spectrum of *allo*-ocimene. These authors did not distinguish between the two forms of *allo*-ocimene but consideration of the Raman data and physical characteristics cited by them would indicate the presence of relatively large concentrations of both the A and B components.

It is also apparent that there is a tendency for many of the lines in the "A" isomer to shift to higher frequencies in the "B" isomer, namely, 151 → 196; 227 → 258; 277 → 296; 335 → 361; 961 → 964; 1082 → 1091; 1231 → 1236; 1347 → 1365; 1627 → 1631; 2911 → 2914. The opposite tendency is shown by the lines 446 → 440; 800 → 790 and 1597 → 1590.

For identification of the "A" isomer in a mixture, one could conveniently use the rather strong, well-defined 1365 line, while the "B" form could be most easily detected by its unique and rather strong line at 1272 cm.$^{-1}$, or alternatively by its lines at 1347 and 1648 cm.$^{-1}$.

Acknowledgment.—The continued interest and advice of the late Dr. S. Palkin, Chief of the Naval Stores Research Division, who originally proposed the project, is gratefully acknowledged.

Summary

Two forms of *allo*-ocimene, designated as A- and B- have been isolated.

Both forms yield with maleic anhydride the same adduct but they exhibit differences in boiling point, freezing point, density and Raman spectra.

Both forms give strong Raman spectra in an exceptionally short exposure time. Each may be detected in a mixture by the characteristic Raman lines at 1365 cm.$^{-1}$ (A-form) and 1272 cm.$^{-1}$ (B-form).

The Raman spectra tend to support the interpretation that these forms are two of the four possible geometric stereoisomers of *allo*-ocimene.

NEW ORLEANS, LA. RECEIVED JULY 30, 1943

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MISSOURI]

The Preparation of Cyclohexanols by Catalytic Reduction of Phenols

BY HERBERT E. UNGNADE AND A. DOUGLAS MCLAREN[1,2]

In connection with another problem it became necessary to prepare alkylcyclohexanols in moderately large quantities. This has been accomplished by the catalytic reduction of alkyl-, alkenyl- and acylphenols with Raney nickel.

Since alkylphenols could be hydrogenated readily to the corresponding cyclohexanols, the chief limitation was the availability of the phenols. The ease of reduction was not greatly affected by substituents in the ring unless two ethyl or *n*-propyl groups occupied the ortho positions (Table I). In the latter cases no cyclohexanols were formed at temperatures above 300°. 2,6-Di-*n*-propylphenol was recovered unchanged but 2,6-diethyl-4-methylphenol underwent hydrogenolysis and reduction of the ring to give 1-methyl-3,5-diethylcyclohexane. The corresponding cyclohexanols could be obtained from the two phenols when the hydrogenation was carried out in the presence of a small amount of a 40% aqueous solution of sodium hydroxide. When the other phenols were reduced in the presence of alkali a slight promoting effect was evidenced in some cases by lower initial reduction temperatures. The promoting effect was lost when the phenolic hydroxyl was methylated (Table II). The formed cyclohexanols consisted predominantly of one of the possible geometric isomers. The same isomer was usually obtained regardless of whether the hydrogenation was carried out in the presence of base or not. An exception was 2-*t*-butyl-4-methylphenol. Higher temperatures were required for reduction in the presence of base, and the product was a mixture of *cis*, *trans* isomers differing only in the position of the hydroxyl group since they could be oxidized to the same cyclohexanone.[3] Only one of the isomers was obtained in the absence of base. The effect of the base in this case may be similar to the inversion observed by Vavon, *et al.*, when the sodium salts of alkylcyclohexanols were heated.[4]

It is interesting to note in this connection that the 2,6-di-*n*-propylcyclohexanol obtained by reduction in presence of alkali was the $1^t,2^c,6^c$-isomer which was prepared by Vavon and Anziani by rearrangement of the $1^c,2^c,6^c$-isomer by heating of the sodium salt.[5]

The effect of alkali was striking in the reduction of *p*-phenylphenol (Table III). The time required for absorption of the same amount of hydrogen in the presence of alkali was one half of that required for the same amount of substance in the absence of alkali. Moreover the ratio of the products was not the same. The percentage of *p*-cyclohexylphenol and *p*-cyclohexylcyclohexanol was smaller and the amount of *p*-phenylcyclohexanol larger when alkali was used as a promoter. It is therefore possible by means of

(1) An abstract of a dissertation submitted by A. Douglas McLaren in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1943.

