[Contribution from the Central Research Laboratory, General Aniline & Film Corporation]

FRIEDEL-CRAFTS REACTIONS WITH γ-VALEROLACTONE. III. SYNTHESIS OF A TETRAMETHYLPHENANTHRENE

WILLIAM L. MOSBY[1]

Received June 26, 1953

During the condensation of γ-valerolactone with *o*- and *p*-xylenes (1) traces of crystalline materials were occasionally observed in the distillation residues. Since it seemed reasonable that these solids might represent products formed by the condensation of more than one valerolactone molecule per molecule of xylene, the deliberate synthesis of such substances was attempted. The following report of this work is incomplete and, unfortunately, the work cannot at present be continued. It is presented now, however, as some of the data obtained may be of interest in other connections.

The condensation of *o*-xylene with two moles of γ-valerolactone may, *a priori*, afford four isomeric dibasic acids, of which only three, however, are capable of cyclization to a diketone. These three acids (I, II, and III) and the corresponding diketones (IV, V, and VI) are shown in Figure 1.

Extension of this reasoning would indicate the structure of the corresponding acid and diketone obtained from *p*-xylene to be either VII and VIII or IX and X, respectively (Figure 2).

In each case, however, only one acid and one diketone was obtained. Since it is known that *o*-xylene is generally disubstituted in the 4,5-positions, structure I seems more likely than either II or III. However, as the two entering groups are quite large, steric repulsion may direct one or (less likely) both groups to alternative positions, and formulas II and III cannot summarily be dismissed. For similar reasons, structure VII is more reasonable than IX for the dibasic acid obtained from *p*-xylene. This acid, on heating, passes through a mesomorphic state (so-called "liquid-crystal") and, on the basis of this behavior, additional support for structure VII may be adduced from the work of Vörlander (2), who has shown that among suitably constituted benzene derivatives the phenomenon of mesomorphism is confined to the *para* isomer. With both *o*- and *p*-xylene, the introduction of a second valeric acid moiety meets considerable steric resistance, as is evidenced by the rather low yields of disubstituted products and considerable quantities of monosubstituted products which accompany them.

Cyclization of the dibasic acids I and VII to the diketones IV and VIII (for the sake of simplification it will be assumed, from this point on, that the two acids and diketones obtained have these structures) is in itself somewhat unusual, insofar as it represents an example of diacylation of the benzene nucleus.[2] Both

---

[1] Present address: American Cyanamid Co., Calco Chemical Division, Bound Brook, N. J.

[2] The most important example of diacylation of a benzene nucleus is the synthesis of anthraquinones by the cyclization of *o*-benzoyl-benzoic acids. In this unique example resonance stabilization of the product favors the cyclization, whereas, under acidic conditions, it is not generally possible to introduce two acyl groups into the benzene nucleus.

diketones are relatively high-melting solids which give high-melting bis-(2,4-dinitrophenylhydrazones). That the diketone obtained from *o*-xylene has structure VI is rendered more improbable by the observation that, on reacting the diketone with hydrazine, there was obtained none of the phthalazine derivative which would be expected from structure VI under these conditions. Although both diketones could obviously exist in *cis-trans* modifications, apparently only one isomer was obtained. No further work has been done on the diketone (obtained from *p*-xylene) whose structure is postulated as VIII.

The ultraviolet absorption spectra of the two diketones are shown in Figure 3. That of compound VIII rather closely resembles the published (3) curve of 1-oxo-1,2,3,4,5,6,7,8-octahydroanthracene in shape and intensity, but shows a bathochromic shift with respect to this substance of about 100 mμ. In the absence of any spectral data on other diacylbenzenes, little additional information may safely be deduced from these curves. The infrared spectra of the two diketones are shown in Figure 4.

Reduction of the diketone IV with lithium aluminum hydride afforded an oil, about 60 % of which crystallized. This evidently is one of the six theoretically possible stereoisomeric forms of XI. The number of stereoisomers of XI which could be obtained in practice is only three, since the ketone IV was apparently a single isomer. Even so, considerable specificity ($>$60 % of one isomer) in the reduction step is noticeable. The diol (XI) was dehydrated by heating with a trace of iodine and this product was dehydrogenated with 10 % palladium-charcoal at 325° for three hours. The over-all yield of these last two steps was about 11 %, indicating considerable resistance to the formation of an aromatic system. Resistance to aromatization has been observed in the dehydrogenation of hydroaromatic systems having substituents which interfere with each other when forced to approach coplanarity.[3] Under the dehydrogenation conditions employed, compound XII exhibited no tendency to dehydrogenate further to form a pyrene derivative. Analyses of the hydrocarbon (XII), its picrate, and its

---

However, in the case of polyalkylbenzenes (*e.g.* durene, *cf.* C. A. Thomas, *Aluminum Chloride in Organic Chemistry*, Reinhold, New York, 1941, page 222), diacylation may occur. The electron-withdrawing influence of the first acyl group is doubtless vitiated by the vicinal alkyl groups which prevent coplanarity of the acyl group and the aromatic nucleus, thereby inhibiting resonance interaction between them, and permitting nuclear attack by a second acyl carbonium ion. [*cf.* R. G. Kadesch and S. W. Weller, *J. Am. Chem. Soc.*, **63**, 1310 (1941); M. J. S. Dewar, *The Electronic Theory of Organic Chemistry*, Oxford, 1949, p. 203; and G. Baddeley, G. Holt and S. M. Makar, *J. Chem. Soc.*, 2416 (1952)]. It is the same situation, essentially, which obtains in the present instances.

