[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. XIV.[1] 9,10-Dialkylphenanthrenes

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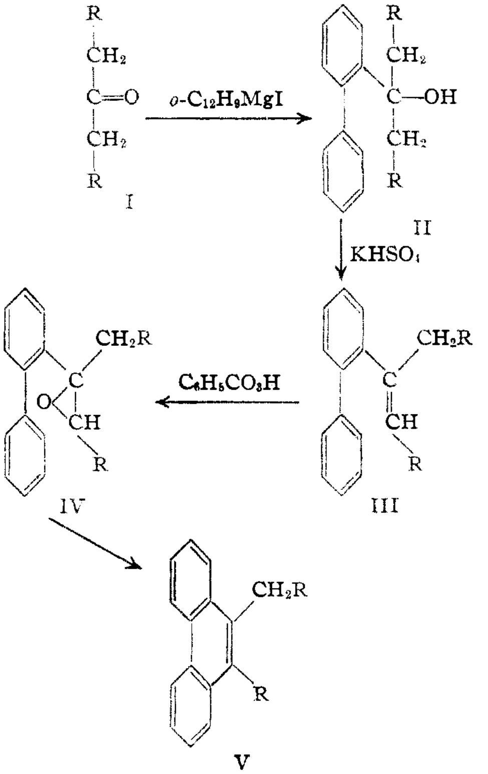
In an earlier paper,[3] we described a new method for the synthesis of 9-alkylphenanthrenes. This method involved, as a first step, the reaction of an aldehyde with 2-biphenylmagnesium iodide. We have now extended this reaction to symmetrical ketones making possible the preparation of some 9,10-dialkylphenanthrenes.

The ketone (I), upon reaction with the biphenylmagnesium iodide, gave a carbinol (II) which was dehydrated by heating with potassium bisulfate. The olefin (III) thus obtained was converted to the oxide (IV) and this was cyclized by the action of hydrobromic and acetic acids.



(R = H, CH_3, C_2H_5, n-C_3H_7)

When the ketone used was acetone, the product was 9-methylphenanthrene. In all of the other cases, the product was a 9,10-dialkylphenanthrene (V). These hydrocarbons are not only new, but are the only known dialkylphenanthrenes with two dissimilar substituents in the central nucleus.

The results of our experiments in this series are summarized in Table I.

TABLE I

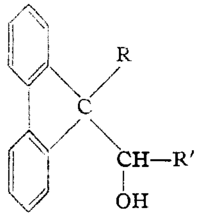
PHENANTHRENES FROM SYMMETRICAL KETONES

Ketone	Alkylphenanthrenes	Yield from ketone, %	Observed m. p., °C. Hydrocarbon	Observed m. p., °C. Picrate
Acetone	Methyl	28	92	154
Diethyl	Methyl-ethyl	26	85	150
Di-*n*-propyl	Ethyl-*n*-propyl	32	69	117
Di-*n*-butyl	*n*-Propyl-*n*-butyl	37	74	99

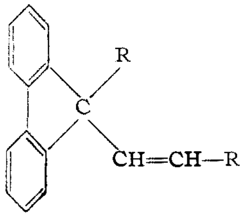
It is worthy of note that the cyclization of the oxide (IV, R = H) of 1-(2-biphenyl)-1-methylethylene may be effected in an over-all yield of 49% by heating it with potassium bisulfate at 160° for only one hour.[4]

Our belief that the three new hydrocarbons are 9,10-dialkylphenanthrenes (V) rests not only upon analogy, but also upon a consideration of the analyses and properties. The latter include the ability to form well-defined picrates and to resist the action of boiling hydrobromic and acetic acids.

As an alternative to a phenanthrene cyclization, the possibility suggests itself that the oxide IV might cyclize to yield a hydroxyalkylfluorene (VI) which might lose water to yield a fluorene derivative of the composition observed. However, the experiments of others[5] indicate that fluorene carbinols of structure VI (R = R′) on dehydration undergo rearrangement to yield phenanthrene hydrocarbons. Further, if the unsaturated fluorene hydrocarbon (VII) were



VI



VII

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[1] For the preceding communication of this series see THIS JOURNAL, **65**, 1646 (1943).

[2] National Research Fellow (participating basis, 1941–1942).

[3] Bradsher and Amore, THIS JOURNAL, **63**, 493 (1941).

[4] A future communication will describe the earlier experiments made by one of us on the scope of the bisulfate-catalyzed cyclization.

[5] Werner and Grob, *Ber.*, **37**, 2894 (1904); Meerwein, *Ann.*, **405**, 129, 173 (1914); Brown and Bluestein, THIS JOURNAL, **62**, 3256 (1940).

formed, it is doubtful that it would remain unchanged under the conditions of the experiment.

In addition to the phenanthrene hydrocarbons, we have prepared 9,9-di-*n*-propylfluorene by the dehydration of 2-biphenyl-di-*n*-propyl carbinol (II, R = C_2H_5) in the presence of sulfuric acid.[6]

Experimental

Preparation of the 2-Biphenylethylenes.—A suitable ketone was added to 1.1 moles of 2-biphenylmagnesium iodide and the mixture refluxed for at least one hour. It was then decomposed with ammonium chloride solution, the ether solution concentrated and the residue distilled under reduced pressure.

