[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Selective Hydrogenation of Derivatives of Naphthalene and Diphenyl

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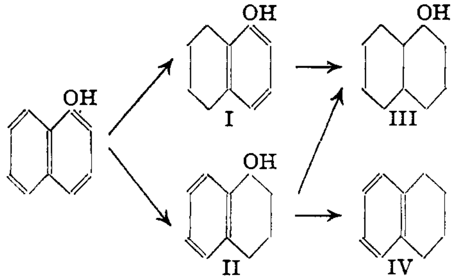
The objective of this investigation has been to ascertain some of the relations of structure, the catalyst and experimental conditions on the relative reactivity toward hydrogen of the two benzenoid nuclei in various hydroxy and alkoxy naphthalenes and diphenyls.

The hydrogenation of naphthalene to tetra- and decahydronaphthalene over nickel, platinum and palladium catalysts has been carried out by a number of investigators.[1-7] Naphthol-1 and naphthol-2 have been hydrogenated over nickel to the decahydronaphthols by Ipatieff[8] and by Leroux[9] among others. Schroeter[10] also obtained a 5,6,7,8-tetrahydronaphthol-1 and Komatsu[11] with reduced copper obtained 1,2,3,4-tetrahydronaphthol-2 with nickel, while Hückel[12] with a platinum catalyst obtained principally 5,6,7,8-tetrahydronaphthol-2. Von Braun studied the hydrogenation of *o*-hydroxydiphenyl and obtained the completely hydrogenated products, 2-phenylcyclohexanol, and products of hydrogenolysis.[13] The hydrogenation of aryl alkyl ethers has been studied by Ipatieff,[14] Marty,[15] Van Duzee[16] and others.

Derivatives of Naphthalene.—Naphthalene was almost quantitatively hydrogenated to tetrahydronaphthalene over either of the two catalysts used in this investigation, *viz.*, Raney nickel and copper–chromium oxide. The difference between these catalysts for this transformation is primarily that the reaction was complete over Raney nickel at 100° after 1.3 hours, while over copper–chromium oxide a temperature of 200° was required for four hours. Another difference between the two catalysts is that hydrogenation begins in the second ring over Raney nickel at 100°, so that if tetralin is desired, the reaction must be interrupted after the addition of two moles of hydrogen per mole of naphthalene. Over copper–chromium oxide the benzenoid nucleus of tetrahydronaphthalene is quite stable even at 200°, so that reaction stops after the addition of two moles of hydrogen to naphthalene.

The naphthols require the same temperature as naphthalene for hydrogenation over copper–chromium oxide (Table I). However, they are much more resistant than naphthalene to hydrogenation over Raney nickel, a temperature of 150° being required for a reasonably rapid rate of reaction under the conditions used. The products formed by the hydrogenation of a naphthol depend upon its structure, the catalyst and other conditions of reaction. The possible products are



That is to say, hydrogen may react first in the non-oxygenated ring to give the phenol I or in the oxygenated ring to give the alcohol, II. Compounds I and II may be hydrogenated further to decahydronaphthol, III, or they may undergo hydrogenolysis to give tetralin, IV. Actually, only the alcohol, II, undergoes this type of reaction to an appreciable extent, since the isomeric phenol, I, is much more stable toward hydrogenolysis. It is possible of course to convert either III or IV into decahydronaphthalene, but these reactions require more drastic conditions and will not be discussed further at this time.

There appears to be a considerable difference between the reactivity toward hydrogen of the two rings in naphthol-1, the ratio of hydrogenation in the non-substituted ring being as 5 to 3 in the oxygenated ring. Actually there was none

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(1) Rowe, *J. Chem. Soc.*, 2441 (1920).

(2) Sabatier and Senderens, *Compt. rend.*, **132**, 1257 (1901).

(3) Leroux, *ibid.*, **139**, 672 (1904).

(4) Willstätter and Krug, *Ber.*, **46**, 527 (1913).

(5) Willstätter and Hatt, *ibid.*, **45**, 1471 (1912).

(6) Skita, *ibid.*, **45**, 3312 (1912).

(7) Lush, British Patent 304,403, Nov. 4, 1927.

(8) Ipatieff, *J. Russ. Phys.-Chem. Soc.*, **39**, 693 (1907), and *C. A.*, **1**, 2877 (1907).

(9) Leroux, *Compt. rend.*, **141**, 953 (1905).

(10) Schroeter, *Ann.*, **426**, 88 (1922).