There are indications that, under favorable circumstances, the resistance of the benzene ring to diacylation may be considerably reduced. For example, it has been shown [F. G. Mann and B. B. Smith, *J. Chem. Soc.*, 1898 (1951) and J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 3046 (1952)] that bis-2-cyano-(and carboxy-) ethylanilines can be cyclized to 1,6-diketojulolidines.

[3] For a discussion of aromatic systems having "interfering" substituents, see refs. 7 and 8; M. S. Newman, *J. Am. Chem. Soc.*, **62**, 2297 (1940); and F. Bell and D. H. Waring, *J. Chem. Soc.*, 2689 (1949).

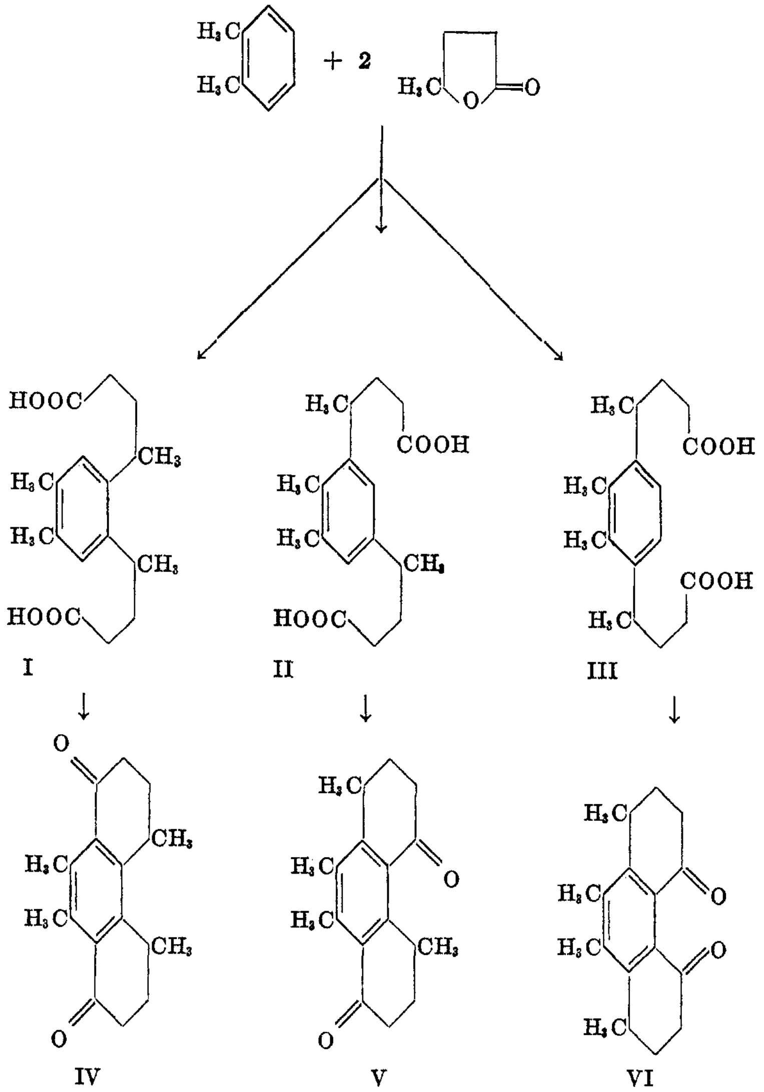


FIGURE 1

trinitrofluorenone derivative agree excellently for the formula $C_{18}H_{18}$—a tetramethylphenanthrene.

Alkyl group migrations are known to occur under Friedel-Crafts' conditions and also during cyclizations with polyphosphoric acid (1). However, the ultraviolet absorption spectrum of compound XII is clearly that of a phenanthrene and not an anthracene, and this fact admits only structures IV, V and VI for consideration as the diketone obtained from *o*-xylene. All other structures which may be written either lead by rearrangement to anthracenes or are derived from dibasic acids incapable of cyclization to a diketone. It is possible that, during the aromatization, migration of one or more methyl groups occurred (4), to give an