The carbinol was mixed with three to four times its weight of potassium hydrogen sulfate and heated for one hour at 160°. The mixture was extracted with benzene and, after evaporation of the solvent, the crude olefin was distilled *in vacuo*. The products obtained in this way still contained a small amount of biphenyl, but were pure enough for further reactions.

TABLE II

SYNTHESIS OF OLEFINS FROM SYMMETRICAL KETONES

R—CH_2—CO—CH_2—R R =	g.	Carbinol II M. p., °C.	Carbinol II B. p., °C.	mm.	Olefin III Yield, g.	% (over-all)	Olefin III B. p., °C.	mm.
H	2.6	71[a]	145–154	7	6.2	71	125–128	7
CH_3	7.8	..	155–157	7	9.3	47	138–141	7
C_2H_5	15.9	68[b]	182–183	11	24.7	71	155–157	8
n-C_3H_7	19.9	..	185–192	8	21.3	55	178–179	7

[a] *Anal.* Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.89; H, 7.50. This compound has recently been reported (m. p. 73°) by Anchel and Blatt, ref. note 6, who prepared it by another method. [b] *Anal.* Calcd. for $C_{19}H_{24}O$: C, 85.03; H, 9.01. Found: C, 85.22; H, 8.56.

TABLE III

PHENANTHRENE HYDROCARBONS DERIVED FROM SYMMETRICAL KETONES

Olefin III R =	g.	Yield of hydrocarbon[a] g.	% from Olefin	% from Ketone	M. p., °C. Hydrocarbon (V)	M. p., °C. Picrate[b]	Anal. of hydrocarbon for:	Calcd. C	Calcd. H	Found C	Found H
H	3.1	1.2	40	28[c]	92	154	[d]				
CH_3	9.3	5	54	26	85	150	$C_{17}H_{16}$	92.68	7.32	92.93	7.17
C_2H_5	24.7	11.2	44	32	69	117	$C_{19}H_{20}$	91.88	8.12	92.08	7.80
n-C_3H_7	21.3	14.3	67	37	74	99	$C_{21}H_{24}$	91.25	8.75	91.25	8.73

[a] With the exception of 9-methyl-10-ethylphenanthrene (V, R = CH_3), which crystallized from methanol as plates, all of the hydrocarbons were obtained as needles from ethanol. [b] The picrates were obtained as yellow-orange needles except in the case of the picrate of 9-*n*-propyl-10-*n*-butylphenanthrene (V, R = *n*-C_3H_7) which formed yellow-orange plates. [c] This is the yield obtained by the hydrobromic acid type of cyclization. [d] The identity of this preparation was established by comparison with an authentic sample (Bradsher and Tess, THIS JOURNAL, **61**, 2184 (1939)).

Oxidation and Cyclization.—The olefin was added to a chloroform solution containing 1.2 moles of perbenzoic acid.[7] The mixture was allowed to stand at 0° for twenty-four hours and, at the end of this period, the amount of unreacted oxidizing agent was determined by titration of a sample, using sodium thiosulfate solution. The acids were removed by washing with sodium bicarbonate solution and the oxide recovered by evaporation of the chloroform. The oxide was dissolved in ten times its volume of acetic acid and to the refluxing solution was added dropwise seven volumes of 34% hydrobromic acid. The mixture was refluxed for sixty to one hundred and twenty hours, the average time being about seventy-two hours. Upon cooling, the hydrocarbons crystallized in the acid mixture and were collected and purified by recrystallization. In a few instances, it was found profitable to distil the mixture *in vacuo* prior to crystallization.

Cyclization of the Oxide of 1-(2-Biphenyl)-1-methylethylene (IV, R = H).—The crude oxide, prepared from 3.1 g. of 1-(2-biphenyl)-1-methylethylene (III, R = H), as described in the general procedure, was heated at 160° for one hour with 12 g. of potassium bisulfate. Water and benzene were added and the product extracted. Upon evaporation of the benzene layer and recrystallization of the residue, 2.1 g. (68%, calculated from the olefin; 49% from the ketone) of 9-methylphenanthrene was obtained, m. p. 92°.

9,9-Di-*n*-propylfluorene.—One gram of 2-biphenyl-di-*n*-propylcarbinol (II, R = C_2H_5) was dissolved in 15 cc. of acetic acid, five drops of concentrated sulfuric acid added and the mixture refluxed for one hour. The mixture was then diluted, the product taken up in ether, and the residue obtained by evaporation of the ether was repeatedly crystallized from methyl alcohol as colorless crystals, m. p. 37–38°.

Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.34; H, 8.98.

Summary

By using a series of symmetrical ketones, the olefin oxide type of cyclization has been extended to the synthesis of some new 9,10-dialkylphenanthrenes.

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[6] This is an example of a general method for the preparation of 9,9-dialkylfluorenes, Anchell and Blatt, THIS JOURNAL, **63**, 1948 (1941).

[7] Braun, *Org. Syntheses*, **13**, 86 (1933).