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Catalytic Dehydrogenation of Hydroaromatic Compounds in Benzene. II

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The study of the aromatization of hydroaromatic compounds with benzene as a hydrogen acceptor[2] was continued with twelve variously substituted compounds as listed in Table I. The data on three of these compounds, *i. e.*, 2-methyl-1-ethyl-3,4-dihydronaphthalene, 2-methyl- and 2-ethyldecalin show that the corresponding naphthalene may be prepared from them in yields of more than 90% of the theoretical with a platinum catalyst. Attempts to aromatize alcohols, *i. e.*, 2-decalol and 2-methyl-1-ethyl-1,2,3,4-tetrahydro-1-naphthol, without loss of oxygen were not so successful. The highest yield of 2-naphthol over any catalyst was only 18–20% from 2-decalol or 2-decalone over a platinum catalyst, while the hydrocarbon 2-methyl-2-ethyl-naphthalene was obtained in 91% yield from the tetrol without any evidence of a phenol. However, a 65% yield of thymol from menthol was obtained[2] over a nickel catalyst.

The dehydrogenation of compounds with quaternary carbon atoms in the rings to be aromatized required more drastic conditions than for simple dehydrogenation. Data for the reaction of six such compounds are given in Table I. Three tetralins carrying two methyls, I, a methyl and an ethyl or a methyl and a phenyl group in the 1,1-position all gave 1-methylnaphthalene, II, but in rather low yields. The nickel on kieselguhr catalyst gave migration rather than elimination of the alkyl group so that 1,2-dimethylnaphthalene, III, was produced from the 1,1-dimethyltetralin. There was a similar migration of a carbon linkage in the aromatization of 1,1-spirocyclopentyl-1,2,3,4-tetrahydronaphthalene, IV, to phenanthrene, V. A methyl or isopropyl group in an angular position of octahydrophenanthrene was eliminated

TABLE I

DEHYDROGENATION OF HYDROAROMATIC COMPOUNDS[a]

Compound	G. catalyst	Temp., °C.	
1,1-Dimethyl-1,2,3,4-tetrahydronaphthalene	0.5 Pt	350	25% 1-Methylnaphthalene 61% No reaction
	3 Ni (CrO)	370	38% 1-Methylnaphthalene 50% No reaction
	3 Ni (k)	350	35% 1,2-Dimethylnaphthalene 35% No reaction
1-Methyl-1-ethyl-1,2,3,4-tetrahydronaphthalene	3 Ni (CrO)	375	35–55% 1-Methylnaphthalene 27% No reaction
1-Methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene	3 Ni (k)	350	12% 1-Methylnaphthalene
1,1-Spirocyclopentyl-1,2,3,4-tetrahydronaphthalene	3 Ni (k)	350	25–40% Phenanthrene
12-Methyl-1,2,3,4,5,6,7,8-octahydrophenanthrene	1 Pt	350	65% Phenanthrene
2-Methyl-12-isopropyl-1,2,3,4,5,6,7,8-octahydrophenanthrene	2 Ni (CrO)	350	50% 2-Methylphenanthrene
2-Methyldecalin	1 Pt	350	91% 2-Methylnaphthalene
2-Ethyldecalin	0.25 Pt	350	94% 2-Ethylnaphthalene
2-Methyl-1-ethyl-1,2,3,4-tetrahydro-1-naphthol	2 Ni (k)	300	66% 2-Methyl-1-ethylnaphthalene
1-Methyl-2-ethyl-3,4-dihydronaphthalene	0.25 Pt	300	91% 1-Methyl-2-ethylnaphthalene
2-Decalol	1 Pt	275	18% 2-Naphthol
2-Decalone	1 Pt	275	20% 2-Naphthol 33% Naphthalene

[a] The dehydrogenations were made on about 5 g. of compound, in 20–40 ml. of benzene for 10–12 hours, in chrome vanadium steel vessels having voids of 62 ml. (platinum catalysts) or 270 ml. (nickel catalysts).

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(1) Allied Chemical and Dye Corporation Fellow, 1941–1942.

(2) (a) Adkins, Richards and Davis, THIS JOURNAL, 63, 1320 (1941); (b) Adkins, Rae, Davis, Hager and Hoyle, *ibid.*, 70, 381 (1948).