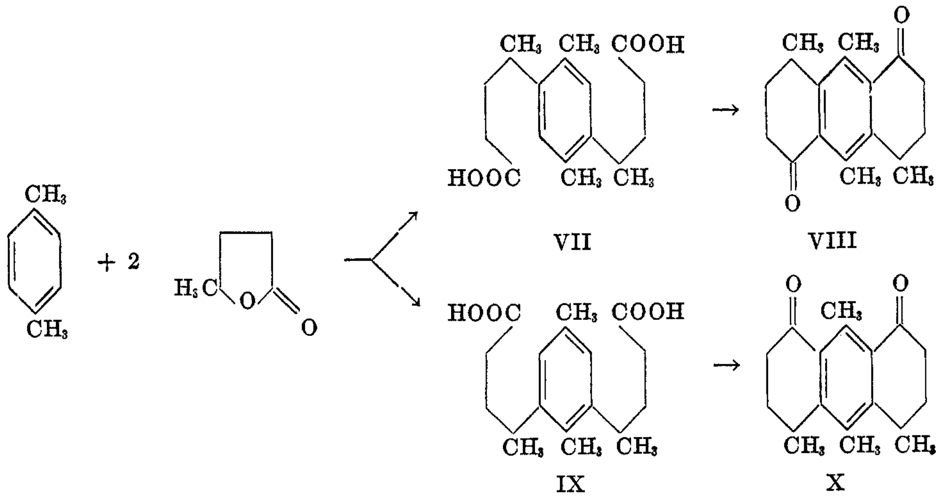


FIGURE 2

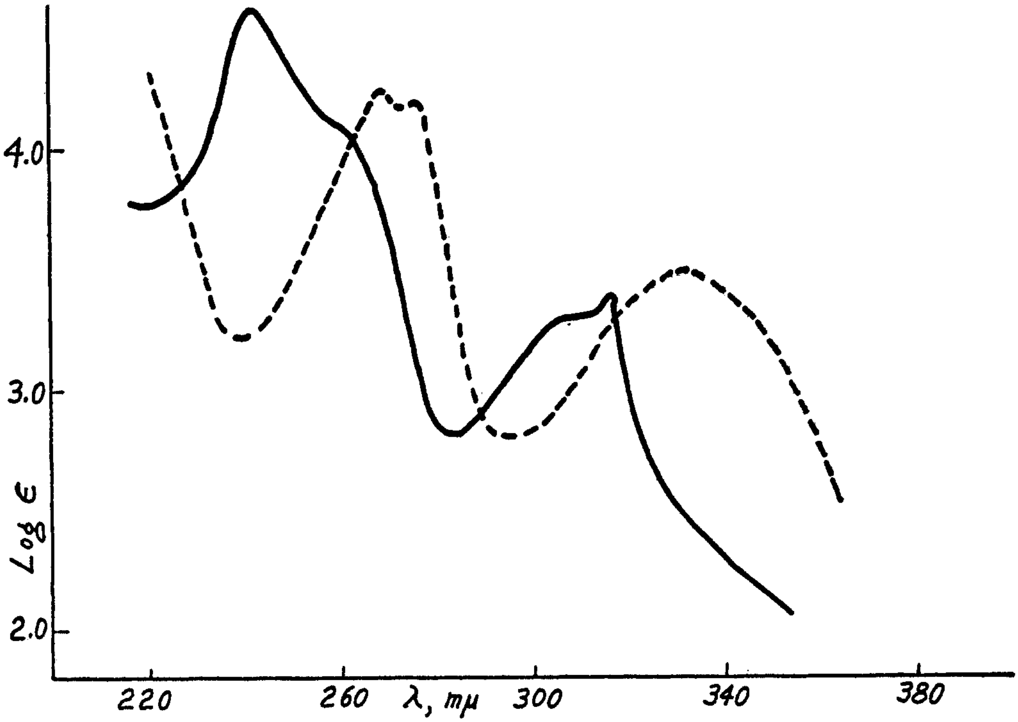


FIG. 3. ULTRAVIOLET ABSORPTION SPECTRA (in isoöctane) OF COMPOUND IV (————) AND VIII (--------).

isomeric tetramethylphenanthrene. The conditions employed here, however, were milder than those which usually seem to effect such rearrangements. This then would seem to limit the probable structure of the tetramethylphenanthrene to the 4,5,9,10-, the 1,5,9,10-, and the 1,8,9,10- isomers (in the order of de-

