

quantitative; m. p. 65–66° after recrystallization from ether-petroleum ether.

**4,7-Dimethoxyhydrindone-1.**—Ten grams of 2,5-dimethoxyhydrocinnamic acid dissolved in 250 cc. of dry benzene was treated with 40 g. of phosphorus pentoxide. The mixture was heated gently with good stirring for two and one-half hours on the steam-bath. After decomposition with water, the aqueous layer was extracted with 300 cc. of ether in small portions. The combined benzene and ether extracts were washed with sodium carbonate solution and water, clarified with charcoal, and evaporated to dryness. The light yellow solid residue weighed 7.5 g. Fractional crystallization from ether gave the pure 4,7-dimethoxyhydrindone-1; m. p. 124.5–125°.

*Anal.* Calcd. for  $C_{11}H_{12}O_2$ : C, 68.71; H, 6.29. Found: C, 68.66; H, 6.50.

**4,7-Dimethoxyhydrindene (XII).**—The 4,7-dimethoxyhydrindone-1 (0.83 g.) was dissolved in 10 cc. of 95% ethanol and reduced with hydrogen and Raney nickel at 150° under a pressure of 1400 pounds for two hours. The solution was filtered and evaporated to 4 cc. Hot water was added to start crystallization and on cooling, 0.69 g. (90%) of 4,7-dimethoxyhydrindene (XII) was obtained; long white needles of m. p. 85–85.5°.

*Anal.* Calcd. for  $C_{11}H_{14}O_2$ : C, 74.13; H, 7.92. Found: C, 74.30; H, 7.96.

**Methylation of 4,7-Hydrindenehydroquinone.**—The hydroquinone (0.45 g.) was dissolved in 3 cc. of methanol and 2.9 cc. of dimethyl sulfate. The mixture was refluxed and a solution of potassium hydroxide (3.6 g. in 18 cc. methanol) was added dropwise with stirring. Refluxing was continued for thirty minutes and the mixture was poured into 80 cc. of ice water. The finely divided precipitate was filtered and recrystallized from dilute ethanol; yield, 0.36 g. An additional recrystallization gave a product melting at 85–85.5°, found by a mixed melting point to be identical

with the sample prepared by the reduction of 4,7-dimethoxyhydrindone-1.

**Measurements.**—The oxidation–reduction potential measurements were carried out by preparing standard 0.003 *M* solutions of the quinones and hydroquinones in a buffer solution consisting of 0.1 *N* acetic acid and 0.1 *N* sodium acetate in 50% aqueous ethanol. For the polarographic measurements, the hydroquinone solutions were diluted to 0.0015 *M* concentration by an equal volume of buffer. For the potentiometric measurements equal volumes of corresponding quinone and hydroquinone solutions were mixed and the potential measured by means of a bright platinum electrode against the same saturated calomel electrode that was used as the reference in the polarographic determinations. In this way, both the *pH* and the ionic strength of the solutions used in both methods of measurement were kept constant at 5.40 and 0.1, respectively.

The method of mixtures was found to be unsatisfactory in the potentiometric measurement of 4,7-hydrindenequinone, undoubtedly because of the noticeable instability of standard solutions of the quinone. Fortunately, however, the quinhydrone was readily accessible and measurement of it dissolved in the standard buffer gave the value (0.641 v.) reported in the table.

### Summary

1. The oxidation–reduction potentials of *o*-xyloquinone, 4,7-hydrindenequinone, and 1,2,3,4-tetrahydronaphthoquinone-5,8 have been measured by two standard procedures.

2. The relatively high value found for the 4,7-hydrindenequinone has been attributed to a positive Mills–Nixon type of partial double bond stabilization.

