unidirectional and fast as shown, *i.e.*, if it were rate determining or were reversible, then change in the alcohol concentration or addition of excess alkoxide ion should have a significant effect on the reduction rate. Pick up of the second electron is considered rate determining[12]; as observed, the presence of a negative charge on the substrate slows the reaction; albeit obscurely, oxygen could assist in the electron transfer here.

(12) It is likely that the pick up of protons is faster than of electrons because of the negatively charged substrate used in this work. For reduction of neutral species protonation could be the slow step.

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KNOXVILLE, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

The Stereochemistry of Hydrogenation of Isomers of Methyl Tetrahydrophthalate and Methyl Phthalate[1,2]

BY SAMUEL SIEGEL AND GEORGE S. MCCALEB

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The hydrogenation of methyl phthalate or methyl Δ^1-cyclohexenedicarboxylate, in the presence of platinum oxide in acetic acid at room temperature yields only *cis*-methyl hexahydrophthalate. The result is independent of the pressure of hydrogen (1 to 200 atm.) and the concentration of the substrate (0.05 to 1.0 mole per liter). Methyl Δ^2-cyclohexenedicarboxylate yields the same result at about 1 atm. of hydrogen, but some of the *trans*-methyl hexahydrophthalate (6 ± 2%) is formed at a pressure of 130 atm. None (within 2%) of the isomeric unsaturated ester is found at the half point of reduction of either the Δ^1- or the Δ^2-ester. The results are consistent with the hypothesis that the hydrogenation of an aromatic compound proceeds stepwise, one of the possible intermediates being the tetrahydro derivative; *e.g.*, the stereochemical evidence does not require that an aromatic ring be saturated during a single period of residence on the catalyst.

The investigation of the stereochemistry of the hydrogenation of methyl phthalate and two isomeric methyl tetrahydrophthalates is part of a program to examine systematically the stereochemistry of the catalytic hydrogenation of aromatic and hydroaromatic compounds.[3] Although considerable data relating to this question are available, it is not sufficiently detailed to be of much use in advancing our understanding of the mechanism of this reaction beyond the qualitative stage which exists at present.[4]

Our first paper in this series[3] dealt with the stereochemistry of hydrogenation of the isomeric xylenes and tetrahydroxylenes. These compounds yield mainly the *cis* isomers of dimethylcyclohexane when reduced in acetic acid in the presence of platinum oxide at room temperature. The largest proportions of the *cis* product are obtained from *o*-xylene (95%) and 1,2-dimethylcyclohexene (82%). This predominance of *cis* products diminishes with the distance separating the substituents, *e.g.*, *m*-xylene, 86% *cis;* and *p*-xylene, 74% *cis*. Because the saturated products do not isomerize under the experimental conditions, the mixture must be formed directly during the reduction of the unsaturated compounds.

Although the isomerization of 1,2-dimethylcyclohexene was not detected under the conditions of the experiment, it yields approximately 18% of *trans*-dimethylcyclohexane. Consequently, the hydrogenation of the olefin must be stepwise, rather than the simultaneous addition of two atoms of hydrogen to one side of the double bond. An intermediate stage in the reduction must provide a path for the formation of both *cis* and *trans* isomers. This is consistent with the mechanistic concepts of Horiuti and Polanyi.[5] The fact that more *trans*-1,3-dimethylcyclohexane than is present in an equilibrium mixture is obtained upon hydrogenating *m*-xylene is evidence that the hydrogenation of the aromatic ring proceeds in steps also, rather than by the simultaneous addition of six hydrogen atoms.[6]

In the present study, the hydrogenation of methyl phthalate, methyl Δ^1-cyclohexenedicarboxylate and methyl Δ^2-cyclohexenedicarboxylate was investigated using platinum oxide as a catalyst and in the solvent acetic acid. The object was to determine whether the ester group gives rise to stereochemical results significantly different from those obtained with methyl groups as substituents on the unsaturated substrates.