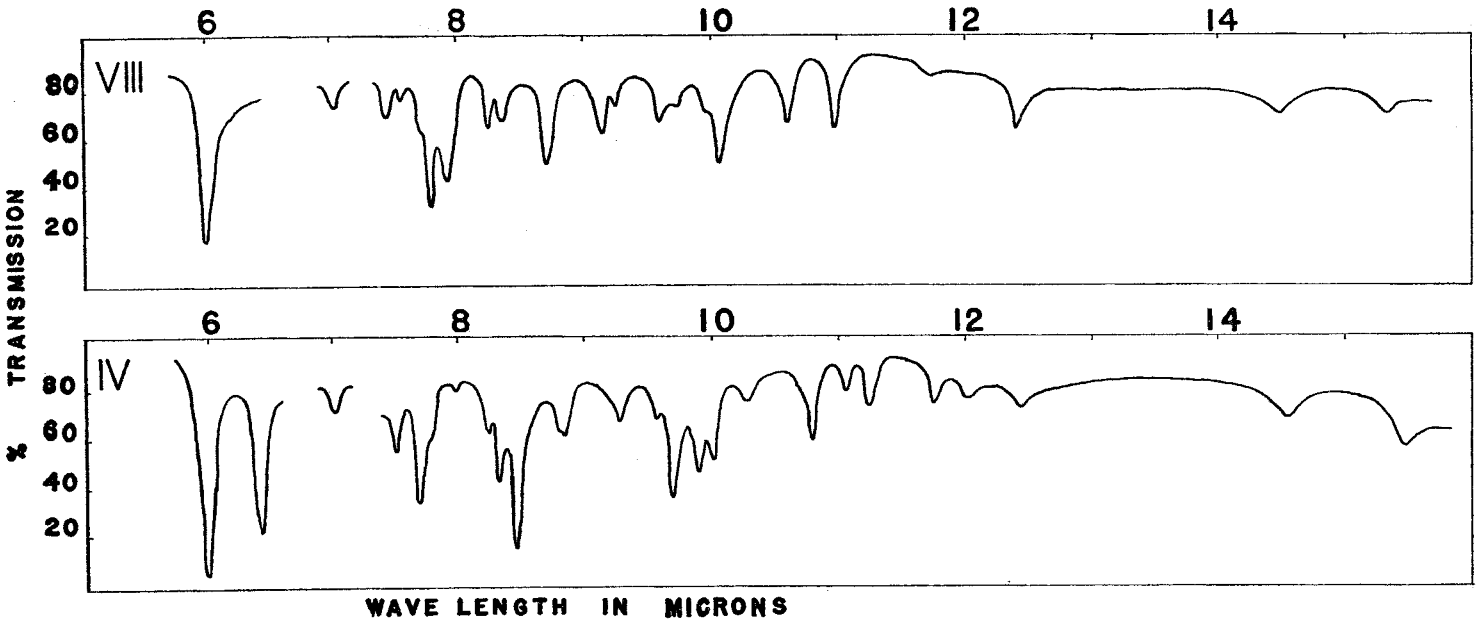
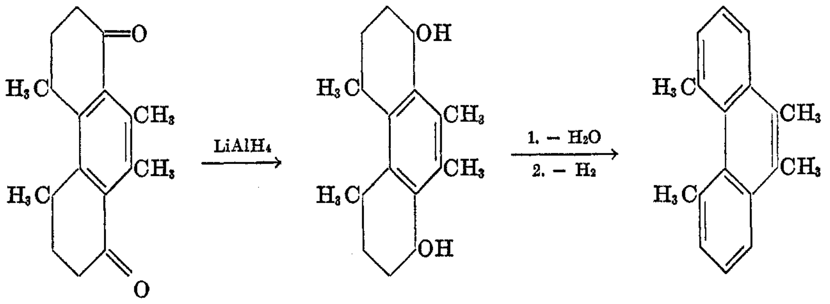


FIG. 4. INFRARED SPECTRA OBTAINED FROM NUJOL MULLS OF 1,5-DIOXO-4,8,9,10-TETRAmethyl-1,2,3,4,5,6,7,8-octahydroanthracene (VIII) and 1,8-Dioxo-4,5,9,10-tetramethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (IV).



