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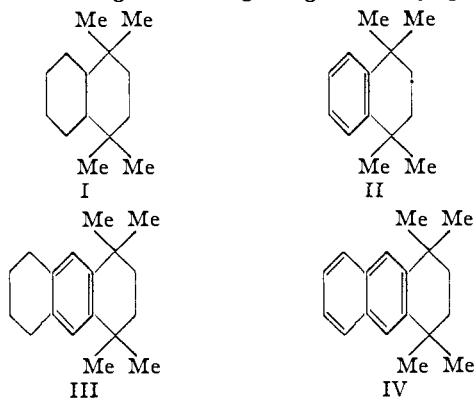
Catalytic Dehydrogenation of Hydroaromatic Compounds in Benzene. III. Compounds Containing Gem Dialkyl Groups

BY HOMER ADKINS AND DAVID C. ENGLAND

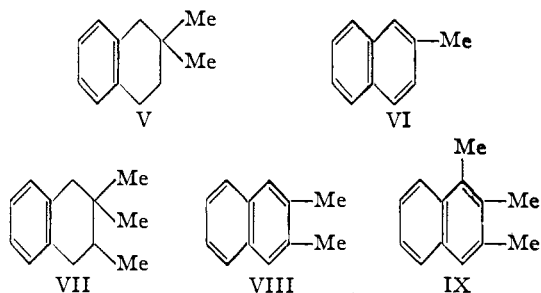
Hydroaromatic compounds may be aromatized in liquid phase in benzene with nickel, platinum or palladium catalysts, the benzene serving as hydrogen acceptor.^{1,2} While gem or angular alkyls are rather stable under the conditions required for simple dehydrogenation, compounds carrying such substituents may be aromatized, with the elimination or migration of alkyl groups.³

The present paper is primarily concerned with the behavior of eleven hydroaromatic derivatives of naphthalene or phenanthrene which carry two alkyl groups on one of the carbon atoms of the nucleus. These compounds in benzene were heated at 350–375° in a closed chrome–vanadium steel vessel over platinum on activated carbon, nickel-on-kieselguhr and nickel-on-nickel chromite catalysts. With possibly one exception the aromatization reaction proceeded more cleanly over the platinum than over the nickel catalysts. The nickel catalysts gave aromatization with each of the eleven compounds but the isolation of the products was in general more difficult, and except for a few cases, the amounts isolated were lower.

More drastic conditions are required to bring about an aromatization if a carbon-to-carbon bond must be ruptured than if only dehydrogenation is required. Thus 2,2-dimethyltetralin (V) is more difficult to dehydrogenate than tetralin itself, and 1,1,4,4-tetramethyltetralin (II) has not been dehydrogenated to any appreciable extent under the conditions employed in this work. 1,1,4,4-Tetramethyldecalin (I) was converted to the corresponding tetralin (II) in 90% yield without formation of significant amounts of methylnaphthalenes. Similarly a tetramethyloctahydroanthracene (III) was converted in 68% yield to the tetramethyl-tetrahydroanthracene (IV) without aromatization of the ring containing the gem methyl groups.



Both 2,2-dimethyltetralin (V) and 2-methyl-2-ethyltetralin were converted to 2-methylnaphthalene (VI) in yields of the order of 40%. The 2-methyl-2-ethyldecalin also gave 2-methylnaphthalene in a yield of the order of 80–85%. Similarly, one of the gem methyl groups was eliminated in 2,2,3-trimethyltetralin (VII) to give 2,3-dimethylnaphthalene (VIII) in a yield of perhaps 80%.



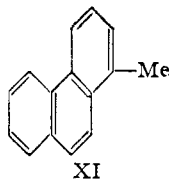
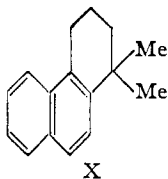
There was evidence of migration as well as elimination of a methyl group and the formation of 1,2,3-trimethylnaphthalene (IX). With a nickel-on-kieselguhr catalyst migration was the chief reaction, the yield of IX being of the order of 40%. This nickel catalyst gave a mixture of two migration products 2,3-dimethylnaphthalene (VIII) and 1,2-dimethylnaphthalene in yields of 50 and 20%, respectively, from V. It also gave the migration product 2-methyl-3-ethylnaphthalene in 30% yield from 2-methyl-2-ethyltetralin and in 20% yield from the decalin.