The only product formed in the presently described hydrogenations of methyl phthalate or the Δ^1-ester is *cis*-methyl hexahydrophthalate. The result is independent of the pressure of hydrogen (1–200 atmospheres) and the concentration of the substrate (0.05–1.0 mole per liter). Methyl Δ^2-cyclohexenedicarboxylate yields the same result at about 1 atmosphere of hydrogen, but some of the *trans*-methyl hexahydrophthalate (6 ± 2%) is formed at a pressure of 130 atmospheres. None (within 2%) of the isomeric unsaturated ester is found at the half point of reduction of either the Δ^1-

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(2) Presented before the division of Organic Chemistry at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958. Abstracted from the M.S. thesis of George S. McCaleb, University of Arkansas, January, 1958.

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or the Δ^2-ester. This is established through gas-liquid partition chromatography and the examination of the ultraviolet spectra of the appropriate materials.

Cursory examination of the data in Table I shows that *trans*-methyl cyclohexanedicarboxylate is produced on reducing the Δ^2-isomer. However, at a pressure of hydrogen of 1 atmosphere, this is due to the presence in the samples used of an impurity (3%) probably *trans*-methyl Δ^3-tetrahydrophthalate which on reduction would give the *trans*-hexahydro derivative. It is reasonable to expect that the Δ^3-ester should hydrogenate more rapidly than either the Δ^1- or Δ^2-isomers because, like the Δ^4-isomer which reacts much faster than the Δ^1- or Δ^2-isomers (see Fig. 1), it has no ester group attached

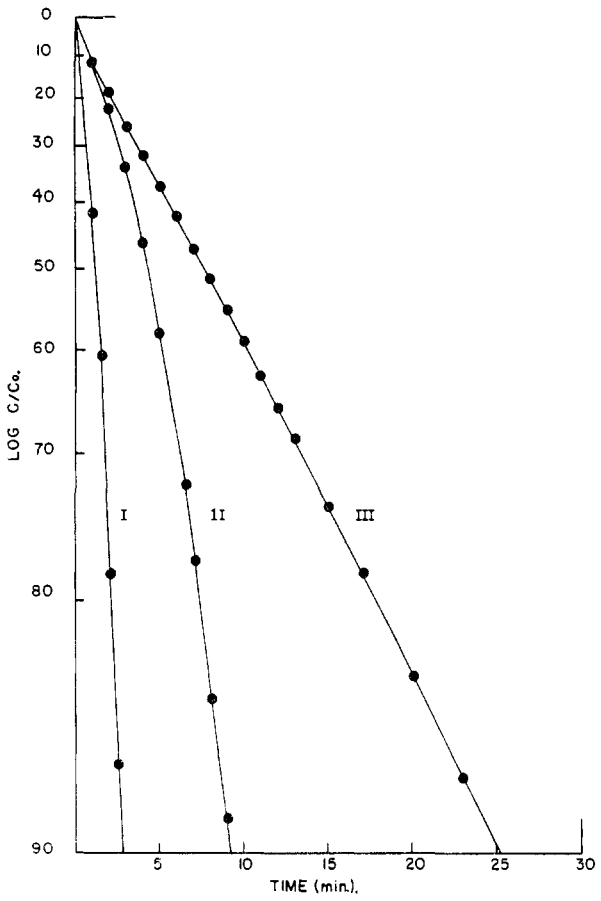

Fig. 1.—Hydrogenation of the Δ^4, Δ^2- and Δ^1-methyl tetrahydrophthalates: I, *cis*-methyl Δ^4-tetrahydrophthalate; II, methyl Δ^2-tetrahydrophthalate; III, methyl Δ^1-tetrahydrophthalate.

to the double bond. Consequently, the impurity should be completely reduced when the hydrogenation is interrupted at 50% of completion. Indeed, none was detected at this point by chromatography, and continued reduction produced exclusively the *cis*-methyl hexahydrophthalate.

