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%.

FAYETTEVILLE, ARK.

[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 $d(\text{ArH})/dt = k(\text{ArH})(\text{M})(\text{ROH})$. The rate constant for the reduction of benzene with lithium and ethanol in liquid ammonia at −34° is 1.40 ± 0.06 l.^{2}/moles^2 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}/moles^2 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

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[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.

[2] (a) Department of Chemistry, Smith College, Northampton, Mass; (b) Mellon Institute, Pittsburgh, Pa.

[3] (a) C. B. Wooster and K. L. Godfrey, THIS JOURNAL, **59**, 596 (1937); (b) A. J. Birch, *J. Chem. Soc.*, 430 (1944); 809 (1945); 593 (1946); 102, 1642 (1947); 1551 (1950); 2556 (1957); (c) A. J. Birch, *Quart. Revs.*, **4**, 69 (1950); *Austral. J. Chem.*, **7**, 256, 261 (1954); **8**, 96 (1955).

[4] (a) R. A. Benkeser, R. E. Robinson, D. M. Sauve and O. H. Thomas, THIS JOURNAL, **77**, 3230 (1955); (b) W. Hückel and Wörffel, *Ber.*, **88**, 338 (1955); **89**, 2098 (1956); (c) G. Stork and W. N. White, THIS JOURNAL, **78**, 4604 (1956); (d) W. S. Johnson, B. Bannister and R. Pappo, *ibid.*, **78**, 6331 (1956); (e) W. Hückel, B. Graf and D. Münkner, *Ann.*, **614**, 47 (1958).

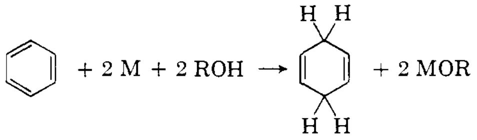
that this direct reaction competes effectively with the reduction of benzene under the reaction conditions employed.

Determination of Order of the Reaction.—In order to study the kinetics of the reduction process, it was necessary to find a means for quenching the reaction in an aliquot of the reaction mixture at definite times, and to settle on a means for analyzing the hydrocarbon products isolated. In view of the results obtained with ammonium chloride, it was at first thought that excess ammonium chloride would serve as an effective quenching agent in the metal-ammonia-alcohol reduction. Several abortive efforts were made in this direction before it was discovered that the most rapid reaction of ammonium chloride was with alkoxide produced during the reduction to regenerate the original alcohol. The rate of reduction was therefore first accelerated then decreased as excess ammonium chloride was added.

A successful method for quenching the reaction was evolved based on the observation (see below) that in a competitive reduction betweeen benzene and sodium benzoate, only the benzoate was reduced. By discharging an aliquot into an ethereal suspension of sodium benzoate, the reduction of benzene by lithium and alcohol in liquid ammonia could be effectively halted. The excess sodium benzoate and dihydrobenzoate then could be removed by extraction of the ethereal layer with water.

The hydrocarbon product from the reduction of substituted benzenes contained more than two compounds. It was therefore desirable to find a method of analysis which would yield not only the fraction of aromatic hydrocarbon reduced, but also the kind and amount of each reduction product obtained. The ideal technique for this purpose proved to be vapor phase chromatography, which was used extensively in all further studies reported in this paper.

The main reaction occurring during the reduction of benzene may be represented by equation 1.



(1)

If the concentration of the benzene, alkali metal and alcohol are initially in the stoichiometric proportions, they may be represented at any time by c, $2c$ and $2c$, respectively. One may then assume an equation of the form

$$-\, \mathrm{d}c/\mathrm{d}t = kc^{\alpha}\,(2c)^{\beta}\,(2c)^{\gamma} = 2^{\beta+\gamma}\,kc^{\alpha+\beta+\gamma} \quad (2)$$

which may be integrated directly to yield

$$c^{1-(\alpha+\beta+\gamma)} - c_0{}^{1-(\alpha+\beta+\gamma)} = (\alpha+\beta+\gamma-1)2^{\beta+\gamma}\,k(t-t_0) \quad (3)$$