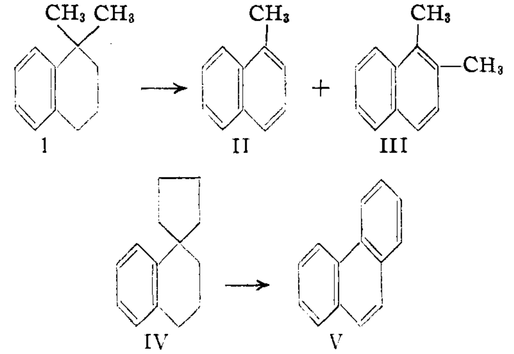
TABLE II

PROPERTIES OF COMPOUNDS

(a) Picrates, (b) trinitrobenzene derivatives, (c) styphnates

Compound	M. p., °C.	Mol. form.	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
1-Methylnaphthalene	−22	(n^{20}_D 1.6180)				
(a)[3]	141–142					
(b)	153–154	$C_{17}H_{13}N_3O_6$	57.46	57.63	3.69	3.77
2-Methylnaphthalene	37–38	(n^{25}_D 1.6086)				
(a)[4]	115–116					
(b)[4]	123					
1,2-Dimethylnaphthalene	(B. p. 139–140 (15 mm.), $n^{16.6}_D$ 1.6105)					
(a)[5]	129.5–130.5					
(b)[6]	147–148					
(c)[6]	142–143					
1-Ethylnaphthalene	−15	(n^{16}_D 1.6089)				
(a)[7]	98.5					
2-Ethylnaphthalene	−7.5	(n^{16}_D 1.6028)				
(a)[8]	76–77					
(b)	88–89	$C_{18}H_{15}N_3O_6$	58.53	58.44	4.08	3.97
1-Methyl-2-ethylnaphthalene	B. p. 140–145 (11 mm.)					
(a)[9]	97					
(b)	98.5–99.5	$C_{19}H_{17}N_3O_6$	59.52	59.69	4.47	4.52
(c)[9]	114					
2-Methyl-1-ethylnaphthalene	B. p. 135–145 (11 mm.)					
(a)[9]	110–111					
(b)	117.5–119.5	$C_{19}H_{17}N_3O_6$	59.52	59.60	4.47	4.49
(c)[9]	141					
2-Methylphenanthrene	55–56					
(a)	118–119					

and a phenanthrene formed under the standard conditions for aromatization.



Experimental Part

The conditions and procedures used for the reactions referred to in the table were essentially the same as those described in the earlier paper. The physical properties and analyses for certain compounds are given in Table II. 2-Decalol, b. p. 140–143° (28 mm.), n^{25}_D 1.4958–1.5000, was prepared by the hydrogenation of 2-naphthol over Raney nickel at 200°. The alcohol (40 g.) was oxidized to 2-decalone (24 g.) (b. p. 123.5–125 (27 mm.), n^{25}_D 1.4885–1.4905) by the procedure described for the preparation of menthone.[10,11] 2-Methyldecalin[12] (b. p. 203–205°, n^{25}_D 1.4712) and 2-ethyldecalin[13] (b. p. 85–87 (7 mm.), n^{25}_D 1.4727) were prepared by hydrogenation at 200° over Raney nickel, from 2-methylnaphthalene and methyl 2-naphthyl ketone, respectively. 1,1-Dimethyl-1,2,3,4-tetrahydronaphthalene, (b. p. 94–95 (12 mm.), n^{25}_D 1.5262); 12-methyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (b. p. 150 (13 mm.), n^{25}_D 1.5510); and 2-methyl-12-isopropyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (n^{25}_D 1.5435) were prepared as described.[14,15,16] Other procedures described below were in general patterned after those of Brunner and Grof[9] or of Bogert, Davidson, Apfelbaum and Perlman.[14,15]

1-Methyl-1-ethyltetralin.[14]—One hundred and sixty grams of 3-phenylpropyl bromide in 300 ml. of dry ether was added to 20 g. of magnesium over a period of fifty minutes. The mixture was refluxed for fifty minutes, and then 72 ml. of methyl ethyl ketone in 72 ml. of dry ether was added over a period of twenty minutes. After thirty minutes of refluxing, the addition product was hydrolyzed with saturated ammonium chloride solution. The ether solution was washed twice with water, dried over anhydrous sodium sulfate and the product (125 g.) distilled at 154–163° (23 mm.), n^{25}_D 1.4970–1.5050.

Eighty-five grams of the alcohol so obtained was cooled to 15° and 85 ml. of cold, concentrated sulfuric acid was added dropwise while the mixture was stirred vigorously

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[3] Darzens and Levy, *Compt. rend.*, **199**, 1131 (1934).

[4] Barbot, *Bull. soc. chim.*, **47**, 1314 (1930).

[5] Schroeter and Lichtenstadt, *Ber.*, **51**, 1601 (1918).

[6] Kloetzel, THIS JOURNAL, **62**, 1708–1713 (1940).