(2) Presented before the Division of Organic Chemistry at the 105th meeting of the American Chemical Society, Detroit, Michigan, April 13, 1943.

(3) Unpublished data by the authors.

(4) Vavon, *et al.*, *Bull. soc. chim.*, (4) **39**, 1142 (1926); (4) **41**, 357 (1927); (4) **45**, 961 (1929).

(5) Vavon and Anziani, *ibid.*, (5) **4**, 1080 (1937).

TABLE I

HYDROGENATION OF ALKYLPHENOLS[a]

Phenol	Moles	T_1,[i] °C.	T_2,[j] °C.	Time, hr.	Yield, %	Cyclohexanol[b]
4-Methyl	1.9	95	130	4	92	*trans*-4-Methyl
	0.88[c,d]	80	115	11	90	*trans*-4-Methyl
3-Ethyl	.66	90	145	7	94	3-Ethyl
4-Ethyl	.19	90	160	4.5	88	4-Ethyl
2-*n*-Propyl	.66	105	150	8	94	*cis*-2-*n*-Propyl
2,4-Dimethyl	.71	135	170	12	91	(1^t)2^c,4^t-Dimethyl
2,5-Dimethyl	.63	125	170	8	94	(1^t)2^c,5^t-Dimethyl
3,4-Dimethyl	.81	125	140	6	98	3,4-Dimethyl
	.41[c,e]	105	135	4	90	3,4-Dimethyl
3,5-Dimethyl	.84	90	125	6	91	(1^t)3^c,5^c-Dimethyl
2,6-Di-*n*-propyl	.1	...	360	1	0	
	.1[c,f]	260	280	3.5	90	(1^t)2^c,6^c-Di-*n*-propyl
4-Methyl-2-*t*-butyl	.36	160	190	7	91	4-Methyl-2-*t*-butyl (liq.)
	.17[c,g]	195	220	5.5	64	4-Methyl-2-*t*-butyl (liq.)
					27	4-Methyl-2-*t*-butyl (sol.)
2,3,5-Trimethyl	.74	95	155	13	90	2,3,5-Trimethyl
2,4,6-Trimethyl	.18	145	200	4.3	30	2,4,6-Trimethyl (solid)[k]
					60	2,4,6-Trimethyl (liquid)
4-Methyl-2,6-diethyl	.08	...	340	1		1-Methyl-3,5-diethylcyclohexane
	.08[c,h]	205	235	1.5	14	4-Methyl-2,6-diethyl (sol.)[k]
					76	4-Methyl-2,6-diethyl (liq.)

[a] All hydrogenations were carried out with 3 g. of Raney nickel. [b] The *cis–trans* isomers were assigned on the basis of properties and derivatives wherever these were described in the literature. [c] Hydrogenation in the presence of the following amounts of 40% aqueous alkali: [d] 1.6 cc., [e] 1.5 cc., [f] 1.0 cc., [g] 1.3 cc., [h] 1.2 cc. [i] T_1, temperature of initial hydrogen uptake. [j] T_2, temperature maintained during the hydrogenation. [k] The solid isomer was separated by freezing out. The separation is not considered to be quantitative. The two isomers give the same cyclohexanone on oxidation and therefore differ only in the configuration around Carbon 1.

TABLE II

HYDROGENATION OF 4-METHYLANISOLE

Moles	T_1,[b] °C.	T_2,[c] °C.	Time, hr.	Yield, %	Product
0.29	155	180	3.7	98	1-Methyl-4-methoxycylohexane
.26[a]	185	220	6.7	85	

[a] Hydrogenation in the presence of 1.6 cc. of 40% aqueous alkali. [b] T_1, temperature of initial hydrogen uptake. [c] T_2, temperature maintained during the hydrogenation.

alkali to promote the reduction of a phenolic ring in the presence of another aromatic nucleus or presumably in the presence of other functions whose reduction is not activated by alkali.

TABLE III

HYDROGENATION OF 4-PHENYLPHENOL

Moles	T_1,[b] °C.	T_2,[c] °C.	Time, hr.	Yield, %	Product
0.295	110	125	6	25.7	4-Cyclohexylphenol
				7.4	4-Phenylcyclohexanol
				59.2	4-Cyclohexylcyclohexanol
.295[a]	95	115	3	16.6	4-Cyclohexylphenol
				30.3	4-Phenylcyclohexanol
				43.2	4-Cyclohexylcyclohexanol

[a] Hydrogenation in the presence of 2 cc. of 40% aqueous alkali. [b] T_1, temperature of initial hydrogen uptake. [c] T_2, temperature maintained during the hydrogenation.