In one experiment (number 25), the hydrogenation of methyl Δ^2-tetrahydrophthalate with a pressure of hydrogen of 136 atmospheres gave only 90% of the expected *cis* compound. The presence of *trans* isomer (7 out of 10%) cannot result from the isomerization of the *cis* isomer after its formation

TABLE I

HYDROGENATION PRODUCTS (*cis*- AND *trans*-METHYL HEXAHYDROPHTHALATES)[a]

Experiment	Substrate	Concn., mole/L	*cis*-Isomer,[b] % D.O.S.	P.P.G.
5	Methyl Δ^1-tetrahydrophthalate	0.050	100	100
8		.050[c]	..	100
7		.050[c]	100	100
6		.050	..	100
18		.500[c]	100	100
27	Methyl Δ^2-tetrahydrophthalate	.020	96	96
2		.050	97	97
4		.050[c]	92	92
20		.500[c]	92	92
30		.250[d]	..	97
1		.500	..	97
3		.500[c]	..	92
25		1.000[e]	91	90
16	Methyl phthalate	0.500[c]	100	100
24		1.000[e]	100	100

[a] The hydrogenations were carried out using platinum oxide and acetic acid at ambient temperature. [b] Two chromatographic columns with different stationary liquid phases were used for analysis. One contained dioctyl sebacate (D.O.S.) and the other polypropylene glycol (P.P.G.). Only the percentage of the *cis* isomer is tabulated: the net product is the *trans* isomer. [c] The unsaturated ester was hydrogenated until one-half the required amount of hydrogen was absorbed. [d] A sample of the half reduced mixture of experiment 20 was hydrogenated completely. [e] In all cases, the pressure of hydrogen was maintained at atmospheric except for experiments 25, 16 and 24 which were conducted at 136, 2 and 267 atmospheres, respectively.

since we have found that the *cis* isomer is not isomerized under these hydrogenation conditions.

Methyl Δ^2-tetrahydrophthalate reacts with hydrogen two and one-half times as rapidly as the Δ^1-ester. Because the Δ^1-ester can add hydrogen from either side of the double bond to give the *cis* product, it should react faster by a statistical factor of two. Therefore, the rate of hydrogenation of methyl Δ^2-tetrahydrophthalate is greater by an intrinsic factor of five.

The stereochemistry of the hydrogenation of hydroaromatic compounds is a function of the constitution of the substituents which are attached to the cycle, because the unsaturated esters yield a larger proportion of the *cis* isomer than do the corresponding substituted dimethylcyclohexenes. Possibly the ester group is effectively larger than the methyl group; or perhaps in the reduction of these methyl tetrahydrophthalates, the intermediate "half-hydrogenated" state does not undergo appreciable isomerization in the manner suggested for the dimethylcyclohexenes.[3] Perhaps methyl substituents on a double bond provide an easy path to the isomerization of the "half hydrogenated states" and this path is not available to the ester group.

The Stereochemistry of the Hydrogenation of Methyl Phthalate.—Methyl phthalate and the tetrahydro derivatives yield only the *cis*-hexahydro product at one atmosphere of hydrogen. This suggests that they are hydrogenated through a common intermediate. Noting that the methyl tetrahydrophthalates react much more rapidly than the aromatic ester suggests the possibility that during the hydrogenation of the latter partially reduced intermediates (possibly methyl tetrahydrophthalate)

could leave the surface of the catalyst and be readsorbed and reduced during a subsequent event. The above stereochemical evidence does not require that an aromatic ring be saturated during a single period of residence on the surface of the catalyst. However, it does not exclude the possibility that an aromatic molecule adds hydrogen atoms stepwise during a single period of residence upon the surface[6] and that one of the intermediates in this process is common to the hydrogenation of the tetrahydro derivatives.[4]

