[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. XVI.[1] Phenanthrene Hydrocarbons from Unsymmetrical Ketones

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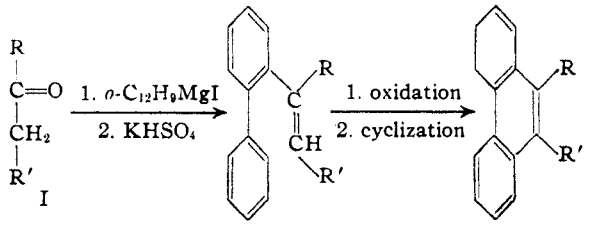
In the synthesis of phenanthrene hydrocarbons by the olefin oxide method, we have used as starting materials only aldehydes[2a] or symmetrical ketones.[2b] If unsymmetrical ketones (I) are used, it is obvious that the outcome of the dehydration reaction, and, by the same token, the structure of the ultimate phenanthrene derivative (III), will be unambiguous only in those cases in



which one group attached to the carbonyl contains no *alpha* hydrogen atom. Two ketones of this type, phenyl *n*-butyl and phenyl undecyl ketones, have been used to prepare the corresponding phenyl-*n*-propyl- and phenyl-*n*-decylphenanthrenes.

Of the unsymmetrical ketones having *alpha* hydrogens on both carbon atoms adjacent to the carbonyl, it was hoped that the methyl ketones (I, R = CH_3) would form a special case. The carbinols derived from them might be expected to lose a hydrogen atom from the adjacent methylene group more readily than from the methyl, and the resulting olefin, upon oxidation and cyclization, would yield 9-methyl-10-alkylphenanthrenes.

It was found that while the olefin obtained from methyl ethyl ketone gave the expected 9,10-dimethylphenanthrene in 39% yield, the olefin from methyl *n*-amyl ketone gave 9-*n*-amylphenanthrene in almost comparable yield (31%), although some of the expected isomer may have been formed.

Experimental

The general procedure was that described previously[2b] for the preparation of phenanthrene hydrocarbons from symmetrical ketones. The experimental data are recorded in the accompanying table.

TABLE I

PHENANTHRENE HYDROCARBONS FROM UNSYMMETRICAL KETONES

Ketone (I)			Olefin (II)					Phenanthrene (III)									
			Yield,		B. p.		Used,	Yield, % from				M. p.,		Analyses, % Calcd.		Found	
R	R'	G.	G.	%	°C.	Mm.	G.	G.	olefin	ketone	From[d]	°C.	Formula	C	H	C	H
C_6H_5	*n*-C_3H_7	20.2	24.4	65	207–208[a]	8	24.4	13.5	64	37	EtOH	148.5–149.5	$C_{23}H_{20}$	93.20	6.80	93.36	6.67
C_6H_5	*n*-$C_{10}H_{21}$	15	13.6	60[b]	242–254	5	13.6	5.3	39	23[c]	MeOH	99–100	$C_{30}H_{44}$	91.31	8.69	91.50	8.78
CH_3	CH_3	10	10.6	36	132–140	9	10.1	4	39	14	HOAc	142.5–143[e]	$C_{16}H_{14}$	93.15	6.85	93.12	6.60
n-C_5H_{11}	H	14	15.4	51	140–160	8	7.3	2.3	31	15	EtOH	69–70[f]					

[a] Recrystallized from ethanol as small colorless needles, m. p. 78–79°. *Anal.* Calcd. for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.60; H, 7.45. (All microanalyses by T. S. Ma, University of Chicago.) [b] Part of the original ketone recovered unchanged. The yield based on ketone consumed was 80%. [c] Based on total ketone. The yield from ketone consumed was 31%. [d] All phenanthrene hydrocarbons crystallized as white needles. [e] Zincke and Tropp, *Ann.*, **362**, 250 (1908), report m. p. 139°. The hydrocarbon formed a picrate, m. p. 193–194°. [f] This was shown to be identical with our earlier preparation (ref. 2b).

Summary

The olefin oxide type of cyclization has been applied to the synthesis of phenanthrene hydrocarbons from unsymmetrical ketones.

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(1) For the preceding communication of this series, see THIS JOURNAL, **65**, 2304 (1943).

(2a) Bradsher and Amore, *ibid.*, **63**, 493 (1941).

(2b) Bradsher and Amore, *ibid.*, **65**, 2016 (1943).