of ice-water. After separation of the organic layer, the aqueous medium was extracted three times with ether. The combined ethereal extracts were washed and dried as usual. Fractional distillation yielded 1-phenyl-2-fluoroethanol (VI) as a colorless oil of b.p. 55–59° (2 mm.), yield 12 g. (79%). It is remarkable that the b.p. of VI is about 30° below that of phenylmethylcarbinol.

Anal. Calcd. for C_8H_9OF: C, 68.6; H, 6.4; F, 13.6. Found: C, 68.6; H, 6.6; F, 13.8.

The carbinol VI gave a crystalline *p*-nitrobenzoate after treatment with *p*-nitrobenzoyl chloride in pyridine. The ester crystallized from ethanol in rods of m.p. 92–93°.

Anal. Calcd. for $C_{15}H_{12}O_4NF$: C, 62.3; H, 4.2. Found: C, 62.3; H, 4.3.

(b) **With Hydrogen and Palladium.**—ω-Fluoroacetophenone (9 g.) in isopropyl alcohol (35 cc.) was reduced at 18° and 693 mm. in the presence of 1.5 g. of palladium-on-charcoal (5%). During 4 hours 1830 cc. was absorbed (calcd. 1760 cc.). The catalyst was filtered off and the weakly acidic solution neutralized with sodium carbonate. Fractionation gave 6.5 g. (71%) of a colorless oil of b.p. 70–75° (12 mm.). Its *p*-nitrobenzoate proved identical with the ester of VI, described under (a).

When HCl was added to the reduction medium, hydrogen absorption continued beyond the theoretical amount and the yield of VI was correspondingly decreased. When the carbinol VI (4 g.) in isopropyl alcohol (25 cc.) was treated under the same conditions as fluoroacetophenone, no hydrogen was absorbed during 4 hours and the starting material was recovered quantitatively.

4. **1,1-Diphenyl-2-chloroethanol.**—This carbinol was prepared from ω-chloroacetophenone (6.5 g.) and phenylmagnesium bromide under the conditions described for the corresponding fluoro derivative. Fractionation gave a colorless oil of b.p. 70–75° (0.3 mm.), which solidified immediately. 1,1-Diphenyl-2-chloroethanol crystallized from petroleum ether–ligroin in prisms of m.p. 65.5°, yield 7.5 g. (76%). The carbinol (1 g.) and maleic anhydride (8 g.) were heated to 195–200° for 6 hours and the light-brown magma dissolved in a small volume of acetic acid. After 48 hours, 0.5 g. of yellow crystals was collected, of m.p. 168–169°, not depressed by admixture of authentic 4-phenylnaphthalene-1,2-dicarboxylic acid anhydride.

The absorption spectra were measured in 95% ethanol with a Beckman ultraviolet spectrophotometer. Carbon and hydrogen determinations for organic fluorine derivatives were carried out by the method of Bodenheimer and Goldstein.[18]

We wish to thank Mrs. M. Goldstein for the micro-analyses and Miss H. Weiler for the spectrographic data.

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[18] W. Bodenheimer and M. Goldstein, *Bull. Res. Council Israel*, III, 53 (1953).

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Aromatic Cyclodehydration. XXVIII.[1] 9,10-Dialkylphenanthrenes by Cyclization of Ketones

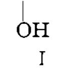
BY CHARLES K. BRADSHER AND WINSTON J. JACKSON, JR.[2]

RECEIVED MARCH 20, 1954

The cyclization of 2-biphenylyl ketones (IV) can be extended to cases where R and R' are normal alkyl groups. Where R or R' is isopropyl, cyclization is accompanied by loss of the isopropyl group. A similar loss of isopropyl group has been observed in an olefin oxide type cyclization.