(11) Komatsu, *Proc. Imp. Acad.* (Japan), **6**, 1947 (1930).

(12) Hückel, *Ann.*, **451**, 109 (1926).

(13) Von Braun, Gruber and Kirschbaum, *Ber.*, **55**, 3664 (1922).

(14) Ipatieff, *J. Russ. Phys.-Chem. Soc.*, **46**, 470 (1914).

(15) Marty, *Compt. rend.*, **187**, 47 (1928).

(16) Van Duzee and Adkins, THIS JOURNAL, **57**, 147 (1935).

TABLE I

HYDROGENATION OF DERIVATIVES OF NAPHTHALENE

Temp., °C.	Time, hrs.	Catalyst	-Naphthalene	% yield of products of various types I	II	III	IV
155	(0.7)	Ni	1-Hydroxy	40^a	..	8^b	30^c
155	6	Ni	1-Hydroxy	19^a	..	34^b	30^c
180	9	CuCr	1-Hydroxy	30^a	35^d	..	10^c
190	(1*)	CuCr	1-Hydroxy	25^a	59^d	..	..
190	4	CuCr	2-Hydroxy	..	87^e	..	..
140	6	Ni	2-Hydroxy	..	55^e	20^f	4^c
150	5	Ni	1-Methoxy	66^g	..	..	26^c
130	10	Ni	1-Ethoxy	82^h	..	..	..
200	4	Ni	1-Dodecoxy	40^i	..	..	25^c
150	1	Ni	2-Methoxy	..	71^j	..	17^c
130	6	Ni	2-Ethoxy	..	77^k	..	..
140	1	Ni	2-Dodecoxy	..	79^l	..	3^c
130	(0.5)	Ni	1-Hydroxy-2-Et	..	78^m	..	5^n
130	(.5)	Ni	2-Hydroxy-1-Et	..	68^o	..	..

* This hydrogenation was carried out at about 350 atm. rather than at 100 to 200 atm. as in the other cases.

[a] 5,6,7,8-Tetrahydronaphthol-1, b. p. 102–104° (2 mm.), m. p. 67–68°.[17] [b] Decahydronaphthol-1, b. p. 87–92° (2 mm.), m. p. 91–92°. [c] Tetralin, b. p. 52–55° (2 mm.). [d] 1,2,3,4-Tetrahydronaphthol-1, b. p. 102–104° (2 mm.).[17] [e] 1,2,3,4-Tetrahydronaphthol-2, b. p. 122–124° (4 mm.).[18] [f] Decahydronaphthol-2, b. p. 115–116° (4 mm.), m. p. 103–104°. [g] 1-Methoxy-5,6,7,8-tetrahydronaphthalene, b. p. 85–88° (3 mm.).[18] [h] 1-Ethoxy-5,6,7,8-tetrahydronaphthalene, b. p. 109–113° (5 mm.).[19] [i] 1-Dodecoxy-5,6,7,8-tetrahydronaphthalene. [j] 2-Methoxy-1,2,3,4-tetrahydronaphthalene, b. p. 115–118° (10 mm.).[18] [k] 2-Ethoxy-1,2,3,4-tetrahydronaphthalene, b. p. 110–115° (5 mm.).[19] [l] 2-Dodecoxy-1,2,3,4-tetrahydronaphthalene. [m] 2-Ethyl-1,2,3,4-tetrahydronaphthol-1. [n] 2-Ethyl-1,2,3,4-tetrahydronaphthalene b. p. 63–65° (0.5 mm.).[20] [o] 1-Ethyl-1,2,3,4-tetrahydronaphthol-2.

of the latter product II found, but undoubtedly it was first formed and then hydrogenolyzed to tetralin since it is a substituted benzyl alcohol. The amount of the phenol of type I isolated depended upon the duration of the reaction; a shorter period (0.7 hour) gave a 40% yield, while a longer period (six hours) converted a good portion of the phenol I first formed to the saturated alcohol III.

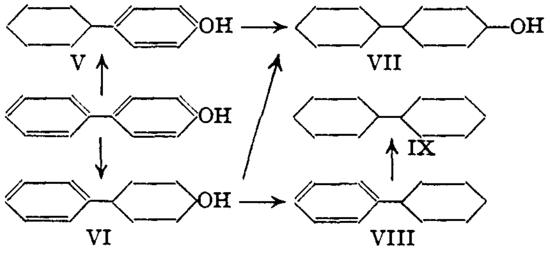
Copper–chromium oxide definitely favors the reaction of the oxygenated ring, the ratio of products instead of being 5 to 3 as over nickel is of the order of 1 to 2. The amount of the alcohol II was particularly high in a very rapid hydrogenation under a higher pressure of 300–350 atm.