From 1,1-dimethyl-1,2,3,4-tetrahydrophenanthrene (X) over nickel (k) there was obtained 1,2-dimethylphenanthrene and from 1,1-diethyl-1,2,3,4-tetrahydrophenanthrene there was evidence for the formation of 1,2-diethylphenanthrene. Thus it may be said that the platinum catalyst brings about aromatization through elimination of an alkyl group while the nickel (k) catalyst aromatizes through inducing migration of an alkyl group from a quaternary carbon atom. The nickel-on-nickel chromite catalyst is intermediate between the platinum (C) and the nickel (k) catalysts; it induces both elimination and migration of alkyl groups.

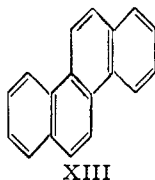
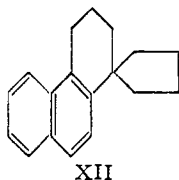
The tetrahydrophenanthrene (X) and the corresponding perhydrophenanthrene were both converted to 1-methylphenanthrene (XI) when aromatized over the platinum catalyst. Similarly the 1-methyl-1-ethyltetrahydrophenanthrene and perhydrophenanthrene lost an ethyl group and gave 1-methylphenanthrene (XI) among other products. The 1,1-diethyl-1,2,3,4-tetrahydrophenanthrene also lost one ethyl group in aromatization and so gave 1-ethylphenanthrene in fair yield and

(1) Adkins, Richards and Davis, *THIS JOURNAL*, **63**, 1320 (1941).
 (2) Adkins, Rae, Davis, Hager and Hoyle, *ibid.*, **70**, 381 (1948).
 (3) Adkins and Davis, *ibid.*, **71**, 2955 (1949).

purity. When the gem methyl groups were in the 2-position of tetrahydrophenanthrene, aromatization was accomplished, but no single product could be isolated or identified, except in the case of the nickel (k) catalyst where a migration product 1,2-dimethylphenanthrene was identified.



1,1-Spirocyclopentano-1,2,3,4-tetrahydrophenanthrene (XII) was aromatized to chrysene (XIII) over all three catalysts to the extent of 15 to 50%. Since this conversion involves a migration of a carbon-to-carbon linkage it is not surprising that the nickel (k) catalyst gave a better yield (50%) than the platinum (C) catalyst (30%), both being superior as in other cases cited in this paper, to the nickel-on-nickel chromite catalyst which gave a 15% yield.



The details as to identification, yields and purity of products are given in the experimental section. The percentage yields given above are approximations, based upon changes in refractive indices as well as weights of purified products isolated. The quantities of one to five grams used in each dehydrogenation did not permit a precise determination of the yield of each product.

The tetralins used in this work were prepared by modifications of a route described by others^{4,5} through the condensation of substituted succinic anhydrides^{6,7} with benzene in the presence of aluminum chloride, followed by a Clemmensen reduction,⁸ ring closure with hydrogen fluoride, and another Clemmensen reduction⁸ of the cyclic ketone so obtained. A similar procedure⁹ using naphthalene instead of benzene was used to prepare 2,2-dimethyl-1,2,3,4-tetrahydrophenanthrene.

The 1,1-disubstituted-1,2,3,4-tetrahydrophenanthrenes were prepared in four steps from 1-chloromethylnaphthalene,¹⁰ the first step being a Grignard reaction with ethylene oxide run in a manner analogous to the procedure described by Wilds¹¹ for the reaction of 1-bromonaphthalene with

ethylene oxide. The resulting 3-(1-naphthyl)-1-propanol was converted to the bromide with phosphorus tribromide¹² from which the Grignard reagent was prepared for reaction with various ketones to give tertiary alcohols. These alcohols were cyclized in 85% sulfuric acid¹³ to give the desired hydrocarbons.

Compounds containing more than one gem dimethyl grouping were prepared using procedures of Bruson and Kroeger.¹⁴

Analytical data and physical constants on compounds not previously reported are given in Tables I and II.