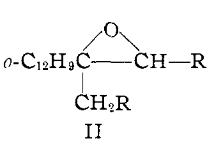
The first 9,10-dialkylphenanthrenes were prepared by Zincke and Tropp[3] who treated phenanthraquinone with alkyl Grignard reagents and dehydrated the resulting glycol to a 10,10-dialkyl-9-phenanthrone. Where the R group was methyl or ethyl, reduction and rearrangement with hydriodic acid yielded the corresponding dialkylphenanthrene, but this reaction failed where R was the propyl group. The same two hydrocarbons were obtained by Meerwein[4] by reduction and rearrangement of 9-methyl-9-acetylfluorene and 9-ethyl-10-propionylfluorene.

Another method[5] involves use of carbinols I which are obtained by the addition of biphenylylmagnesium iodide to symmetrical ketones. Dehydration and epoxidation of the carbinols yields the epoxides II which may be cyclized to 9,10-dialkylhydrocarbons (V, X = H; R' = CH_2R). This is clearly a method which cannot be adopted to the unambiguous synthesis of any desired 9,10-dialkylphenanthrene derivative.



$$o\text{-}C_{12}H_9\underset{\displaystyle OH}{\underset{|}{C}}(CH_2R)_2$$

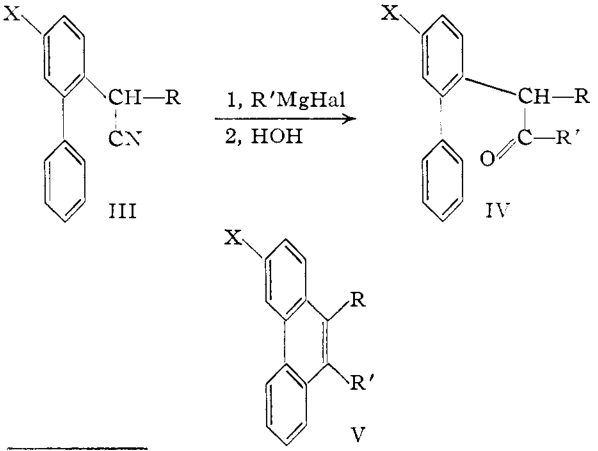
I



$$o\text{-}C_{12}H_9\underset{\displaystyle CH_2R}{\underset{|}{C}}\overset{O}{\text{———}}CH\text{—}R$$

II

The method which has been developed recently[6,7] for the synthesis of 9-alkyl-10-arylphenanthrene derivatives gave promise of being sufficiently general to permit the preparation of diverse kinds of 9,10-dialkylphenanthrenes. The present investigation was undertaken to determine the limitations of the method.



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[1] For the preceding communication of this series, see THIS JOURNAL, **76**, 734 (1954).

[2] Public Health Service Fellow of the National Cancer Institute, 1950–1952.

[3] T. Zincke and W. Tropp, *Ann.*, **362**, 242 (1908); H. Meerwein, *ibid.*, **396**, 200 (1913).

[4] H. Meerwein, *ibid.*, **405**, 129 (1914).

[5] C. K. Bradsher and S. T. Amore, THIS JOURNAL, **65**, 2016 (1943); **66**, 1280 (1944).

[6] C. K. Bradsher and W. J. Jackson, Jr., *ibid.*, **73**, 3235 (1951).

[7] C. K. Bradsher and W. J. Jackson, Jr., *ibid.*, **74**, 4880 (1952).

TABLE I

PREPARATION OF KETONES, $C_{12}H_9CHRCOR'$ (IV)