where the subscript zero refers to the concentration at time t_0. Assumptions inherent in this derivation are (1) that a single reaction path predominates and (2) that no large concentrations of intermediates or irreversible side reaction products occur. If equation 3 applies, a plot of $c^{1-(\alpha+\beta+\gamma)}$ *versus* time will give a straight line intercepting the zero-time axis at $c_0{}^{1-(\alpha+\beta+\gamma)}$. By assuming successively values of -1, -2, -3, etc., for $1-(\alpha+\beta+\gamma)$, it can be demonstrated that for the reduction of benzene with lithium and ethanol a good fit for a straight line is obtained in the case of $1\text{-}(\alpha+\beta+\gamma) = -2$. The reaction is therefore of third order. A typical set of data for a kinetic run is given in Table II, and is plotted in Fig. 1.

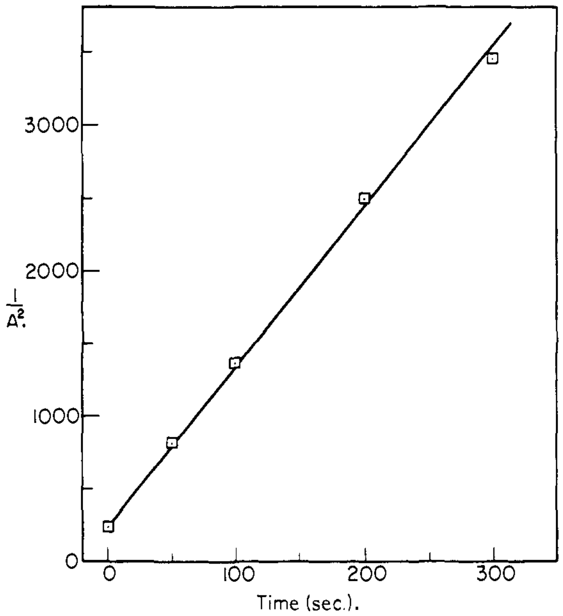


Fig. 1.—Third-order plot of reduction of benzene with lithium and ethanol in stoichiometric quantities.

Although it seemed quite probable that the coefficients α, β and γ were all equal to unity, it was especially important to establish this for β, the order with respect to alkali metal concentration. Both β and γ were determined by the differential method of van't Hoff, for the case of *t*-butyl alcohol and lithium reduction of benzene. A typical set of data for a kinetic run is given in Table II, and is plotted in Fig. 1. In each case, doubling the initial concentration of reactant very nearly doubled the initial rate. Since the reaction is so fast (benzene is essentially completely reduced in 300 seconds when the initial concentrations of benzene, lithium and *t*-butyl alcohol are 0.1 *M*, 0.2 *M*, and 0.2 *M*, respectively) it was not possible to obtain aliquots in which less than 4–10% reduction had taken place. The data are nevertheless unambiguous, as is shown in Table III and Fig. 2. The order is unity both with respect to alcohol and with respect to alkali metal. The rate law may therefore be expressed as

TABLE II

REDUCTION OF BENZENE (0.066 *M*) WITH LITHIUM (0.132 *M*) AND ETHANOL (0.132 *M*) IN LIQUID AMMONIA

Time, sec.	c (concn. of benzene)	$1/c$	$1/c^2$	$1/c^3$ ($\times 10^{-2}$)
0	0.066	15.2	230	35
50	.035	28.6	816	229
100	.027	27.0	1372	507
200	.020	50.0	2500	1250
300	.017	58.9	3460	2040

$$-d(\text{ArH})/dt = k(\text{ArH})(\text{M})(\text{ROH}) \qquad (4)$$

where (ArH) is the concentration of aromatic hydrocarbon, (M) the concentration of metal and (ROH) the concentration of alcohol. This rate law is valid when the concentration of aromatic is in the range 0.02–0.10 *M*.