Experimental

Hydrogenations.—2-Methyl-2-ethyl-1,2,3,4-tetrahydronaphthalene (14.4 g., n_D^{25} 1.5208) was hydrogenated over Raney nickel at 225° under 3000 p. s. i. to give 2-methyl-2-ethyldecalin (14.2 g., n_D^{25} 1.4782, d_4^{25} 0.8880). The molecular refraction is 57.5 as compared with a calculated value of 57.8. 1,1-Dimethylperhydrophenanthrene and 1,1-diethylperhydrophenanthrene were prepared by the hydrogenation of the corresponding tetrahydrophenanthrenes over Raney nickel at 250° and 3000 p. s. i. The products of the first hydrogenations were rehydrogenated once or twice in methylcyclohexane in order to obtain the perhydrophenanthrene free of less completely hydrogenated products. 1,1,4,4-Tetramethyl-1,2,3,4-tetrahydronaphthalene (10.4 g., n_D^{25} 1.5192) was hydrogenated over Raney nickel at 250° under 3000 p. s. i. to give 1,1,4,4-tetramethyldecalin (10 g. b. p. 100–103° (11 mm.), n_D^{25} 1.4732, d_4^{25} 0.8816). The molecular refraction was thus 61.8 as compared with a calculated value of 62.4. A mixture of stereoisomers of 1,1,4,4,5,5,8,8-octamethylperhydroanthracene (m. p. 100–110° from alcohol) was prepared by the hydrogenation of the corresponding octahydroanthracene over Raney nickel at 340° for four hours at 3000 p. s. i. The hydrogenation of 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthalene over Raney nickel in methylcyclohexane at 250° gave a mixture of stereoisomers of the corresponding perhydronaphthalene (m. p. 162–167° from chloroform-alcohol). 2,5-Dimethyl-3-hexyn-2,5-diol was hydrogenated at 27–75° over Raney nickel at 3000 p. s. i. to give a quantitative yield of 2,5-dimethyl-2,5-hexanediol.

Procedures of Dehydrogenation, Isolation and Characterization.—The dehydrogenations were carried out in a chrome-vanadium steel reaction vessel having a void of 270 ml. In general about 2 g. of the compound to be dehydrogenated in 5 ml. of benzene was heated for eight to twelve hours at 350–375° with 0.25 g. of a platinum-on-carbon catalyst carrying about 0.06 g. of reduced platinum. Where other conditions were used it is noted in the summary of experimental results given below. A nickel-on-nickel chromite (2 g.) and a nickel-on-kieselguhr catalyst (2 g.) were used also with all compounds, but the results are not given below in detail except in a few cases. The benzene was usually thiophene free. A little thiophene is advantageous with nickel catalysts.²

The products of reaction were removed from the steel vessel with ether, the catalyst separated by centrifuging, the solution decolorized with activated carbon and the solvents removed under reduced pressure. Usually a solid product was isolated by crystallization at about –80° from petroleum ether (b. p. 40–60°) using a "Dry Ice technique."¹¹ From the amount of solid isolated and/or the refractive index of the residue an estimate of the percent aromatization could be made. The formation of picrates, styphnates and trinitrobenzene derivatives served also to separate and characterize aromatic products. The hydrocarbon was conveniently recovered from these de-

(4) Clemo and Dickenson, *J. Chem. Soc.*, 255 (1937).

(5) Sengupta, *J. prakt. Chem.*, 151, 82 (1938).

(6) Higson and Thorpe, *J. Chem. Soc.*, 89, 1465 (1906).

(7) Inglis, *ibid.*, 99, 544 (1911).

(8) Martin, *THIS JOURNAL*, 58, 1440 (1936).

(9) Sengupta, *J. prakt. Chem.*, 152, 9 (1939).

(10) Cambron, *Can. J. Research*, 17B, 10 (1939).

(11) Wilds, *THIS JOURNAL*, 64, 1424 (1942).

(12) Hoch, *Bull. soc. chim.*, [5] 6, 268 (1938).

(13) Perlman, Davidson and Bogert, *J. Org. Chem.*, 1, 295 (1936).

(14) Bruson and Kroeger, *THIS JOURNAL*, 62, 36 (1940).