IV XI XII

FIGURE 5

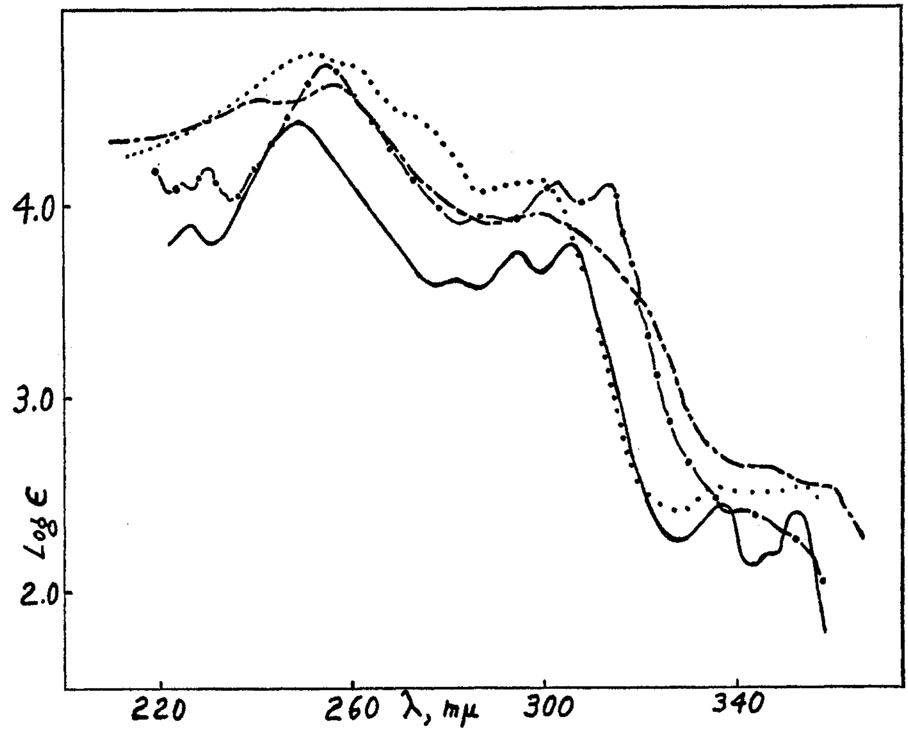


FIG. 6. ULTRAVIOLET ABSORPTION SPECTRA OF SOME METHYL PHENANTHRENES: ••••• 9,10-Dimethyl- (in absolute ethanol); •—•— 4,5-Dimethyl- (in 95% ethanol); ——— 1,4,5-Trimethyl- (in 95% ethanol), and —-— 4,5,9,10-Tetramethyl- (in absolute methanol).

creasing probability). The ultraviolet absorption spectrum of the $C_{18}H_{18}$ compound resembles those of 9,10-dimethyl- (5) and 4,5-dimethyl-phenanthrene (6) and 1,4,5-trimethylphenanthrene (7) which are shown in Figure 6. It is almost devoid of fine structure, a phenomenon which might be expected in a substance having the structure postulated (XII), since intramolecular strain (such as would result here from the methyl groups in positions 4 and 5) is known[4] often to suppress fine structure. The infrared spectra of phenanthrene, 4,5-dimethylphenanthrene, 9,10-dimethylphenanthrene, and of compound XII are shown in Figure 7.

Thus the evidence in favor of structure XII for the tetramethylphenanthrene (and structure IV for the diketone) is consistent though inconclusive. Irrefutable evidence for or against structure XII might be obtained by oxidation of the tetramethylphenanthrene to a dimethyl-9,10-phenanthraquinone and conversion of this to the phenazine. A comparison could then be made with the material thus obtained by Newman and Whitehouse (8) from 4,5-dimethylphenanthrene. Unfortunately, insufficient product was available for this oxidation.

Acknowledgment. The author wishes to thank Professor M. S. Newman for many helpful discussions and for a sample of 4,5-dimethylphenanthrene; Professor R. B. Sandin for a generous sample of 9,10-dimethylphenanthrene, and Dr. R. Norman Jones for very kindly making available from his file the ultraviolet spectra of several polymethylphenanthrenes. Thanks are also due to Miss Patricia Roxbury for valuable technical assistance; Dr. Henry Hemmendinger and Mrs. Janet Schwar for the ultraviolet spectra; Dr. S. T. Gross and Mrs. A. Balderston for the infrared spectra and Messrs. L. T. Lohr, L. J. Frauenfelder and T. E. Bonstein for the analytical data.

EXPERIMENTAL[5]

2,5-p-Xylene-bis(γ-methylbutyric acid) (VII). A mixture of 106 g. (1.0 mole) of *p*-xylene and 350 ml. of chlorobenzene was stirred, while 200 g. (2.0 moles) of γ-valerolactone and 280 g. (2.1 moles) of powdered anhydrous aluminum chloride were added slowly at about equal rates. When all of the reactants had been mixed, the solution was refluxed gently for about 15 minutes, then cooled and poured onto a mixture of ice and dilute hydrochloric acid. The hydrolysis mixture was allowed to stand overnight, then filtered, and the rubbery white curds were washed with water. The product was dissolved in excess hot potassium hydroxide solution and subjected to steam-distillation. The distillation residue was adjusted to approximately *p*H 7 and filtered from aluminum salts, etc. The filtrate was treated with charcoal, filtered, and the filtrate was acidified and allowed to cool. The mixture was filtered and the product was washed with cold water then slurried into a distillation flask with a little xylene. The xylene and water were removed *in vacuo* and the residue was vacuum-distilled. The first fraction obtained was 133 g., b.p. 120–140° (0.30–0.35 mm.) after which the temperature fell, then rose, and at 200–235° (0.5–1.0 mm.) there was collected 46.2 g. (15.1% yield) of product, which crystallized in the receiver. Recrystallization of the 46.2 g.-fraction from methanol (and decolorization with charcoal) gave 17.5 g. of white crystals with an additional crop of 18 g. of less pure material obtained from the mother liquors.

A sample for analysis was recrystallized from acetic acid. When heated, the acid changes

---

[4] Numerous examples may be found in the compilation of R. A. Friedel and M. Orchin (Ref. 3). See also E. Clar, *Aromatische Kohlenwasserstoffe*, Springer, Berlin, 2nd. Ed., 1952, pp. 90–92; R. N. Jones, *J. Am. Chem. Soc.*, **63**, 313 (1941) and W. L. Mosby, *J. Am. Chem. Soc.*, **75**, 3348 (1953).

