converted to disintegration per minute (d.p.m.) by measurement of the exact counting efficiencies with calibrated tritium solutions.

Acknowledgments.—The author is grateful to Dr. V. P. Guinn for furnishing the radioactivity measurements, to E. L. Sanborn and J. R. Weaver

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# A Study of the Catalytic Hydrogenation of Hydroxybenzenes over Platinum and Rhodium Catalysts

BY HILTON A. SMITH AND BILLY L. STUMP

The catalytic hydrogenation of phenol, catechol, resorcinol, hydroquinone, phloroglucinol and pyrogallol has been studied with platinum and rhodium catalysts. The rates of reduction are of the same order as those found for corresponding methyl- and methoxybenzenes. Some cleavage occurs in the reduction process, the amount depending on both temperature and catalyst. While ketones are produced during the reduction of the phenols, the kinetic evidence indicates that the mechanism of formation of cyclohexanols from the phenols does not require ketone intermediates. It is suggested that cyclohexenols are formed as intermediates, and that these may be reduced to form cyclohexanols, cleaved to form cyclohexanes, or isomerized to form cyclohexanones.

It has been recognized for many years that when phenol undergoes hydrogenation, the predominant product may be cyclohexanol, benzene or cyclohexane, depending on the catalyst employed and the reaction. Under certain conditions and with specific catalysts, cyclohexanone may be isolated during the course of the reaction, and the role of this compound as an "intermediate" in phenol hydrogenation has been investigated.

Vavon and Berton[1] were the first to isolate cyclohexanone as an "intermediate" in the hydrogenation of phenol. They hydrogenated phenol and the cresols over platinum black and isolated the cyclohexanones formed by reaction of the ketone with semicarbazide to produce the semicarbazone derivative. Coussemant and Jungers[2] made a thorough study of the kinetics of catalytic hydrogenation of phenol over Raney nickel. On the basis of the results obtained in these investigations, the following reaction mechanism has been proposed
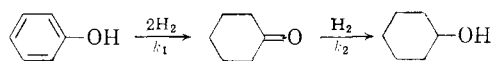
Wicker[3] hydrogenated o-, m-, p-cresol, and the corresponding methylcyclohexanones in acetic acid over Adams platinum catalyst at 20°. Stereochemical evidence obtained indicated that these hydroxy compounds do not hydrogenate via a ketone intermediate. It was the purpose of this research to extend the study of phenol hydrogenations to include the isomeric dihydroxybenzenes, catechol, resorcinol and hydroquinone, to find out whether ketones or diketones are formed during the course of the reaction and, if so, in what amounts.

Of interest also was the cleavage of hydroxyl groups from the aromatic ring during the course of hydrogenation. Smith and Thompson[4] made a sys-

tematic study of the cleavage reaction of the methoxyl group from an aromatic nucleus during hydrogenation, and it was felt that an extension of this study to include hydroxyl cleavage would lead to a further understanding of the reaction. A possible mechanism for the cleavage of the carbon-to-oxygen bond during such catalytic hydrogenations is: The methoxybenzene, anisole for example, is adsorbed on the catalyst surface where hydrogenation takes place to give a methoxycyclohexene as a short-lived intermediate. This intermediate may undergo cleavage and hydrogenation to give cyclohexane and methanol, or it may undergo simple hydrogenation to give methoxycyclohexane. These two reactions would probably occur simultaneously until the double-bonded molecules were saturated.

Finally, it was the purpose of this research to extend the kinetic data for catalytic hydrogenation of hydroxybenzenes.

Experimental

Commercial preparations of platinum oxide were obtained from the American Platinum Works, Newark, N. J., and Goldsmith Brothers, Chicago, Ill. The 5% rhodium-on-alumina catalyst was obtained from Baker and Co., Inc., Newark, N. J.

Glacial acetic acid was purified by fractionation of du Pont C.P. acid through an 8-foot Vigreux column. Commercial hydrogen obtained from the National Cylinder Gas Co. was used without further purification. This hydrogen has been shown previously to be satisfactory for kinetic studies.