TABLE I
 ANALYTICAL DATA AND PHYSICAL CONSTANTS

Compound	n_D^{25}	d_4^{25}	M_D Calcd.	M_D Found	B. p. or m. p. °C.	Mol. form.	Analyses, %				
							Carbon		Hydrogen		
							Calcd.	Found	Calcd.	Found	
1,1-Dimethyl-1,2,3,4-tetrahydrophenanthrene	1.6035	1.031	67.2	71.6	122-123	1	C ₁₆ H ₁₈	91.37	91.53	8.63	8.58
1,1-Dimethylperhydrophenanthrene	1.4960	0.9289	69.5	69.3	103-106	1	C ₁₆ H ₂₂	87.20	87.40	12.80	12.90
1,1-Methylethyl-1,2,3,4-tetrahydrophenanthrene	1.6007	1.029	71.9	74.7	144-145	2	C ₁₇ H ₂₀	91.00	90.92	9.00	8.99
1,1-Methylethylperhydrophenanthrene	1.5015	0.9404	74.1	73.5	123-125	1.5	C ₁₇ H ₂₀	87.12	87.42	12.88	12.78
1,1-Diethyl-1,2,3,4-tetrahydrophenanthrene	1.5990	1.027	76.4	79.1	146-147	1.1	C ₁₈ H ₂₂	90.69	91.00	9.31	9.39
1,1-Spirocyclopentano-1,2,3,4-tetrahydrophenanthrene	1.5200	0.9325	55.3	56.8	160-164	0.5	C ₁₈ H ₂₀	91.50	91.49	8.50	8.61
2,2,3-Trimethyl-1,2,3,4-tetrahydronaphthalene	1.5200	0.9325	55.3	56.8	64	0.4	C ₁₈ H ₁₈	89.61	89.25	10.39	10.31
2-Methyl-2-ethyldecalin	1.4782	0.8880	57.8	57.5			C ₁₈ H ₂₄	86.58	86.47	13.42	13.37
1,1,4,4-Tetramethyldecalin	1.4732	0.8816	62.4	61.8	100-103	11	C ₁₈ H ₂₆	86.60	86.30	13.40	13.30
2,2-Dimethyl-1,2,3,4-tetrahydrophenanthrene					45-46.5		C ₁₆ H ₁₈	91.43	91.42	8.57	8.42
1,1,4,4-Tetramethyl-1,2,3,4-tetrahydroanthracene					82.5-84		C ₁₈ H ₂₂	90.75	90.81	9.25	9.29
α -Methyl- α -phenylsuccinic acid					156-158		C ₁₁ H ₁₂ O ₄	63.45	63.45	5.81	5.76
γ -Phenyl- γ -keto- α,α,β -trimethylbutyric acid					133.5-136		C ₁₃ H ₁₆ O ₂	70.89	71.10	7.31	7.23
γ -Phenyl- α,α,β -trimethylbutyric acid					115-120		C ₁₃ H ₁₈ O ₂	75.70	75.76	8.78	8.97
1,1,4,4,5,5,8,8-Octamethylperhydroanthracene					100-110		C ₂₂ H ₄₀	86.84	86.94	13.16	12.97
1,1,4,4,7,7,10,10-Octamethylperhydronaphthalene					162-167		C ₂₆ H ₄₆	87.2	86.8	12.8	12.5