Allyl or propenylphenols which are readily available through the Claisen allyl ether rearrangement have been converted in good yields to alkylcyclohexanols. The reduction was found to take place in two steps. Isolation of the alkylphenol was not necessary. The addition of alkali shortened the time required for the saturation of the side-chain, lowered the initial temperature for the reduction of the ring and reduced the time required for the saturation of the ring. The experimental data are summarized in Table IV.

TABLE IV

HYDROGENATION OF ALKENYLPHENOLS

Phenol	Moles	T_1,[c] °C.	T_2,[d] °C.	Time, hr.	Yield, %	Product
2-Allyl	0.77	30	50	0.4	95	2-*n*-Propylphenol
2-Allyl	.37	30	50	0.4		
		100	140	11.0	91	*cis*-2-*n*-Propylcyclohexanol[a]
2-Allyl	.37[b]	30	50	0.3		
		85	130	5.6	90	*cis*-2-*n*-Propylcyclohexanol[a]
2-Propenyl	.53	30	50	6.5		
		105	160	2.5	95	*cis*-2-*n*-Propylcyclohexanol[a]
2,6-Diallyl	.39	30	50	2.75	99	2,6-Di-*n*-propylphenol

[a] The hydrogenation was continued until no more hydrogen was absorbed, then the temperature was raised to the next reduction stage. [b] Hydrogenation in the presence of 1.5 cc. of 40% aqueous alkali. [c] T_1, temperature of initial hydrogen uptake. [d] T_2, temperature maintained during the hydrogenation.

It was shown some years ago[6] that *p*-propionylphenol can be converted to 4-propylcyclohexanol

(6) Harris, D'Ianni and Adkins, THIS JOURNAL, 60, 1467 (1938).

TABLE V

HYDROGENATION OF ACYLPHENOLS[a]

Phenol	Moles	T_1,[c] °C.	T_2,[d] °C.	Time, hr.	Yield, %	Products
2-Acetyl	0.37	70	180	5.8	87	*cis*-2-Ethylcyclohexanol
4-Acetyl	.018	65	90	5.0	86	4-Ethylphenol
4-Acetyl	.34[e]	45	50	11.0	31	4-Ethylphenol
					48	4-(1-Hydroxyethyl)-cyclohexanol[b]
4-Acetyl	.23[e]	65	160	3.0	67	4-Ethylcyclohexanol
					21	4-(1-Hydroxyethyl)-cyclohexanol
2-Acetyl-4-methyl	.73	85	115	12.0	87	2-Ethyl-4-methylphenol
2-Acetyl-4-methyl-6-ethyl	.21	85	135	9.5	83	2,6-Diethyl-4-methylphenol
2-Propionyl	.39	105	180	6.5	81	*cis*-2-*n*-Propylcyclohexanol
2-Propionyl	.33	60	110	3.0	83	2-*n*-Propylphenol
2-Propionyl	.34[e]	55	65	10.3	34	2-*n*-Propylphenol
					46	2-(1-Hydroxypropyl)-cyclohexanol
2-Propionyl	.31[e]	60	140	2.25	72	*cis*-2-*n*-Propylcyclohexanol
					23	2-(1-Hydroxypropyl)-cyclohexanol
2-Propionyl	.32[e]	55	220	5.2	67	*cis*-2-*n*-Propylcyclohexanol
					23	2-(1-Hydroxypropyl)-cyclohexanol

[a] All hydrogenations with 3 g. of Raney nickel and 100 cc. of ethanol. [b] The authors are indebted to Dr. Austin Patterson for his advice in naming these compounds. [c] T_1, temperature of first hydrogen uptake. [d] T_2, temperature maintained during the hydrogenation. [e] Hydrogenation in the presence of 2 cc. of 40% aqueous alkali.

