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The Catalytic Hydrogenation of the Benzene Nucleus. VI. The Hydrogenation of Compounds with Two Benzene Rings

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In earlier publications in this series, the kinetics of the catalytic hydrogenation of the benzene nucleus in compounds containing only one phenyl group have been reported. The purpose of the present paper is to report similar studies on a number of compounds containing more than one such group. In a compound such as diphenyl or diphenylmethane, the hydrogenation curve shows no discontinuity at the half-hydrogenation point, when the reaction is carried out in acetic acid using Adams platinum catalyst. This might be due to the fact that once the compound is adsorbed on the catalyst, both rings are reduced before desorption occurs. If, on the other hand, the reaction proceeds by steps, with all of the original compound being hydrogenated to an intermediate containing one phenyl and one cyclohexyl group, and subsequently the intermediate being hydrogenated to the fully reduced product, then the lack of a break in the hydrogenation curve could only be explained if the rates of hydrogenation of the original and the intermediate compounds were the same.

The rates for diphenylacetic acid and phenylcyclohexylacetic acid have already been reported,[1] and are equal, within experimental error. The hydrogenation of methyl and ethyl diphenylacetate has also been studied by two other workers using nickel catalysts.[2,3] The hydrogenation was reported to proceed only as far as the ester of phenylcyclohexylacetic acid, although the second benzene nucleus can be reduced in the presence of platinum. Methyl benzilate could also be reduced only to the methyl ester of phenylcyclohexylacetic acid when nickel was used as a catalyst. Miescher and Hoffmann[4] have reported that benzilic acid can be hydrogenated to phenylcyclohexylglycolic and dicyclohexylglycolic acids using platinum as a catalyst. However, experimental details are not given, and there is some question as to the identity of their products.

Experimental

Diphenyl, diphenylmethane, dibenzyl, diphenylacetic acid, mandelic acid, and triphenylmethane were obtained from the Eastman Kodak Company. The diphenyl was recrystallized from methanol and then distilled through an 18-inch Vigreux column. Dibenzyl and triphenylmethane were recrystallized from ethanol. The diphenylmethane was fractionated before use. Mandelic acid and diphenylacetic acid were used directly. 1,1-Diphenylethane was obtained by the catalytic hydrogenation over nickel of 1,1-diphenylethylene, which had been prepared from bromobenzene and ethyl acetate by a Grignard reaction.[5] The diphenylethane was fractionated in an eight-foot Vigreux column. **1,6-Diphenylhexane** was prepared from γ-phenyl-*n*-propyl alcohol, which was converted to the bromide using phosphorus tribromide, and thence to the desired product by means of sodium in dry ether.[6] The product was fractionated in a small Vigreux column.

Phenylcyclohexylmethane, 1-phenyl-1-cyclohexylethane, cyclohexyldiphenylmethane, and phenylcyclohexylacetic acid were all prepared by partial hydrogenation of the corresponding diphenyl or triphenyl compound. **Phenylcyclohexane** was synthesized from cyclohexene and benzene.[7] The product was fractionated in the eight-foot column.

Benzilic acid was prepared as follows: Benzoin was prepared from benzaldehyde by the method of Adams and Marvel.[8] This was converted to benzil by oxidation with nitric acid.[9] Rearrangement to benzilic acid using alcoholic potassium hydroxide[10] with subsequent recrystallizations from benzene, water, and methanol-water mixtures gave a product which melted from 148–150°. Oxidation of the benzoin by the method of Ballard and Dehn[11] with subsequent conversion to benzilic acid and recrystallization gave a product with similar melting range. A sample of benzilic acid was converted to ethyl benzilate by the reaction of potassium benzilate with ethyl iodide. The ester was fractionated under reduced pressure in an eight-foot Vigreux column, and the middle 60% of the distillate saponified. The acid obtained from this process was treated with active charcoal (in ethanol solution), and recrystallized three times from benzene, three times from methanol-water mixtures, and twice from ligroin. The resulting material melted from 148–150° as before. It was concluded that the melting range was caused by decomposition of the acid, and not by extraneous impurities.