TABLE II

ANALYSIS OF (a) PICRATES AND (b) TRINITROBENZENE DERIVATIVES

Compound	M. p., °C.	Mol. form.	% Carbon		% Hydrogen	
			Calcd.	Found	Calcd.	Found
1,1-Spirocyclopentano-1,2,3,4-tetrahydrophenanthrene (a)	96-97	C ₂₄ H ₂₃ O ₂ N ₃	61.92	61.87	4.99	4.91
1,1-Spirocyclopentano-1,2,3,4-tetrahydrophenanthrene (b)	125-126	C ₂₄ H ₂₃ O ₆ N ₃	64.13	64.16	5.12	5.11
1,2,3-Trimethylnaphthalene (a)	141-142	C ₁₉ H ₁₇ O ₇ N ₃	57.13	57.12	4.26	4.40
2,2-Dimethyl-1,2,3,4-tetrahydrophenanthrene (b)	112-115	C ₂₂ H ₂₁ O ₆ N ₃	62.41	62.38	4.96	4.86
1-Methylphenanthrene (b)	160-161	C ₂₁ H ₁₅ O ₆ N ₃	62.22	62.46	3.70	3.72
1,2-Diethylphenanthrene (b)	137-138	C ₂₄ H ₂₁ O ₆ N ₃	64.42	64.85	4.74	4.78
2-Methyl-3-ethylnaphthalene (a)	131.5-133.5	C ₁₉ H ₁₇ O ₇ N ₃	57.13	57.26	4.26	4.36
2-Methyl-3-ethylnaphthalene (b)	131-131.5	C ₁₉ H ₁₇ O ₆ N ₃	59.51	59.47	4.44	4.45

rivatives by dissolving in the proper solvent (benzene for picrate and petroleum ether for trinitrobenzene derivatives) and passing through a tower packed with activated alumina. Thus, small amounts of low melting aromatic hydrocarbons were conveniently purified by preparing a higher melting derivative such as the picrate, recrystallizing to purity and recovering the hydrocarbon by passing the picrate in benzene solution through an alumina tower. The picric acid was adsorbed on the alumina and the purified hydrocarbon could be recovered by evaporation of the benzene. After determination of its refractive index and/or melting point other derivatives could be prepared.

Results of Dehydrogenations

2,2-Dimethyltetralin (1.54 g., n_D^{25} 1.5188) gave 1.27 g. of product n_D^{25} 1.5410, which after crystallization gave 0.44 g. crystals and 0.75 g. of oil n_D^{25} 1.5330. The crystalline product was characterized as 2-methylnaphthalene through the formation of the trinitrobenzene derivative which after three crystallizations from methanol showed a m. p. 123-125.5°. The m. p. of the derivative was not lowered when mixed with an authentic sample. Decomposition of the derivative over alumina gave a sample of 2-methylnaphthalene m. p. above 25° which gave a picrate m. p. 113-114° corresponding to that reported.¹⁵

2-Methyl-2-ethyltetralin (1.4 g., n_D^{25} 1.5170) gave a product (1.1 g., n_D^{25} 1.5595) which yielded 0.4 g. of crystals melting at room temperature and 0.67 g. of an oil n_D^{25} 1.5520. The crystals were characterized as 2-methylnaphthalene as described above.

2,2-Dimethyltetralin (2.9 g.) over the nickel (k) catalyst gave 1.03 g. m. p. 90-92° and 0.88 g. of an oil n_D^{25} 1.5950. The solid after four recrystallizations from methanol showed a m. p. 102-103.5° and gave a trinitrobenzene derivative m. p. 134.5-136.5°. These values correspond to those for 2,3-dimethylnaphthalene. 1,2-Dimethylnaphthalene was identified in the oil through the formation of the trinitrobenzene derivative m. p. 144-148°

and comparison of it with an authentic compound. A few milligrams of the hydrocarbon was recovered from the derivative and converted to the picrate m. p. 124-128°.

2-Methyl-2-ethyltetralin and the corresponding decalin, over the nickel (k) catalyst, gave aromatic oils from which derivatives of 2-methyl-3-ethylnaphthalene (n_D^{25} 1.6003) were prepared. The yields of this compound were estimated to be 20-30%. The picrate m. p. 131.5-133.5°, styphnate m. p. 118-119°, and trinitrobenzene derivative m. p. 131-133.5° were unreported to a quinone mixture m. p. 64-68° prepared as by Karrer,¹⁶ served to identify it as 2-methyl-3-ethylnaphthalene.

2-Methyl-2-ethyldecalin (2.3 g., n_D^{25} 1.4775) gave a product (2.1 g., n_D^{25} 1.5450) from which was obtained 1.53 g. of 2-methylnaphthalene (m. p. 23-25°) and 0.23 g. of oil. The 2-methylnaphthalene was characterized as described above.

