

THE HYDROGENATION OF AROMATIC KETONES WITH HYDROGEN AND COPPER-CHROMIUM OXIDE CATALYST

DOROTHY NIGHTINGALE AND HERSCHEL D. RADFORD^{1, 2}

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A number of aromatic ketones have been reduced to the corresponding carbinols and alkylbenzenes in good yields by means of hydrogen and copper-chromium oxide catalyst. When the ketones were hydrogenated at temperatures of 100–130°, the product was the secondary carbinol. This carbinol was in turn hydrogenated at 180–195° without solvent or at 200–250° with solvent to the aromatic hydrocarbon. The data for these reductions are summarized in Tables I, II, and III.

The presence of one, two, or three methyl groups on the benzene nucleus and the branching of the alkyl group had little effect on the temperature at which the carbonyl group was reduced to carbinol. *n*-Butyrophenone, *p*-methyl-*n*-butyrophenone, and the three dimethyl-*n*-butyrophenones were reduced to carbinols at 110–130° during two hours. With two methyl groups *ortho* to the carbonyl group in the two mesitylene ketones only a slight increase in temperature was necessary. The relatively small variations in reduction temperature may perhaps be due to variations in pressure or to catalyst poisons rather than to a hindering effect of the methyl groups.

As a matter of interest, the reduction study was extended to include representative phenolic aldehydes and ketones and methoxyaldehydes listed in Table III. The *o*- and *p*-methoxybenzaldehydes were reduced to the corresponding methoxybenzyl alcohols at 110–125°, the same temperature range required for the reduction of aromatic ketones to alcohols, and *p*-methoxybenzyl alcohol yielded *p*-cresol methyl ether at 185° in methanol solution.

When the hydroxyl group was not methylated and was *ortho* or *para* to the aldehyde group, *o*- and *p*-cresol were obtained at 110–130°, while *m*-hydroxybenzaldehyde required a temperature of 185° to form *m*-cresol. At 250°, *o*-hydroxybenzaldehyde yielded a small amount of 2-methylcyclohexanol. To minimize possible polymerization of the intermediate hydroxybenzyl alcohols, methanol was used as solvent for the reduction of the phenolic aldehydes.

The *o*- and *p*-hydroxyacetophenones and the *o*- and *p*-hydroxypropiofenones were also reduced to alkylphenols at 110–130°. This reaction should furnish a convenient method for the preparation of alkylphenols.

From these data it appears that when a phenolic group is *ortho* or *para* to the carbonyl group of an aromatic aldehyde or ketone, the carbinol group is

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² DuPont Fellow, 1947–1948. Present address, Pan American Refining Corporation, Texas City, Texas.

reduced to the methylene group at the temperature (110–130°) at which the non-phenolic aldehydes and ketones are reduced to carbinols. A phenolic group *meta* to the carbonyl group appears to have no effect on the course of the reduction of the phenolic aldehyde, and a temperature of 185° was required to convert the carbonyl to methylene.

The results from the hydrogenation of ten of the aromatic ketones with Raney nickel as catalyst indicate that it is of limited usefulness in the preparation of aromatic hydrocarbons. Ketones such as acetophenone and propiophenone could be hydrogenated at 65–85° and 200 atm. to yield a product containing up to 75% of aromatic hydrocarbon and variable amounts of aromatic carbinol and naphthene carbinol. Higher temperatures increased the proportion of naphthene carbinol. Some of the ketones derived from *m*-xylene such as 2,4-

TABLE I
HYDROGENATION OF AROMATIC KETONES TO CARBINOLS

COMPOUND	TEMP., °C.	TIME, HRS.	YIELD, WT., %	PRODUCTS
Acetophenone ^a	100–120	0.1	63	Methylphenyl carbinol
			5	Ethylbenzene
<i>n</i> -Butyrophenone ^b	120–130	2.0	74	<i>n</i> -Propylphenylcarbinol
			18	<i>n</i> -Butylbenzene
4-Methyl- <i>n</i> -butyrophenone ^b	110–125	2.0	89	(4-Methylphenyl)propylcarbinol
			6	1-Methyl-4- <i>n</i> -butylbenzene
2,4-Dimethyl- <i>n</i> -butyrophenone ^a	110–130	2.2	90	(2,4-Dimethylphenyl)- <i>n</i> -propylcarbinol
			2	1,3-Dimethyl-4- <i>n</i> -butylbenzene
2,4-Dimethyl- <i>n</i> -caprophenone ^b	175	2.2	92	(2,4-Dimethylphenyl)- <i>n</i> -amylcarbinol
			5	1,3-Dimethyl- <i>n</i> -hexylbenzene
Acetomesitylene ^a	110–130	1.5	96	(2,4,6-Trimethylphenyl)methylcarbinol
Propiomesitylene ^a	135	1.5	87	(2,4,6-Trimethylphenyl)ethylcarbinol

^a The ketone (0.25 mole) in 100 ml. of anhydrous methanol was reduced with hydrogen at 220–240 atm. using 4.0 g. of copper-chromium oxide catalyst.

