



Chloromethylation. The chloromethylation of β-chloroethylbenzene proceeded smoothly to yield a mixture of *ortho* and *para* (β-chloroethyl)benzyl chloride. There was no apparent participation of the β-chlorine in alkylations under the conditions employed. Yields of 85% were obtained under optimum conditions. This reaction was reported previously by Kulka and Van Stryk,[4] but they did not report the separation of the two isomers. We have

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[1] Presented at the meeting of the Connecticut Valley Section of the American Chemical Society, November 19, 1960.

[2] Present address: Film Research Department, E. I. du Pont de Nemours and Company, Wilmington, Del.

[3] W. S. Emerson, J. W. Heyd, V. E. Lucas, W. I. Lyness, G. R. Owens, and R. W. Shortridge, *J. Am. Chem. Soc.*, 69, 1905 (1947).

[4] M. Kulka and F. G. Van Stryk, *Can. J. Chem.*, 33, 1130 (1955).