2,2,3-Trimethyltetralin (1.08 g., n_D^{25} 1.5200) gave a product (1.0 g.) which yielded 0.77 g. of crystalline but impure 2,3-dimethylnaphthalene and a liquid (0.2 g., n_D^{25} 1.5720). Recrystallization of the crude 2,3-dimethylnaphthalene from petroleum ether (b. p. 40-60°) yielded 0.5 g., m. p. 95-99° and three crystallizations from methanol gave 0.2 g., m. p. 104-105°. The m. p. reported is 102°. The picrate, m. p. 123-124.5° and the trinitrobenzene derivative m. p. 137-138° were also prepared and found to agree with those reported.¹⁷ From another run there was obtained 0.3 g. of crystalline 2,3-dimethylnaphthalene and 0.41 g. of oil n_D^{25} 1.5570. From the oil a picrate was prepared which after two recrystallizations from methanol melted at 138-142° and showed no lowering when mixed with the picrate of 1,2,3-trimethylnaphthalene m. p. 141-142° obtained from the nickel (k) run below. Therefore it was concluded that some of this hydrocarbon was present in the dehydrogenation product. 2,2,3-Trimethyltetralin (1 g.) over the nickel (k) catalyst gave 0.52 g. of an oil n_D^{25} 1.5725. A picrate m. p.

(15) Barbot, *Bull. soc. chim.*, **47**, 1317 (1930).(16) Karrer and Epprecht, *Helv. chim. acta*, **23**, 277 (1940).(17) Thiele and Troutman, *Ber.*, **68B**, 2247 (1935).

141–142° and the styphnate m. p. 136–139° corresponding to 1,2,3-trimethylnaphthalene were obtained.

1,1,4,4-Tetramethyldecalin (2.6 g., n_D^{25} 1.4732) gave 2.3 g. of a product n_D^{25} 1.5210. This value is similar to that of 1,1,4,4-tetramethyltetralin, n_D^{25} 1.5180, and identical with the product from an attempted dehydrogenation of the tetralin. There was also fair agreement in the densities, *i. e.*, d_4^{25} 0.9215 as compared with 0.9244 for the authentic tetralin.

1,1-Dimethyl-1,2,3,4-tetrahydrophenanthrene (2 g., n_D^{25} 1.6035) gave 1.1 g. of crystals and 0.58 g. of oil n_D^{25} 1.6092. After two crystallizations from petroleum ether (b. p. 60–68°) the 1-methylphenanthrene (0.47 g.) had a m. p. 115–117° and after three recrystallizations from methanol the m. p. was 118–119°. The picrate m. p. 135.5–137°, the styphnate m. p. 150.5–152°, and the trinitrobenzene derivative m. p. 160–161° were obtained. These values correspond with those of 1-methylphenanthrene and its derivatives.

1,1-Dimethyl-1,2,3,4-tetrahydrophenanthrene (2 g., n_D^{25} 1.6035) over the nickel (k) catalyst gave 0.6 g. of crystals which after three recrystallizations from methanol melted at 136–140°. The picrate melted at 151–153°. These values are in agreement with those reported for 1,2-dimethylphenanthrene.¹⁸

1,1-Dimethylperhydrophenanthrene (2.3 g., n_D^{25} 1.4940) gave 1.17 g. of crude 1-methylphenanthrene and 0.93 g. of oil n_D^{25} 1.5885. Crystallization and characterization as described above gave 0.68 g. of 1-methylphenanthrene m. p. 83–95° which was purified to 0.24 g., m. p. 116–117°.

1-Methyl-1-ethyl-1,2,3,4-tetrahydrophenanthrene (2 g., n_D^{25} 1.6002) gave 1 g. of a solid and 0.58 g. of an oil n_D^{25} 1.6138. Purification and characterization of the solid product, as described above for 1-methylphenanthrene, showed it to consist primarily of that compound. The quantities obtained were low, *i. e.*, 0.33 g., m. p. 99–107°, and 0.10 g., m. p. 117–120°.

1-Methyl-1-ethyl-perhydrophenanthrene (1.6 g., n_D^{25} 1.5010) gave 1.21 g. of a solid and an oil n_D^{25} 1.6145. Purification and characterization of the solid product as described above, indicated that 1-methylphenanthrene was produced along with other compounds in the dehydrogenation.