Phenylcyclohexylglycolic acid was prepared as follows: Benzoyl cyanide (100 g.)[12] was dissolved in 400 ml. of absolute ethanol, and the solution saturated at 10° with hydrogen chloride. After standing five days it was diluted with water, and extracted with ether. The ether layer was washed with sodium bicarbonate solution and distilled under reduced pressure, yielding 56 ml. of ethyl phenylglyoxylate, b. p. 105–106° (1 mm.). To 40 g. of this ester dissolved in dry ether was added slowly with vigorous stirring a solution of cyclohexylmagnesium bromide[13] made from one mole of bromocyclohexane and one equivalent of magnesium. The mixture was heated under reflux for one hour, poured into a mixture of ice and dilute sulfuric acid and the ether layer dried and evaporated. The remaining liquid was distilled under reduced pressure, yielding 45 ml. of ethyl phenylcyclohexylglycolate, b. p. 172–173° (10 mm.). Thirty grams of phenylcyclohexylglycolic acid was obtained from this ester by saponifica-

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[1] Smith, Alderman and Nadig, THIS JOURNAL, **67**, 272 (1945).

[2] Miescher and Hoffmann, *Helv. Chim. Acta*, **24**, 458 (1941); *cf.* Swiss Patent 217,225.

[3] L. Sandoval, *Ciencia* (*Mex.*), **4**, 107 (1943).

[4] Miescher and Hoffmann, U. S. Patents 2,265,184 and 2,265,185.

[5] Allen and Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1941, p. 226.

[6] The authors are indebted to Mr. Sigmund Wolfson who carried out this preparation.

[7] Corson and Ipatieff, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 151.

[8] Adams and Marvel, *Org. Syntheses*, **1**, 33 (1920).

[9] *Ibid.*, **1**, 25 (1920).

[10] *Ibid.*, **1**, 29 (1920).

[11] Ballard and Dehn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 89.

[12] Oakwood and Weisgerber, "Org. Syntheses," **24**, 14 (1944).

[13] Gilman and Zoellner, THIS JOURNAL, **53**, 1945 (1931).

TABLE I

BOILING POINTS, MELTING POINTS AND NEUTRAL EQUIVALENTS OF COMPOUNDS HYDROGENATED

Reactant	B. p. cor. °C.	Mm.	M. p. cor., °C.	Neutral equivalent Found	Neutral equivalent Theory
Diphenyl			68.9–69.6		
Diphenylmethane	264.0	743	26.6		
1,1-Diphenylethane	150.9–151.4	29			
Dibenzyl			52.5–53.0		
1,6-Diphenylhexane	203.8–204.1	16			
Triphenylmethane			92.6–93.8		
Phenylcyclohexane	135.2	46.5			
Phenylcyclohexylmethane	132.7	19			
1-Phenyl-1-cyclohexylethane	131.6	10			
Cyclohexyldiphenylmethane			62.0–63.6		
Diphenylacetic acid[a]			147.5	212.0	212.2
Di-(γ-phenylpropyl)-acetic acid[a]			52.5	294.2	296.4
Phenylcyclohexylacetic acid			142.5	217.7	218.3
Benzilic acid			148–150	228.0	228.2
Phenylcyclohexylglycolic acid			167–168	234.0	234.3
Mandelic acid			120.3–120.8	151.9	152.1

[a] Smith, Alderman and Nadig, THIS JOURNAL, 67, 272 (1945).

TABLE II

MELTING POINTS, BOILING POINTS AND NEUTRAL EQUIVALENTS OF HYDROGENATION PRODUCTS

Completely reduced product	B. p. cor. (distn. temp.) °C.	Mm.	M. p. cor.	Neutral equivalent Found	Neutral equivalent Theory
Dicyclohexyl	131.4–132.0	31			
Dicyclohexylmethane	131.0	19			
1,1-Dicyclohexylethane	128.4–128.8	10			
1,2-Dicyclohexylethane	273.6	736			
1,6-Dicyclohexylhexane	197.6–198.0	16			
Tricyclohexylmethane	200.7	7	58.2–59.4		
Dicyclohexylacetic acid[a]			138.6	224.8	224.3
Di-(γ-cyclohexylpropyl)-acetic acid[a]			49.0	309.9	308.5
Dicyclohexylglycolic acid			173	240	240.3
Cyclohexylglycolic acid			137.2–137.6	158.7	158.2

[a] Smith, Alderman and Nadig, THIS JOURNAL, 67, 272 (1945).

tion procedures. The acid, when recrystallized from benzene and methanol–water mixtures, melted from 167–168°, and had a neutral equivalent of 234. Upon hydrogenation, it yielded dicyclohexylglycolic acid.