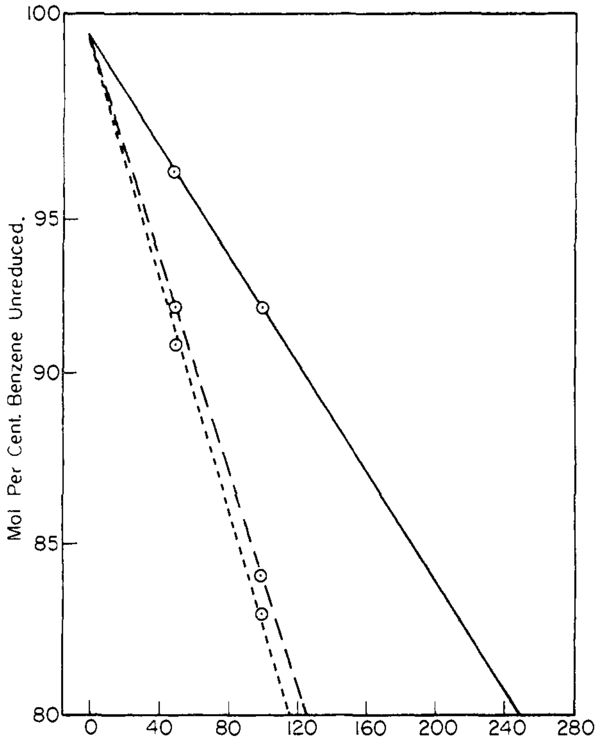


Fig. 2.—Determination of kinetic order by the van't Hoff method.

Effect of Proton Source, Nature of Metal and Added Salts on Rates of Reduction.—Using the same technique, kinetics were observed for the reduction of benzene with lithium and both butanol and ethanol at −34° and at *ca.* −75°. The reaction in these cases was surprisingly fast even at low temperatures. The relative rates of reduction with lithium, sodium and potassium were compared and found to decrease in that order, reductions with lithium being much faster than with the other two metals. The effect of added salts also was investigated. The addition of lithium bromide to a sodium reduction accelerated the rate by more than sixty-fold, while addition of sodium chloride or sodium bromide to a lithium reduction slowed the reaction slightly. The addition of sodium bromide to a sodium reduction was practically without effect.

Table III

Determination of Kinetic Order

Kinetic run	Moles/l. benzene	Moles/l. lithium	Moles/l. *t*-BuOH	% Ether volume	Reaction time, sec.	Mole % benzene remaining
2	0.061	0.122	0.122	6.6	50	96.0
					100	92.0
2A	.061	.122	.244	6.6	50	91.0
					100	83.0
2B	.061	.244	.122	6.6	50	92.0
					100	84.1

In each of these cases, the data provided satisfactory linear third order plots. The rate constants evaluated from the slopes of these plots are summarized in Table IV.

Table IV

Third-order Rate Constants for Metal–Ammonia–Alcohol Reductions of Benzene

Alkali metal	Alcohol	Added salt, moles	Temp., °C.	k, l.²/moles² sec.
Li	*t*-BuOH	.....	−34	0.10
Li	*t*-BuOH	.....	−74	0.015
Li	Ethanol	.....	−34	1.40
Li	Ethanol	.....	−76	0.40
Na	Ethanol	.....	−34	.0064
K	Ethanol	.....	−34	.0015
Li	Ethanol	NaCl, 2	−34	.33
Li	Ethanol	NaCl, 4	−34	.34
Li	Ethanol	NaBr, 2	−34	.56
Na	Ethanol	LiBr, 1.9	−34	.41
Na	Ethanol	NaBr, 2	−34	.0067

Competitive Reductions.—If a mixture of two aromatic hydrocarbons is reduced each will obey the appropriate rate law. If it is supposed that the law is that shown in equation 4 above, then the laws governing the reduction of the two hydrocarbons may be written

$$-ds/dt = k[s][M][ROH] \qquad (5)$$

and

$$-ds'/dt = k'[s'][M][ROH] \qquad (6)$$

where s and s′ represent the two species involved. Since they are present in the same reaction mixture, the concentration of metal and alcohol to which they are exposed at any time is the same for both, and one may divide equation 5 by equation 6 to obtain

$$\frac{ds}{ds'} = \frac{ks}{k's'} \qquad (7)$$

from which by direct integration is obtained

$$\frac{k}{k'} = \frac{\ln (s/s_0)}{\ln (s'/s_0')} \qquad (8)$$

where the subscript zero refers to the concentrations at some initial time, t_0. If the ratio $\ln (s/s_0)/\ln(s'/s_0')$ is constant, this provides further support for the idea that the mechanisms of the two reductions are similar, and that the rate law is of the same form. Furthermore, the implication is that the order of the reaction with respect to the species s is one, although there is no guarantee that the step in which it enters is not subsequent to the rate-determining step.[5]

Measurements of k/k_{benzene} were made for a number of substituted benzenes by the competition method. Analysis of the complex reaction product was generally simple, when the vapor phase chromatographic technique was used.