Matheson (Coleman and Bell Division) phenol was fractionated through a 2-foot Vigreux column and the fraction boiling at 181.6° (745.8 mm.) was used. Eastman Kodak Co. white label catechol and Merck and Co., Inc., hydroquinone were purified by recrystallization from benzene. Melting points are 108.5° and 175.4–176.6°, respectively. Matheson (Coleman and Bell Division) resorcinol was recrystallized from toluene (m.p. 111.2–111.6°). Eastman Kodak Co. white label phloroglucinol and cyclohexanone were used without further purification. Baker Chemical Co. pyrogallol was recrystallized from an ethanol–benzene solution (m.p. 136°).

A much simpler method than has been reported previously was used to prepare dihydroresorcinol. Ten grams of resorcinol was hydrogenated at room temperature in 20 ml. of water containing 4.36 g. of sodium hydroxide over 2.0

(1) G. Vavon and A. L. Berton, *Bull. soc. chim.*, **37**, 296 (1925).

(2) F. Coussemant and J. C. Jungers, *Bull. soc. chim. Belges*, **59**, 295 (1950).

(3) R. J. Wicker, *J. Chem. Soc.*, 3299 (1957).

(4) H. A. Smith and R. G. Thompson, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 727.

g. of 5% rhodium-on-alumina catalyst. The initial pressure was 50 p.s.i.g. The reaction ceased after 37% of the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration and the reaction mixture was treated with concentrated hydrochloric acid until the solution was acidic to congo red test paper. Chilling the solution in the refrigerator produced 8.90 g. (87.4% yield) of dihydroresorcinol, m.p. 104–105°. Recrystallization from benzene was necessary to remove traces of sodium chloride from the product, but the melting point was not raised.[5]

Several hydrogenations of catechol were made in methanol over 5% rhodium-on-alumina catalyst, and the percentage ketone present was studied as a function of percentage reaction. This was accomplished by stopping the hydrogenations at various degrees of completion, removing the catalyst and solvent, and treating the residue which remained with phenylhydrazine. 2-Hydroxycyclohexanone phenylhydrazone, m.p. 117.4–118°,[6] was isolated in each case. The percentage ketone present in the reaction mixture reached a maximum of 16 at 50% completion. When the reactions were repeated using acetic acid solvent in place of methanol, the percentage ketone present in the reaction mixture reached a maximum of 23%, again at 50% reaction. It appears, then, that 2-hydroxycyclohexanone is formed in the hydrogenation of catechol, rather than the diketone 1,2-cyclohexanedione.

Catechol was hydrogenated in acetic acid over Adams platinum and in the presence of semicarbazide hydrochloride. A white solid was isolated from this reaction mixture which melted at 198–199° and, from an elemental analysis, appeared to be 2-hydroxycyclohexanone semicarbazone dihydrate.

Anal. Calcd. for $C_7H_{17}N_3O_4$: C, 40.56; H, 8.27; N, 20.28. Found: C, 40.6; H, 7.9; N, 20.42.

Several hydrogenations of resorcinol were carried to varying degrees of completion over both Adams platinum and 5% rhodium-on-alumina catalysts, but in no case was it possible to isolate a ketone intermediate.

Hydroquinone was hydrogenated to 40% completion in acetic acid over 5% rhodium-on-alumina. The residue which remained after removing the catalyst and solvent was dissolved in ethanol and treated with 2,4-dinitrophenylhydrazine. Crystals were obtained which melted at 157° after recrystallization from a methanol–water mixture. The derivative was analyzed as 4-hydroxycyclohexanone 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_{12}H_{14}N_4O_5$: C, 48.98; H, 4.80; N, 19.04. Found: C, 48.93; H, 4.71; N, 19.10.

This reaction established the fact that 4-hydroxycyclohexanone rather than 1,4-cyclohexanedione is the ketone formed during the hydrogenation of hydroquinone.

The ketones cyclohexanone and 1,3-cyclohexanedione were hydrogenated over both platinum oxide and 5% rhodium-on-alumina.

A modified Parr low pressure reduction apparatus was employed for all hydrogenation reactions. The general procedure was the same as that previously discussed.[7] Initial hydrogen pressure was approximately 50 p.s.i.g. with changes in pressure of 5 to 15 p.s.i. during the course of a reaction. As solvent, 25 ml. of glacial acetic acid was employed for all runs. The weights of catalyst and acceptor were 0.1–0.3 and 1.0 g., respectively. During each run the reaction bottle was enclosed in a metal jacket through which water from a constant temperature bath (±0.1°) was circulated.