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

## Catalytic Dehydrogenation of Hydroaromatic Compounds with Benzene<sup>1</sup>

BY HOMER ADKINS, LAWRENCE M. RICHARDS AND JAMES W. DAVIS

Linstead and his associates have in recent years developed the catalytic method<sup>2</sup> for the dehydrogenation of hydroaromatic compounds so that it has been found useful in several laboratories, especially in structural studies. Linstead's method involves passing the vapors of the hydroaromatic compound over platinum or palladium at 300 to 350°. In most instances the compound to be dehydrogenated was passed over 2 g. of the metal on a suitable support, at the rate of about

0.3 g. per hour. It has been our objective to develop a method for catalytic dehydrogenation in the liquid phase that can be used for high molecular weight compounds and upon a scale suitable for preparational work.

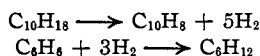
A method for catalytic dehydrogenation in the liquid phase in a closed system necessitates a hydrogen acceptor to prevent the reverse reaction. Even in the vapor phase at one atmosphere pressure we have found that the dehydrogenation of tetradecahydrophenanthrene does not go completely to phenanthrene at 325°. At superatmospheric pressures of hydrogen, in the temperature range 300–350°, the equilibrium is far on the

(1) This investigation was supported by the Wisconsin Alumni Research Foundation.

(2) Linstead, Millidge, Thomas, Walpole and Michaelis, *J. Chem. Soc.*, 1146–1157 (1937), 1127–1147 (1940). References are given to earlier work by Ipatieff, Zelinski and others.

side of the hydroaromatic compound. While ethylene was a good hydrogen acceptor for the dehydrogenation of alcohols,<sup>3</sup> it has not been useful in the dehydrogenation of hydroaromatic compounds.<sup>4</sup>

The ideal hydrogen acceptor should be readily available, stable against polymerization, highly unsaturated, and should react irreversibly with hydrogen under the conditions of its use. When the problem is so stated, benzene is an obvious answer, and in fact it has proved to be an excellent oxidizing agent or hydrogen acceptor. The reaction of benzene with hydrogen to give cyclohexane is of course a reversible process, but it so happens that cyclohexane does not undergo dehydrogenation to an appreciable extent under conditions where substituted cyclohexanes react relatively rapidly. Thus the dehydrogenation of decalin, with a suitable catalyst, goes practically to completion in the presence of benzene at 350°.



Cyclohexanol,  $\beta$ -decalol, several mono- and di-substituted cyclohexanols, tetradecahydrophenanthrene and bicyclohexyl have been rather completely (50 to 90%) converted to the corresponding aromatic hydrocarbons, over platinum, by this process.

However, the use of platinum as a catalyst is not attractive because of the cost of the metal and the necessity of recovering it after use. A number of procedures therefore were devised for the preparation of nickel catalysts. The support and method of preparation of a nickel catalyst make a good deal of difference in its activity. Charcoal, kieselguhr, pure alumina from aluminum isopropoxide, and alumina precipitated by sodium hydroxide have proved to be satisfactory supports. The nickel in these instances was precipitated as the hydroxide or carbonate with sodium or ammonium hydroxide or ammonium carbonate, and then reduced with hydrogen. Another very active catalyst "nickel on chromium oxide" was made by reduction of nickel chromite, obtained by the decomposition of nickel ammonium chromate.

The effectiveness of these catalysts in dehydrogenating decalin,  $\beta$ -decalol, and  $\beta$ -decalone has served as a basis for rating their activity. Decalin was used as a test compound because it is dehydrogenated only by the most active catalysts.

(3) Reeve and Adkins, *THIS JOURNAL*, **62**, 2874 (1940).

(4) Adkins and Reid, *ibid.*, **68**, 741 (1941).

The comparison of catalysts for the dehydrogenation of  $\beta$ -decalol is interesting, because, while the

TABLE I  
COMPARISON OF CATALYSTS (350°)