Figure 3 shows typical vapor phase chromatographic elution curves obtained in the reductions of benzene (3A) and mesitylene (3B). In cases where the substituted benzene was reduced at a rate much

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(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 243 ff.

slower than that of benzene, additional competition experiments were preformed in which the substance was reduced in competition with a substituted benzene of intermediate reactivity. Rate ratios obtained this way checked satisfactorily with those obtained directly.

In Table V are presented the values obtained for k_1/k_{benzene} for a number of substituted benzenes.

TABLE V

REACTION RATE CONSTANTS FOR A NUMBER OF SUBSTITUTED BENZENES RELATIVE TO BENZENE

Compound	k/k_{benzene}[a]	Compound	k/k_{benzene}[a]
p-Di-butylbenzene	<0.005[b]	*p*-Xylene	0.30
Mesitylene	.017	Dimethylaniline	.30
t-Butylbenzene	.050	Tetralin	.38
o-Xylene	.050	Toluene	.65
i-Propylbenzene	.10	Indane	.94
Aniline	.10	(Benzene)	(1.00)
n-Butylbenzene	.21	Anisole	3.28
Ethylbenzene	.25	Sodium benzoate	>200[c]
m-Xylene	.28		

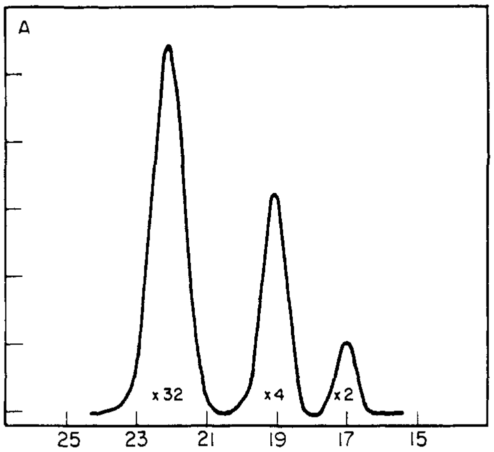
[a] Probable error ±10%. [b] No reduction of *p*-di-*t*-butylbenzene detectable. [c] No reduction of benzene detectable.

Competition experiments involving benzene, toluene and isopropylbenzene have been reported by Hückel, Graf and Münkner.[4e] Since in their experiments the hydrocarbon and alcohol were added together and over a relatively long period of time, the exact kinetic significance is not clear. Application of equation 8 to their results, however, gives the following ratios: $k_{\text{toluene}}/k_{\text{benzene}} = 1.0$; $k_{\text{isopropylbenzene}}/k_{\text{benzene}} = 0.11$; $k_{\text{isopropylbenzene}}/k_{\text{toluene}} = 0.13$. These are in general agreement with the data from Table V, which lead to the values 0.65, 0.10 and 0.15 for the same ratios.

Identification of Products.—Major products have previously been recognized and characterized[3b,4b,e] for many of these reductions. In the expectation that the structures of the minor products and the amounts in which they are produced might be helpful in discerning the detailed path of the reaction, a considerable effort was expended on their identification and assay.

In the typical experiment, a sample of the aromatic hydrocarbon (the purity of which was checked by vapor phase chromatography) was reduced using lithium (1 to 6 moles) and ethanol under standard conditions. The ethereal solution of the product was subjected directly to vapor phase chromatographic analysis. The separated products could be characterized by retention time and spectroscopic examination of the individual fractions trapped in cold solvent as they came off the column. In a number of cases samples of the minor product were synthesized independently for the purpose of comparing the spectra and retention times with the products from the reductions. In a few cases nuclear magnetic resonance was helpful in characterizing the major products.

