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GENERAL ANILINE AND FILM CORPORATION]

FRIEDEL-CRAFTS REACTIONS WITH γ-VALEROLACTONE. II. A SYNTHESIS OF 1-METHYL- AND 1,4-DIMETHYL-ANTHRACENES[1]

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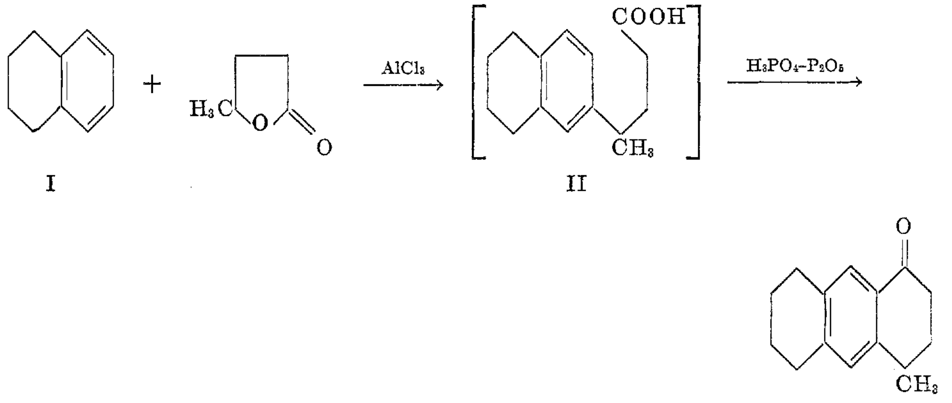
As part of a program to study the reactions of lactones and aluminum chloride with aromatic systems, tetralin was found to react smoothly with γ-valerolactone, and the substituted valeric acid so formed was cyclized, without isolation, by means of polyphosphoric acid as shown below. The major product of the reaction is derived from attack upon the 6-position of the tetralin nucleus.



I II III

When III was hydrogenated in ethanol using a 10% palladium-charcoal catalyst, a nearly quantitative yield of 1-methyl-1,2,3,4,5,6,7,8-octahydroanthracene was obtained. This material could not be induced to crystallize[3] however, and it seems probable that this may result from the presence of traces of isomeric impurities (chiefly 4-methyl-1,2,3,4,5,6,7,8-octahydrophenanthrene accruing originally from attack of the valeric acid moiety upon the 5-position of the tetralin nucleus,[4] or the 1-methyl isomer formed by cyclization of II in this position).

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[1] For Part I see *J. Am. Chem. Soc.*, **74**, 2564 (1952).

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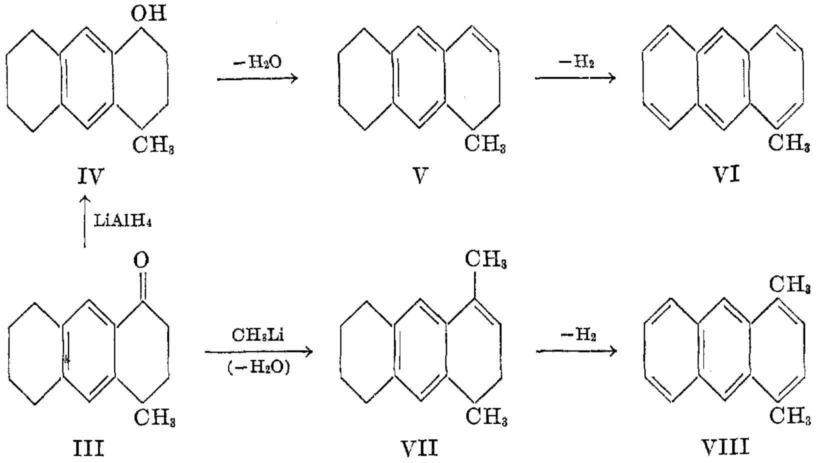
[3] The melting point 64–66° is given by von Braun, Bayer, and Fieser [*Ann.*, **459**, 287 (1927)], who prepared this compound by the catalytic reduction of 1-methylanthraquinone.