Experimental

Preparation of Methyl Δ^1-Tetrahydrophthalate (Methyl 1-Cyclohexene-1,2-dicarboxylate).—Δ^1-Tetrahydrophthalic anhydride was prepared according to the procedure of Bailey and Amstutz.[7] The anhydride (40 g.) was dissolved in a small amount of water and neutralized (phenolphthalein indicator) with a dilute solution of sodium hydroxide until the pink color remained for 30 minutes. An excess of a solution of silver nitrate was added with stirring. The white precipitate was collected, washed with methanol and ether, and dried for four days in an evacuated desiccator containing phosphorus pentoxide (weight of dry salt, 92 g.). The salt was suspended in absolute ether (500 ml.) and treated dropwise with methyl iodide (150 g.) in absolute ether (200 ml.) over a period of 3 hours. The reaction mixture was heated on the steam-bath during this time. After an additional 12 hours of refluxing, the mixture was cooled and the silver iodide was removed by filtration. The ether was evaporated and the product distilled. The methyl Δ^1-tetrahydrophthalate (48 g., 92%) distilled at 86–88° (0.03–0.04 mm.). d^{25}_4 1.1352. The chromatographic analysis showed no impurity. *Anal.* Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.35; H, 7.10.

Preparation of Methyl Δ^2-Tetrahydrophthalate (Methyl 2-Cyclohexene-1,2-dicarboxylate).—The procedure described by Baeyer[8] was followed for the preparation of Δ^2-tetrahydrophthalic acid. Phthalic anhydride (8 g.) and sodium bicarbonate (17 g.) were dissolved in 68 ml. of water. A 3% sodium amalgam (260 g.) was added immediately to the mixture which was refluxed for 4.5 hours on a steam-bath. The reaction mixture then was cooled to room temperature and concentrated hydrochloric acid was added until the mixture was slightly acidic. After standing overnight at room temperature, the reaction mixture was filtered through Celite. Crystals of Δ^2-tetrahydrophthalic acid formed upon addition of excess dilute sulfuric acid to the filtrate. Two recrystallizations of the solid from water gave Δ^2-tetrahydrophthalic acid (9 g.) melting at 214–215° (lit.[9] m.p. 215°).

The Δ^2-tetrahydrophthalic acid was converted to the methyl ester *via* the reaction of methyl iodide with the silver salt of the acid as described for methyl Δ^1-tetrahydrophthalate. The methyl Δ^2-tetrahydrophthalate distilled at 92.5–93° (1 mm.). d^{25}_4 1.1388. The yield was 26.7 g. (79%). *Anal.* Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.58; H, 7.24.

The chromatographic analysis of methyl Δ^2-tetrahydrophthalate showed a 3% impurity which had not been completely removed by distillation. This impurity is believed to be *trans*-methyl Δ^3-tetrahydrophthalate because its corresponding acid is formed in the sodium amalgam reduction of *o*-phthalic acid along with the Δ^2-acid.[9] Furthermore, it has a retention time on polypropylene glycol which falls between *cis*-methyl Δ^4-tetrahydrophthalate and the Δ^1- or Δ^2-esters and is converted to *trans*-methyl hexahydrophthalate upon hydrogenation.

***cis*-Methyl Δ^4-tetrahydrophthalate** was prepared from *cis*-Δ^4-tetrahydrophthalic anhydride *via* the silver salt.

***cis*-Methyl hexahydrophthalate** was prepared *via* the action of methyl iodide on the silver salt of the acid as above. The acid was obtained by the hydrogenation of *cis*-Δ^4-tetrahydrophthalic acid according to Jenkins and Costello.[10] The acid was purified by repeated recrystallizations from water yielding material of m.p. 191°. lit.[10] 192°.

Preparation of *trans*-Hexahydrophthalic Acid (*trans*-Cyclohexane-1,2-dicarboxylic Acid).—A sample of *cis*-hexahydrophthalic acid (18 g.) was refluxed with 85% phosphoric acid (100 ml.) for 5 hours. The reaction mixture was poured into 600 ml. of water and allowed to cool. Crystals of the *trans*-acid (18 g., 97%) formed and after two recrystallizations from water had a m.p. of 218–220°; lit.[11] m.p. 215–216° and 227–228°.[12]

Preparation of *trans*-Methyl Hexahydrophthalate (*trans*-Methyl Cyclohexane-1,2-dicarboxylate).—The procedure reported by Smith and Fort[13] was followed for the synthesis of *trans*-methyl hexahydrophthalate. The isolated product was distilled at 135° (17 mm.). Crystallization of the material with a benzene–petroleum ether mixture gave crystals which melted at 31°, lit.[12] 31°.