Catalyst	From decalin,		From $\beta$ -decalol	
	% $\text{C}_{10}\text{H}_8^a$	% $\text{C}_{10}\text{H}_8$	% $\text{C}_{10}\text{H}_{18}$	% $\text{C}_{20}\text{H}_{14}$
Pt (char.)	87	38 <sup>c</sup>	?	?
Pt (char.)	..	33 <sup>b,c</sup>	?	?
Ni(Cr <sub>2</sub> O <sub>3</sub> )	78	22 <sup>c</sup>	28	11
Ni(Cr <sub>2</sub> O <sub>3</sub> )	..	32 <sup>b,c</sup>	17	30
Ni(Al <sub>2</sub> O <sub>3</sub> ) I	0	71	27	0
Ni(Al <sub>2</sub> O <sub>3</sub> ) II	11	54	35	0
Ni(Al <sub>2</sub> O <sub>3</sub> ) III	0	65	20	6
Ni(Al <sub>2</sub> O <sub>3</sub> ) IV	36	60	21	16
Ni (char.)	34	58	42	0
Ni (kies.)	62	63	35	0

<sup>a</sup> The figures in this column refer to % conversion of decalin to naphthalene, *i. e.*, allowance was made for mechanical losses. The figures in the other columns give the % yield of a given compound actually isolated. <sup>b</sup>  $\beta$ -Decalone, not  $\beta$ -decalol, was the compound dehydrogenated. <sup>c</sup>  $\beta$ -Naphthol was produced in 15-20% yields over platinum from either  $\beta$ -decalol or  $\beta$ -decalone, while nickel on chromium oxide gave similar yields of an aromatic compound containing twenty or more carbon atoms in each molecule.

TABLE II

DEHYDROGENATION OF HYDROCARBONS (350°)

Hydrocarbon (catalyst)	% Yield of products	
Tetralin (Ni) <sup>a</sup>	100	Naphthalene
Decalin (Pt)	73	Naphthalene
Decalin (Ni)	72	Naphthalene
$\beta$ -Methyldecalin (Ni)	14	$\beta$ -Methylnaphthalene
<i>p</i> -Menthane (Ni)	28	<i>p</i> -Cymene
Bicyclohexyl (Pt)	53	Biphenyl
Bicyclohexyl (Ni)	83	Biphenyl
3-Cyclohexylpropene-1 (Ni)	36	Propylbenzene
	37	Propylcyclohexane
3-Cyclohexylpropene-1 (Pt)	30	Propylbenzene
	60	Propylcyclohexane
Tricyclohexylmethane (Ni)	25	Triphenylmethane
	25	Dicyclohexylphenylmethane
	x	Diphenylcyclohexylmethane
Tetradecahydrophenanthrene (Pt)	89	Phenanthrene
Tetradecahydrophenanthrene (Ni)	65	Phenanthrene
<i>as</i> -Octahydrophenanthrene (Ni) <sup>a</sup>	100	Phenanthrene
Dodecahydrotriphenylene (Ni)	33	Triphenylene (pure)
	50	Triphenylene (impure)
Hydrindane (Ni)	48	Hydrindene
1-Ethylhydrindane (Ni)	75	1-Ethylhydrindene
1-Cyclohexylhydrindane (Ni)	63	1-Phenylhydrindene

<sup>a</sup> Nickel on alumina I, the other nickel catalyst was on chromium oxide.