1,1-Diethyl-1,2,3,4-tetrahydrophenanthrene (2 g., n_D^{25} 1.5960) gave 0.72 g. of crystals and 0.77 g. of oil n_D^{25} 1.6210. 1-Ethylphenanthrene, 0.37 g., m. p. 60–61.5° was obtained by recrystallization of the product from methanol. Further recrystallization gave a sample m. p. 62.5–63° corresponding with that previously reported.¹⁹ The above run repeated over a nickel (k) catalyst gave an oil n_D^{25} 1.6355. A trinitrobenzene derivative after six recrystallizations from methanol melted at 137–138° (0.1 g.). It gave the correct carbon and hydrogen analyses for the trinitrobenzene derivative of 1,2-diethylphenanthrene.

2,2-Dimethyl-1,2,3,4-tetrahydrophenanthrene (0.5 g., m. p. 45–46.5°) gave 0.4 g. of a product which formed a picrate that melted at 120–123° after being twice recrystallized from methanol. The m. p. of the picrate of 2-

methylphenanthrene is 118–119°. The m. p. of a mixture of the two samples was 118–120°. Analysis of the picrate for carbon and hydrogen indicated that it was a mixture derived from a mono- and a dimethylphenanthrene. The hydrocarbon(s) recovered from the picrate over alumina showed a m. p. 65–75° which is higher than that of 2-methylphenanthrene, m. p. 53–54°.

2,2-Dimethyl-1,2,3,4-tetrahydrophenanthrene (1.06 g.) over nickel (k) catalyst gave 0.82 g. of solid. Four recrystallizations from methanol gave crystals melting at 142–143°, the reported melting point of 1,2-dimethylphenanthrene.¹⁸

1,1,4,4-Tetramethyl-1,2,3,4,5,6,7,8-octahydroanthracene (5 g., m. p. 88–91°) at 350° gave 4.8 g. of a solid product. Recrystallizations from ethanol gave 3.3 g. of 1,1,4,4-tetramethyl-1,2,3,4-tetrahydroanthracene m. p. 78–81° or 1.6 g., m. p. 82.5–84°. This compound reacted with 2,5-dichloro-2,5-dimethylhexane in the presence of aluminum chloride to give 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene.

A sample of 1,1,4,4,7,7,10,10-octamethylperhydro-naphthacene (2 g., m. p. 162–167°) gave upon dehydrogenation a product which after crystallization from toluene amounted to 1.2 g. of product m. p. 160–170°. After five recrystallizations there was obtained 0.05 g., m. p. 295–298° of a compound that is probably 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene.

1,1,4,4,5,5,8,8-Octamethylperhydroanthracene resisted dehydrogenation even to the octamethyloctahydroanthracene under the conditions used in this work. This might be expected since the reverse hydrogenation was so difficult to accomplish, *i. e.*, 340° was required.

1,1-Spirocyclopentano-1,2,3,4-tetrahydrophenanthrene (0.8 g., m. p. 56–58°) gave after evaporative distillation of the dehydrogenation product 0.17 g., m. p. 200–244°. This solid could be crystallized from benzene to m. p. 250–251° and the melting point was not lowered on mixing with an authentic sample of chrysene m. p. 251–252°.

The above experiment was repeated using nickel (k) as catalyst and there was obtained after evaporative distillation 0.23 g., m. p. 240–250°.

Summary

Eleven tetralins, decalins, tetrahydrophenanthrenes and perhydrophenanthrenes carrying gem dialkyl groups have been prepared. These compounds have been aromatized in the liquid phase with benzene and platinum and nickel catalysts to substituted naphthalenes or phenanthrenes. The platinum catalyst brings about aromatization almost exclusively through elimination of an alkyl group and hydrogen, while the nickel-on-kieselguhr catalyst brings about aromatization through the catalysis of the migration of a carbon linkage. The latter catalyst, for example, brings about a rather clean transformation of 1,1-spirocyclopentano-1,2,3,4-tetrahydrophenanthrene to chrysene.

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(18) Haworth, *J. Chem. Soc.*, 457 (1934).

(19) Haworth, *ibid.*, 460 (1934).