General Procedures for Hydrogenation.—A semi-micro hydrogenation apparatus similar to that described by Vandenheuvel[14] was constructed to study the relative rates of reduction of unsaturated compounds. This apparatus allowed the determination of the fraction hydrogenated with a precision of about 1% under near isobaric conditions. The reductions were carried out at a pre-set pressure of approximately 730 mm. of mercury at a temperature of 26 ± 0.5°. The buret readings were taken at minute intervals.

The Δ^1- and Δ^2-isomers of methyl tetrahydrophthalate (0.0025 and 0.025 mole) were hydrogenated in 50 ml. of glacial acetic acid in contact with 80 mg. of commercial platinum oxide (The American Platinum Works) at 26–27° and atmospheric pressure. Additional reductions of methyl Δ^2-tetrahydrophthalate (0.0125 mole and 150 mg. of catalyst) and methyl phthalate (0.0125 mole and 300 mg. of catalyst) were carried out in 10 ml. of acetic acid at 136 and 267 atm., respectively. An Aminco high pressure shaking autoclave was employed in the latter experiments.

Isolation of Products.—The catalyst was filtered and the acetic acid solution was poured into a separatory funnel containing 300 g. of ice. The cold mixture was immediately neutralized with an equivalent amount of sodium hydroxide. After a saturated solution of sodium chloride was added, the solution was extracted with ether and dried over anhydrous magnesium sulfate. Careful removal of the ether by distillation yielded the mixture of methyl hexahydrophthalates and in the case of an incomplete reduction, the saturated mixture plus the original unsaturated ester. The recovery of reaction products was performed without appreciable loss.

Analytical Methods.—The absorbance of standard samples of the methyl Δ^1- and Δ^2-tetrahydrophthalates and methyl phthalate (0.084 mg./cc. of "spectrographic" cyclohexane) was examined in the region of 230–300 mμ with a Beckman model DU spectrophotometer equipped with a hydrogen discharge lamp and 1-cm. silica cells. At this concentration, the *cis*- and *trans*-hexahydrophthalates do not absorb appreciably and therefore do not interfere with the analysis. Neither the Δ^1- nor the Δ^2-tetrahydrophthalates have maxima in their absorption spectra in this region; however, the Δ^1-ester begins to absorb at longer wave lengths, about 265 mμ, while the Δ^2-ester reaches the same weak absorption at 250 mμ. Consequently, the spectral region 230–250 mμ was used to detect the presence of one in the other component. From reference curves, it is possible to distinguish between the above compounds in mixtures within an error of 3–4%.

The presence of methyl phthalate can be detected from the maxima occurring at about 275–280 mμ.

An apparatus employing gas–liquid partition chromatography was constructed along lines described by Dimbat, Porter and Stross,[15] but was modified in several ways. The stream of carrier gas was shunted before reaching the sampling port, one path leading to the reference side of the thermal conductivity cell and the other to the sample injector system.[16] This allowed both reference and measuring filaments to operate at the same pressure. A one millivolt recorder was used. The chromatograph columns were

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constructed from copper tubing, 25 feet in length and 0.25 inch in diameter. Helium was used as the carrier gas. Several liquid stationary phases on 50–60 mesh fire brick were investigated in order to separate the products and reactants formed in the hydrogenation of the methyl tetrahydrophthalates. The most useful found were dioctyl sebacate (W. C. Hardesty Co., Inc., Dover, Ohio) and polypropylene glycol 2025 (Carbide and Carbon Chemicals Co., New York, N.Y.). Operating at a temperature of 200° and a flow of helium of 140 ml. per minute, the *cis* and *trans* isomers of methyl hexahydrophthalate gave peaks at 166 and 154 minutes on dioctyl sebacate (D.O.S.) and 160 and 148 minutes on polypropylene glycol (P.P.G.), respectively. The retention time for the unsaturated esters was much greater. The Δ^1- and Δ^2-isomers of methyl tetrahydrophthalate gave peaks at 223 and 217 minutes, respectively, on D.O.S., and 231 and 225 minutes, respectively, on P.P.G. The ratio of isomers was taken as the ratio of the areas under the respective peaks. These areas can be obtained satisfactorily by multiplying the height of the peak by the width of the peak at half height. A comparison of the prepared standards indicated an accuracy of ±1%.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Kinetics of the Metal–Ammonia–Alcohol Reductions of Benzene and Substituted Benzenes[1]

