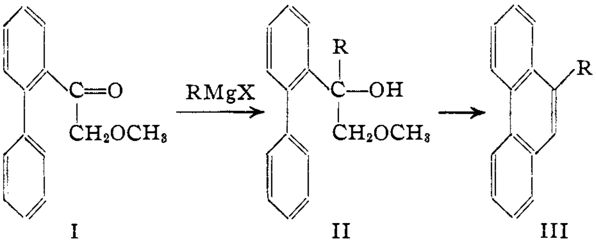
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. IX.[1] 9-Alkylphenanthrenes

BY CHARLES K. BRADSHER AND SALVATORE T. AMORE

Of the large number of compounds reported to have estrogenic activity, one of the simplest is 9-ethylphenanthrene.[2] For this reason, it seemed desirable to develop syntheses suitable for the preparation of substituted 9-ethylphenanthrenes and further to prepare some other, untested, 9-alkylphenanthrenes.

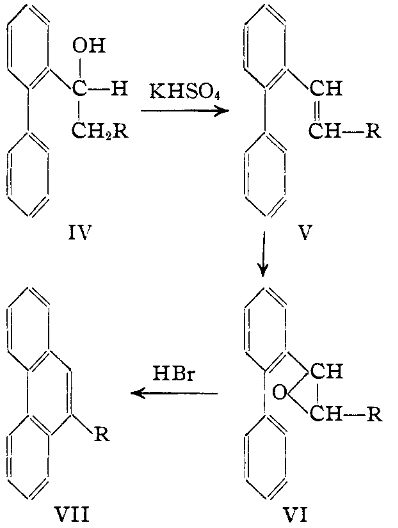
The first general method of synthesis employed is an extension of one used previously by Bradsher and Tess[3] for the preparation of 9-methylphenanthrene. A suitable Grignard reagent was treated with 2-(ω-methoxyaceto)-biphenyl (I) and the resulting carbinol (II) cyclized to the hydrocarbon (III) by the action of boiling hydrobromic and acetic acids. The ethyl, *n*-propyl, *n*-butyl and benzylphenanthrenes were prepared by this method. In an attempt to prepare 9-isopropylphenanthrene, the isopropylmagnesium bromide used evidently reacted chiefly by reduction for the only crystalline product obtained was identified as phenanthrene.[4]



($R = C_2H_5$, n-C_3H_7-, n-C_4H_9, $C_6H_5CH_2$)
β-Methoxycarbinol method

The second general method of synthesis employed is an extension of the olefin oxide method used previously to prepare 9,10-cyclohexenophenanthrene[5] and with limited success in the synthesis of phenanthrene.[4] A Grignard reagent prepared from 2-iodobiphenyl was treated with a suitable aldehyde and the resulting carbinol (IV) dehydrated with potassium bisulfate.

The olefin (V) was oxidized with monoperphthalic acid and the crude oxide (VI) cyclized with the hydrobromic and acetic acids to give the hydrocarbon (VII).



($R = C_2H_5$, n-C_3H_7, i-C_3H_7, n-C_4H_9, n-C_5H_{11})
Olefin oxide method

It will be seen that the two general methods should make it possible to prepare both the 9- and 10-alkyl derivatives from a single *substituted* 2-iodobiphenyl. The results obtained by both methods are summarized in Table I.

TABLE I

9-Alkyl-phenanthrene	Yield,[6] % β-Methoxy carbinol method	Yield,[6] % Olefin oxide method	Observed, m. p., °C. Hydrocarbon	Observed, m. p., °C. Picrate	Previously reported m. p. Hydrocarbon	Previously reported m. p. Picrate
C_2H_5	54	41	63	124	63	124[7]
n-C_3H_7	51	26	58	99	74	134[8]
i-C_3H_7	0	28	42	110		
n-C_4H_9	40	21	81		58	99.5[8]
n-C_5H_{11}		25	70			
$C_6H_5CH_2$	70		153		153[9]	

Of the six hydrocarbons which we prepared, four have been reported previously. Two of these four, the 9-*n*-propyl- and 9-*n*-butylphenanthrenes, were reported by Miller and Bachman[8] as having been obtained by the action of 9-phenanthrylmagnesium bromide on the corresponding alkyl bromides. As may be seen by reference to Table I, our preparations of these two hydrocar-

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[1] For the preceding paper of this series see THIS JOURNAL, **62**, 3140 (1940).

[2] Thayer, MacCorquodale and Doisy, *J. Pharmacol.*, **59**, 48 (1937).

[3] Bradsher and Tess, THIS JOURNAL, **61**, 2184 (1939).

[4] It has been demonstrated (Bradsher and Wert, *ibid.*, **62**, 2806 (1940)) that reduction of the ketone and cyclization of the resulting carbinol yields phenanthrene.

[5] Bradsher, *ibid.*, **61**, 3131 (1939).

[6] The yields by the carbinol method are calculated from the 2-(ω-methoxyaceto)-biphenyl; by the olefin oxide method, from the aldehyde.

[7] Mosettig and van de Kamp, THIS JOURNAL, **55**, 3442 (1933).