Naphthol-2 over either catalyst was preferentially hydrogenated in the oxygenated ring, although here again copper–chromium oxide was more favorable to the reaction of this ring than was nickel. In fact, with copper–chromium oxide the alcohol of type II was the only product found in the reaction mixture, the yield isolated being 87%.

The ethers of naphthol-1 were, like the parent phenol, preferentially hydrogenated in the non-oxygenated ring. The ethers of naphthol-2 were hydrogenated only in the oxygenated ring. Under the most favorable conditions the yields of the tetrahydronaphthyl ethers were 80%. The hydrogenation of the ethers was carried out over Raney nickel, since the ethers would not undergo hydrogenation over copper–chromium oxide. When the temperature with the latter catalyst was raised sufficiently to give reaction, naphthalene was formed by hydrogenolysis from the ethers.

Thus, substitution in the 2-position as contrasted with the 1-position favors the hydrogenation of the oxygenated ring. Similarly the use of copper–chromium oxide as compared with Raney nickel favors the oxygenated ring. If the 1- and 2-positions are occupied by an ethyl and a hydroxyl group in either of the two possible combinations then the oxygenated ring is hydrogenated to the exclusion of the non-oxygenated ring.

Derivatives of Diphenyl.—The types of compound which are formed by the hydrogenation of a monohydroxy diphenyl are shown below



These involve the same possibilities as in the case of the naphthols except that the ultimate hydrogenation product, dicyclohexyl, was isolated in the hydrogenation of the diphenyl derivatives.

Using nickel as the catalyst, the non-oxygenated ring was preferentially hydrogenated in the case of the 4-hydroxydiphenyl and its ethers (Table II). On the contrary, in 2-hydroxydiphenyl and its ethers the oxygenated ring was the more reactive toward hydrogen. The 3-hydroxydiphenyl was like the 2-hydroxy in that the oxygenated ring was the more receptive toward hydrogenation; in fact the alcohol of type VI was the only product which could be isolated. However, from the ethyl ether of 3-hydroxydi-

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(17) Brochet, *Bull. soc. chim.*, **4**, 1231 (1922).

(18) Schroeter, *Ann.*, **426**, 17 (1922).

(19) Bamberger, *Ber.*, **23**, 217 (1890).

(20) Bogert, THIS JOURNAL, **57**, 157 (1935).

phenyl the phenol ether and the alcohol ether were produced in similar amounts. Thus there is a marked difference between the relative reactivities of the two rings in this phenol and in its ether.

TABLE II

HYDROGENATION OF DERIVATIVES OF DIPHENYL

Temp., °C.	Time, hrs.	Catalyst	-Diphenyl	% yield of products of various types V	VI	VII	VIII	IX
160	9.5	Ni	2-Hydroxy*	..	16[a]	50[b]	..	4[c]
150	4.0	Ni	2-Methoxy	..	23[d]	30[e]	..	18[c]
150	6.0	Ni	2-Ethoxy	..	24[f]	36[g]	..	18[c]
225	6.0	CuCr	2-Ethoxy	(22% diphenyl)			55[h]	..
150	3.0	Ni	2-Cetoxy	..	19[i]	..	..	47[c]
130	(1.5)	Ni	2-Hydroxy-5-Et	..	74[j]	..	6[k]	..
160	(0.5)	Ni	3-Hydroxy	..	79[l]	..	..	..
160	4.0	Ni	3-Hydroxy	..	..	89[m]	..	..
140	3.5	Ni	3-Ethoxy*	29[n]	27[o]	..	..	13[e]
160	5.0	Ni	4-Hydroxy	..	..	78[p]	..	..
160	(0.7)	Ni	4-Hydroxy	43[q]	13[r]	17[s]	..	..
240	9.0	CuCr	4-Hydroxy	..	52[r]	..	..	..
150	3.3	Ni	4-Methoxy*	37[t]	..	41[u]	..	8[c]
150	6.5	Ni	4-Ethoxy	27[v]	..	24[w]	..	10[c]
150	1.0	Ni	4-Cetoxy	67[x]	..	..	..	10[c]