The relationship between pressure drop and moles of hydrogen reacted was determined by the hydrogenation of benzoic acid which is known to require three moles of hydrogen per mole. Determination of the rate constant for benzoic acid hydrogenation with platinum oxide allowed a comparison of the rate constants with previous results with this catalyst.

(5) Since preparation of this article, this procedure has also been reported by B. Esch and H. J. Schaeffer, *J. Am. Pharm. Assoc., Sci. Ed.*, **49**, 786 (1960).

(6) W. Pritzkow, *Chem. Ber.*, **87**, 1668 (1954).

(7) H. A. Smith, D. M. Alderman and F. W. Nadig, *J. Am. Chem. Soc.*, **67**, 272 (1945); H. A. Smith and E. F. H. Pennekamp, *ibid.*, **67**, 276, 279 (1945).

Experimental Calculations

The hydrogenation of hydroxybenzenes was found to be first order with respect to hydrogen pressure, zero order with respect to concentration of hydrogen acceptor and directly proportional to the weight of catalyst used. The reaction rate is given by[8]

$$- dP/dt = kP/V$$

where P is the pressure, k is the specific rate constant, V is the volume of the system and t is time. Values of k were obtained by multiplying by $-2.303 V$ the slope of the straight line of a log P *vs.* t plot. All rate constants are referred to 1.0 g. of catalyst ($k_{1.0}$), the units of $k_{1.0}$ being liters/minute. As previously noted in catalytic hydrogenations, there was often a slow drift from linearity after 60–80% reaction. This was undoubtedly due to a poisoning or decay of the active catalyst surface. Rate constants were reproducible within 5%. Activation energies were obtained from the usual Arrhenius plots.

Results and Discussion

In platinum-catalyzed hydrogenations of benzene, methylbenzenes and methoxybenzenes (acetic acid solvent, ordinary pressures and temperatures), it has been shown that the reactions are first order in hydrogen pressure, zero order in concentration of acceptor and directly proportional to catalyst weight.[4,6] The same kinetic picture was exhibited by the hydroxybenzenes. The hydrogenation rates for methylbenzenes decrease with the number of substituents, so that the rate for benzene > toluene> *o*-xylene > hemimellitene. For compounds with the same number of substituents, the one with a symmetrical arrangement has the highest rate, the vicinal isomer has the lowest rate, and the unsymmetrical isomer an intermediate rate: *p*-xylene > *m*-xylene > *o*-xylene. There exists an overlapping of these factors such that a symmetrical compound with a number of substituents has a higher rate than a vicinal isomer with one less substituent: mesitylene > *o*-xylene. Similar behavior was noted for methoxybenzenes.[4]

As shown in Table I, the rate constants for the hydrogenation of hydroxybenzenes reveal the same effect of symmetry, number of substituents, etc., as for the methylbenzenes. The relative rates are

TABLE I

COMPARISON OF RATE CONSTANTS AT 30° FOR HYDROGENATIONS OVER PLATINUM

Compound	$k_{1.0}$[a]	$\dfrac{k_{hydroxyl}}{k_{methyl}}$[b]	$\dfrac{k_{hydroxyl}}{k_{methoxyl}}$[c]
Phenol	0.1620	0.90	1.02
Catechol	.1330	1.43	1.58
Resorcinol	.1611	1.12	1.59
Hydroquinone	.2072	1.10	1.29
Pyrogallol	.0951	2.26	2.11

[a] The $k_{1.0}$ is in l. g.$^{-1}$ min.$^{-1}$ and is given per unit weight of catalyst. [b] Calculated using data obtained from Smith and Pennekamp.[7] [c] Calculated using data obtained from Smith and Thompson.[4]

not only in the same order, but fair agreement in actual values also exists. An exception is found

(8) H. A. Smith and J. F. Fuzek, *J. Am. Chem. Soc.*, **70**, 3743 (1948).

with the trisubstituted compounds, where the hydroxyl compound hydrogenates about twice as rapidly as the methyl compound. It is interesting to note, too, that reduction of catechol is somewhat faster than that for o-xylene. Any difference in steric requirements would be manifested with these two compounds, and this probably accounts for the results observed here.