TABLE III

## DEHYDROGENATION OF CYCLOHEXANOLS AND DERIVATIVES

Cyclohexanol (catalyst) <sup>a</sup>	% Yield of products
Cyclohexanol (Pt, 275°)	25 Phenol
Cyclohexanone (Pt, 275°)	27 Phenol
4- <i>n</i> -Pr-cyclohexanol (Pt, 300°)	58 <i>n</i> -Pr-benzene 6 <i>n</i> -Pr-cyclohexane
4- <i>n</i> -Bu-cyclohexanol (Pt, 300°)	68 <i>n</i> -Bu-benzene 4 <i>n</i> -Bu-cyclohexane
4- <i>n</i> -Bu-cyclohexanol (Ni)	28 <i>n</i> -Bu-benzene 12 <i>n</i> -Bu-cyclohexane 12 <i>p</i> - <i>n</i> -Bu-phenol 37 Dimer
2- <i>n</i> -Bu-cyclohexanol (Ni)	15 <i>n</i> -Bu-benzene 18 <i>o</i> - <i>n</i> -Bu-phenol
2,6-Di-Et-cyclohexanone (Ni)	50 2,6-Di-Et-phenol 9 2,6-Di-Et-benzene 3 2,6-Di-Et-cyclohexane
2-Me-6- <i>n</i> -Pr-cyclohexanol (Pt, 330°)	80 2-Me-6- <i>n</i> -Pr-benzene 7 2-Me-6- <i>n</i> -Pr-cyclohexane 3 2-Me-6- <i>n</i> -Pr-phenol
2-Me-6- <i>n</i> -Pr-cyclohexanol (Ni)	11 2-Me-6- <i>n</i> -Pr-benzene 6 2-Me-6- <i>n</i> -Pr-cyclohexane 35 2-Me-6- <i>n</i> -Pr-phenol
4-Me-2- <i>n</i> -Pr-cyclohexanol (Pt, 330°)	66 4-Me-2- <i>n</i> -Pr-benzene 16 4-Me-2- <i>n</i> -Pr-cyclohexane
4-Me-2- <i>n</i> -Pr-cyclohexanol (Ni)	26 4-Me-2- <i>n</i> -Pr-benzene 9 4-Me-2- <i>n</i> -Pr-cyclohexane 20 4-Me-2- <i>n</i> -Pr-phenol
3-Me-6- <i>n</i> -Bu-cyclohexanol (Pt, 330°)	72 3-Me-6- <i>n</i> -Bu-benzene
4-Cyclohexyl-cyclohexanol (Pt)	82 Biphenyl
2-Cyclohexylidene-cyclohexanone (Ni)	39 Biphenyl 19 2-Hydroxybiphenyl 15 "Aromatic oil"
Menthol (Pt, 330°)	46 <i>p</i> -Cymene 24 <i>p</i> -Menthane
Menthol (Ni)	65 Thymol 3 <i>p</i> -Cymene
Menthone (Ni)	63 Thymol 3 <i>p</i> -Cymene
$\alpha$ -Decalol (Ni)	23 Naphthalene 22 Decalin 3 Binaphthyl 29 "Aromatic oil"
$\beta$ -Ethoxydecalin (Ni, 300°)	67 Naphthalene
2-Methoxybicyclohexyl (Ni)	71 Biphenyl
4-Cyclohexylbutanol-2 (Ni)	18 <i>n</i> -Bu-benzene 22 <i>n</i> -Bu-cyclohexane

<sup>a</sup> The nickel was on chromium oxide; the temperature of reaction was 350° unless otherwise noted.

alcohol is more easily dehydrogenated than decalin, there is a considerable variation in the proportion of the products depending upon the catalyst used. A part of the data upon the comparison of catalysts is summarized in Table I. The results of other dehydrogenations are given in Tables II and III.

## Comparison of Catalysts

Nickel on chromium oxide or on kieselguhr proved the most active of the nickel catalysts against decalin. However, chromium oxide was quite unsatisfactory as a support for nickel with  $\beta$ -decalol, as binaphthyl and other condensation products were formed. These condensation reactions did not occur to an appreciable extent when the nickel was supported on alumina or on kieselguhr. Tentatively the conclusion may be drawn that chromium oxide is the best support for nickel in the dehydrogenation of the saturated hydrocarbons which are very resistant toward dehydrogenation while alumina, co-precipitated with nickel hydroxide, is the best support for the preparation of the aromatic hydrocarbons from hydroaromatic alcohols and ketones. The use of pure alumina from an aluminum alkoxide did not offer any advantage over precipitated alumina. The nickel on kieselguhr was a little less active than nickel on chromium oxide for decalin, and less active than nickel on alumina for  $\beta$ -decalol. However, since the chromium oxide supported catalyst was almost valueless against  $\beta$ -decalol, and the alumina supported catalyst was inactive toward decalin, kieselguhr is probably the best catalyst support for the dehydrogenation of a variety of types of organic compounds.