[4] The ratio of isomers obtained by electrophilic attack upon tetralin varies considerably with the nature of the attacking species, although evidence exists [Berthier and Pullman, *Bull. soc. chim. France*, 88 (1950)] of predilection for the 6-position. It would seem, *ceteris paribus*, that cations having large interference radii favor attack at the 6-position, whereas smaller cations give products containing larger amounts of the more hindered 5-isomers. Thus, on succinoylation under Friedel-Crafts conditions, tetralin yields a 73% yield of the 6-isomer [Fieser, *et al.*, *J. Am. Chem. Soc.*, **70**, 3197 (1948)]. The chloromethylation of

The products obtained in good yield from subsequent reactions, shown below indicate that the amount of this isomeric impurity present in III is not great. The partial dehydrogenation of compounds V and VII to give tetrahydroanthracenes was attempted, using palladium-charcoal as the dehydrogenation catalyst. From the mixtures thus obtained, however, only the anthracenes (VI and VIII) were isolated.



The ultraviolet absorption spectra of VI and VIII (Figure 1) show successive bathochromic shifts of the longer wave length maxima (with respect to those of anthracene) often characteristic of methyl substitution. The shift is smaller than that observed in the case of 9-methyl- (1) and 9,10-dimethyl-anthracenes (1, 2), respectively, as would be expected,[5] since in these latter examples substituents are located in those positions of the anthracene nucleus having the greatest conjugating power (3). Also, 1,4-dimethylanthracene exhibits at 293 mμ, a small additional peak, which is not visible in anthracene or the other methyl derivatives mentioned above. Figure 2 shows the infrared absorption spectra of compounds VI and VIII.

EXPERIMENTAL[6]

1-Oxo-4-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (III). A mixture of 264 g. (2.00 moles) of tetralin and 100 g. (1.00 mole) of γ-valerolactone was stirred in a three-necked

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tetralin was recently reinvestigated [Baltazzi, *Bull. soc. chim. France*, 167 (1953)], and found to give a 60% yield of product containing the 5- and 6-isomers in the approximate ratio of 1:2. Colonge and Rochas [*Bull. soc. chim. France*, 827 (1948)] have isolated, from the treatment of tetralin with ethylene oxide and aluminum chloride, a 47% yield of product containing nearly equal quantities of the 5- and 6-tetrahydronaphthylethanols. However, in most of its substitution reactions, tetralin behaves more in accordance with the generalizations outlined above.

[5] The relation between spectra and structures of the methyl 1,2-benzanthracenes has been discussed admirably by Badger [*J. Chem. Soc.*, 2500 (1949) and 1112 (1952)]. For a brief discussion of such shifts in the polymethylnaphthalene series, see W. L. Mosby, *J. Am. Chem. Soc.*, in press.

[6] All melting points were taken in Pyrex capillaries using Anschütz thermometers and a Hershberg apparatus.

flask equipped with a reflux condenser and a hydrogen chloride trap. To the mixture there was added portionwise, 140 g. (1.05 moles) of anhydrous aluminum chloride (powder). After introduction of all of the aluminum chloride, the reaction mixture was warmed gently until the evolution of hydrogen chloride abated. The mixture was then poured onto ice, and the product was extracted with ether. The combined ethereal extracts were washed with a very dilute hydrochloric acid solution saturated with sodium chloride, then dried over magnesium sulfate. Vacuum stripping removed the ether and permitted recovery of about 115 g. of unreacted tetralin.

The residual light brown oil was warmed and dissolved in 750 g. of polyphosphoric acid which had been preheated to 90°. The mixture was stirred and heated to 140°, then poured into warm water and the product was extracted with ether. The combined ethereal extracts were washed well with dilute sodium carbonate solution, then water, and finally were dried over magnesium sulfate and stripped of solvent *in vacuo*. Vacuum distillation of the residue gave 152 g. (71% yield), b.p. up to 135° (0.01 mm.). Redistillation afforded 107 g. (50% yield) of colorless liquid, b.p. 113–115° (0.01 mm.), n_D^{26} 1.5790.