Dicyclohexylglycolic acid was obtained in 97-99% yields by hydrogenation of either benzilic acid or the phenylcyclohexylglycolic acid using platinum catalyst and acetic acid solvent. If the recrystallized acid was heated slowly, it underwent a change of state at 160°. The crystals melted, and almost immediately recrystallized in a different modification. The resulting solid melted sharply at 173°. Miescher and Hoffmann[1] claim a melting point of 143–144° while Danilow and Venus-Danilowa[14] obtained a value of 162–163°. For proof of structure of the compound resulting from this research, the following evidence was obtained: neutral equivalent, 240 (theoretical 240); molecular weight by boiling point elevation in ethyl acetate, 239 (theoretical 240). Reaction with methylmagnesium iodide showed two active hydrogens. The product obtained by complete hydrogenation over Raney nickel at 150° was dicyclohexylacetic acid, m. p. 138°, mixed melting point with an authentic sample, 138°.

Table I gives the reactants used together with their melting points, boiling points, and neutral equivalents.

The acetic acid used as a solvent in hydrogenation runs was prepared by fractionation in a five-foot helix-packed still. The platinum catalyst was prepared by standard methods.[15] The hydrogenations were carried out in a standard low-pressure Parr catalytic reduction apparatus.

After the reaction was complete, the product was recovered either by distilling the acetic acid solvent or by diluting it with water to make the product insoluble. The product was then recrystallized or distilled. The pertinent data are given in Table II.

Experimental Calculations and Results

As in previous hydrogenation experiments dealing with the benzene nucleus, all of the reactions were zero order with respect to the hydrogen acceptor, first order with respect to hydrogen pressure, and directly proportional to the weight of catalyst used. Therefore rate constants were calculated from the equation

$$\log p^0_{H_2}/p_{H_2} = kt/2.303\ V$$

where $p^0_{H_2}$ represents the initial hydrogen pressure, p_{H_2} represents the hydrogen pressure at time t, and V is the volume of the hydrogen gas in the system. Individual values of the rate constant, k, were obtained by plotting $\log p^0_{H_2}/p_{H_2}$ against t, and multiplying the slope of the line thus ob-

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[14] Danilow and Venus-Danilowa, *Ber.*, **62**, 2653 (1929).

[15] Adams, Voorhees and Shriner, "Org. Syntheses," **8**, 92 (1928).

tained by $2.303V$.[16] Figure 1 shows typical plots from which rate constants were calculated. These constants, all referred to one gram of standard catalyst,[1] are given in Table III. The values are given at 30°, although the actual runs were made at temperatures varying from 25 to 32.5°. Corrections to 30° were made by means of the Arrhenius equation, using an activation energy of 7400 calories per mole.[17]

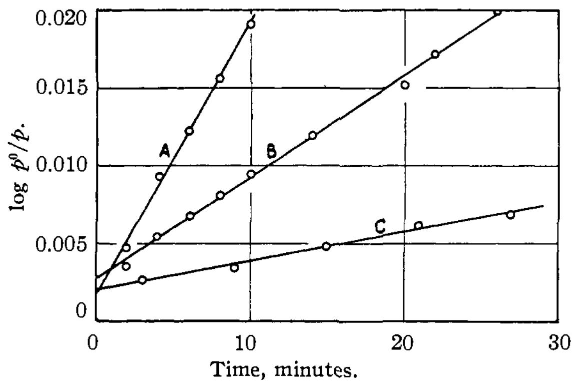

Fig. 1.—Hydrogenation plots for A, dibenzyl; B, diphenyl; and C, cyclohexyldiphenylmethane. For each run, 50 ml. of acetic acid, 0.2 g. of PtO_2 and 64 p. s. i. initial H_2 pressure were employed.

Discussion of Rate Data

An examination of the results given in Table III indicates two significant facts. First, substitution of a benzene nucleus into a molecule already containing one such nucleus usually causes a considerable decrease in the hydrogenation rate. This fact is clearly shown in Table IV. It appears that, in general, the retarding influence is reduced as the phenyl groups are removed farther away from each other.