Platinum is, at least for certain compounds, active at a lower temperature than the most active nickel catalyst so far prepared. It gave a higher yield of naphthalene and phenanthrene from decalin and tetradecahydrophenanthrene, respectively. The substituted cyclohexanols gave higher yields of aromatic hydrocarbons, less contaminated with saturated hydrocarbons, over platinum than over nickel. Platinum also gave a better yield of  $\beta$ -naphthol from  $\beta$ -decalol than did nickel.

Nickel proved better than platinum in several respects. Nickel was outstandingly superior to platinum in dehydrogenating cyclohexanols or cyclohexanones without dehydration. The phenol corresponding to the cyclohexanol was obtained with nickel in all the dehydrogenations of this type of compound, the average yield being about 35%. In the cases of menthol and menthone, the phenol (thymol) was isolated in a yield of about 63% of the theoretical, while platinum gave only traces of the phenol. Platinum gave a lower yield of biphenyl from bicyclohexyl than nickel, and platinum gave little or no dehydrogenation

of tricyclohexylmethane and 2-methoxydicyclohexyl, while nickel gave good yields of triphenylmethane and biphenyl from these compounds.

### Structure and Course of Reactions

Early in the course of this investigation, it seemed possible that the difference in the rate of dehydrogenation of saturated hydrocarbons and of saturated hydroaromatic alcohols might be due to the fact that the first stage in the reaction of the alcohols was dehydration. The unsaturated hydrocarbon so formed would undergo dehydrogenation more rapidly than a saturated hydrocarbon. In order to avoid dehydration and thus perhaps obtain higher yields of phenols, a comparison was made of the dehydrogenation of cyclohexanol and cyclohexanone over platinum, of menthol and menthone over nickel and of  $\beta$ -decalol and  $\beta$ -decalone over both platinum and nickel. The rate and proportion of products was found however to be similar for the ketone and alcohol. The exception to this general statement was that  $\beta$ -decalone gave more binaphthyl than did  $\beta$ -decalol. These facts suggest that the alcohol undergoes a rather rapid dehydrogenation to the ketone and that the dehydrogenation of the ring is a subsequent reaction. Since the formation of binaphthyl probably depends upon the condensation of a ketone, the amount of binaphthyl formed would be greater where the concentration of ketone is originally high.

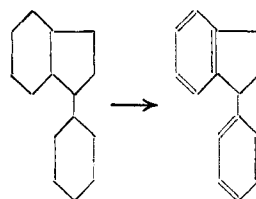
As would be anticipated from the foregoing, there is a considerable difference between the dehydrogenation of an alcohol and its ether. Attempts to dehydrogenate 2- and 4-methoxybicyclohexyl over platinum were unsuccessful although the dehydrogenation of a corresponding alcohol went readily. The 2-methoxybicyclohexyl went readily over nickel as did  $\beta$ -ethoxydecalin. It is noteworthy that in this latter case no condensation products were found such as were produced from  $\beta$ -decalol under similar conditions. No aromatic ether was found and naphthalene was the only product.

The formation of 20 to 42% yields of decalin in the dehydrogenation of  $\beta$ -decalol over various nickel catalysts is striking. Decalin might be formed by hydrogenation of octalin or disproportionation of di- $\beta$ -decalyl ether, either of which might be formed by dehydration of  $\beta$ -decalol. The inactivation of the catalyst by the water so formed may account in part for the failure of the

catalyst to dehydrogenate the decalin to naphthalene.

The number of compounds submitted to the conditions for dehydrogenation described in this paper is not large enough to justify many conclusions about the relation of structure to ease of dehydrogenation. Compounds containing an aromatic nucleus, such as tetralin and *as*-octahydrophenanthrene, undergo dehydrogenation so rapidly that little attention has so far been paid to them in this investigation. One compound, 3-cyclohexylpropene-1, having unsaturation in a side chain, underwent dehydrogenation over nickel to propylbenzene. However, propylcyclohexane also was formed, presumably by disproportionation of the cyclohexylpropene. Over platinum there was no evidence for dehydrogenation of this compound as the proportion of propylbenzene and propylcyclohexane was in accord with a disproportionation, *i. e.*, 2 parts of the saturated for 1 part of unsaturated compound.