R	R′	Yield, %	M.p. or b.p., °C.	Mm.	$n^{25}D$	Formula	Analysis of ketone, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
CH_3	CH_3	88[a]	151[b]	5	1.5718	$C_{16}H_{16}O$	85.67	85.79	7.19	7.33
CH_3	C_2H_5	77	152–155	4	1.5663	$C_{17}H_{18}O$	85.67	85.80	7.61	7.44
CH_3	n-C_3H_7	88	150–154	3	1.5565	$C_{18}H_{20}O$	85.67	85.88	7.99	8.28
CH_3	i-C_3H_7	29[c]	77–78			$C_{18}H_{20}O$	85.67	85.64	7.99	8.04
CH_3	n-C_4H_9	92	170–173	5	1.5505	$C_{19}H_{22}O$	85.67	85.74	8.33	8.12
C_2H_5	C_2H_5	88	133–138	1	1.5572	$C_{18}H_{20}O$	85.67	85.52	7.99	8.25
C_2H_5	i-C_3H_7	[d]	134–139	1	1.5584[e]	$C_{19}H_{22}O$		[f]		
n-C_3H_7	CH_3	70[g]	53–55			$C_{18}H_{20}O$	85.67	86.44[h]	7.99	8.28
n-C_3H_7	n-C_3H_7	83	146–152	1	1.5448	$C_{20}H_{24}O$	85.67	85.82	8.63	8.79
i-C_3H_7	CH_3	84	131–137	1	1.5582	$C_{18}H_{20}O$	85.67	86.00	7.99	7.98
i-C_3H_7	C_2H_5	87[i]	135–143	1	1.5538	$C_{19}H_{22}O$	85.67	86.22[h]	8.33	8.10

[a] All alkyl halides were bromides except methyl iodide. [b] This compound crystallized after standing several days, m.p. 38–43°. [c] Yield of product cystallized from petroleum ether as white prisms, m.p. 74–77°. When the oil obtained by concentrating the mother liquor was refluxed with alcoholic potassium hydroxide solution and acidified, some α-(2-biphenylyl)-propionic acid was obtained. [d] The yield, based on the assumption that the product was entirely ketone, was 70%; however, when 1.0 g. was cyclized with a hydrobromic–acetic acid mixture, 0.5 g. of α-(2-biphenylyl)-butyric acid was obtained, indicating the presence of a considerable quantity of unchanged nitrile with the ketone. Also a very small amount of α-(2-biphenylyl)-butyraldehyde, isolated as the 2,4-dinitrophenylhydrazone, was present with the ketone. [e] This value was above that of the pure compound since starting material was present. [f] The compound was not analyzed since starting material also was present. [g] Yield of compound melting at 51–54.5°. [h] A satisfactory analysis of the 2,4-dinitrophenylhydrazone was obtained. [i] A small amount of nitrile (VI, X = H; R = i-C_3H_7) was present with the ketone.

The alkylated nitriles III (X = H) were prepared in yields of 72–91%, with an average of 83%. In addition to the methyl[1] and ethyl[6] derivatives (III) already described, the propyl and isopropyl were prepared. By addition of the appropriate Grignard reagents to the above nitriles, eleven ketones of structure IV (X = H) were prepared.

As may be seen in Table I, in the two cases where R′ was the isopropyl group, the yields were low (about 30%) and a small amount of nitrile remained unchanged. In the nine remaining cases, the yields were 70–92% with an average yield of 84%. The low yields obtained with isopropylmagnesium bromide may be due in part to tautomerism of the nitrile with destruction of a portion of the Grignard reagent, but a part of the loss may be due to reduction. Preparation of a 2,4-dinitrophenylhydrazone from a crude sample of 4-(2-biphenylyl)-2-methylpentanone yielded a mixture, 10% of which was the dinitrophenylhydrazone of α-(2-biphenylyl)-butyraldehyde (IV, X = H; R = C_2H_5; R′ = H).

Those ketones (IV, X = H) having no isopropyl group cyclized in 86–100% (average 92%) to the expected 9,10-dialkylphenanthrenes. This was accomplished in most cases by refluxing the ketone in a hydrobromic–acetic acid medium for 0.5 to 1.5 hours, allowing the mixture to cool and collecting the product which crystallized. In the preparation of the 9,10-dimethylphenanthrene, refluxing was stopped after only three minutes since by that time the high melting hydrocarbon had crystallized from the boiling solution. The results are summarized in Table II.