TABLE III

RATE CONSTANTS FOR THE HYDROGENATION OF COMPOUNDS STUDIED

Compound	*k* (liters/g. min.)
n-Alkylbenzenes[a]	0.1152
Biphenyl	.0541
Diphenylmethane	.0629
1,1-Diphenylethane	.0474
1,2-Diphenylethane (dibenzyl)	.0806
1,6-Diphenylhexane	.1143
Triphenylmethane	.0135
Phenylcyclohexane	.0614
Phenylcyclohexylmethane	.0665
1-Phenyl-1-cyclohexylethane	.0366
Cyclohexyldiphenylmethane	.0129
Phenyl-substituted normal aliphatic acids[b]	.1108
Diphenylacetic acid[b]	.0182
Di-(phenylpropyl)-acetic acid	.0554
Benzilic acid	.0146
Mandelic acid	.0481
Phenylcyclohexylacetic acid[b]	.0191
Phenylcyclohexylglycolic acid	.0163

[a] For propylbenzenes and higher homologs. *Cf.* Smith and Pennekamp, THIS JOURNAL, **67**, 276 (1945). [b] *Cf.* Smith, Alderman and Nadig, *ibid.*, **67**, 272 (1945).

The second interesting result is shown clearly in Table V. It appears that the substitution of a cyclohexyl group for a phenyl group has essentially no influence on the rate of hydrogenation. With the exception of 1,1-diphenylethane, the substitution of a cyclohexyl for a phenyl group results in a value of the rate constant which is unchanged almost within experimental error. It is possible that a trace of catalyst poison is responsible for the one exception, although great care was taken to prevent this.

These results can be explained if one assumes that only one benzene nucleus is adsorbed on the catalyst in any of the polyphenyl compounds, and that the remaining nucleus decreases the rate because of steric factors. Thus, an increase in the number of benzene nuclei would cause a decrease in the hydrogenation rate and, in addition, the substitution of the cyclohexyl group for the phenyl group would have little influence. This suggestion is particularly interesting in reference to biphenyl, where the two benzene rings are in resonance with each other, and where one would probably expect that both of these groups would be simultaneously adsorbed on the catalyst surface in a flat position. However, it has already been suggested that resonance in a single benzene ring is destroyed when adsorption on platinum takes place,[17] and a similar condition would probably be indicated for the biphenyl molecule.

Partial Hydrogenation Experiments

In view of the previous finding that the substitution of a cyclohexyl group for one of the phenyl groups in a polyphenyl compound did not affect the rate of hydrogenation, it follows that rate measurements can give no evidence as to whether these compounds are hydrogenated completely before they are desorbed from the catalyst, or whether one phenyl is hydrogenated, the compound then desorbed, and subsequently the other phenyl or phenyls are reduced. In order to investigate the mechanism of hydrogenation of such materials, several polyphenyl compounds were hydrogenated to that point which would be equivalent to the saturation of one ring only. The hydrogenations were then stopped, and the products analyzed. Four methods of analysis were used; they were fractional distillation, spectrophotometry, esterification and identification of the products.

The half-hydrogenation products of biphenyl, diphenylmethane, 1,1-diphenylethane and 1,2-diphenylethane were analyzed by fractional distillation methods. Figure 2 shows the results for diphenylmethane and Figure 3 those for biphenyl. The fractionations were carried out in a

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(16) Fuzek and Smith, THIS JOURNAL, **70**, 3743 (1948).

(17) Smith and Meriwether, *ibid.*, **71**, 413 (1939).

TABLE IV

INFLUENCE OF PHENYL SUBSTITUTION ON HYDROGENATION RATE

Mono-substituted	k_m	Di-substituted	k_d	Ratio, k_m/k_d
Benzene	0.290	Biphenyl	0.0541	5.4
Toluene	.178	Diphenylmethane	.0629	2.8
Ethylbenzene	.130	1,1-Diphenylethane	.0474	2.7
Diphenylmethane	.0629	Triphenylmethane	.0135	4.7
Phenylcyclohexylmethane	.0665	Cyclohexyldiphenylmethane	.0129	5.2
Phenylacetic acid	.1108	Diphenylacetic acid	.0182	6.1
Mandelic acid	.0481	Benzilic acid	.0146	3.3
Ethylbenzene	.130	1,2-Diphenylethane	.0806	1.6
n-Hexylbenzene	.115	1,6-Diphenylhexane	.1145	1.0