Braude, Jackman and Linstead[6] observed that 1,4-dihydrobenzene is oxidized readily by benzoquinone in homogeneous solution. This forms the basis of a convenient diagnostic test which was of considerable help in identifying the peaks in the vapor phase chromatograms: benzene solutions of quinone and 1,4-dihydrobenzenes first warmed then cooled yield a black precipitate of quinhydrone.



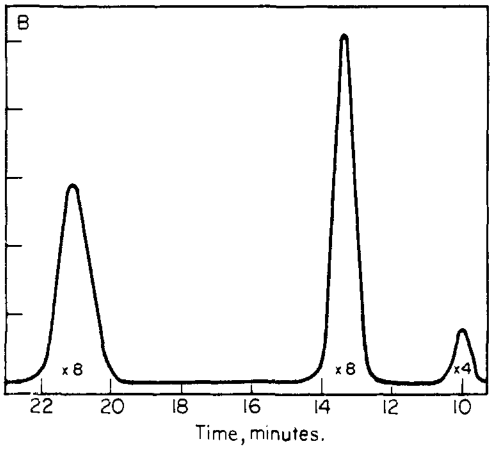


Fig. 3A.—Vapor phase chromatogram of the reduction products of benzene using stoichiometric amounts of lithium and ethanol. The analysis was performed utilizing a 4-meter "A" column at a temperature of 92°. The three components in order of increasing retention time are cyclohexene, benzene and 1,4-dihydrobenzene, recorded at sensitivities of 2, 4 and 32, respectively.

Fig. 3B.—Vapor phase chromatogram of the reduction products of mesitylene using three moles of lithium metal per mole of mesitylene and ethanol as a proton source. The analysis was performed using a 4-meter "A" column at a temperature of 160°. The components in order of increasing retention time are *cis*-tetrahydromesitylene, 1,4-dihydromesitylene and mesitylene, recorded at sensitivities of 4, 8 and 8, respectively.

The results of the analyses are given in Table VI.

The case of anisole is exceptional and deserves special mention. In the vapor phase chromatographic analysis of the products it was noted that the half-width of the peak for the third component (2,5-dihydroanisole) was greater than that for the fourth component (unreduced anisole). Upon close scrutiny this revealed itself as arising from the thermal isomerization of the unconjugated material to a conjugated isomer during its passage through the hot column. By refluxing the unconjugated isomer in an atmosphere of air, it could be converted to a mixture of anisole and the conjugated isomer.

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[6] E. A. Braude, L. M. Jackman and R. P. Linstead, *J. Chem. Soc.*, 3564 (1954).

TABLE VI

MAJOR AND MINOR REDUCTION PRODUCTS

Hydrocarbon	Products	Mole % with molar Li ratio 1 Li	2 Li
Benzene	1,4-Dihydrobenzene	50.6	94.0
	Cyclohexene	0.3	0.8
	Benzene	49.1	5.2
Toluene	2,5-Dihydrotoluene	47.5	88.2
	1-Methyl-1-cyclohexene	1.0	2.0
	3-Methyl-1-cyclohexene	0.2	0.5
	4-Methyl-1-cyclohexene	0.5	1.0
	Toluene	50.8	8.3
		2 Li	4 Li
Ethylbenzene	2,5-Dihydroethylbenzene	84.0	93.7
	1-Ethyl-1-cyclohexene	4.0	6.3
	Ethylbenzene	12.0	..
Isopropylbenzene	2,5-Dihydroisopropylbenzene	62.3	
	1-Isopropyl-1-cyclohexene	5.2	
	Isopropylbenzene	32.5	
t-Butylbenzene	2,5-Dihydro-*t*-butylbenzene	37.3	
	Unidentified	4.9	
	t-Butylbenzene	57.8	
t-Butylbenzene[a]	2,5-Dihydro-*t*-butylbenzene	60.6	
	Unidentified	10.9	
	t-Butylbenzene	28.5	
Anisole	2,5-Dihydroanisole	52.0	85.7
	1-Methoxy-1-cyclohexene	7.1	9.6
	Cyclohexene	2.7	4.7
	Anisole	38.2	..
p-Xylene	2,5-Dihydro-*p*-xylene	72.5	95.9
	1,4-Dimethyl-1-cyclohexene	3.1	4.1
	p-Xylene	24.4	..
o-Xylene	3,6-Dihydro-*o*-xylene	41.8	77.5
	1,4-Dihydro-*o*-xylene	8.4	14.3
	2,3-Dimethyl-1-cyclohexene	0.9	1.5
	o-Xylene	48.9	8.2
			6 Li
m-Xylene	1,4-Dihydro-*m*-xylene	4.6	5.4
	2,5-Dihydro-*m*-xylene	83.0	91.7
	1,3-Dimethyl-1-cyclohexene and 2,4-dimethyl-1-cyclohexene	2.9	2.9
	m-Xylene	9.5	..
			3 Li
Mesitylene	1,4-Dihydromesitylene	51.5	80.3
	cis-Tetrahydromesitylene	3.1	4.8
	Mesitylene	45.5	14.9
			2 Li
1-Methoxy-2-cyclohexene	Cyclohexene	100	