* 20 to 30% of this compound was recovered unchanged after the hydrogenation. [a] 2-Phenylcyclohexanol-1, b. p. 115–117° (4 mm.), m. p. 54–55°. [b] 2-Cyclohexylcyclohexanol-1, b. p. 107–109° (4 mm.).[21] [c] Dicyclohexyl, b. p. 62–65° (1 mm.). [d] 2-Methoxy-1-phenylcyclohexane. [e] 2-Methoxy-1-cyclohexylcyclohexane. [f] 2-Ethoxy-1-phenylcyclohexane. [g] 2 - Ethoxy - 1 - cyclohexylcyclohexane. [h] Phenylcyclohexane, b. p. 76–78° (2 mm.). [i] 2-Cetoxy-1-phenylcyclohexane. [j] 5-Ethyl-1-phenylcyclohexanol-2. [k] 5-Ethyl-1-phenylcyclohexane, b. p. 103–107° (3 mm.). [l] 3-Phenylcyclohexanol-1, b. p. 140–144° (5 mm.).[22] [m] 3-Cyclohexylcyclohexanol-1, b. p. 127–129° (5 mm.), m. p. 43–44°. [n] 1-Ethoxy-3-cyclohexylbenzene. [o] 1-Ethoxy-3-phenylcyclohexane. [p] 4-Cyclohexylcyclohexanol-1, b. p. 115–117° (2 mm.), m. p. 101–102°. [q] 4-Cyclohexylphenol, b. p. 132–135° (4 mm.), m. p. 130–131°.[23] [r] 4-Phenylcyclohexanol-1, b. p. 132–135° (4 mm.), m. p. 117–118°. [s] 4-Cyclohexylcyclohexanol-1, b. p. 115–117° (2 mm.), m. p. 101–102°. [t] 4-Methoxy-1-cyclohexylbenzene, b. p. 114–116° (4 mm.), m. p. 59°. [u] 4-Methoxy-1-cyclohexylcyclohexane. [v] 4-Ethoxy-1-cyclohexylbenzene, b. p. 130–131° (3 mm.), m. p. 42°. [w] 4-Ethoxy-1-cyclohexylcyclohexane. [x] 4-Cetoxy-1-cyclohexylbenzene.

There is a difference in the relative reactivity of the two rings in 4-hydroxydiphenyl depending upon whether the catalyst is Raney nickel or copper-chromium oxide. With the first mentioned catalyst the non-oxygenated ring is the more reactive, while with the oxide catalyst the oxygenated ring is first hydrogenated.

The fact that copper–chromium oxide is more active for the hydrogenation of the oxygenated as compared with the non-oxygenated ring in naphthols and hydroxydiphenyls may be rationalized by the assumption that this catalyst reduces a phenol through its ketone form, for it is well known that this catalyst is relatively more active toward ketones than toward benzenoid nuclei. Similarly in the three cases where there is a difference between the relative ease of hydrogenation of the two rings in the phenol and in its ether, the difference may be ascribed to the fact that the phenol can ketonize and thus facilitate the hydrogenation of the oxygenated ring. The ether of a phenol cannot ketonize, so that, if there is any difference between the phenol and its ether, the ether will show more hydrogenation in the non-oxygenated ring.

A comparison of the amounts of the products shows that in general hydrogenation proceeded further with less hydrogenolysis in the case of the diphenyl than with the naphthalene derivatives. The phenols and their ethers do not readily undergo hydrogenolysis but the benzyl alcohols and ethers are easily cleaved by hydrogen, *i. e.*, $\mathrm{Ph}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{OH} \longrightarrow \mathrm{Ph}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H} + \mathrm{H_2O}$. The hydrogenation of the oxygenated ring in a naphthol-1 gives a substituted benzyl alcohol, which therefore is readily cleaved. Such a compound cannot be formed from a hydroxydiphenyl, for if the oxygenated ring is hydrogenated the alcohol thus produced from 2-hydroxydiphenyl is a phenethyl alcohol. Such an alcohol is much more resistant to cleavage than a benzyl alcohol, since the activating group ($>\mathrm{C}{=}\mathrm{C}<$) is further removed from the carbon to oxygen linkage. The alcohols produced by the hydrogenation of the oxygenated ring of 3- and 4-hydroxy-diphenyl are gamma phenylpropyl or delta butyl alcohols and so are resistant to hydrogenolysis.