by reduction with Raney nickel at 200°. More recently Smith and Rouault[7] were able to hydrogenate 2-(2′,6′-dimethylheptanoyl)-4-methylphenol and 2-lauroyl-4-methylphenol in practically quantitative yields by a two stage reduction. In our hands both ortho and para acylphenols gave excellent yields of alkylphenols at about 110° when the hydrogenation was carried out in alcoholic solution. When the temperature was raised to 180° the ring could be saturated without previous isolation of the alkylphenol. Attempts to stop the hydrogenation at the first reduction stage, the (1-hydroxylalkyl)-phenols, were unsuccessful. The products were mixtures of alkyl and acylphenols. In the presence of alkali ortho and para acylphenols absorbed hydrogen rapidly between 45 and 65°. The products consisted of mixtures of alkylphenols and hydroxyalkylcyclohexanols. The second reduction stage (110°) gave a mixture of alkylcyclohexanols and hydroxyalkylcyclohexanols. Further increase in temperature up to 220° did not change the products or their ratio (Table V).

The experimental data allow the conclusion that the hydrogenation of the phenolic ring as well as that of the carbonyl group is activated by alkali. The latter case has been studied previously by Delépine and Horeau.[8]

The results cannot be entirely accounted for unless it is assumed that the hydrogenation of one function is affected by the presence of the other. Thus, the hydrogenation of the phenolic ring during the first reduction stage takes place at temperatures appreciably below those required for alkylphenols even in the presence of base. This effect is ascribed to the acyl group.

During the second stage the hydroxylalkylcyclohexanols are partially converted to alkylcyclohexanols by hydrogenolysis of the side-chain hydroxyl group. Simultaneously the alkylphenols formed in the first stage undergo complete saturation. Since heating to higher temperatures does not bring about further hydrogenolysis (after all phenolic rings have been reduced), it is proposed that this reaction is catalyzed by the sodium phenolate still present during the second stage. The resistance of the dihydric alcohol to further hydrogenation is not surprising since the side-chain hydroxyl group is no longer on a carbon directly connected to an aromatic nucleus[9] and is, therefore, not expected to undergo hydrogenolysis below 200°.[10] Further aspects of these reactions are now under investigation.

Acknowledgment.—The authors wish to express their thanks to the University Research Council for funds to purchase apparatus and chemicals necessary for this investigation.

Experimental[10a]

The hydrogenations reported in the tables were carried out in general at 100–300 atm. with Raney nickel in a steel chamber equipped with a copper liner having a total capacity of 500 cc.[11] The temperature of initial hydrogen absorption was determined by plotting temperature against pressure. The data chosen for the tables were for catalysts with as near the same age as possible since Raney nickel was found to lose some of its activity upon aging, as evidenced by higher initial hydrogenation temperatures required with some older catalysts for the same sample of starting-material.

Hydrogenation of Alkyl and Alkenylphenols.—Most of the phenols were obtained from commercial sources and were purified in addition to the usual methods by distillation from Raney nickel. *o*-*n*-Propylphenol and 2,6-di-*n*-

(7) Smith and Rouault, THIS JOURNAL, **65**, 745 (1943).

(8) Delépine and Horeau, *Bull. soc. chim.*, (5) **4**, 31 (1937).

(9) Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, New York, N. Y., 1943, Vol. I, p. 805.

(10) Schröter, *Angew. Chem.*, **54**, 252 (1941).

(10a) All melting points are uncorrected.

(11) American Instrument Company, Silver Springs, Maryland.

TABLE VI

Cyclohexanol	B. p., °C.	M. p., °C.	Phenyl urethan, m. p., °C.	α-Naphthyl urethan, m. p., °C.	Nitrogen, % Found	Nitrogen, % Calcd.
trans-4-Methyl[a]	167–170		124–124.5	156.5–157.5	4.81	4.95
cis-2-Ethyl[14]	180–182		99–99.8	151–153.5	4.92	4.72
3-Ethyl[b]	191.5–192			98.5–99.5	4.70	4.72
4-Ethyl[15]	191–192		114–115	139.5–140.5	4.92	4.72
cis-2-*n*-Propyl[16]	201.5–202		94–95	103–104	4.39	4.5
(1[t])2[c],4[t]-Dimethyl[c]	176.5–177.5		95–96	152.5–153.5	4.72	4.72
(1[t])2[c],5[t]-Dimethyl[18]	179–180.5		116–117	172–173.5	4.64	4.72
3,4-Dimethyl	188–189.5		96–97[d,19]	162–163	4.90	4.72
(1[t])3[c],5[c]-Dimethyl[20]	181–183	8–9.8	106–107.5	141–143	4.67	4.72
2-*t*-Butyl-4-methyl[e]	215–216			130–131[g]	4.06	4.15
2-*t*-Butyl-4-methyl[f]		112–113		130.5–131.5[g]	4.07	4.15
(1[t])2[c],6[c]-Di-*n*-propyl[5]	241–242	109–110	145.5–146.5	137–138	4.01	3.97
2,3,5-Trimethyl[h]	196–197			148–149[i]	4.3	4.5
2,4,6-Trimethyl[j]	182–184	70.5–71		197.5–198	4.35	4.5
2,6-Diethyl-4-methyl[k]	219–220	86–87		143.5–144	3.91	4.15