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

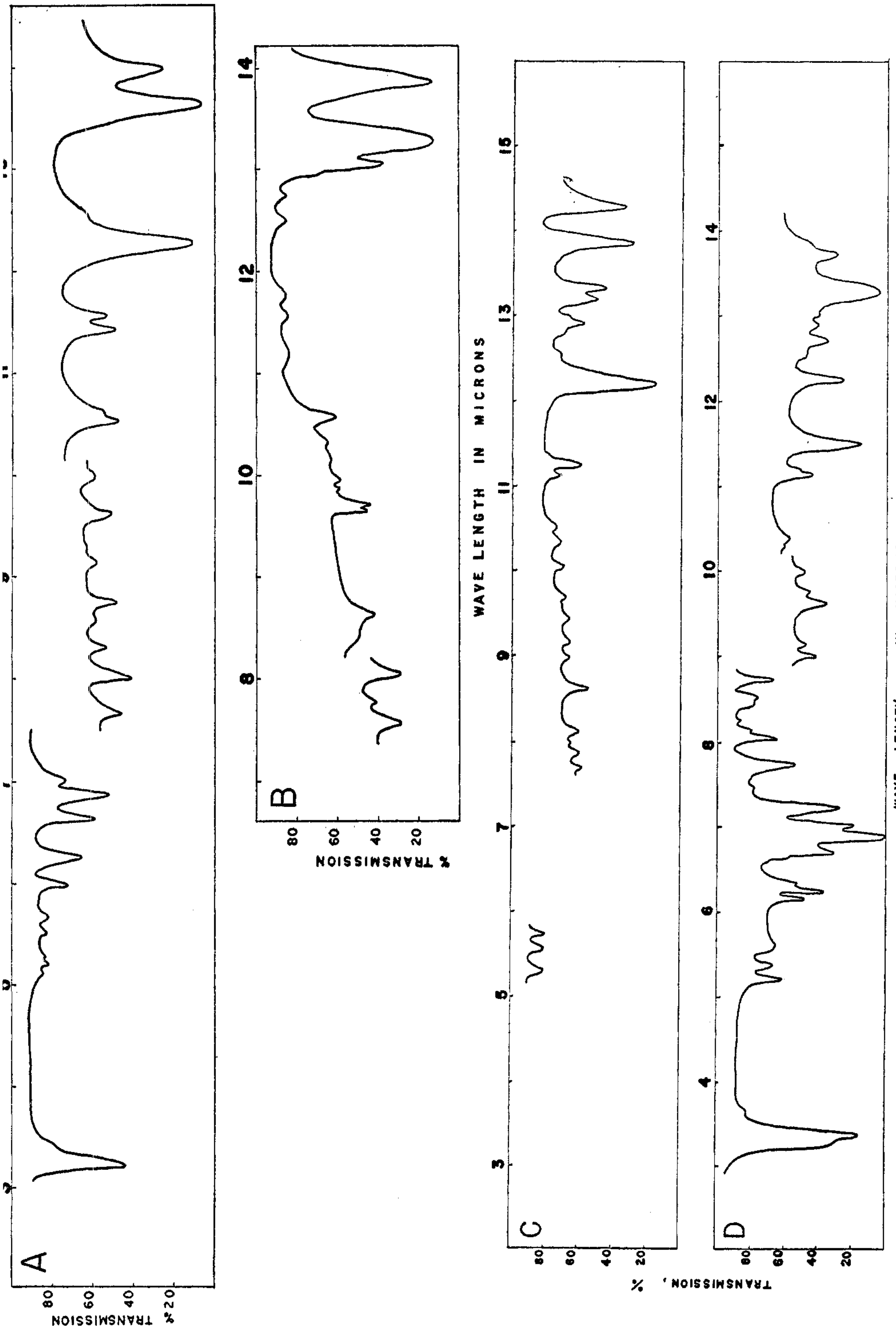


FIG. 7. INFRARED SPECTRA OF PHENANTHRENE (A), 9,10-DIMETHYLPHENANTHRENE (B), 4,5-DIMETHYLPHENANTHRENE (C), and 4,5,9,10-Tetramethylphenanthrene (D). The 3.0–7.5 μ portion of curve A and the 3.0–8.9 μ range of curve D were obtained from carbon tetrachloride solutions. The 7.5–14.5 μ portion of curve A, the 8.9–15.0 μ portion of curve D, and the whole of curves B and C were obtained from Nujol mulls.

to a mesomorphic state ("liquid crystal") at 200.6–202.0°, which then clears and yellows slowly up to 219.0°.

Anal. Calc'd for $C_{18}H_{26}O_4$: C, 70.6; H, 8.44.

Found: C, 70.4; H, 8.63.

1,5-Dioxo-4,8,9,10-tetramethyl-1,2,3,4,5,6,7,8-octahydroanthracene (VIII). To 250 g. of polyphosphoric acid, preheated to 100°, was added 8.8 g. of VII. Stirring was continued while the mixture was heated to 145° over a 15-minute period. It was then poured into water and the yellow flocculent precipitate was filtered, washed successively with water, acetone, and methanol, and dried. Two recrystallizations from toluene afforded 4.9 g. (63% yield) of nearly white platelets, m.p. 223.5–225°. The melting point was unchanged by additional recrystallizations from toluene or ethanol.