The correspondence between hydroxy- and methoxybenzene rate constants can also be seen from the data in Table I. The o- and m- dihydroxy compounds hydrogenate about 1.6 times as rapidly as the corresponding methoxyl compounds. This difference in rates may be attributable to the difference in size of the hydroxyl and methoxyl groups, but the extensive formation of ketones during the course of the hydrogenation of the hydroxybenzenes could be an equally important factor. Especially noteworthy is the fact that the ratio of the rate constants for hemimellitene and 1,2,3-trimethoxybenzene is about one, while the ratio of the rate constant for pyrogallol to either of these compounds is greater than two.

The rates of hydrogenation at 30° for the hydroxybenzenes using 5% rhodium-on-alumina show the same general effect of symmetry as observed for the corresponding compounds with platinum. Table II shows a comparison of the rate constants of hydroxybenzenes with those of methoxybenzenes over 5% rhodium-on-alumina. The relative rates are in the same order, and fair correspondence of values also exists.

TABLE II

COMPARISON OF RATE CONSTANTS AT 30° FOR HYDROGENATIONS OF HYDROXYBENZENES AND METHOXYBENZENES OVER 5% RHODIUM-ON-ALUMINA

Compound	$k_{1.0}{}^a$	$\frac{k_{hydroxyl}}{k_{methoxyl}}{}^b$
Phenol	0.0687	0.78
Catechol	.0145	.46
Resorcinol	.0311	.86
Hydroquinone	.0363	1.00

[a] The $k_{1.0}$ in l. g.$^{-1}$ min.$^{-1}$ and is given per unit weight of total catalyst. [b] Calculated from data obtained from Smith and Thompson.[4]

In Table III are shown the moles of hydrogen absorbed for each mole of compound hydrogenated. Included are values both for platinum and for 5% rhodium-on-alumina catalysts. Hydrogenation of

TABLE III

CLEAVAGE OF HYDROXYL GROUPS AS A FUNCTION OF TEMPERATURE

Compound	Over Adams platinum Temperature[a] 20°	30°	40°	50°	Over 5% Rh-on-alumina Temperature[a] 20°	30°	40°	50°
Phenol	3.19	3.22	3.31	3.38	3.04	3.01	2.99	3.04
Catechol	3.61	3.63	3.66	3.68	3.04	2.94	3.10	3.13
Resorcinol	3.91	4.00	4.03	4.07	3.07	3.16	3.16	3.16
Hydroquinone	3.95	3.97	4.05	4.05	3.29	3.18	3.14	3.21
Phloroglucinol	3.28	3.48	3.54	3.64	2.78	2.85	2.88	2.81
Pyrogallol	3.57	3.70	3.72	3.83	3.12	3.22	3.24	3.24

[a] Values are given in moles of hydrogen absorbed per mole of acceptor.

the ring requires three moles of hydrogen per mole of acceptor, while ring-hydrogenation accompanied by complete hydroxyl cleavage requires 4, 5 and 6 moles for the mono-, di- and trihydroxybenzenes,

respectively. It is obvious that the extent of cleavage is dependent upon both the catalyst and the temperature. Hydrogenolysis is quite extensive over Adams platinum catalyst and appears to be a linear function of reaction temperature. The results obtained indicate that the higher reaction temperature and use of platinum oxide catalyst promote cleavage, while low temperatures and the use of rhodium on alumina combine to retard cleavage during hydrogenation. It can also be seen from the data in Table III that the o-isomer undergoes less cleavage than the m- or p- isomers. This may be due to a slight steric inhibition of cleavage for the o-isomer. These results parallel those reported earlier for hydrogenation of methoxybenzenes over rhodium and platinum catalysts.[4]

Table IV shows the hydrogenation rates as a function of temperature for the hydroxybenzenes.