[a] Proton source = *t*-butyl alcohol; all others with ethanol.

This might explain the observation of Wilds and Nelson[7] that the conjugated isomer was obtained by fractionation of the products from the reduction of anisole.

In a separate experiment it was demonstrated that the conjugated isomer is reduced quickly and quantitatively to yield a mixture of cyclohexene and 1-methoxycyclohexene in the approximate ratio 1:2. The reduction to cyclohexene presumably occurs *via* 3-methoxycyclohexene as an intermediate. It also was demonstrated in a separate experiment that 3-methoxycyclohexene is quickly and quantitatively reduced to cyclohexene.

Discussion.—The most important proposals which have been made with respect to the mechanism of the reduction are those of Baeyer,[8] Willstätter[9] and Birch.[3c]

It was proposed by v. Baeyer that the dissolving metal reacted with the solvent to produce "nascent" hydrogen atoms, which were very reactive and added to organic compounds before they combined to form molecular hydrogen. This theory has now been largely abandoned, since it can be shown that reduction occurs in systems from which molecular hydrogen is not released in the absence of the substrate. Recently, however, this idea has been advanced in a modified form by Hückel, Graf and Münkner.[4e] They suggest that the first step in the reduction of benzene in homogeneous medium may involve the addition of a hydrogen atom (perhaps as the result of a three-body collision involving a benzene molecule, an ammonium ion and an electron). This would be followed by the addition of an electron to give an anion which would then quickly accept a proton to give the dihydrobenzene. They point out that under the usual Birch conditions (addition of aromatic dissolved in alcohol to sodium dissolved in liquid ammonia) the yield is sharply lowered when certain metals (*e.g.*, copper) are added, and that these metals exert a catalytic effect on the reaction of the alkali metals with the alcohols to yield molecular hydrogen.

Willstätter[9] made a careful study of the course of the reduction by sodium amalgam. He suggested that the reaction was initiated by the addition of metallic sodium to the double bond, followed by hydrolysis by the solvent. This theory has received considerable support from studies of the addition of the alkali metals to polynuclear aromatic hydrocarbons in inert media.

Birch has suggested[3c] that the reactive intermediate is formed by the transfer of one or two electrons to the aromatic nucleus, giving a radical anion or a dianion, respectively. These intermediates would be very strong bases, and would react promptly with proton donors. In earlier publications, Birch favored the dianion as an intermediate over the anion-radical, but more recently has suggested that the anion-radical would be preferred under some conditions.

That the anion-radical occurs in solution has been most elegantly demonstrated by Lipkin, *et al.*,[10] and by Tuttle and Weissman[11] using the technique of electron paramagnetic resonance. When naphthalene in tetrahydrofuran solution is allowed to react with sodium a solution is obtained which gives

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[7] H. L. Wilds and N. A. Nelson, THIS JOURNAL, **75**, 5361 (1953).

[8] A. v. Baeyer, *Ann.*, **155**, 267 (1870).

[9] R. Willstätter, F. Seitz and E. Bumm, *Ber.*, **61**, 871 (1928).

[10] D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).