Anal. Calc'd for $C_{18}H_{22}O_2$: C, 80.0; H, 8.15.

Found: C, 80.1; H, 8.33.

The *bis-(2,4-dinitrophenylhydrazone)* was prepared by adding to a refluxing solution of the diketone in ethanol, a solution of 2,4-dinitrophenylhydrazine reagent. The orange precipitate was filtered hot, washed well with ethanol, and dried. Owing to the extreme insolubility of this derivative, no suitable solvent for its recrystallization was found. When introduced into a melting-point bath at 312° it melts with vigorous decomposition at 313°; but, if put into the bath below 310°, it blackens without melting below 335°.

Anal. Calc'd for $C_{30}H_{30}N_8O_8$: C, 57.1; H, 4.76; N, 17.8.

Found: C, 57.1; H, 4.75; N, 17.7.

1,8-Dioxo-4,5,9,10-tetramethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (IV). A mixture of 106 g. (1.0 mole) of *o*-xylene, 200 g. (2.0 moles) of γ-valerolactone, and 350 ml. of chlorobenzene was stirred in a three-necked flask having a reflux condenser equipped with a trap for absorption of hydrogen chloride. Gradually, 280 g. (2.10 moles) of powdered anhydrous aluminum chloride was added, and the mixture finally was refluxed for a few minutes, then hydrolyzed. The product was extracted with ether, and the combined ethereal extracts were washed with very dilute hydrochloric acid saturated with sodium chloride, dried over magnesium sulfate, and stripped of ether *in vacuo*. To the warm brown residue was added 500 g. of polyphosphoric acid which had been preheated to 100°. The mixture was stirred and heated to 135°, then cooled to 100° and poured into water. The oil was taken up in ether, washed well with dilute sodium carbonate solution, dried as before, and stripped of solvent. Vacuum-distillation of the residue gave two fractions: I, 99.2 g., b.p. 90–135° (0.25 mm.), consisting chiefly of 4,6,7-trimethyl-1-tetralone; and II, 69.1 g., b.p. 135–190° (0.25 mm.) [largely at 175–180° (0.25 mm.)], which contained the product, and solidified on cooling. Fraction II was triturated first with ethanol, then with successive portions of methanol, whereby 40.4 g. of white solid was obtained. Two recrystallizations of this material from ethanol and one from xylene gave white rectangular plates or blades, m.p. 188.6–189.6°.

Anal. Calc'd for $C_{18}H_{22}O_2$: C, 80.0; H, 8.15.

Found: C, 80.0; H, 8.15.

The *bis-(2,4-dinitrophenylhydrazone)* was prepared like that of compound VIII (described above). It melted at 276.5–277.0°.

Anal. Calc'd for $C_{30}H_{30}N_8O_8$: C, 57.1; H, 4.76; N, 17.8.

Found: C, 57.8; H, 5.25; N, 17.1.

1,8-Dihydroxy-4,5,9,10-tetramethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (XI). A solution of 2.0 g. (0.0526 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether was stirred under nitrogen in a three-necked flask equipped with a reflux condenser (Drierite guard tube) and an addition-funnel of the pressure-equalizing type. To it was added slowly through the addition-funnel a warm solution of 13.5 g. (0.50 mole) of the diketone IV in 300 ml. of xylene. The cloudy mixture was then refluxed and stirred for two hours, and allowed to stand overnight at room temperature. The reaction mixture was hydrolyzed by the addition of very dilute hydrochloric acid, and after the insertion of a solvent "take-off" between the flask and the condenser, the bulk of the ether was removed by distillation. The xylene layer was separated from the residue and washed with dilute hydrochloric acid, then with a dilute solution of sodium bicarbonate, and finally it was dried with magnesium sulfate. The xylene was removed *in vacuo* and the residue was allowed to stand, whereupon it solidified partly. There was obtained 8.5 g. (62% yield) of solid and 5.0 g. of oil. The solid portion, after recrystallization from cyclohexane, melted at 113.5–114.5°.

Anal. Calc'd for $C_{18}H_{26}O_2$: C, 78.8; H, 9.49.
Found: C, 78.7; H, 9.40.

4,5,9,10-Tetramethylphenanthrene (XII). To 4.0 g. of the solid diol (XI) in a small Claisen flask was added a tiny crystal of iodine. The flask was heated until the evolution of water had ceased, and the contents were then subjected to vacuum-distillation. There was obtained 2.6 g. (70% yield) of pale yellow viscous oil. To the oil was added 0.5 g. of 10% palladium-charcoal and the mixture was heated in a bath at 325° for three hours, while a stream of carbon dioxide was bubbled through it. The product was extracted with benzene, filtered, and stripped of solvent, whereupon it crystallized. Four recrystallizations from methanol (the first with charcoal) resulted in 0.4 g. (15.6% yield based on crude diene or 11.7% based on the diol used) of short white acicular crystals, m.p. 85.8–86.4°.