Bicyclohexyl and *p*-menthane underwent dehydrogenation to biphenyl and *p*-cymene, respectively, but the rate of reaction was so slow in the case of menthane that it is improbable that a mono-alkyl substituted cyclohexane would undergo dehydrogenation. Hydrindane, 1-ethylhydrindane and 1-cyclohexylhydrindane all underwent a smooth dehydrogenation, *e. g.*



As noted above the cyclohexanols readily underwent dehydrogenation to give the corresponding aromatic hydrocarbon and phenol.

The catalytic dehydrogenation of hydroaromatic compounds containing angular or gem dimethyl groups will be discussed in a subsequent paper. For the present it will suffice to state that such structures are relatively stable under the conditions of dehydrogenation described in this paper.

### Experimental Details

**Procedures for Dehydrogenation and Separation of Products.**—The general procedure for carrying out the dehydrogenations was as follows: The compound to be dehydrogenated (5 to 10 g.) and thiophene-free benzene (10 to 40 ml.) were placed in a steel reaction vessel having a

void of 60 to 270 ml. The steel reaction vessels<sup>5,6</sup> were the same as those used for catalytic hydrogenations under pressure except that the gage-valve assembly was replaced by a simple valve and the bent steel tube within the vessel was omitted. The air in the reaction vessel was displaced with carbon dioxide, the catalyst (2 g.) added, the vessel closed and nitrogen admitted to a pressure of about 60 atmospheres. The use of carbon dioxide is not necessary if a platinum catalyst is used. The vessel was then heated (300 to 350°) for the necessary length of time, usually ten hours. The pressure within the reaction vessel was approximately 150 atmospheres.

The conditions of dehydrogenation used in the studies reported herewith were no doubt often excessive with respect to temperature and duration of reaction. This is particularly true for the cyclohexanols. The yields are affected by the purity of the compound and of the benzene used. They are also dependent, especially with nickel catalysts, upon the free space in the reaction vessel. Yields, for example, were higher in a vessel having a void of 270 ml. than in one of 100 ml. A large excess of benzene seemed to be disadvantageous, while larger amounts of catalyst had a favorable effect on the yield. The use of nitrogen at 50 to 150 atmospheres is probably not necessary but better yields were obtained in some instances when it was used than when it was not.

The reaction mixture was rinsed from the bomb with ether or benzene, and the catalyst removed by centrifuging. When there were no low boiling products, the solvents were removed on the steam-bath, and the last traces under diminished pressure.

Crystalline products were separated from non-crystalline products by crystallization from petroleum ether (b. p. 40–60°) at –80°. This separation was conveniently carried out using a sintered glass funnel fitted with a suction flask attached by means of a three-way stopcock to a source of gaseous carbon dioxide and a suction pump. A slow stream of carbon dioxide was allowed to flow up through the sintered glass plate which was covered to a depth of 2–3 mm. with petroleum ether. After bubbles started coming up through the liquid, the mixture to be separated was rinsed into the funnel with petroleum ether, and the sides of the funnel were rinsed down, the volume of the solution being brought up to about 15–20 ml. Solid carbon dioxide was then packed around the funnel, and the solution allowed to cool. When crystallization was complete, the stopcock was turned to connect the flask with the suction line, and the crystals on the sintered plate were sucked free of solvent. They were then washed by turning on the stream of carbon dioxide and rinsing in more solvent. When the solvent was cold, it was again drawn off. A 50–50 mixture of decalin and naphthalene treated in this way yields about 90% of the naphthalene, m. p. 78–80°. The decalin so obtained holds in solution about 10% of its weight of naphthalene.

Aromatic products which form picrates were separated from non-aromatic products by treatment with picric acid. The mixture, 4–5 g., was refluxed with a slight excess of picric acid in about 25 ml. of petroleum ether (b. p. 60–68°) for one hour. This was then cooled in ice and filtered and

(5) Adkins, *THIS JOURNAL*, **55**, 4272 (1933).