TABLE II

9,10-DIALKYLPHENANTHRENES (VIII) BY CYCLIZATION OF KETONES VII

R	R	Reflux time, hr.	Yield, %	Crystal form[a]	Observed m.p., °C. Hydrocarbon	Picrate[b]
CH_3	CH_3	(3 min.)[c]	87	Needles	143.5–144.5[d]	192–193
CH_3	C_2H_5	1	86	Plates	82.5–84[e]	148–149
CH_3	C_3H_7	1.5	100	Powder	92.5–93.5[f]	118.5–119.5
CH_3	C_4H_9	1	92	Needles	89–89.5[g]	89–91[h]
C_2H_5	C_2H_5	1.5	91	Flakes	105–106[i]	118–119
C_3H_7	CH_3	0.5	100	Powder	92.5–93.5[j]	118.5–119.5
C_3H_7	C_3H_7	9[k]	89	Needles	95.5–96.5[l]	99–102[h]

[a] All hydrocarbons were recrystallized from ethanol. The picrates were obtained as orange needles from ethanol. [c] The product began crystallizing from the refluxing acid mixture during the second minute. [d] Bradsher and Amore[5] reported a melting point of 142.5–143° for the hydrocarbon and 193–194° for the picrate. [e] Bradsher and Amore[5] found that the hydrocarbon melted at 85° and the picrate at 150°. [f] *Anal.* Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.36; H, 7.63. [g] *Anal.* Calcd. for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.88; H, 8.25. [h] The picrate dissociated on attempted recrystallization from ethanol. [i] Zincke and Tropp[8] reported a melting point of 105–106° for the hydrocarbon. The picrate has not previously been reported. [j] The mixed melting point of this compound and the n-propylmethylphenanthrene derivative showed no depression. [k] Since the ketone was not completely soluble in the boiling acid mixture, 30 ml. of acetic acid was used instead of 20 ml. [l] *Anal.* Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.34; H, 8.49.

To ascertain the effectiveness of cyclization with sulfuric acid, two ketones were cyclized by the action of concentrated sulfuric acid at 0° for five minutes. 9-Ethyl-10-methylphenanthrene (V, X = H; R = CH_3; R′ = C_2H_5) and 9-n-propyl-10-methylphenanthrene were obtained in 66% yield from 2-(2-biphenylyl)-hexanone (IV, X = H; R = CH_3; R = C_3H_7). The yields and purity of product were both inferior to those obtained in the hydrobromic–acetic acid cyclization.

The cyclodehydration of isopropyl ketones IV in hydrobromic–acetic acid was anomalous, for when either R or R′ was isopropyl this group was eliminated on cyclization. The reaction was decidedly slower than in the previous cases, for whereas cyclization was generally complete in less than an hour in the examples in Table II, it took at least 24 hours when R or R′ was isopropyl. The yields in the combined cyclization–elimination reaction are shown in Table III.

In order to obtain more information regarding the loss of an isopropyl group during cyclization,

TABLE III

9-ALKYLPHENANTHRENES FROM KETONES

Ketones (X = H) R	R′	9-Alkyl-phenanthrene	Yield, %
CH_3	i-C_3H_7	Methyl	71
C_2H_5	i-C_3H_7	Ethyl	25[a]
i-C_3H_7	CH_3	Methyl	56[b]
i-C_3H_7	C_2H_5	Ethyl	52[c]

[a] This yield is low since alkylated nitrile (III, X = H; R = C_2H_5) was present with the ketone. On refluxing 1 g. of the ketone–nitrile mixture with hydrobromic and acetic acids, the acid corresponding to the nitrile (0.5 g.) was obtained with the hydrocarbon. It is possible that a small part of the yield is from the cyclization of a little α-(2-biphenylyl)-butyraldehyde (IV, X = H; R = C_2H_5; R′ = H) which was also present with the ketone. [b] A small amount of α-(2-biphenylyl)-β-methylbutyric acid also was isolated, indicating that a little α-(2-biphenylyl)-β-methylbutyronitrile (III, X = H; R = $(CH_3)_2CH$) was present with the ketone (IV, X = H; R = $(CH_3)_2CH$; R′ = CH_3). [c] In addition to the hydrocarbon, some α-(2-biphenylyl)-β-methylbutyric acid was isolated, indicating the presence of some nitrile (III, X = H; R = $(CH_3)_2CH$) with the ketone.