^b No solvent.

dimethyl-*n*-butyrophenone and 2,4-dimethylisobutyrophenone required a temperature of 175–195° at 240 atm. for reduction to the aromatic hydrocarbon in 80% yield, while 2,4-dimethyl-*n*-caprophenone reduced with a different preparation of catalyst at 160° to yield a mixture of naphthene hydrocarbon and aromatic hydrocarbon. Adkins (1) reports that acetomesitylene is stable toward Raney nickel at 150° but at 160° we have obtained a 22% yield of ethylmesitylene along with methyl (2,4,6-trimethylphenyl)carbinol. Propiomesitylene reduced similarly.

The addition of small amounts of aqueous sodium hydroxide or sodium 2,6-di-*n*-propylphenol did not facilitate the reduction of these ketones as it did with phenolic ketones (2).

Apparently the activity of the catalyst and to some extent the number of alkyl groups present on the aromatic nucleus affect the course of the reduction when Raney nickel is used as the catalyst.

TABLE II
HYDROGENATION OF AROMATIC KETONES AND CARBINOLS TO HYDROCARBONS^a

COMPOUND	TEMP., °C.	TIME, HRS.	YIELD, WT. %	PRODUCTS
Acetophenone	235		83	Ethylbenzene
<i>n</i> -Butyrophenone	240		74	<i>n</i> -Butylbenzene
4-Methylacetophenone	250-270	0.5	91	<i>p</i> -Ethyltoluene
4-Methylpropiofenone	250-270	1.25	83	<i>p-n</i> -Butyltoluene
2,4-Dimethylacetophenone	250	0.5	84	1,3-Dimethyl-4-ethylbenzene
2,4-Dimethylpropiofenone	250	0.5	74	1,3-Dimethyl-4- <i>n</i> -propylbenzene
2,4-Dimethyl- <i>n</i> -butyrophenone	250	1.5	86	1,3-Dimethyl-4- <i>n</i> -butylbenzene
2,4-Dimethylisobutyrophenone	250-260	0.5	83	1,3-Dimethyl-4-isobutylbenzene
2,4-Dimethylisovalerophenone	250-260	0.5	89	1,3-Dimethyl-4-isoamylbenzene
2,4-Dimethyl- <i>n</i> -caprophenone	250	0.5	91	1,3-Dimethyl- <i>n</i> -hexylbenzene
2,4-Dimethylisocaprophenone	250	0.5	87	1,3-Dimethyl-4-isohexylbenzene
3,4-Dimethyl- <i>n</i> -butyrophenone	250	0.5	77	1,2-Dimethyl-4- <i>n</i> -butylbenzene
2,5-Dimethyl- <i>n</i> -butyrophenone	250	0.5	86	1,4-Dimethyl-2- <i>n</i> -butylbenzene
Propiomesitylene	250	0.5	82	<i>n</i> -Propylmesitylene
Phenylmethylcarbinol	250	0.75	89	Ethylbenzene
Phenyl- <i>n</i> -propylcarbinol	180-195	2.0	88	<i>n</i> -Butylbenzene
(4-Phenylmethyl)- <i>n</i> -propylcarbinol)	180-190	2.0	93	1-Methyl-4- <i>n</i> -butylbenzene
(2,4-Dimethylphenyl)- <i>n</i> -propylcarbinol)	180-195	2.1	95	1,3-Dimethyl-4- <i>n</i> -butylbenzene
(2,4-Dimethylphenyl)- <i>n</i> -amylcarbinol)	180-195	2.0	95	1,3-Dimethyl-4- <i>n</i> -hexylbenzene
(2,4,6-Trimethylphenyl)methylcarbinol	180-195	1.75	43	1,3,5-Trimethyl-2-ethylbenzene
			44	Unchanged carbinol

^a The ketones (0.25 mole) in 100 ml. of anhydrous methanol were reduced with hydrogen at 300 to 340 atm. using 4.0 g. of copper-chromium oxide catalyst. The carbinols (0.25 mole) were reduced in the absence of solvent with hydrogen at 270 atm. using 4.0 g. of copper-chromium oxide catalyst.