[a] 3,5-Dinitrobenzoate, m. p. 137.2–138.7°.[13] [b] $n^{25}D$ 1.4600, d^{25} 0.9094, M_D (calcd.) 38.47, M_D (found) 38.56. *Anal.* Calcd. for $C_{18}H_{16}O$: C, 75.00; H, 12.50. Found: C, 74.69; H, 12.52. [c] The exact configuration of this compound is uncertain since the literature data are conflicting.[17] [d] *Anal.* Calcd. for $C_{15}H_{21}NO_2$: N, 5.68. Found: N, 5.74. [e] *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.65; H, 13.06. Found: C, 77.79; H, 13.00. $n^{25}D$ 1.4661; d^{25}_4 0.9002; M_D(calcd.) 52.32; M_D(found) 52.30. [f] *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.65; H, 13.06. Found: C, 77.35; H, 12.94. [g] Mixed melting point 111–113.5°. [h] *Anal.* Calcd. for $C_9H_{18}O$: C, 76.06; H, 12.7. Found: C, 75.7; H, 12.9. $n^{25}D$ 1.4572; d^{25} 0.9002; M_D(calcd.) 43.09; M_D(found) 42.97. [i] *Anal.* Calcd. for $C_{20}H_{25}ON_2$: C, 77.1; H, 8.03. Found: C, 76.8; H, 7.54. [j] *Anal.* Calcd. for $C_9H_{18}O$: C, 76.05; H, 12.65. Found: C, 75.73; H, 12.99. [k] *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.65; H, 12.94. Found: C, 77.54; H, 12.78.

TABLE VII

ALKYLPHENOLS OBTAINED BY HYDROGENATION OF ALKENYL AND ACYLPHENOLS

Phenol	B. p., °C.	Mm.	Derivative	M. p., °C.
4-Ethyl	213–216	739	Aryloxyacetic acid	94–94.5[24]
2-*n*-Propyl	214–216	740	Phenylurethan	109–110[25]
2,6-Di-*n*-propyl	247.5–249	740	Phenlyurethan	126.5–127[26]
2-Ethyl-4-methyl	131–133	135	Aryloxyacetic acid	130.5–131.5[27]
2,6-Diethyl-4-methyl	133–134	23	Benzoate	100.5–101.5[28]

propylphenol were obtained by hydrogenation of the corresponding allyl compounds, and 2-*t*-butyl-4-methylphenol by alkylation of *p*-cresol with *t*-butyl alcohol.[12] Mesitol was prepared by hydrolysis of bromomesitylene, 4-ethyl- and 2,6-diethyl-4-methylphenol by hydrogenation of the corresponding acylphenols.

All phenols were hydrogenated in the absence of solvents. The pertinent data for the cyclohexanols are given in Table VI.

1-Methyl-3,5-diethylcyclohexane.—B. p. 175–176.5°, $n^{25}D$ 1.4345, d^{25}_4 0.7841; M_D (calcd.) 50.80; M_D (found) 51.21. *Anal.* Calcd. for $C_{11}H_{22}$: C, 85.71; H, 14.28. Found: C, 85.55; H, 14.49.