The water produced by hydrogenolysis tends to retard nuclear hydrogenation,[24] and hence the occurrence of hydrogenolysis is unfavorable to hydrogenation. This probably accounts in part for the smaller degree of hydrogenation of the naphthalene derivatives. In addition, the benzenoid ring in a tetralin is certainly more resistant to hydrogenation than the phenyl group in a cyclohexylbenzene.

The Hydrogenation of Aryl Ethers.—Van Duzee reported that dodecyl phenyl ether did not undergo hydrogenation over Raney nickel even at 250°, although it was well known that several other alkyl phenyl ethers were readily hydro-

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(21) Von Braun, *Ann.*, **477**, 143 (1930).

(22) Duff and Ingold, *J. Chem. Soc.*, 67 (1934).

(23) Kursanoff, *Ann.*, **318**, 325 (1901).

(24) Zartman and Adkins, THIS JOURNAL, **54**, 1668 (1932).

TABLE III

HYDROGENATION OF ETHERS OF PHENOLS OVER RANEY NICKEL

Figures in parentheses represent recovered ether

Ether	Moles	Hours	Temp., °C.	% yield
Phenyl dodecyl	0.11	4	160	17 Dodecyl alcohol 69 Dodecoxycyclohexane
Phenyl cetyl	.10 (.01)	4	190	21 Cetyl alcohol 62 Cetoxycyclohexane
p-Tolyl methyl	.32 (.08)	12	170	62 1-Methyl-4-methoxycyclohexane
p-Tolyl cetyl	.08 (.02)	5	170	26 Cetyl alcohol 44 1-Cetoxy-4-methylcyclohexane
o-Cyclohexylphenyl cetyl	.06	6	180	15 Dicyclohexyl 10 Cetyl alcohol 57 1-Cetoxy-2-cyclohexylcyclohexane

TABLE IV

PREPARATION AND PROPERTIES OF VARIOUS ETHERS

RONa + R'X = ROR' + NaX, where R'X is dimethyl or diethyl sulfate, or cetyl iodide or dodecyl bromide. Solids were recrystallized from ethanol (*a*), petroleum ether (60 to 70°) (*b*), or a mixture of ethanol and acetone (*c*).

R	R'	% yield	B. p., °C.	Mm.	n^{25}D or m. p.
1-Naphthyl	Methyl[25]	70	101–102	3	1.6940
2-Naphthyl	Methyl[26]	70	145–148	16	71–72° *a*
1-Naphthyl	Ethyl[27]	77	136–138	14	1.5953
2-Naphthyl	Ethyl[28]	84	130–132	5	37–38° *a*
2-Diphenyl	Methyl[29]	89	121–122	2	28–29° *b*
4-Diphenyl	Methyl[30]	32	.....	..	88–89° *a*
2-Diphenyl	Ethyl[29]	87	128–132	6	33–34° *b*
3-Diphenyl	Ethyl[31]	90	157–158	8	34–35° *a*
4-Diphenyl	Ethyl	71	185–188	13	73–74° *a*
4-Tolyl	Methyl[32]	92	55–57	9	1.5060
1-Naphthyl	Dodecyl	60	210–211	3	1.5325
2-Naphthyl	Dodecyl	54	225–228	4	49–50° *a*
4-Diphenyl	Cetyl	62	250–255	2	88–89° *b*
2-Diphenyl	Cetyl	52	257–262	3	41–42° *c*
Phenyl	Dodecyl[16]	73	166–167	3	25–26° *a*
Phenyl	Cetyl[33]	67	.....	..	41–42° *a*
4-Tolyl	Cetyl	37	199–201	2	43–44° *a*
4-Cyclohexylphenyl	Cetyl	67	284–285	7	57–58° *a*
2-Cyclohexylphenyl	Cetyl	58	278–282	8	38–40° *c*
Cyclohexyl	Dodecyl	36	154–155	3	1.4510
Cyclohexyl	Cetyl	44	195–196	3	1.4625
2-Cyclohexylphenyl	Cetyl	58	278–282	8	39–40°
4-Cyclohexylphenyl	Cetyl	67	284–285	9	57–58°
5,6,7,8-Tetrahydro-1-naphthyl	Methyl	61	85–88	3	1.5440
5,6,7,8-Tetrahydro-1-naphthyl	Ethyl	60	107–109	4	1.5361
5,6,7,8-Tetrahydro-1-naphthyl	Dodecyl	30	203–206	3	1.5005
1,2,3,4-Tetrahydro-2-naphthyl	Ethyl	40	110–112	5	1.5200
1,2,3,4-Tetrahydro-2-naphthyl	Dodecyl	34	200–203	3	1.4972
4-Cyclohexylphenyl	Methyl[34]	64	114–116	4	58–59°
4-Cyclohexylphenyl	Ethyl[34]	57	130–131	3	41–42°
2-Cyclohexylphenyl	Ethyl[34]	59	97–99	1	....