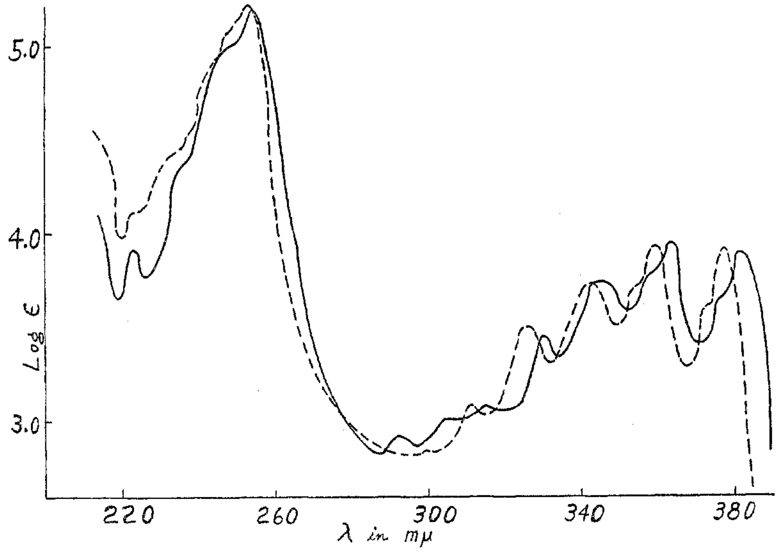

FIG. 1. THE ULTRAVIOLET ABSORPTION SPECTRA OF 1-METHYLANTHRACENE (VI, broken line) AND 1,4-DIMETHYLANTHRACENE (VIII, solid line), EACH IN ISOÖCTANE

Anal. Calc'd for $C_{15}H_{18}O$: C, 84.0; H, 8.40.

Found: C, 84.1; H, 8.46.

The *semicarbazone* was prepared and recrystallized from ethanol. It melted at 202–203° dec.

Anal. Calc'd for $C_{16}H_{21}N_3O$: C, 70.7; H, 7.75; N, 15.5.

Found: C, 70.5; H, 7.84; N, 15.5.

The *2,4-dinitrophenylhydrazone* melted at 209–210° after recrystallization from xylene.

Anal. Calc'd for $C_{21}H_{22}N_4O_4$: C, 64.0; H, 5.58; N, 14.21.

Found: C, 63.9; H, 5.69; N, 14.02.

1-Hydroxy-4-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (IV). To a stirred solution of 2.00 g. (0.053 mole) of lithium aluminum hydride in 100 ml. of dry ether, under nitrogen, there was added dropwise, a solution of 21.4 g. (0.10 mole) of III in 150 ml. of dry ether. The mixture was stirred for one hour at room temperature, then hydrolyzed by the addition of very dilute hydrochloric acid. The ether layer was separated and washed successively

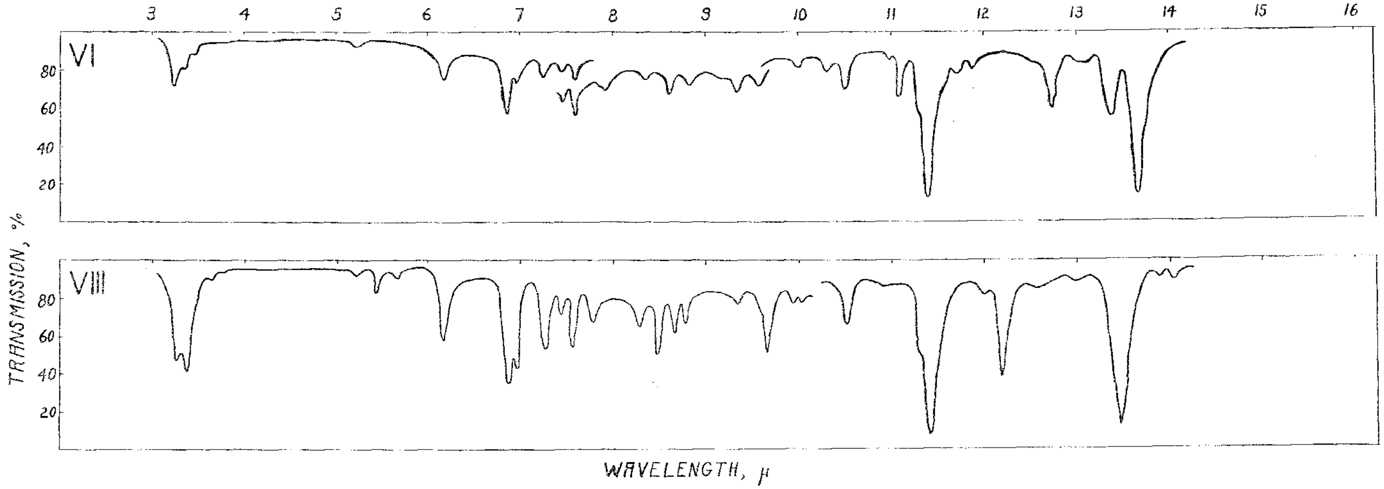

FIG. 2. THE INFRARED SPECTRA OF 1-METHYLANTHRACENE (VI) AND 1,4-DIMETHYL-ANTHRACENE (VIII). The curve of VI was obtained from a carbon tetrachloride solution in the 3.0–7.4 range, and from a Nujol mull in the 7.4–14.0 range. The curve of VIII represents a carbon tetrachloride solution in the 3.0–10.0 range and a Nujol mull in the 10.0–14.0 range

with dilute hydrochloric acid and dilute sodium bicarbonate solution, and finally was dried with magnesium sulfate. The ether was removed and the product vacuum-distilled, giving 18.3 g. (85% yield), b.p. 140-145° (0.4 mm.), n_D^{25} 1.5699.