2-(5-methoxy-2-biphenylyl)-4-methylpentanone-3 (IV, X = OCH_3; R = CH_3; R′ = $CH(CH_3)_2$) was prepared and cyclized. This ketone was obtained by a series of reactions analogous to those used in preparing the ketones previously discussed. The action of isopropylmagnesium bromide on α-(5-methoxy-2-biphenylyl)-propionitrile (III, X = OCH_3; R = CH_3) produced the expected ketone (IV, X = OCH_3; R = CH_3; R′ = $CH(CH_3)_2$] in 34% yield. The ketone was an easily purified crystalline solid. When a sample of this ketone was refluxed with hydrobromic and acetic acid, it underwent cyclization, elimination of the isopropyl group and cleavage of the ether linkage to produce a 72% yield of 3-hydroxy-10-methylphenanthrene (V, X = OH; R = CH_3; R′ = H). This product was identical with that obtained by cyclizing α-(5-methoxy-2-biphenylyl)-propionaldehyde[1] (IV, X = OCH_3; R = CH_3; R′ = H).

The facile elimination of an isopropyl group from ketones of type IV suggested an explanation for a hitherto unexplained observation of Amore.[8] He had treated diisobutyl ketone with 2-biphenylylmagnesium iodide and carried out a phenanthrene synthesis proceeding as usual from the crude carbinol (I, R = $(CH_3)_2CH$) *via* the olefin and the epoxide (II, R = $(CH_3)_2CH$). He found that cyclization yielded a hydrocarbon, m.p. 95–96°, which did not have the composition calculated for 9-isopropyl-10-isobutylphenanthrene, the expected product. It has now been found that the previously unidentified hydrocarbon is 9-isobutylphenanthrene.

The mechanism of the dealkylative cyclization poses some interesting problems, but speculation appears useless until it can be established whether dealkylation occurs at the ketone or dihydrophenanthrene stages[9] or takes place after the alkyl-isopropylphenanthrene actually has been formed. It is hoped that the last hypothesis can be tested by synthesis of a 9-alkyl-10-isopropylphenanthrene followed by a study of its stability in boiling hydrobromic and acetic acids.

Experimental

α-(2-Biphenylyl)-valeronitrile (III, X = H; R = C_3H_7).—The sodio derivative of 2-biphenylylacetonitrile (38.6 g.) was alkylated with *n*-propyl bromide as described in the case of the lower homologs.[6,7] Purified by fractionation, 42 g. (89%) of a light yellow oil, b.p. 159–160° (3 mm.), was obtained, n^{25}_D 1.5609.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.76; H, 7.28. Found: C, 86.97; H, 7.19.

α-(2-Biphenyl)-valeric Acid.—Twelve grams of the nitrile (above) was hydrolyzed by refluxing with 20% alcoholic potassium hydroxide for a total of 60 hours. The alkaline solution was diluted, washed with methylene chloride and acidified. Crystallized three times from petroleum ether, 5.4 g. (42%) of product, m.p. 78–81°, was obtained. The analytical sample melted at 80–81°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.28; H, 7.07.

The methylene chloride, containing the neutral impurities was washed with water, dried and concentrated. Crystallization of the residue afforded 0.6 g. of colorless needles, m.p. 101–102.5°. The analytical sample, recrystallized from hexane, m.p. 101.5–102.5°, contained nitrogen and had the composition expected for the amide.

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.59; H, 7.56. Found: C, 80.72; H, 7.71.

α-(2-Biphenylyl)-β-methylbutyronitrile (VI, X = H; R = i-C_3H_7).—By a procedure very similar to that used in making the isomeric biphenylylvaleronitrile (2-biphenylyl)-acetonitrile was alkylated with isopropyl bromide. Worked up in the usual way the product (79% yield) was a very viscous light yellow oil, b.p. 131–138° (1 mm.). The analytical sample boiled at 138° (1 mm.), n^{25}_D 1.5614. The analysis for the nitrile was less satisfactory than that for its hydrolysis product.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.76; H, 7.28. Found: C, 87.26; H, 7.50.