TABLE V

COMPARISON OF RATES OF HYDROGENATION OF CORRESPONDING PHENYL- AND CYCLOHEXYL-SUBSTITUTED COMPOUNDS

Phenyl-substituted	k_p	Cyclohexyl-substituted	k_c	Ratio k_p/k_c
Biphenyl	0.0541	Phenylcyclohexane	0.0614	0.88
Diphenylmethane	.0629	Phenylcyclohexylmethane	.0665	0.95
1,1-Diphenylethane	.0474	1-Phenyl-1-cyclohexylethane	.0366	1.3
Triphenylmethane	.0135	Diphenylcyclohexylmethane	.0129	1.05
Diphenylacetic acid	.0182	Phenylcyclohexylacetic acid	.0191	0.95
Benzilic acid	.0146	Phenylcyclohexylglycolic acid	.0163	0.90

twenty-inch Vigreux column. The platinum catalyst was filtered from the acetic acid solution of the partially hydrogenated material, and the solvent removed by distillation in the same column. A synthetic mixture containing diphenylmethane and dicyclohexylmethane, and one containing 1,1-diphenylethane and 1,1-dicyclohexylethane were also fractionated in order to show that separation could be achieved with the apparatus employed.

The results of the fractionation experiments showed that the half-hydrogenated products of diphenylmethane and 1,1-diphenylethane were essentially pure phenylcyclohexylmethane and 1-phenyl-1-cyclohexylethane respectively. Half-hydrogenated diphenyl yielded about 60% of phenylcyclohexane. The distillation curve for 1,2-diphenylethane was unsatisfactory for analytical purposes, but indicated that a mixture was present.

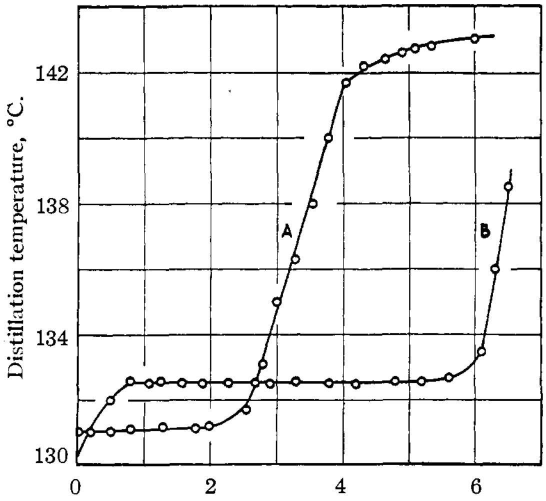

Fig. 2.—Distillation curves at 19 mm. pressure: A, synthetic mixture of 3 ml. of dicyclohexylmethane plus 4 ml. of diphenylmethane; B, 6.5 ml. of half-hydrogenated diphenylmethane.

Analysis of half-hydrogenated diphenylacetic acid depended on the fact that diphenylacetic acid is esterified at a measurable rate under conditions where dicyclohexylacetic acid is not esterified at all.[18] If one assumes that phenylcyclohexylacetic acid does not esterify at all, then the total esterification rate of a mixture of the three acids will be caused by any diphenylacetic acid present.

Two samples of diphenylacetic acid were hydrogenated until an amount of hydrogen gas equivalent to half that necessary to saturate both rings had been adsorbed. The catalyst was removed by filtration, and the acetic acid solvent

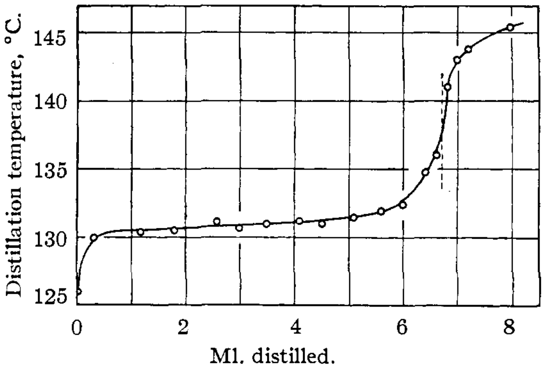

Fig. 3.—Distillation of 8.5 ml. of half-hydrogenated diphenyl; fraction between 0 and 6.7 ml. is a mixture of dicyclohexyl and phenylcyclohexane; remainder is diphenyl.