[7] Froschl and Harlass, *Monatsh.*, **59**, 280 (1932).

[8] Levy, *Compt. rend.*, **192**, 1397 (1931).

[9] Brunner and Grof, *Monatsh.*, **64**, 78–79 (1934).

[10] "Organic Syntheses," Coll. Vol. 1, p. 333, John Wiley and Sons, Inc., New York, N. Y., 1941.

[11] Leroux, *Compt. rend.*, **141**, 46 (1900).

[12] Weissenberger, *Z. anorg. allgem. Chem.*, **153**, 33 (1926).

[13] Levy, *Compt. rend.*, **192**, 1397–1399 (1931).

[14] Bogert, Davidson and Apfelbaum, THIS JOURNAL, **56**, 961 (1934).

[15] Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 288 (1936).

[16] Orcutt and Bogert, *ibid.*, **4**, 543 (1939).

and the temperature kept below 25°. Ten minutes after all the acid had been added, the mixture was diluted with water and ether. The ether solution was washed with a sodium carbonate solution, dried and distilled from sodium. The yield was 48.6 g., b. p. 125.5° (23 mm.), n^{25}D 1.5250–1.5260. The product was redistilled from sodium through a modified Widmer column to give 34 g., b. p. 127–127.5° (23 mm.), n^{25}D 1.5255.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.55; H, 10.35.

1-Methyl-1-phenyltetralin.[14]—A Grignard reagent was prepared as before from 125 g. of 3-phenylpropyl bromide in 225 ml. of ether and 72 ml. of acetophenone in 70 ml. of dry ether added over a period of twenty minutes. After one hour of refluxing, the addition compound was hydrolyzed with dilute sulfuric acid and the ether solution washed with water. The low boiling material was removed by distillation, and the crude alcohol cyclized as described above. There was obtained 73.2 g. or a 55% yield; b. p. 141–147° (2 mm.), n^{25}D 1.5850–1.5855. The product was redistilled from sodium to give 67 g., b. p. 129–131° (1 mm.), n^{25}D 1.5853, d^{25}_4 1.042. MD calcd.: 71.32. Found: 71.6. *Anal.* Calcd. for $C_{17}H_{18}$: C, 91.83; H, 8.17. Found: C, 91.60; H, 8.23.

1,1-Spirocyclopentyltetralin.[15]—A Grignard reagent was prepared as before from 160 g. of 3-phenylpropyl bromide and 71 ml. of cyclopentanone in 70 ml. of dry ether was added over a period of thirty minutes. After one hour of refluxing, the addition product was hydrolyzed with saturated ammonium chloride solution; the ether solution was washed with water, dried and distilled. The alcohol so obtained boiled at 150–170° (25 mm.), n^{25}D 1.5200. The alcohol was cyclized by treatment with an equal volume of cold concentrated sulfuric acid as for methylethyltetralin. The tetralin was distilled from sodium through a modified Widmer column. The yield was 23.1 g., b. p. 158° (24 mm.), n^{25}D 1.5535. *Anal.* Calcd. for $C_{14}H_{18}$: C, 90.25; H, 9.75. Found: C, 89.91; H, 9.74.

2-Methyl-1-tetralone.[9]—Nineteen and one-half grams of potassium was powdered in 500 ml. of xylene in a 1 l. three-necked flask fitted with a dropping funnel, a reflux condenser and a Hershberg stirrer. The mixture was cooled and 87 g. of diethyl methylmalonate was added over a period of ten minutes. After one hour, 93 g., of β-phenethyl bromide was added and the mixture was refluxed and stirred for twelve hours in an oil-bath at 150–160°. The xylene solution was washed with water, dried and distilled, and there was obtained 85 g. of diethyl methyl-β-phenethylmalonate, b. p. 188–192° (17 mm.), n^{25}D 1.4818–1.4820.

Ninety-three grams of this ester was hydrolyzed by refluxing it ninety minutes with 56 g. of potassium hydroxide in 200 ml. of 50% aqueous alcohol. After water was added and the alcohol was distilled off, the solution was acidified to congo red with concentrated hydrochloric acid. The solid acid which precipitated was dissolved in ether and the aqueous solution was extracted with ether. The ether solutions were combined, washed with water, dried with anhydrous sodium sulfate and the ether distilled. The acid was heated to 180° and distilled after carbon dioxide ceased to be evolved. The yield of γ-phenyl-α-methylbutyric acid was 48.9 g. or 82%, b. p. 176–178° (17 mm.), n^{25}D 1.5093–1.5100, plus 4.9 g., b. p. 178–183° (17 mm.). To 53.8 g. of this acid dissolved in 250 ml. of dry benzene was added 80 g. of phosphorus pentachloride, the solution refluxed thirty minutes, cooled, and 70 ml. of stannic chloride in 70 ml. of benzene added slowly. After twenty-five minutes the mixture was poured into 250 ml. of concentrated hydrochloric acid. The benzene solution was separated and washed with three 100 ml. portions of 10% hydrochloric acid, followed by three 100 ml. portions of a 5% sodium carbonate solution, dried and distilled. The yield (71%) was 34.2 g., b. p. 136–138° (16 mm.), n^{25}D 1.5538.