α-(2-Biphenylyl)-β-methylbutyramide.—A sample of the nitrile (VI, X = H; R = i-C_3H_7) above was hydrolyzed by refluxing for 24 hours in 20% alcoholic potassium hydroxide solution. Dilution of the reaction mixture gave a 93% yield of a cream-colored powder, m.p. 140–142.5°. The analytical sample crystallized from cyclohexane as white needles, m.p. 143.5–144.5° which gave a positive test for nitrogen.

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.59; H, 7.56. Found: C, 80.86; H, 7.40.

A sample of the amide was refluxed in 20% alcoholic potassium hydroxide for 85 hours and upon dilution of the solution was recovered unchanged.

α-(2-Biphenylyl)-β-methylbutyric Acid.—The amide above (50 mg.) was refluxed for 48 hours with 10 ml. of acetic acid and 5 ml. of 48% hydrobromic acid. Upon dilution of the reaction mixture, 44 mg. of small tan plates, m.p. 157–164°, crystallized from solution. The analytical sample was obtained as white granular crystals from hexane, m.p. 168–169°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.60; H, 7.47.

Preparation of Ketones. General Procedure.—To a Grignard reagent prepared from 1.4 g. of magnesium turnings and 0.06 mole of alkyl halide in 25 ml. of dry ether was added 0.029 mole of the alkylated nitrile in 30 ml. of dry ether. The mixture was refluxed with stirring for six hours, during which time a finely divided solid formed. After the mixture was decomposed with 50 ml. of 2 *N* hydrochloric acid, it was heated on a steam-bath with stirring for one-half hour to remove the ether and hydrolyze the imine hydrochloride to the ketone. This product was then taken up in methylene chloride and the methylene chloride solution washed with water and sodium bicarbonate solution, dried with magnesium sulfate and concentrated. The residual oil was fractionated under reduced pressure to yield in most cases a colorless oil. In one instance the ketone was not distilled since it crystallized. These results are summarized in Table I.

Preparation of the 2,4-dinitrophenylhydrazones was carried out in the usual way. Yields were 70–80% except when the ketones were hindered, and all 2,4-dinitrophenyl-

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(8) S. T. Amore, Ph.D. Dissertation, Duke University, 1944.

(9) By dihydrophenanthrene stage we imply a dialkyl-9,10-dihydrophenanthryl ion (or ions) which may gain aromatic character through loss of an isopropyl ion.

TABLE IV

2,4-DINITROPHENYLHYDRAZONES OF KETONES

R	R′	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3	CH_3	154–155[a]	$C_{22}H_{20}O_4N_4$	65.33	65.43	4.99	4.92
CH_3	C_2H_5	148.5–149.5[b]	$C_{22}H_{22}O_4N_4$	66.01	66.12	5.30	5.35
CH_3	*i*-C_3H_7	136.5–137.5[b]	$C_{24}H_{24}O_4N_4$	66.65	66.84	5.59	5.81
CH_3	*n*-C_4H_9	120–121[b]	$C_{25}H_{26}O_4N_4$	67.25	67.40	5.87	5.86
C_2H_5	C_2H_5	139–140[b]	$C_{24}H_{24}O_4N_4$	66.65	66.89	5.59	5.67
C_2H_5	*i*-C_3H_7	164.5–165.5[a]	$C_{24}H_{26}O_4N_4$	67.25	67.24	5.87	6.07
n-C_3H_7	CH_3	138.5–139.5[b]	$C_{24}H_{24}O_4N_4$	66.65	66.56	5.59	5.93
n-C_3H_7	*n*-C_3H_7	102.5–104[a]	$C_{26}H_{28}O_4N_4$	67.13	67.82	6.13	6.31
i-C_3H_7	CH_3	138–139[b]	$C_{24}H_{24}O_4N_4$	66.65	66.45	5.59	5.70
i-C_3H_7	C_2H_5	136–137[a]	$C_{25}H_{26}O_4N_4$	67.25	67.50	5.87	5.92

[a] Yellow-orange needles. [b] Yellow-orange plates.

hydrazones were recrystallized from ethanol. Results are given in Table IV.