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[18] Smith and Burn, THIS JOURNAL, **66**, 1494 (1944).

completely evaporated. Esterification analyses were made by treating samples from each run with methanol at 50° in the presence of hydrochloric acid catalyst. The method was essentially that used in earlier experiments,[18] except that the concentrations of organic acid and of catalyst were different from those previously used. Runs were made under comparable conditions with diphenylacetic acid, mixtures of diphenylacetic and dicyclohexylacetic acids, and with phenylcyclohexylacetic acid. The results are given in Table VI.

Table VI

Esterification of Diphenylacetic Acid and Hydrogenated Products in Methanol

For all runs, the temperature was 50.0° and the concentration of the HCl catalyst was 0.01 *M*.

Material esterified	Original concn., moles/liter	Rate constant[a]
Diphenylacetic acid	0.10	0.00957
Diphenylacetic acid plus phenylcyclohexylacetic acid	.05 .05	.00490
Half-hydrogenated diphenylacetic acid, no. 1	.10[b]	.00059
Half-hydrogenated diphenylacetic acid, no. 2	.10[b]	.00047
Phenylcyclohexylacetic acid	.10	.00054

[a] The rate constants were calculated from the equation

$$k = \frac{(r + a)\ln a/(a - x) - x}{(\text{catalyst})rt}$$

where a is the initial concentration of organic acid, x is the concentration of ester formed after time, t, and $r = 0.42$ [*cf.* Smith and Reichardt, This Journal, **63**, 605(1941)]. The units of the rate constants are liters moles^{-1} sec.^{-1}
[b] These concentrations were calculated assuming a molecular weight of 218.3.

On the basis of the runs with diphenylacetic acid, it appears that the half-hydrogenated product can have a maximum of 5% of this material, and hence a minimum of 90% phenylcyclohexylacetic acid. The experiments with samples of the latter acid indicate that essentially all of the esterification rate can be accounted for by the reactivity of this material and hence the half-hydrogenated product is essentially pure phenylcyclohexylacetic acid.

When triphenylmethane was reduced with enough hydrogen to saturate only one benzene ring, the platinum filtered out, and the acetic acid solution poured into water, an oily layer separated which on standing in the refrigerator for several days became crystalline. The melting range of the crystalline material indicated that it was primarily a single compound. When recrystallized several times from methanol, the product melted at 62.0–63.6°. The literature reports a melting point of 56.5° for diphenylcyclohexylmethane.[19]

When di-(phenylpropyl)-acetic acid was half-hydrogenated, and the product recovered in the usual manner, an oily layer was obtained which could not be crystallized. This was thought to indicate that a mixture was present.

The half-hydrogenated benzilic acid was analyzed by a colorimetric method, details of which will be given later. The analysis showed that approximately 65% of the material present when enough hydrogen had been taken up to reduce one benzene nucleus was phenylcyclohexylglycolic acid.

Thus, for every compound for which satisfactory analysis was made, the partial hydrogenation product was found to be mainly a compound with only one ring saturated, and in three cases this was essentially the only material present. It would appear that the polyphenyl compound must be desorbed after one ring is saturated, and that the original material is adsorbed in preference to the partially saturated material, even though the rates of hydrogenation of the two are the same. If the differences in these adsorptions are sufficiently great, one may obtain practically pure material with only one saturated benzene nucleus.

The fact that, on nickel catalyst, the esters of diphenylacetic and benzilic acids may be hydrogenated only as far as the esters of phenylcyclohexylacetic acid[2,3] may be explained on the same basis.

Summary

The kinetics of the catalytic hydrogenation of sixteen compounds each containing more than one benzene nucleus have been investigated. All hydrogenations were carried out in acetic acid solution using Adams platinum catalyst, and first order rate constants referred to one gram of standard catalyst were tabulated.

The results indicate that, in general, the rate of hydrogenation decreases with the number of phenyl groups present. In addition, substitution of a cyclohexyl group for a phenyl group has no influence on the rate of hydrogenation.

Partial hydrogenation experiments indicate that the mechanism of the hydrogenation of compounds containing several nuclei is a stepwise reaction involving saturation of only one benzene nucleus at a time. In some cases it is possible to isolate intermediate cyclohexyl compounds in almost the theoretical quantities even though no change in rate occurs.

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[19] Schmidlin and von Escher, *Ber.*, **45**, 892 (1912).