genated. It is now known that dodecyl phenyl ether may be hydrogenated at 160° (see Table III) but at the time this investigation was begun it seemed possible that a large alkoxy group on an aromatic nucleus might protect the latter from hydrogenation. Therefore the hydrogenation of several methyl, ethyl, dodecyl and cetyl ethers of phenol, cresol, naphthols, hydroxydiphenyls, and cyclohexylphenols has been investigated. The resulting data are recorded in Tables I, II and III. A survey of these data shows that while in a number of cases a higher temperature was required for the hydrogenation of cetyl and dodecyl ethers as compared with methyl and ethyl, there is no evidence that the larger alkyl groups protected the oxygenated ring against hydrogenation. The higher temperature required in some cases for the hydrogenation of the dodecyl and cetyl ethers is disadvantageous since more hydrogenolysis occurs. There is, therefore, no advantage and in some cases a disadvantage in

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(25) Staedel, *Ann.*, **217**, 42 (1883).

(26) Staedel, *ibid.*, **217**, 43 (1883).

(27) Kamm, THIS JOURNAL, **39**, 1245 (1917).

(28) Orndorff, *Am. Chem. J.*, **13**, 162 (1891).

(29) Hönigschmid, *Monatsh.*, **22**, 570 (1901).

(30) Werner, *Ann.*, **322**, 167 (1902).

(31) Jacobson and Loeb, *Ber.*, **36**, 4083 (1903).

(32) Gerber. *Chem. Zentr.*, II, **80**, 1511 (1909).

(33) Eijkman, *Rec. trav. chim.*, **12**, 1182 (1893).

(34) Bodroux, *Ann. chim.*, **11**, 511–582 (1929).

TABLE V

PHYSICAL CONSTANTS AND ANALYTICAL DATA

Compound	B. p., °C.	Mm.	n^{25}_D	d^{25}_{25}	MR_D		Carbon, %		Hydrogen, %	
					Obsd.	Calcd.	Found	Calcd.	Found	Calcd.
1-Methyl-4-methoxycyclohexane	149–153	741	1.4340	0.8703	38.37	38.59	74.91	74.92	12.57	12.58
Cyclohexyl-dodecyl ether	153–154	3	1.4507	.8561	84.35	84.50	80.37	80.51	13.56	13.52
1-Dodecoxynaphthalene	210–211	3	1.5325	.9546	101.4	101.4	84.47	84.54	10.38	10.33
1-Dodecoxy-5,6,7,8-tetrahydronaphthalene	204–207	3	1.5005	.9341	99.66	99.63	83.49	83.50	11.44	11.39
1-Cetoxy-4-methylcyclohexane	184–186	3	1.4557	.8533	107.7	107.52	81.64	81.57	13.44	13.71
2-Dodecoxy-1,2,3,4-tetrahydronaphthalene	205–207	4	1.4971	.9362	98.84	99.63	83.40	83.50	11.46	11.39
Cetoxycyclohexane	188–190	2	1.4627	.8639	103.3	102.9	81.48	81.48	13.57	13.58
1-Phenyl-2-ethoxycyclohexane	110–113	4	1.5065	.9653	62.90	62.81	82.42	82.30	9.80	9.80
1-Phenyl-2-methoxycyclohexane	105–107	3	1.5082	.9791	57.93	58.20	82.29	82.10	9.34	9.47
1-Cyclohexyl-2-ethoxycyclohexane	109–110	4	1.4775	.9266	64.09	63.99	79.87	80.00	12.15	12.38
1-Cyclohexyl-2-methoxycyclohexane	103–106	4	1.4883	.9456	59.75	59.39	79.74	79.59	12.14	12.24
1-Cyclohexyl-4-ethoxycyclohexane	115–116	4	1.4747	.9248	63.91	63.99	80.05	80.00	12.38	12.38
1-Cyclohexyl-4-methoxycyclohexane	105–108	4	1.4797	.9341	59.59	59.39	79.58	79.59	12.33	12.24
2-Ethyl-1,2,3,4-tetrahydronaphthol-1	120–121	2	1.5495	1.0440	53.69	53.47	81.82	81.82	9.31	9.09
3-Ethoxy-1-phenylcyclohexane	100–101	1	1.5103	0.9698	62.94	62.80	82.14	82.30	9.80	9.88
3-Methoxy-1-cyclohexylbenzene	105–106	1	1.5175	.9785	63.10	62.80	82.19	82.30	9.84	9.88
2-Phenyl-4-ethylcyclohexanol-1	134–136	3	1.5294	1.0050	62.03	62.67	82.37	82.35	10.03	9.80
2-Cetoxydiphenyl	258–261	3		m. p. 41–42°			85.20	85.28	10.77	10.75
4-Cetoxydiphenyl	253–255	3		m. p. 88–89°			85.31	85.28	10.70	10.75
4-Ethoxydiphenyl	185–188	14		m. p. 73–74°			84.74	84.80	7.16	7.12
2-Dodecoxynaphthalene	225–228	4		m. p. 48–49°			84.49	84.54	10.27	10.33
4-Cetoxytoluene	199–201	2		m. p. 43–44°			83.16	83.05	12.16	12.14
4-Cetoxy-1-cyclohexylbenzene	240–243	2		m. p. 57–58°			83.87	83.94	12.08	12.04
1,2,3,4-Tetrahydro-1-ethylnaphthol-2	128–129	2		m. p. 88–89°			81.82	81.82	9.07	9.09
2-Cetoxy-1-phenylcyclohexane	225–227	2		m. p. 29–30°			83.83	83.94	12.04	12.04