[8] Miller and Bachman, *ibid.*, **57**, 766 (1935).

[9] Bachmann, *ibid.*, **56**, 1353 (1934).

bons have properties different from those observed by the previous authors. The most reasonable explanation for this discrepancy seems to be that they have confused the identity of their samples.[10]

One other observation of interest is that 9-alkylphenanthrenes containing more than three carbon atoms in the side chain do not form picrates under the ordinary conditions. This suggests that picrate formation is somehow associated with the C_9-C_{10} double bond of the phenanthrene nucleus.

Experimental

Preparation of 9-Alkylphenanthrenes by the β-Methoxycarbinol Method.—An ether solution containing 10 g. of 2-(ω-methoxyaceto)-biphenyl[11] was added slowly to a Grignard reagent prepared from 0.06 mole of an alkyl halide and the mixture refluxed for thirty minutes. At the end of this period, the mixture was decomposed by the action of ice-cold 20% ammonium chloride solution. The ether layer was separated and evaporated. The crude carbinol thus obtained was taken up in 120 cc. of glacial acetic acid and this solution added dropwise to 60 cc. of boiling 40% hydrobromic acid over the period of several hours. After a total of twenty-four hours of refluxing, the mixture was cooled. At this point the crude hydrocarbon usually crystallized and was collected; otherwise the mixture was diluted and extracted with ether to obtain the hydrocarbon. The crude hydrocarbon obtained by either of these methods was purified by vacuum distillation followed by crystallization from a suitable solvent. A summary of the results is shown in Table II.

TABLE II

PREPARATION OF ALKYLPHENANTHRENES BY THE β-METHOXYCARBINOL METHOD

Alkyl halide	9-Alkyl phenanthrene	Crystallized from	Crystalline form	M. p., °C.	Yield, %
CH_3CH_2Br	Ethyl	Methanol	Needles	60–61	53
n-C_3H_7Br	n-Propyl	Methanol	Plates	57.5–58	51
i-C_3H_7Br[a]					
n-C_4H_9Cl	n-Butyl	Methanol	Needles	79.5–80.5	40
$C_6H_5CH_2Cl$	Benzyl[b]	Acetic acid	Prisms	152.5–153	70

[a] The only product obtained in this case after repeated recrystallization melted at 98–99° and gave no depression of melting point when mixed with an authentic specimen of phenanthrene.

[b] *Anal.* Calcd. for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 94.19; H, 6.02.

Synthesis of 9-Alkylphenanthrenes by the Olefin Oxide Method

Preparation of the 2-Biphenylethylenes (V).—A suitable aldehyde was treated with 1.2 moles of a Grignard reagent and the mixture refluxed for thirty minutes. It was then decomposed with ammonium chloride solution. The ether solution was concentrated. In some cases, the crude carbinol thus obtained was submitted to vacuum distillation, in others it was dehydrated directly. In either case 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 then extracted with benzene and after evaporation of the solvent, the crude olefin was distilled *in vacuo*. The products obtained in this manner contained a small amount of biphenyl, but were pure enough for further reactions. Our results are summarized in Table III.

TABLE III

SYNTHESIS OF OLEFINS

R =	R—CH_2CHO, g.	R—CH_2—CH(OH)$C_{12}H_9$, b. p. °C.	Mm.	R—CH=CH—$C_{12}H_9$ yield, g.	% Yield (over-all)	B. p. °C.	Mm.
C_2H_5	3.6	142–145	15–18	10	96	148–152	6
n-C_3H_7	5	160–165	6	5.3	42	155–160	7
i-C_3H_7	5			9.3	73	163–174	6
n-C_4H_9	2.6			4.1	59	155–164	7
n-C_5H_{11}	4.6	195–200	14	5	50	168–174	4–6

TABLE IV

PREPARATION OF 9-ALKYLPHENANTHRENES BY THE OLEFIN OXIDE METHOD[a]

Olefin $\begin{matrix}C_{12}H_9—CH\\ \|\\ R—CH\end{matrix}$	g.	Yield of hydrocarbon g.	Yield of hydrocarbon % from olefin	Yield of hydrocarbon % from aldehyde	M. p., °C. Hydrocarbon	M. p., °C. Picrate	Anal. of hydrocarbon Calcd. for:	Calcd. C	Calcd. H	Found C	Found H
C_2H_5	5	2.1	43	41	62–63	123–124	$C_{16}H_{14}$	93.15	6.85	93.15	7.01
n-C_3H_7	5	3.3	66	26	57–58	98–99	$C_{17}H_{16}$	92.68	7.32	92.38	7.25
i-C_3H_7	5.1	3.5	69	28	41–42	109–110	$C_{17}H_{16}$	92.68	7.32	92.61	7.22
n-C_4H_9	2.3	0.8	34	21	80–81		$C_{18}H_{18}$	92.25	7.75	92.36	7.47
n-C_5H_{11}	2.9	1.4	53	25	69–70		$C_{19}H_{20}$	91.88	8.12	91.72	8.03

[a] With the exception of n-propylphenanthrene, which crystallized as plates, all the hydrocarbons were obtained as colorless needles from methanol. In the case of the isopropylphenanthrene, it was found convenient to use a mixture of ether and methanol.