1-Methyl-4-methoxycyclohexane.—B. p. 146–148.5°, $n^{20}D$ 1.4333.[21]

Hydrogenation of *p*-Phenylphenol.—A solution of 50 g. of *p*-phenylphenol (Eastman Kodak Co.) in 50 cc. of ethanol was hydrogenated in the presence of 3 g. of Raney nickel until a total of 1200 lb. of hydrogen had been absorbed at 115°. A subsequent run with addition of 2 cc. of 40% aqueous alkali was made under identical conditions. After removal of the solvent the mixture of products was taken up in benzene and petroleum ether and extracted with 10% aqueous alkali. Acidification of the alkaline extract gave *p*-cyclohexylphenol which melted at 129.2–130.5° after crystallization from benzene–petroleum ether.[22] Fractional crystallization of the remaining benzene–petroleum ether solution gave *p*-phenylcyclohexanol. m. p. 116–117°, and *p*-cyclohexyl-cyclohexanol, m. p. 98–99°.[22] *p*-Phenylcyclohexanol was converted to the corresponding ketone, m. p. 77–78°, by oxidation with sodium dichromate and sulfuric acid.[23]

Hydrogenation of Acylphenols.—The acylphenols used in this investigation were prepared by the Fries rearrangement of the phenol esters. No special purification was necessary even though carbon disulfide was used in the procedure. The hydrogenations were carried out in 100 cc. of ethanol with 3 g. of Raney nickel catalyst. The products were separated by fractional distillation under reduced pressure. The constants of the phenols are listed in Table VII.

4-(1-Hydroxyethyl)-cyclohexanol.—B. p. 129–133° (2 mm.), m. p. 91–92.2°. *Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.66; H, 11.01. Found: C, 66.32; H, 10.87. 3,5-

(12) Chichibabin, *Compt. rend.*, **198**, 1239 (1934).
(13) Skita and Faust, *Ber.*, **64**, 2878 (1931).
(14) Vavon and Mitchovitch, *Bull. soc. chim.*, (4) **45**, 961 (1939).
(15) v. Braun, Mannes and Reuter, *Ber.*, **66**, 1499 (1933).
(16) Vavon and Anziani, *Bull. soc. chim.*, (4) **41**, 1638 (1927).
(17) Skita, *Ann.*, **427**, 275 (1922); Godchot and Bedos, *Compt. rend.*, **180**, 751 (1925).
(18) Skita, *Ber.*, **56B**, 2234 (1923).
(19) Sabatier and Mailhe, *Ann. chim.*, (8) **10**, 527 (1907).
(20) Skita and Faust, *Ber.*, **72B**, 1127 (1939); v. Braun and Anton, *ibid.*, **60B**, 2442 (1927).
(21) Cornubert and Le Bihan, *Bull. soc. chim.*, **43**, 74 (1928); Musser and Adkins, THIS JOURNAL, **60**, 664 (1938).
(22) Musser and Adkins, THIS JOURNAL, **60**, 666 (1938).
(23) Braun and Weissbach, *Ber.*, **64B**, 1785 (1931).
(24) Kruber and Schmitt, *Ber.*, **64**, 2272 (1931).
(25) Claisen, *Ann.*, **418**, 89 (1919).
(26) Claisen, *ibid.*, **418**, 93 (1919).
(27) Niederl, *et al.*, THIS JOURNAL, **59**, 1113 (1937).
(28) v. Auwers and W. Mauss, *Ann.*, **460**, 240 (1928).

Dinitrobenzoate, m. p. 210–212°. *Anal.* Calcd. for $C_{22}H_{20}N_4O_{12}$: C, 49.62; H, 3.95. Found: C, 49.94; H, 4.11.

2-(1-Hydroxypropyl)-cyclohexanol.—B. p. 256–259°, $n^{25}D$ 1.4788, d^{25}_4 1.0060; M_D (calcd.) 44.61; M_D (found) 44.65. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.35; H, 11.39. Found: C, 67.96; H, 11.42. 3,5-Dinitrobenzoate, m. p. 162.5–164°. *Anal.* Calcd. for $C_{23}H_{22}O_{12}N_4$: C, 50.54; H, 4.04. Found: C, 50.71; H, 4.48.

Summary

1. Alkylcyclohexanols are readily obtained by the hydrogenation of alkyl-, alkenyl- and acylphenols in the presence of Raney nickel.

2. The hydrogenation of di-ortho substituted phenols is promoted by small amounts of alkali.

3. The hydrogenation of alkenyl and acylphenols may be conducted at low temperatures to give good yields of alkylphenols.

4. The hydrogenation of acylphenols gives alkylphenols or alkylcyclohexanols depending upon the temperature. In the presence of alkali a mixture of alkylphenol and hydroxyalkylcyclohexanol is obtained at low temperatures and a mixture of alkylcyclohexanol and hydroxylalkylcyclohexanol at high temperatures.