TABLE IV

REACTION RATES AND ACTIVATION ENERGIES FOR HYDROGENATIONS OF HYDROXYBENZENES

Compound	T, °C.	Over Adams platinum $k_{1.0}$, l. min.$^{-1}$	ΔH_a, kcal. mole^{-1}	Over 5% Rh-on-alumina $k_{1.0}$, l. min.$^{-1}$	ΔH_a, kcal. mole^{-1}
Phenol	20	0.1361	4.49	0.0445	6.61
	30	.1620		.0687	
	40	.2050		.1044	
	50	.2434		.1249	
Catechol	20	.1015	4.62	.0102	6.43
	30	.1330		.0145	
	40	.1748		.0211	
	50	.2281		.0282	
Resorcinol	20	.1177	5.51	.0177	7.84
	30	.1611		.0311	
	40	.2129		.0442	
	50	.2856		.0633	
Hydroquinone	20	.1571	4.40	.0221	6.49
	30	.2072		.0363	
	40	.2611		.0445	
	50	.3175		.0653	
Phloroglucinol	20	.0211	9.67	.00471	10.82
	30	.0378		.00807	
	40	.0614		.0150	
	50	.1001		.0263	
Pyrogallol	20	.0628	6.54	.00463	8.25
	30	.0951		.00757	
	40	.1390		.0116	
	50	.1687		.0174	

Activation energies were calculated from the "least-squares" slopes of activation energy plots. For each compound, the activation energy was greater for hydrogenation with the supported rhodium catalyst than with Adams platinum. The low rate constants and high activation energies for phloroglucinol may be attributed to resonance stabilization of this compound in the keto form.

The results reported here indicate that 2-hydroxy- and 4-hydroxycyclohexanone are formed during the hydrogenation of catechol and hydroquinone, respectively. No evidence for ketone formation was found in the hydrogenation of resorcinol. Kinetically speaking, cyclohexanone and 1,3-cyclohexanedione could be intermediates in the platinum-catalyzed hydrogenations of phenol and resorcinol, since the rate constants for these

TABLE V

COMPARISONS OF RATE CONSTANTS AND CLEAVAGES AT 30° FOR HYDROGENATIONS OF HYDROXYBENZENES AND KETONES

	Over Adams platinum			Over 5% Rh-on-alumina		
Compound	$k_{1.0}$, 1. min.$^{-1}$	Moles H$_2$ / Mole cmpd.	Moles H$_2$ / Mole, hydroxyl groups	$k_{1.0}$,, 1. min.$^{-1}$	Moles H$_2$ / Mole cmpd.	Moles H$_2$ / Mole, hydroxyl groups
Phenol	0.1620	3.22	0.22	0.0687	2.96	0.00
Cyclohexanone	.1937	1.12	.12	.0452	0.92	.00
Resorcinol	.1611	4.00	.50	.0311	3.16	.08
1,3-Cyclohexanedione	.1949	3.13	.56	.1081	2.13	.07

ketones are greater than the rate constants for the corresponding hydroxyl compounds; Table V. However, the rate constant for cyclohexanone is two-thirds that of phenol for hydrogenation over 5% rhodium-on-alumina (see Fig. 1). The kinetic behavior found for the hydrogenation of phenol rules out the possibility of cyclohexanone being an intermediate over this catalyst.
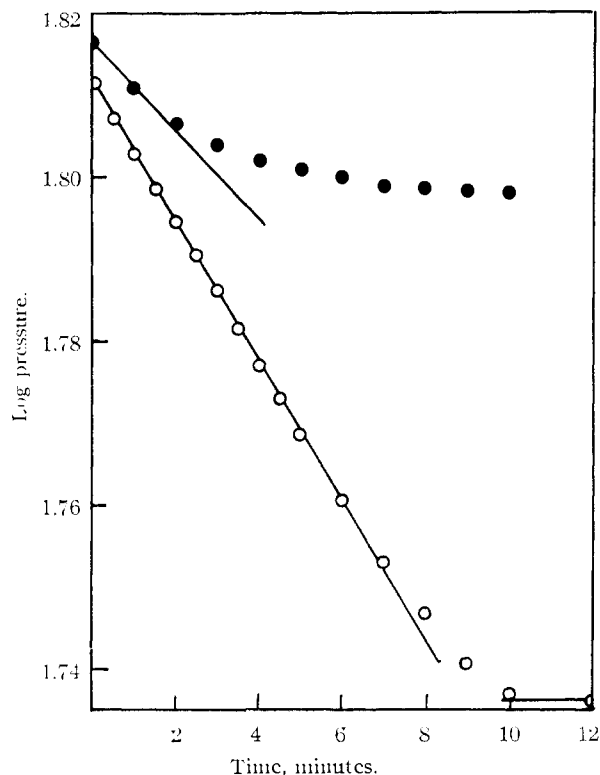
Fig. 1. Comparison of the rate of hydrogen absorption by phenol (O) and cyclohexanone (●) over 5% rhodium-on-alumina catalyst.