2-Ethyl-1-tetralone[9] was prepared by the same method as 2-methyl-1-tetralone. From 20 g. of potassium, 94 g. of ethyl diethylmalonate and 93 g. of β-phenethyl bromide there was obtained 70 g. or 48% of diethyl ethyl-β-phenethylmalonate, b. p. 160–180° (4 mm.). A much lower yield was obtained when benzene instead of xylene was used as the solvent.

Hydrolysis and decarboxylation of 102.8 g. of this ester gave 62.5 g. of 93% of α-ethyl-γ-phenylbutyric acid, b. p. 146–161° (3 mm.), n^{25}D 1.5010–1.5055. The ethylphenylbutyric acid (10.3 g.) was dissolved in 30 ml. of concentrated sulfuric acid, heated to 90° for 2.5 hours on the steam-bath, cooled, diluted with water and extracted with ether. The ether solution was washed with sodium carbonate solution, dried and the ether removed. The yield was 7.8 g. or 84%, which upon distillation gave a faintly yellow liquid, b. p. 147–148° (15 mm.), n^{25}D 1.5460–1.5458. The combined yield of pure redistilled ketone from several cyclizations was 70%.

1-Ethyl-2-methyl-1-tetralol.—A Grignard reagent was prepared from 17.5 g. of ethyl bromide and 3.9 g. of magnesium in 70 ml. of ether. 2-Methyl-1-tetralone (20 g.) in 50 ml. of dry ether was added over a period of ten minutes and the solution refluxed six hours. The addition product was hydrolyzed with ice-cold dilute sulfuric acid, the ether solution washed with dilute sulfuric acid, a sodium carbonate solution and dried. The solid remaining after the distillation of the ether was recrystallized twice from acetone at about −70°. The yield of alcohol was 16.1 g. or 68%, m. p. 65–67°. *Anal.* Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 82.27; H, 9.53.

1-Ethyl-2-methyl-3,4-dihydronaphthalene was prepared by dehydration of the filtrates from the crystallization of 1-ethyl-2-methyl-1-tetralol. The acetone was removed and the residue distilled from potassium bisulfate. The yield (26%) was 5.7 g., b. p. 125–130° (15 mm.). The crude product was redistilled from sodium to give 4.47 g., b. p. 121–127° (13 mm.), n^{25}D 1.5660.

1-Methyl-2-ethyl-3,4-dihydronaphthalene.—Methylmagnesium iodide was prepared from 23 g. of methyl iodide and 3.9 g. of magnesium in 70 ml. of ether, to which was added 21.8 g. of 2-ethyl-1-tetralone in 50 ml. of dry ether and the mixture refluxed thirty minutes. The addition product was decomposed with a saturated ammonium chloride solution and the ether solution washed with water and dried. The thick oil left after the distillation of the ether did not crystallize. This oil was distilled from potassium bisulfate. The crude product below 135° (15 mm.) was redistilled from sodium. The yield was 16.6 g. or 79%, b. p. 132° (14 mm.), n^{25}D 1.5658.

The m. p. of the trinitrobenzene derivative of 1,2-dimethylnaphthalene (148°) is the same as the m. p. of a mixture of 30% of the compound and 70% of the trinitrobenzene derivative of 1-methylnaphthalene. Mixtures of intermediate composition melt lower with a minimum of 147°. The mixtures containing a higher proportion of the derivative of 1-methylnaphthalene melt for 80% at 149.5°, 90% at 151° and the pure compound at 154°.

Summary

The method of aromatizing hydroaromatic compounds over nickel or platinum catalysts with benzene as a hydrogen acceptor has been applied to several substituted hydronaphthalenes and hydrophenanthrenes. Aromatization has in some cases involved the rupture of linkages to a quaternary carbon. The nickel on kieselguhr catalyst has been found to bring about aromatization through catalysis of migration as in the formation of phenanthrene from 1,1-spirocyclopentyltetralin. The platinum and nickel on nickel chromite catalysts brought about aromatization through elimination of an alkyl group on the quaternary carbon.

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