hydrogenating the ethers of higher molecular weight.

Experimental Part

The hydrogenations reported in the tables were carried out in general at 100–200 atm. in the apparatus and with the catalysts which have been used for some time in this Laboratory.[35] The quantities of material used in each hydrogenation (Tables I and II) were in most cases 0.25 to 0.30 of a mole. In a few experiments a somewhat larger or lesser amount was used. The figures in Tables I and II indicating the duration of reaction are in some cases enclosed in parentheses to indicate that the reaction was stopped while hydrogen was still being absorbed. Approximately 5 g. of copper–chromium oxide or 4 g. of Raney nickel per 0.25 mole of hydrogen acceptor was used in all hydrogenations. Approximately 60 ml. of dioxane or dry ethanol was used as a reaction medium in each hydrogenation.

The phenols were obtained from commercial sources and were purified in the usual way. In addition they were distilled from Raney nickel. Dodecyl and cetyl alcohols were obtained by the hydrogenation of pure ethyl laurate or palmitate over copper–chromium oxide.[35] Dodecyl bromide, b. p. 134–135° (6 mm.), d^{25}_D 1.4550, and cetyl iodide, b. p. 173–175° (3 mm.), were made as described in "Organic Syntheses."[36] The ethers were prepared by the Williamson reaction, starting with 0.1 to 0.5 mole of sodium in each preparation. The yields and properties of the products are given in Table IV.

The 1-ethylnaphthol-2 and 2-ethylnaphthol-1 were prepared in yields of approximately 90% by the hydrogenation of the corresponding acetylnaphthols. In a typical hydrogenation 50 g. of 2-acetylnaphthol-1 in 75 ml. of ethanol, with 5 g. of copper–chromium oxide at 140°, under a pressure of 150 atm. of hydrogen, was hydrogenated within one hour. This process gives a much higher yield of purer product than does the reduction of the ketone with zinc and an acid.

1-Acetylnaphthol-2, b. p. 130–132° (2 mm.), m. p. 63–64° (from petroleum ether), was obtained (62 g.) by the reaction of 120 g. of 2-naphthyl acetate (b. p. 132–134° at 2 mm., m. p. 68–69°) in 200 ml. of carbon bisulfide and 120 g. of anhydrous aluminum chloride.[37,38] In a similar way 2-acetylnaphthol-1, b. p. 110–115° (0.5 mm.), m. p. 96–97°, was obtained (146 g.) from 1-naphthyl acetate, b. p. 114–116° (1 mm.), m. p. 43–44°, (242 g.) and 250 g. of anhydrous aluminum chloride without, however, the use of carbon bisulfide as a solvent.

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(35) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, 1937.

(36) "Organic Syntheses," **1**, 17 (1921); **15**, 29 (1935).

(37) Fries, *Ber.*, **54**, 711 (1921).

(38) Stoughton, THIS JOURNAL, **57**, 202 (1935).