Anal. Calc'd for $C_{15}H_{20}O$: C, 83.3; H, 9.30.

Found: C, 83.4; H, 9.30.

1-Methyl-1,2,5,6,7,8-hexahydroanthracene (V). A small crystal of iodine was added to 16.0 g. (0.074 mole) of IV contained in a small Claisen flask which was then gently warmed until dehydration was complete. When all of the water had carefully been driven out of the flask, a tiny lump of sodium metal was introduced, and the product then was vacuum-distilled, giving 14.4 g. (98% yield) b.p. 100-102° (0.2 mm.), n_D^{25} 1.5845.

Anal. Calc'd for $C_{15}H_{18}$: C, 90.90; H, 9.09.

Found: C, 90.89; H, 9.10.

1-Methylanthracene (VI). Dehydrogenation of the hexahydroanthracene V was accomplished by heating 5.4 g. of it with 0.5 g. of 10% palladium charcoal in a bath at 290-300° for one hour while bubbling a stream of carbon dioxide through the mixture. The cooled mixture was diluted with benzene, filtered and the filtrate was stripped of solvent. The yellow residue was dissolved in ethanol and converted to the picrate, giving 6.3 g. of brick-red crystals (55% yield) m.p. 112-114°. After two recrystallizations from methanol, the picrate was dissolved in benzene and passed through a column of alumina to regenerate the hydrocarbon. The benzene eluate was stripped of solvent *in vacuo*, and the yellow residue was dissolved in petroleum ether (b.p. 30-65°) and chromatographed on a column of alumina. White crystals of 1-methylanthracene, m.p. 83-84° [lit. 86° (4); 85-86° (5); 77° (6)] were obtained on evaporation of the eluate.

The *picrate* crystallized from methanol in red needles, m.p. 115.6-116.2° [lit. 113-115° (4, 5, 6)].

The *styphnate*, on recrystallization from methanol, formed red needles, m.p. 176.4-177.0°.

Anal. Calc'd for $C_{21}H_{15}N_3O_8$: C, 57.6; H, 3.43; N, 9.72.

Found: C, 57.5; H, 3.62; N, 9.60.

The *trinitrofluorenone derivative*, after two recrystallizations from benzene, gave dark red microneedles, m.p. 219.0-219.8°.

Anal. Calc'd for $C_{28}H_{17}N_3O_7$: C, 66.3; H, 3.35; N, 8.28.

Found: C, 66.43; H, 3.22; N, 8.34.

1,4-Dimethyl-3,4,5,6,7,8-hexahydroanthracene (VII). A suspension of 3.47 g. (0.50 mole) of clean lithium wire pieces in 100 ml. of anhydrous ether was stirred under nitrogen, and cooled in a Dry Ice-acetone bath, while 37.0 g. (0.26 mole) of methyl iodide in 100 ml. of anhydrous ether was added dropwise. The mixture was stirred until the lithium had dissolved (*ca.* two hours), then the cooling bath was removed. A solution of 21.4 g. (0.10 mole of III in 100 ml. of anhydrous ether was added dropwise over the period of one hour, with continued stirring. The reaction mixture was then decomposed with very dilute hydrochloric acid. The ether layer was separated and washed successively with very dilute hydrochloric acid, then dilute sodium bicarbonate solution, and finally was dried over magnesium sulfate. The ether was removed and the residue was heated with a small crystal of iodine until the evolution of water had ceased. A small piece of sodium metal was then added to the residue and the product was distilled, giving 17.2 g. (81% yield), b.p. 110-112° (0.4 mm.), n_D^{23} 1.5795.

Anal. Calc'd for $C_{16}H_{20}$: C, 90.56; H, 9.44.

Found: C, 90.45; H, 9.40.