Oxidation and Cyclization.—The olefin in ether solution was oxidized by the action of 2–3 moles of monoperphthalic acid.[12] After twelve hours, the acids were removed by

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(10) Dr. Bachman has very kindly undertaken a comparison of our compounds with his. The report of his investigation has been made the subject of another communication (Bachman and Hoaglin, THIS JOURNAL, 63, 621 (1941)).

(11) Bradsher and Schneider, *ibid.*, 60, 2960 (1938).

(12) Böhme, *Ber.*, 70, 379 (1937).

extraction with sodium bicarbonate solution. The ether was then evaporated and the crude oxide taken up in ten times its volume of acetic acid. The acetic acid solution was added dropwise to half as much boiling 40% hydrobromic acid. The mixture was refluxed for twenty-four hours, after which the hydrocarbon was isolated as in the case of the β-methoxycarbinol method. A summary of our results is given in Table IV. In every case in which the same hydrocarbon was prepared by both methods, the two preparations were shown to be identical by mixed melting point determinations.

Summary

Using the new method of ring closure, two hydrocarbons, 9-*n*-amyl- and 9-isopropylphenanthrene, never previously reported, have been synthesized.

The synthesis of 9-*n*-propyl- and 9-*n*-butylphenanthrene has shown that previous reports of these two hydrocarbons are erroneous.

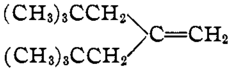
DURHAM, N. C. RECEIVED AUGUST 10, 1940

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Isolation and Properties of 1,1-Dineopentylethylene, a Component of Triisobutylene[1]

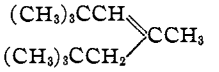
BY PAUL D. BARTLETT, GEORGE L. FRASER AND ROBERT B. WOODWARD[2]

From the ozonolysis of triisobutylene McCubbin[3] reported the isolation of trimethylacetaldehyde, methyl neopentyl ketone, dineopentyl ketone, and an inert compound, b. p. 158–162° at 23 mm., which was assumed to be 3,3-di-*t*-butylbutanone-2 because it could be oxidized to an acid, m. p. 69–71°, apparently identical with the one to which Butlerow[4] assigned the structure of methyl-di-*t*-butylacetic acid (I). These facts were consistent with the conclusion, drawn by McCubbin, that triisobutylene was a mixture of the three isomers 1,1-dineopentylethylene (II), 1-methyl-1-neopentyl-2-*t*-butylethylene (III), and 1,1-dimethyl-2,2-di-*t*-butylethylene (IV), providing that the ozonolysis of IV could involve molecular rearrangement yielding a ketone of the same number of carbon atoms.



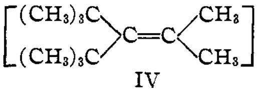
$((CH_3)_3CCH_2)_2C{=}CH_2$

II



$(CH_3)_3CCH{=}C(CH_3)CH_2C(CH_3)_3$

III



$[((CH_3)_3C)_2C{=}C(CH_3)_2]$

IV

A little later Conant and Wheland[5] showed that the chromic acid oxidation of triisobutylene yields two 12-carbon acids instead of the 11-carbon acid (I) which Butlerow believed he had. Whitmore and his co-workers[6] established the structures of these acids as dineopentylacetic acid (V), m. p. 89°, and methyl-*t*-butylneopentylacetic acid (VI), m. p. 129°, and pointed out that they must have been produced by molecular rearrangement from II and III, respectively. At the same time the evidence for the existence of IV as a component of triisobutylene was invalidated, since this rested upon Butlerow's incorrect structure I.

Such oxidative rearrangements are not known to occur except with acidic oxidizing agents. Thus it might be possible that if any of the compound IV existed in triisobutylene, it might be oxidized under vigorous conditions by alkaline permanganate to hexamethylacetone. This would not only be good structural evidence but would provide a superior way of preparing hexamethylacetone. With this in mind we treated triisobutylene with a calculated excess of hot 30% permanganate solution containing potassium hydroxide with stirring for seven hours, long after the first vigorous reaction had ceased. Although excess permanganate remained and the solution was not unduly viscous, half of the original triisobutylene appeared to remain unchanged. The oil was isolated by steam distillation, dried and distilled through a Widmer column. The entire material boiled constantly at 177.7–178°.

The unoxidized residue was shown to be one of the components of the triisobutylene, comprising about 50% of the original material. Its density, refractive index, molecular refractivity, and analysis are correct for a hydrocarbon $C_{12}H_{24}$. It is completely resistant to neutral or alkaline permanganate, but is attacked by dichromate and

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[1] Presented before the San Francisco Section of the American Chemical Society, September 12, 1940.

[2] Member of the Society of Fellows.

[3] McCubbin, THIS JOURNAL, **53**, 356 (1931).

[4] Butlerow, *Ber.*, **12**, 1482 (1879).

[5] Conant and Wheland, THIS JOURNAL, **55**, 2499 (1933).

[6] Whitmore and Laughlin, *ibid.*, **56**, 1128 (1934); Whitmore and Wilson, *ibid.*, **56**, 1397 (1934).