Anal. Calc'd for $C_{18}H_{18}$: C, 92.3; H, 7.68.
Found: C, 92.5; H, 7.51.

The *picrate* formed orange micro-needles, which, after two recrystallizations from methanol, melted at 164–165°.

Anal. Calc'd for $C_{24}H_{21}N_3O_7$: C, 62.25; H, 4.54; N, 9.08.
Found: C, 62.15; H, 4.69; N, 9.11.

The *TNF-derivative* was recrystallized from benzene in red microneedles, m.p. 185.0–185.5°.

Anal. Calc'd for $C_{31}H_{23}N_3O_7$: C, 67.8; H, 4.19; N, 7.65.
Found: C, 67.7; H, 4.10; N, 7.70.

Ultraviolet absorption spectra. The curves shown in Figures 3 and 6 were obtained with a Cary recording spectrophotometer. Tables of values of $\lambda_{max.}$ and $\lambda_{min.}$ together with the corresponding intensities (log ϵ) are given below. Inflections ("shoulders") are parenthesized.

COMPOUND	λ_{max}, μ	Log ϵ	λ_{min}, μ	Log ϵ
1,5-Dioxo-4,8,9,10-tetramethyl-1,2,3,4,5,6,7,8-octahydroanthracene (VIII)	225	4.09	240	3.20
	268	4.21	273	4.16
	276	4.17	294	2.78
	331	3.47		
1,8-Dioxo-4,5,9,10-tetramethyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (IV)	242	4.59	(260)	(4.10)
			284	2.81
	(307)	(3.30)		
	316	3.34		
4,5,9,10-Tetramethylphenanthrene (XII)	239	4.53	246	4.52
	256	4.62	289	3.90
	300	3.95		
	(340)	(2.65)		
	345	2.62		
	360	2.53		

Infrared absorption spectra. The band positions of the infrared spectra shown in Figures 4 and 7 are tabularized below. The relative intensities of the bands may be estimated by reference to the curves in Figures 4 and 7. Points of inflection or shoulders are parenthesized.

Compound VIII

5.981
7.047
7.435
7.570
(7.705)
7.806
7.930
8.244
8.375
8.711
9.116
9.251
9.597
9.728
9.960
10.060
10.604
10.964
11.709
12.406
14.492
15.349

Compound IV

5.981
6.431
7.097
7.513
7.692
(7.794)
7.981
8.244
8.319
8.460
8.787
8.842
9.242
9.565
9.695
9.891
10.000
10.293
10.787
11.049
11.235
11.743
12.004
12.437
14.545
15.455

Phenanthrene

3.236
5.510
5.682
5.977
6.262
6.645
6.863
7.013
7.663
8.013
8.306
8.562
8.753
9.141
9.615
9.975
10.537
(10.610)
11.415
11.554
12.269
13.642
13.985

9,10-Dimethylphenanthrene

7.55
7.76
8.04
(8.44)
8.62
9.64
9.70
9.86
9.96
10.17
10.33
10.58
11.10
11.57
11.75
12.50
12.74
(12.94)
13.07
13.28
13.87

4,5-Dimethylphenanthrene

5.291
5.479
5.698
7.675
7.843
7.968
8.110
8.606
8.993
9.174
9.434
9.690
10.04
10.33
10.526
11.142
11.248
12.217
(12.578)
(12.795)
12.911
(12.995)
13.333
13.869
14.285

4,5,9,10-Tetramethylphenanthrene (XII)

(3.268)
3.378
(3.656)
5.210
5.391
5.618
6.169
6.269
6.349
(6.631)
6.716
6.892
7.037
7.230
7.479
7.74
8.059
8.150
8.268
8.418
8.547
8.757
8.980
9.140
9.625
9.78
9.99
10.298
10.395
11.148
11.49
12.277
(12.55)
12.722
12.936
(13.03)
13.306
13.717

Easton, Penna.

REFERENCES

(1) Mosby, *J. Am. Chem. Soc.*, **74,** 2564 (1952).
(2) Vörlander, *Ber.*, **40,** 4527 (1907).
(3) Friedel and Orchin, *Ultraviolet Spectra of Aromatic Compounds*, Wiley, New York, 1951, Curve No. 61.
(4) *Cf.* Plattner, *Dehydrogenation with Sulfur, Selenium, and Platinum Metals* in *Newer Methods of Preparative Organic Chemistry*, Interscience, New York, 1948, pp. 39–40.
(5) Curve drawn from data given by Greenhow, McNeil and White, *J. Chem. Soc.*, 992 (1952).
(6) Ref. 3, Curve No. 352.
(7) Newman and Hussey, *J. Am. Chem. Soc.*, **69,** 3023 (1947).
(8) Newman and Whitehouse, *J. Am. Chem. Soc.*, **71,** 3664 (1949).