1,4-Dimethylanthracene (VIII). Compound VII was dehydrogenated by heating 8.53 g. of it with 0.9 g. of 10% palladium charcoal in a bath at 290-300° for one hour, while bubbling a stream of carbon dioxide through the mixture. The reaction mixture was cooled, diluted with benzene and filtered, and the filtrate was stripped of solvent *in vacuo* to give 7.2 g. of pale yellow crystals, m.p. 65.6-70.0°. This material was recrystallized twice from ethanol, then converted to the picrate which was recrystallized twice from ethanol. The picrate was dissolved in benzene and the hydrocarbon regenerated by passage over a column of alumina. The benzene was removed from the eluate, and the pale yellow product was dissolved in petroleum ether (b.p. 20–40°) and chromatographed on an alumina column. The progress of the product band was checked by observing the column under ultraviolet light while it was developed with a solution of 1:100 ethanol:petroleum ether. Traces of yellow-and brown-fluorescing impurities were more tightly held on the column, and were separated from the product. The effluent solution was vacuum-stripped and the residue was crystallized from ethanol to give long needles with a slight yellow color, but which appeared greenish in reflected light owing to a rather strong blue fluorescence. The product melted at 73–74° [lit. 74° (4); 76° (7)].

Anal. Calc'd for $C_{16}H_{14}$: C, 93.2; H, 6.80.
Found: C, 93.3; H, 6.77.

The *picrate*, after recrystallization from ethanol, forms red needles, m.p. 139–140° [lit. 140° (4)].

The *styphnate* melted at 176.6–177.2° after recrystallization from ethanol.

Anal. Calc'd for $C_{22}H_{17}N_3O_8$: C, 58.54; H, 3.80; N, 9.31.
Found: C, 58.71; H, 3.98; N, 9.22.

The *trinitrofluorenone derivative*, after one recrystallization from benzene melted at 224–225°.

Anal. Calc'd for $C_{29}H_{19}N_3O_7$: C, 66.79; H, 3.67; N, 8.06.
Found: C, 66.90; H, 3.50; N, 8.08.

The ultraviolet absorption spectra shown in Figure 1 were obtained from solutions of compounds VI and VIII in isoöctane using a Cary recording spectrophotometer, Model 11. The following table shows the positions of absorption maxima and minima, and the corresponding values of log ϵ. Points of inflection ("shoulders") are parenthesized.

1-METHYLANTHRACENE				1,4-DIMETHYLANTHRACENE			
λ_{max}, mμ	log ϵ	λ_{min}, mμ	log ϵ	λ_{max}, mμ	log ϵ	λ_{min}, mμ	log ϵ
212	4.56	220	3.98	214	4.10	220	3.65
(222)	(4.10)			223	3.91	226	3.77
(250)	(5.12)			(237)	(4.38)		
253	5.22	293	2.81	(250)	(5.00)		
299	2.84	302	2.82	254	5.19	288	2.82
311	3.08	316	3.01	293	2.91	298	2.87
326	3.45	332	3.31	305	3.01	308	2.99
343	3.74	350	3.45	315	3.07	322	3.04
(354)	(3.71)			330	3.45	335	3.34
359	3.93	369	3.28	345	3.75	353	3.56
(373)	(3.61)			(360)	(3.80)		
377	3.92			364	3.94	372	3.20
				(378)	(3.67)		
				382	3.90		

Infrared absorption spectra. The curves shown in Figure 2 were obtained from compounds VI and VIII using a Perkin Elmer Model 12A instrument. The curve for compound VI was obtained from a Nujol mull in the 7.4–14.1 μ range,, and from a carbon tetrachloride solution in the 3.0–7.8 μ range, using a 4-mil cell. The curve for compound VIII represents a Nujol mull in the 10.2–14 μ range and a carbon tetrachloride solution in the 3.0–10.2 μ range (3-mil cell). The positions of all of the absorption bands within the range investigated for the two compounds are tabularized below. The corresponding values of per cent transmission can be obtained by reference to the curves in Figure 2.

POSITION OF INFRARED ABSORPTION BONDS, IN μ

1-METHYLANTHRACENE

3.24	6.96	8.36	10.30	11.70
3.36	7.25	8.61	10.50	11.87
3.48	7.45	8.83	10.97	12.72
5.22	7.59	9.35	11.08	13.06
6.18	7.86	9.58	11.28	13.38
6.86	7.92	10.00	11.38	13.66

1,4-DIMETHYLANTHRACENE

3.26	6.87	8.47	10.02	12.18
3.38	6.96	8.66	10.71	12.57
3.65	7.26	8.78	10.91	12.99
5.23	7.43	9.36	11.28	13.47
5.44	7.56	9.65	11.40	13.88
5.68	7.78	9.92	11.99	14.04
6.17	8.28			

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SUMMARY

A description is given of the condensation of γ-valerolactone with tetralin and conversion of the product to 1-methyl- and 1,4-dimethyl-anthracenes. Information on the spectra and on derivatives of the two anthracenes is given.

EASTON, PA.

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