TABLE III
HYDROGENATION OF METHOXY- AND PHENOLIC ALDEHYDES AND KETONES^a

COMPOUND	TEMP., °C.	TIME, HRS.	YIELD, WT. %	PRODUCTS
<i>o</i> -Hydroxybenzaldehyde	123-135	2.3	86	<i>o</i> -Cresol
<i>p</i> -Hydroxybenzaldehyde	110-125	1.5	73	<i>p</i> -Cresol
			8	<i>p</i> -Hydroxybenzyl alcohol
<i>m</i> -Hydroxybenzaldehyde	110-125	2.0	4	<i>m</i> -Cresol
			84	<i>m</i> -Hydroxybenzyl alcohol
<i>o</i> -Methoxybenzaldehyde	110-125	2.0	88	<i>o</i> -Methoxybenzyl alcohol
<i>p</i> -Methoxybenzaldehyde	130		83	<i>p</i> -Methoxybenzyl alcohol
<i>p</i> -Methoxybenzyl alcohol	185	2.5	85	<i>p</i> -Methylanisole
<i>o</i> -Hydroxyacetophenone	115-130	2.2	91	<i>p</i> -Ethylphenol
<i>o</i> -Hydroxypropiofenone	115-125	0.25	89	<i>o</i> -Propylphenol
<i>p</i> -Hydroxyacetophenone	140	0.5	75	<i>p</i> -Ethylphenol
<i>p</i> -Hydroxypropiofenone	115-125	3.5	79	<i>p-n</i> -Propylphenol

^a The compound (0.25 mole) in 100 ml. of methanol was reduced with hydrogen at 220 to 240 atm. using 4.0 g. of copper-chromium oxide catalyst.

Five ketones derived from toluene and *m*-xylene were reduced by the modified Wolff-Kishner method (3). Of the chemical methods for reducing aromatic ketones to hydrocarbons, this method has been the most satisfactory. Yields were good, and the aromatic hydrocarbon was free of olefins and carbinols which are by-products of the Clemmensen reduction.

TABLE IV
PHYSICAL CONSTANTS OF COMPOUNDS NOT DESCRIBED IN THE LITERATURE

	B.P., °C.	MM.	n_D^{20}	FORMULA	CALC'D		FOUND	
					C	H	C	H
2,4-Dimethyl- <i>n</i> -caprophenone.....	133	5	1.5170	C ₁₄ H ₂₀ O	82.30	9.87	82.08	9.89
2,4-Dimethylisocaprophenone.....	120	5	1.5123	C ₁₄ H ₂₀ O	82.30	9.87	82.25	9.76
Ethylcyclohexylcarbinol.....	96	18	1.4688	C ₉ H ₁₈ O	75.99	12.76	75.93	12.8
<i>n</i> -Propylcyclohexylcarbinol.....	115	40	1.4652	C ₁₀ H ₂₀ O	76.84	12.91	77.02	12.66
(4-Methylphenyl)- <i>n</i> -propylcarbinol.....	98	4	1.5137	C ₁₁ H ₁₆ O	80.44	9.82	80.31	9.96
(2,4-Dimethylphenyl)- <i>n</i> -propylcarbinol.....	142	19	1.5151	C ₁₂ H ₁₈ O	80.90	10.11	80.73	10.37
(2,4-Dimethylphenyl)isopropylcarbinol.....	138	18	1.5155	C ₁₂ H ₁₈ O	80.90	10.11	80.98	10.41
(2,4-Dimethylphenyl)isobutylcarbinol.....	145	25	1.5120	C ₁₃ H ₂₀ O	81.25	10.41	81.10	10.61
(2,4-Dimethylphenyl)- <i>n</i> -amylcarbinol.....	122	2	1.5125	C ₁₄ H ₂₂ O	81.50	10.75	81.38	10.98
(3,4-Dimethylphenyl)- <i>n</i> -propylcarbinol.....	139	11	1.5183	C ₁₂ H ₁₈ O	80.84	10.18	80.87	10.26
(2,4,6-Trimethylphenyl)methylcarbinol ^a	93	2		C ₁₁ H ₁₆ O	80.44	9.82	80.35	9.86
(2,4,6-Trimethylphenyl)methylcarbinol.....	112	5	1.5271	C ₁₂ H ₁₈ O	80.84	10.18	80.74	10.37
1,3-Dimethyl-4- <i>n</i> -hexylbenzene.....	102	2	1.4962	C ₁₄ H ₂₂	88.35	11.65	88.50	11.65
1,3-Dimethyl-4-isoethylbenzene.....	96	2	1.4928	C ₁₄ H ₂₂	88.35	11.65	88.32	11.76
1,2-Dimethyl-4- <i>n</i> -butylbenzene.....	93	8	1.4989	C ₁₂ H ₁₈	88.82	11.18	88.76	11.12
1,4-Dimethyl-2- <i>n</i> -butylbenzene.....	85	6	1.4996	C ₁₂ H ₁₈	88.82	11.18	88.84	11.16
1-(2,4-Dimethylphenyl)-1-butene....	110	20	1.3340	C ₁₂ H ₁₆	90.00	10.00	89.94	10.12