BY A. P. KRAPCHO[2a] AND A. A. BOTHNER-BY[2b]

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A study of the metal–ammonia–alcohol reduction of benzene and some substituted benzenes has shown that over a limited range of concentration the rate of reduction of aromatic compound is governed by the law $d(ArH)/dt = k(ArH)(M)(ROH)$. The rate constant for the reduction of benzene with lithium and ethanol in liquid ammonia at −34° is 1.40 ± 0.06 l.²/moles² sec., and the energy of activation is 2.7 kcal./mole. With *t*-butyl alcohol as proton source, the rate constant at −34° is 0.10 ± 0.01 l.²/moles² sec. and the energy of activation is 4.4 kcal./mole. Relative rates of reduction of benzene and fourteen substituted benzenes have been obtained. Bulky alkyl substituents lower the rate of reduction, and increase the proportion of cyclohexenes in the product. The addition of lithium bromide increases the rate of sodium and alcohol reduction of benzene sixty-four-fold. A probable mechanism for the reaction as it proceeds under the usual Birch conditions is presented.

Introduction.—The reduction of aromatic compounds with a combination of an alkali metal and an alcohol or other proton source in a medium of liquid ammonia or low molecular weight amine is a synthetic procedure of great utility.[3] Its flexibility and usefulness has attracted increasing attention in recent times.[4] In previous investigations of this reaction, attention has been centered on characterization of the major products,[3b] on achieving optimum conditions for high yields in specific cases,[4a,c,d] and on discerning the probable mechanism of the reaction by means of product studies.[3c,4b,e] Other aspects of the reaction which might be expected to cast light on the mechanism include the kinetics, and the composition and proportions of minor products. An investigation of these topics forms the subject matter of this report.

Effect of Proton Source on Yield.—In Table I are assembled data on several preliminary experiments in which were determined the effect of variations in the kind and amount of alcohol or acid used as a proton source on the yield of reduced hydrocarbon.

TABLE I

EFFECT OF PROTON SOURCE ON YIELD OF REDUCED HYDROCARBON IN SEVERAL REACTIONS

Hydrocarbon	Molar proportion and kind of proton source	Analytical method[a]	Reduction,[b] %
Benzene	2 NH_4Cl	VPC	3
Benzene	2 NH_4Cl	R	3
Benzene	2 NH_4Cl	UV	2
Benzene	3 EtOH	VPC	94
Benzene	4 EtOH	R	92
Benzene	1.4 EtOH	VPC	50[c]
Benzene	5 H_2O	VPC	36
Toluene	2 EtOH	VPC	88
Toluene	Excess H_2O	VPC	28
Toluene	2 NH_4Cl	UV	2
Toluene	4 *i*-PrOH	UV	96
Toluene	4 *t*-BuOH	UV	91

[a] VPC = vapor phase chromatography; R = refractometry; UV = ultraviolet spectroscopy. [b] Major reduction product only. [c] One mole of lithium; all other experiments with 2 moles of lithium.

In these reductions, lithium and benzene or toluene were dissolved in the ammonia, usually with a little added ether to render solution complete, and the proton source then added as rapidly as possible. Analyses of the hydrocarbon products were performed by one or more of these methods: refractometry, ultraviolet spectroscopy and vapor phase chromatography.

The data reflect a general trend toward lower yields with more strongly acidic proton sources. Although ammonium chloride gives good results in the reduction of polynuclear hydrocarbons, its use in the present cases leads to almost no reduction. Unlike alcohols,[3c,4d] both ammonium chloride and water react rapidly with alkali metals dissolved in liquid ammonia. It seems very likely

(1) Abstracted in part from the thesis submitted by A. P. Krapcho to Harvard University in partial fulfillment of the requirements for the Ph.D. degree, 1957.

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