(6) Adkins, "Reactions of Hydrogen, etc.," University of Wisconsin Press, Madison, Wis., 1937, p. 31.

the picrate washed with cold petroleum ether. When the hydrocarbons were volatile in steam, the picrates were decomposed by distilling them in steam from an alkaline solution. Picrates of hydrocarbons not volatile in steam were decomposed by refluxing with a 10% sodium hydroxide solution.

The picrate separation was more complete than the crystallization at –80° and was of necessity used for the more soluble and lower melting hydrocarbons. The carbon dioxide–petroleum ether separation was faster and more convenient and very satisfactory for naphthalene, phenanthrene and biphenyl unless the proportion of aromatic compound was less than 20%. The preparation of picrates in petroleum ether instead of in alcohol<sup>4</sup> makes possible a more accurate determination of small amounts of a hydrocarbon.

Mixtures containing phenols and volatile hydrocarbons in ether or benzene (as rinsed from the bomb) were first extracted several times with 2% sodium hydroxide solution until removal of the phenol was complete. The remaining hydrocarbons were then obtained pure by distilling the ether and benzene from sodium through a Podbielniak column. This was found to be the most practical method of removing the last traces of benzene without losing any of the hydrocarbons. The hydrocarbons were then distilled at about 1 mm. pressure into a receiver cooled in dry-ice. The ratio of aromatic to hydroaromatic product was estimated from the refractive index and density of the mixture. Oxidation to the corresponding phthalic acid was also sometimes used to estimate the aromaticity. The C<sub>10</sub> compounds from  $\beta$ -decalol were separated from the C<sub>20</sub> compounds by steam distillation.

**Platinum Catalyst.**—The platinum catalyst was prepared by a procedure suggested by Linstead<sup>2</sup> but not described in detail. A water solution of hydrochloroplatinic acid containing an equivalent of 2 g. of platinum or 5.34 g. of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was placed in an evaporating dish and the volume of the solution reduced to 15–20 ml. by evaporation on the steam-bath. To this solution was added 6 g. of charcoal and evaporation continued until the paste formed at first became powdery. It was well to stir the paste frequently, especially just before it began to dry. When this was properly done, there were no orange deposits of H<sub>2</sub>PtCl<sub>6</sub> visible on the evaporating dish. The powder was dried several hours at 120° and then reduced in a slow current of hydrogen two hours at 100°, six hours at 135° and two hours at 300°. This reduction was conveniently carried out in a 19 mm., thick-walled Pyrex tube about 30 cm. long heated in an electric furnace. The catalyst was allowed to cool in the tube before the current of hydrogen was turned off. The cold catalyst was placed in a stoppered container and stored in a desiccator. The charcoal support was prepared by treating 100 g. of Norit with 500 ml. of warm 10% nitric acid for about twelve hours, filtering and suspending the charcoal three or four times in 500 ml. of hot distilled water and filtering each time. It was then dried several hours at 120°.

**Nickel Catalysts.**—All of the nickel catalysts were stored in the oxidized forms and reduced only as needed. Usually 2-g. portions were reduced in a current of commercial hydrogen for forty-five minutes at 450° in a horizontal glass tube with an external thermocouple.

The nickel on kieselguhr catalyst was made according to the procedure developed in this Laboratory several years ago.<sup>7,8</sup> Nickel on charcoal and nickel on alumina IV were prepared by a similar procedure. The charcoal was prepared as for the platinum catalyst while the alumina was obtained as for the "alumina II" catalyst. Other nickel catalysts were prepared as described below.

**Nickel Chromite.**—One hundred and twenty ml. of concd. ammonium hydroxide was added to a solution of 75.6 g. of ammonium dichromate,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , in 210 ml. of water. A solution of 178.4 g. of hydrated nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in 110 ml. of water was then added with vigorous stirring with the solutions at room temperature. The resultant paste was heated to  $90^\circ$  on a hot-plate or steam-bath with occasional stirring, and filtered immediately with suction. The filter cake was pressed as dry as possible and dried for twelve hours at  $75\text{--}80^\circ$ . The dried salt (133 g.) was pulverized in a mortar to a fine powder and decomposed in a casserole in five batches as described for the decomposition of copper chromite.<sup>6</sup> After the completion of each decomposition the casserole was heated to a cherry-red heat for a minute. The resulting powder was stirred for thirty minutes with 200 ml. of a 20% acetic acid solution and then washed with 1600 ml. of distilled water in four portions, by suspension and filtration. The filter cake was dried for twelve hours at  $125\text{--}130^\circ$ , and ground to a fine powder (64 g.).