In the case in which R = CH_3 and R′ = *n*-C_3H_7, a constant-melting product could not be obtained. Where R = C_2H_5 and R′ = *i*-C_3H_7 a mixture of flat orange needles and small yellow needles was obtained. The yellow needles, which made up about 10% of the mixture, melted at 174–176° and showed no depression of melting point with the 2,4-dinitrophenylhydrazone of α-(2-biphenylyl)-butyraldehyde.

9,10-Dialkylphenanthrenes by the Cyclization of Ketones. General Procedure.—To 1.0 g. of the ketone dissolved in 20 ml. of hot acetic acid was added 10 ml. of 48% hydrobromic acid. Since in all cases except that of 9,10-dimethylphenanthrene the product melted below the temperature of the refluxing acid solution, it partially separated from solution as an oil while the mixture was refluxed the required length of time. After the mixture had cooled to room temperature, the oil solidified and the hydrocarbon in solution crystallized. This product was collected and washed with water. Sometimes the yield could be increased slightly by diluting the acidic mother liquor with water, but usually the additional amount obtained this way was negligible. That portion of the product which crystallized from solution was fairly pure. However, the portion which had been an oil in the hot solution and had solidified on cooling melted 0.5 to 5 degrees lower. The results are summarized in Table II.

2-(5-Methoxy-2-biphenylyl)-4-methylpentanone-3 (IV, X = OCH_3; R = CH_3; R′ = $(CH_3)_2CH$).—A solution of 5.7 g. of α-(5-methoxy-2-biphenylyl)-propionitrile[1] in dry ether was added to an excess of isopropylmagnesium bromide and the mixture refluxed for six hours and worked up in the usual way. Fractionation yielded 5.6 g. of an oil, b.p. 159–161° (1 mm.), which solidified on standing and was recrystallized from petroleum ether as colorless prisms m.p. 78–80.5°, yield 2.3 g. (34%). The analytical sample melted at 81.5–82.5°.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 81.05; H, 8.10.

3-Hydroxy-10-methylphenanthrene (V, X = OH; R = CH_3; R′ = H).—When 0.45 g. of the above ketone was refluxed for 48 hours in the usual hydrobromic–acetic acid mixture 0.30 g. (90%) of violet feathery needles, m.p. 129–135°, was obtained. A single recrystallization yielded 0.24 g. (72%) of white feathery needles, m.p. 138–140°. Further recrystallization yielded material, m.p. 141–142°, which did not depress the melting point of an authentic sample.[1]

3-Methoxy-10-methylphenanthrene was obtained by methylation of the phenanthrol (above) in alkaline solution with dimethyl sulfate. The analytical sample was obtained from ethanol as clusters of small white needles, m.p. 74–75.5°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.45; H, 6.62.

9-Isobutylphenanthrene by Cyclization of Crude 1-Isobutyl-1-(2-biphenylyl)-2-isopropylethylene Oxide.[10]—Crude diisobutyl-2-biphenylylcarbinol (I, R = $(CH_3)_2CH$) obtained from diisobutyl ketone by the Grignard reaction, was dehydrated by heating for one hour at 160° with three parts by weight of potassium bisulfate. The resulting olefin, b.p. 155–163° (7 mm.), was oxidized with perbenzoic acid and worked up as previously described.[5] The crude oxide was refluxed with 60 ml. of acetic acid and 40 ml. of 48% hydrobromic acid for a total of 135 hours. On cooling, this yielded 1 g. of solid material which was purified by repeated recrystallization from methanol. The pure sample consisted of white needles, m.p. 95–96°, which showed no depression of melting point when mixed with an authentic[1] sample of 9-isobutylphenanthrene.

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[10] We are indebted to S. Thomas Amore for this experiment.