The products of reaction were in general separated by fractional distillation through Widmer or modified Widmer columns carrying spirals 15 cm. in length.[39] Solid products were recrystallized. The products were characterized by analysis and by comparison of their physical constants with those reported in the literature or found for substances prepared by other methods. A considerable number of ethers were prepared by the Williamson synthesis in order that their properties might be compared with those of products of hydrogenation (Table IV).

The structure of a number of compounds was ascertained by oxidizing them to a benzoic or a substituted benzoic acid. For this purpose 1 to 2 g. of the compound was oxidized with potassium permanganate in the usual manner. Benzoic acid, m. p. 120–121°, was obtained from 1-phenyl-2-methoxycyclohexane, 1-phenyl-2-ethoxycyclohexane, 1-phenyl-3-ethoxycyclohexane, cetyl ether of 1-phenyl-2-hydroxycyclohexane and 1-phenyl-2-hydroxy-5-ethylcyclohexane. Phthalic anhydride, m. p. 129–131°, was obtained from 2-ethyl-1,2,3,4-tetrahydro-1-naphthol and 1-ethyl-1,2,3,4-tetrahydro-2-naphthol. *m*-Ethoxybenzoic acid,[40] m. p. 136–137°, was obtained from 1-cyclohexyl-3-methoxybenzene, *p*-ethoxybenzoic acid,[41] m. p. 195–196°, from *p*-cyclohexylphenetole, *o*-ethoxybenzoic acid,[41] m. p. 19–20°, from 1-cyclohexyl-2-ethoxybenzene and *o*-methoxybenzoic acid,[42] m. p. 98–100°, from 1-cyclohexyl-2-methoxybenzene.

Summary

The monohydroxynaphthalenes and diphenyls and their ethers have been submitted to partial hydrogenation over Raney nickel and copper–chromium oxide. Over Raney nickel hydrogenation takes place exclusively in the oxygenated ring of naphthol-2 and of 2- and 3-hydroxydiphenyl, while naphthol-1 and 4-hydroxydiphenyl accept hydrogen in both rings, but predominantly in the non-oxygenated ring. The ethers of naphthol-1, and of 3- and 4-hydroxydiphenyl over Raney nickel show a greater tendency to react in the non-oxygenated ring than do the phenols.

The phenols showed a much greater tendency to hydrogenate in the oxygenated ring over copper–chromium oxide. This fact coupled with the inactivity of the ethers toward hydrogen over copper–chromium oxide leads to the conclusion that with this catalyst the hydrogenation of the phenol in the oxygenated ring involves the tautomeric ketone.

While no effort has been made to prepare in high yields the completely hydrogenated alcohols and ethers corresponding to the five phenols referred to above, there is no doubt that they may be made in excellent yields by catalytic hydrogenation over Raney nickel, with the possible exception of those from naphthol-1 for which a yield of 34% is reported.

Tetralin has been made for the first time over copper–chromium oxide. This catalyst has the advantage in this case over Raney nickel that further hydrogenation does not occur at 200°. Tetralin may be made with Raney nickel at 100° or lower.

It has been shown that there is no great difference between the ease of hydrogenation of methyl, ethyl, dodecyl and cetyl aryl ethers.

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(29) Martha E. Smith and Adkins, THIS JOURNAL, **60**, 657 (1938).

(40) Fritsch, *Ann.*, **329**, 71 (1903).

(41) Cohen and Dudley, *J. Chem. Soc.*, **97**, 1737 (1910).

(42) Graebe, *Ann.*, **340**, 210 (1905).

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydrogenation of Pyrones[1]

BY RALPH MOZINGO AND HOMER ADKINS

The chromones, flavonols and anthocyanidins offer an attractive field for studies in selective hydrogenation which may be of some value to synthetic organic chemistry. To that end the reaction of hydrogen with various pyrones has been investigated.

It has been observed many times in this Laboratory that rapid hydrogenations give better yields of the chief product and fewer products due to side or subsequent reactions. This matter becomes of decisive importance in the hydrogenation of compounds containing several functional groups. Impurities, inadequate amounts of catalyst, inactive catalysts, too low temperatures or pressures, or a poor choice of solvent may serve to prolong the period of reaction to such an extent that a hopeless mixture of products is obtained. On the other hand, too high a temperature may induce reactions which could otherwise be avoided. Most of the hydrogenations described in this paper were carried out at the lowest temperature at which a rapid hydrogena-

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