**Nickel on Alumina I.**—A sodium aluminate solution was prepared by adding a solution of 131.5 g. of sodium hydroxide in 300 ml. of water to 321 g. of hydrated aluminum nitrate,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , dissolved in 500 ml. of water. This solution was heated on a steam-bath and a solution of 71.5 g. of hydrated nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in 300 ml. of water and 30 ml. of concd. nitric acid was added with vigorous stirring. The resulting paste was heated for one-half hour on the steam-bath and filtered. The filter cake was washed four times by suspending in 800 ml. of hot water and filtering. The light blue filter cake was then dried at  $125\text{--}130^\circ$  for twelve hours and the dry material (79 g.) was ground to a fine powder.

**Nickel on Alumina II.**—One hundred and fifty grams of distilled aluminum isopropoxide was dissolved in 500 ml. of anhydrous isopropyl alcohol, with refluxing if necessary. This solution was placed in a large evaporating dish on a steam-bath and hydrolyzed by adding, with vigorous stirring, a solution of 60 ml. of water in 140 ml. of isopropyl alcohol. The resulting paste was evaporated to dryness on the steam-bath and finally dried at  $130^\circ$  for twelve hours. The dried material was ground to a powder and yielded 47 g. of snow white, fluffy, hydrated alumina.

A solution of 16.8 g. of nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in 78 ml. of water was ground with 14.2 g. of hydrated alumina prepared as above, until the paste was homogeneous. To

this paste was added with stirring 60 ml. of a solution containing 0.40 mole of ammonium hydroxide. The bluish paste was stirred until homogeneous, filtered with suction, and washed with 50 ml. of water. The filter cake was suspended in 200 ml. of hot water, stirred for five minutes, filtered, and washed with 50 ml. of water. The washed material was dried at  $130^\circ$  for twelve hours and ground to a powder (17 g.).

**Nickel on Alumina III.**—A solution of 16.2 g. of hydrated nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in 50 ml. of water was ground with 15 g. of hydrated alumina, prepared as in II above, until the paste was homogeneous. The water was removed on a steam-bath and finally at  $130^\circ$  for twelve hours. The dried product was ground to a fine powder (26 g.).

### Summary

A catalytic process has been described in which hydroaromatic compounds containing a completely or partially saturated benzene, naphthalene, or phenanthrene nucleus are dehydrogenated to the corresponding aromatic compounds in good yields. Twenty-eight representative compounds including hydrocarbons, alcohols, ketones and ethers, have been dehydrogenated and the results summarized in the tables. The process consists in heating the hydroaromatic compound at  $300$  to  $350^\circ$  in the liquid phase under nitrogen with benzene in the presence of a nickel or platinum catalyst. Under these conditions benzene takes up the hydrogen from the hydroaromatic compound and thus serves as an hydrogen acceptor or oxidizing agent. Various methods have been described for preparing nickel catalysts. It has been found that nickel on chromium oxide is perhaps the most active catalyst for the dehydrogenation of those saturated hydrocarbons which are particularly resistant to reaction. Nickel on alumina or nickel on kieselguhr, however, are better catalysts for the dehydrogenation of substituted cyclohexanols because they show less tendency to induce condensations. Platinum in some cases was active at a lower temperature than nickel, but it was not active for the dehydrogenation of certain compounds. Nickel gave much better yields of phenols than did platinum, which converted cyclohexanols to aromatic hydrocarbons.

(7) Covert, Connor and Adkins, *THIS JOURNAL*, **54**, 1651 (1932).

(8) Adkins, "Reactions of Hydrogen, etc.," p. 19.