Over rhodium, 1,3-cyclohexanedione might be an intermediate in resorcinol hydrogenations, since the rate constant for this ketone is much greater than the rate constant for the hydroxyl compound. However, a consideration of Fig. 2 shows that this ketone hydrogenates stepwise, and the rate constant determined from the slope of the last portion of this curve is 1.8 times smaller than the rate constant for resorcinol. Too, the rate curve for the hydrogenation of resorcinol is linear over virtually the entire course of the reaction. This rules out the possibility that 1,3-cyclohexanedione is an intermediate in this hydrogenation.

Gilman and Cohn[9] included in their study of rhodium as a hydrogenation catalyst some experiments

with hydroxybenzenes. They observed an increase in rate of reduction of hydroquinone and resorcinol when the reaction was approximately five-sixths completed. This increase was not observed in the experiments reported here. It should be noted that Gilman and Cohn employed water as a solvent.
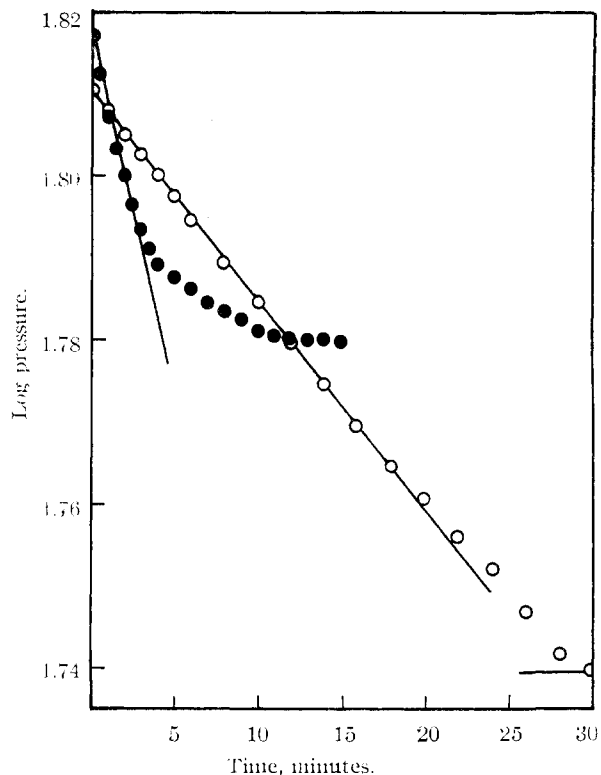

Fig. 2. Comparison of the rate of hydrogen absorption by resorcinol (O) and 1,3-cyclohexanedione (●) over 5% rhodium-on-alumina catalyst.

From the data which have been collected on the hydrogenation and hydrogenolysis of hydroxybenzenes, the following reaction mechanism is suggested. The hydroxybenzene, phenol for example, is adsorbed on the catalyst surface where hydrogenation takes place to give hydroxycyclohexenes as short-lived intermediates. These short-lived intermediates may or may not be desorbed from the catalyst surface, i.e., the hydroxycyclohexene may react with an additional mole of hydrogen to give a cyclohexanol without desorbing into the reaction mixture where it would compete with the unreacted phenol for adsorption. The intermediate hydroxycyclohexene may undergo cleavage to cyclohexene and water or ring hydrogenation to

(9) G. Gilman and G. Cohn, "Advances in Catalysis, Vol. IX," Academic Press, Inc., New York, N. Y., 1957, p. 736.

give cyclohexanol. The reactions probably occur simultaneously until the double-bonded molecules are saturated.
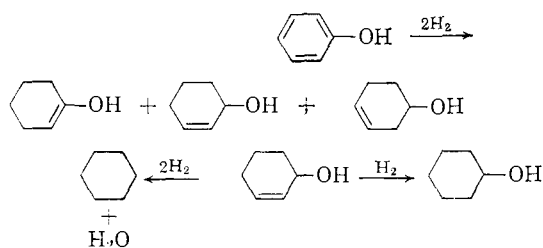

Three hydroxycyclohexene intermediates are possible, and these are shown above. The 1-hydroxy-cyclohexene-1 is the tautomeric form of cyclohexanone.
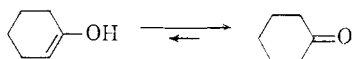
This tautomerization would be expected to take place since the keto form is more stable than the enol form by about 18 kcal. mole^{-1}.[3] This could account for the presence of ketones in the reaction mixture without claiming that cyclohexanone is a reaction intermediate in the usual sense.