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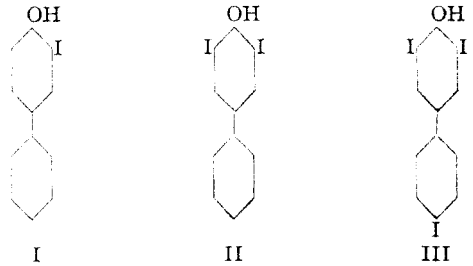
[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF TEXAS AND THE UNIVERSITY OF OKLAHOMA]

The Iodination of 4-Hydroxybiphenyl[1a]

BY J. C. COLBERT,[1b] H. W. HOUGHTON,[1b] H. R. SCHMIDT[2] AND J. L. ABERNETHY[2]

Although the chlorination[3] and bromination[4,5] of 4-hydroxybiphenyl have been investigated, the only iodine derivative of this phenol mentioned in the literature appears to be 4′-iodo-4-hydroxybiphenyl[6] obtained by use of the Sandmeyer reaction.

On the basis of the results of chlorination and bromination, it was anticipated that iodination of 4-hydroxybiphenyl would cause the first iodine atom to enter the 3-position, thereby yielding 3-iodo-4-hydroxybiphenyl (I); the second atom would enter the 5-position, with the resultant formation of 3,5-diiodo-4-hydroxybiphenyl (II); and, finally, the third atom would enter the 4′-position, giving rise to 3,5,4′-triiodo-4-hydroxybiphenyl (III).



I II III

Introduction of a solution of iodine dissolved in potassium iodide into a solution of 4-hydroxybiphenyl in sodium hydroxide[7] gave rise to I. However, when an attempt was made to diiodinate 4-hydroxybiphenyl using the same procedure, II could not be isolated from the reaction products. Instead, a compound which gave an analysis very close to a monoiodinated derivative was obtained. This substance decomposed at temperatures above 170°. Since it is known that on heating diiodinated phenols[8] with sodium hydroxide, two molecules undergo condensation with loss of hydrogen, *i. e.*, aristol formation takes place, it seemed plausible that a similar reaction had taken place during the attempted diiodination of 4-hydroxybiphenyl. Consequently a Rast molecular weight of this product was determined. This indicated that the molecular weight was approximately double that of a monoiodo-4-hydroxybiphenyl and suggested that aristol formation had taken place. No further attempt was made to prove its structure.

Iodination of 4-hydroxybiphenyl in an ammonium hydroxide solution gave rise to I. Further iodination introduced iodine in the 5-position, hence yielding II. This procedure is known to be more satisfactory than the procedure in which sodium hydroxide is used, in that in most instances very little aristol formation takes place with iodinated phenols.

Iodination with iodine monochloride gave rise to I, and further iodination gave rise to II. Attempts to triiodinate 4-hydroxybiphenyl were unsuccessful.

The benzoates of I and II were prepared by benzoylation of these substances with benzoyl chloride in pyridine. It was found that benzoylation of I took place readily, whereas benzoylation of II was somewhat more difficult. This latter

(1a) In 1938 at the University of Oklahoma an attempt was made to apply the detailed method of iodination of a phenol used by Harington in the synthesis of thyroxin to the iodination of 4-hydroxybiphenyl. This method made use of a solution of iodine in potassium iodide which was added to the ammoniacal solution of the phenol. In work initiated independently at the University of Texas in 1942 an attempt was made to iodinate this substance in a sodium hydroxide solution. This was abandoned, however, in favor of iodination with iodine monochloride. Shortly after this latter work was under way it was learned through correspondence that the iodination had been accomplished at the University of Oklahoma. The present paper presents the results of the investigations conducted independently at both institutions.

(1b) University of Oklahoma, Norman, Oklahoma.

(2) University of Texas, Austin, Texas.

(3) Colbert, Meigs and Mackin, THIS JOURNAL, **56**, 202 (1934).

(4) Raiford and Colbert, *ibid.*, **47**, 1456 (1925).

(5) Bell and Robinson, *J. Chem. Soc.*, 1128 (1927).

(6) Angelletti and Gatti, *Gazz. chim. ital.*, **58**, 630–635 (1929).

(7) Harington and Barger, *Biochem.*, **21**, 169 (1927); **22**, 1429 (1928).

(8) Bordeianu, *Chem. Abs.*, **30**, 1760 (1936).