^a M.p. 72-72.5°

EXPERIMENTAL³

All of the carbonyl compounds were refluxed over Raney nickel and distilled from the nickel as the final step in their purification.

Several of the carbinols were prepared for reference purposes by the reduction of the ketones with aluminum isopropoxide (4). When 2,4-dimethyl-*n*-butyrophenone was reduced with aluminum isopropoxide, the product was the olefin, 1-(2,4-dimethylphenyl)-1-butene.

The copper chromium oxide catalyst was prepared by the usual method (5). The Raney nickel catalyst was prepared by the method of Mazingo (6).

Hydrogenations. (a) *With copper-chromium oxide.* The hydrogenations were carried out in a rocking steel autoclave.⁴ Normally, 0.25 mole of ketone, aldehyde, or alcohol and 4 g.

³ The semimicro carbon-hydrogen analyses are by Richard A. Carpenter and Karl T. Zilch.

of copper chromium oxide were placed in a copper liner having a total capacity of 500 ml. When a solvent was used, 100 ml. of anhydrous analytical reagent methanol was added. Yields were nearly identical with or without methanol except in the case of the phenolic aldehydes, which formed variable amounts of resinous products when they were reduced without solvent.

The temperature at which hydrogen was first absorbed was noted by plotting pressure against temperature. When the carbinol was the desired product, the temperature was held at this point until the pressure became constant. If the hydrocarbon was to be the final product and methanol was the solvent, the temperature was raised to 200–250° and held there until reduction was complete. Without solvent, the carbinol was usually reduced to hydrocarbon at 180–195°. The reaction time listed in the tables represents the interval of time from the start of the reaction at room temperature until the pressure became constant.

The contents of the liner were washed out with methanol if it had been used as solvent, or with benzene if no solvent had been used, and filtered. When the reduction products (notably the monoalkylbenzenes) formed azeotropic mixtures with methanol, the reaction mixture was diluted with an equal volume of water, the oily layer was separated, and the aqueous layer was extracted three times with small portions of benzene. The benzene extracts were combined with the oily layer, the solution was dried and fractionated through a micro column of approximately fifteen theoretical plates with a reflux ratio of 5:1 to 10:1 depending on the closeness of the boiling points of the compounds to be separated.

(b) *Reductions with Raney nickel.* The reductions were carried out and the products isolated as described above. Usually 0.25 mole of ketone, 3 g. of Raney nickel, and 60 cc. of anhydrous methanol were placed in the copper liner. The initial hydrogen pressure was approximately 200 atm. at room temperature.

The known hydrocarbons, carbinols, and alkylphenols were identified by their physical constants or by their derivatives. The physical constants and analyses of compounds not previously described in the literature are listed in Table IV.

SUMMARY

Aromatic ketones and methoxy aromatic aldehydes may be hydrogenated over copper-chromium oxide catalyst at an initial hydrogen pressure of 220–340 atm. to form the corresponding carbinol at 110–130° or the alkylbenzene or cresol at 184–250°. Yields are nearly quantitative.

The *o*- and *p*-hydroxybenzaldehydes were reduced to *o*- and *p*-cresol at 110–130° while *m*-hydroxybenzaldehyde required a temperature of 185° to form *m*-cresol.

The *o*- and *p*-hydroxy ketones were reduced to alkylphenols at 110–130°.

Raney nickel is of limited usefulness as a catalyst for the reduction of aromatic ketones to alkylbenzenes.

COLUMBIA, MISSOURI

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⁴ American Instrument Co., Silver Spring, Md.