Similar reaction routes for the dihydroxybenzenes can be shown to explain the results obtained in the course of this study. Consider as an example the reaction route for the hydrogenation of catechol
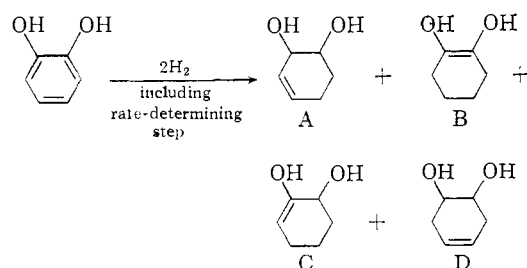
Intermediates B and C undergo tautomerization to 2-hydroxycyclohexanone

when desorbed from the catalyst into the reaction mixture. Experiments performed during this research have shown that 2-hydroxycyclohexanone is formed during the hydrogenation of catechol. Intermediate A has a double-bond β-γ to a hydroxyl group and renders this group labile to hydrogenolysis. Intermediate D makes the least contribution to the over-all reaction. If steric factors are important at all in determining the course of the reaction, intermediate B would be expected to predominate. This would account for the fact that catechol cleaves less rapidly than do resorcinol and hydroquinone.

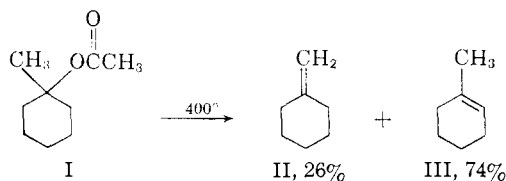## Pyrolytic cis Eliminations. II. Eliminations of Axial and Equatorial Acetates[1]

BY C. H. DEPUY AND R. W. KING

cis- and trans-1-methyl-4-t-butylcyclohexyl acetates have been prepared and a study made of the relative amounts of exo and endo olefin formed in the pyrolyses of these conformationally pure esters. It was shown that there are no conformational effects on the direction of elimination in the pyrolysis of these esters, both isomers giving the same exo/endo product ratio as was found in the pyrolysis of 1-methylcyclohexyl acetate. Relative rate studies on these same two acetates and on cis- and trans-4-t-butylcyclohexyl acetate showed that the ease of pyrolysis depends mainly on the ground state energy of the acetates, since with the 1-methyl-4-t-butylcyclohexyl acetates the equatorial ester undergoes elimination more readily, while the axial ester is the more reactive of the 4-t-butylcyclohexyl acetates.

When 1-methylcyclohexyl acetate (I) is pyrolyzed at 400°, it is smoothly converted into a mixture of methylenecyclohexane (II) and 1-methylcyclohexene (III). Although it was at first thought that the former of these olefins was the predominant product of this elimination, more recent studies

have shown that the internal olefin III makes up 74% of the olefinic product.[2] The preponderance of 1-methylcyclohexene has been ascribed to the fact that pyrolytic eliminations from esters have transition states with appreciable double bond character[3] and that the well-known greater stability of internal over external olefins in the cyclohexane series[4] accounts for its ease of formation. Nevertheless, in more complicated systems exo olefin has been reported to be the major product of elimination. Thus Maali acetate (IV) decomposes

(1) Part I, C. H. DePuy, C. A. Bishop and C. N. Goeders, J. Am. Chem. Soc., **83**, 2151 (1961). This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) (a) D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, ibid., **81**, 643 (1959); (b) W. J. Bailey and W. F. Hale, ibid., **81**, 651 (1959); (c) R. A. Benkeser and J. J. Hazdra, ibid., **81**, 228 (1959).

(3) C. H. DePuy and R. W. King, Chem. Revs., **60**, 431 (1960).

(4) H. C. Brown, J. H. Brewster and H. Shechter, J. Am. Chem. Soc., **76**, 467 (1954).