[11] T. R. Tuttle and S. I. Weissman, THIS JOURNAL, **80**, 5342 (1958).

rise to electron paramagnetic resonance absorption. A hyperfine splitting of the electron absorption line by the protons of the naphthalene indicate that a single electron is transferred from sodium to naphthalene in such solutions, and remains attached to a single molecule for long periods of time. Addition of naphthalene to the solution broadens the lines, indicating that an exchange process is occurring, so that it is necessary to postulate a mobile equilibrium. The solutions of sodium naphthalenide in tetrahydrofuran or ethylene glycol dimethyl ether are green, and it is not possible to alter this color by the addition of more sodium. On the other hand, while addition of 0.1 mole of sodium or lithium to naphthalene in liquid ammonia solutions produces a green solution, further addition of up to 2 moles of metal produces orange-red solutions, which apparently contain the dianion.[12] It is possible to form the dianion from phenanthrene even in tetrahydrofuran.[13] It is difficult to form even the radical-anion from benzene.[11,14] From the experiments which have been reported in the literature, it is apparent that at least three factors are important in assessing the probable stability of the anion radical and the dianion in solution: (1) the resonance possibilities for distributing the charge or charges over the molecule, (2) the specific solvating capacity of the solvent for the anions and (3) the extent to which the counter ions may be solvated or held in ion-pairs with the negatively charged species.

For the reduction of benzene and alkylbenzenes with alkali metal and alcohol in liquid ammonia solutions, it seems probable that the sequence of events is as represented in steps 1 through 5, Fig. 4. In this scheme, solvation by ammonia is represented by the symbol (s); the degree of solvation will vary from one species to the next. In step 1, the dissolved metal dissociates to form "solvated electrons." Recent investigations employing nuclear magnetic resonance have indicated that in concentrated solutions the electrons are in weakly bound states with the solvated cation,[15] analogous to expanded s-orbitals. In dilute solutions more complete dissociation may occur. In step 2, a reversible equilibrium is set up, in which the electron is transferred to the aromatic ring, and the ion-pair I now consists of the solvated metal ion and the solvated anion-radical. In step 3, the rate-determining step, the anion-radical reacts with a molecule of alcohol to release metal alkoxide, and form a radical intermediate. In rapid subsequent steps this intermediate acquires an additional electron, and abstracts a proton from either alcohol or solvent to yield the 1,4-dihydro or the 1,2-dihydro derivative. The latter is further reduced to cyclohexene.

This mechanism accommodates the accumulated experimental evidence reasonably well. In particular, the following points seem worthy of discussion.

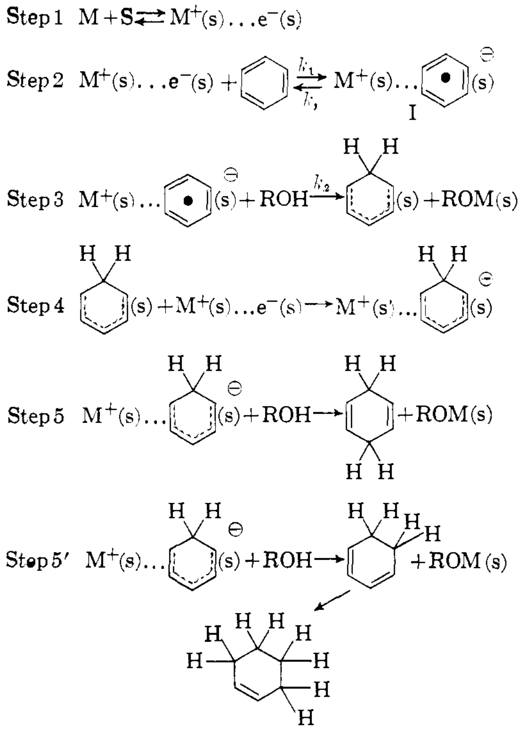

Fig. 4.—Probable steps in the reduction of benzene by metal and alcohol in liquid ammonia at −34°.

Assuming the steps as stated to be correct, standard kinetic treatment gives the equation

$$\frac{d[\mathrm{ArH}]}{dt} = \frac{k_1k_2[\mathrm{ArH}][\mathrm{M}][\mathrm{ROH}]}{k_{-1} + k_2[\mathrm{ROH}]} \qquad (9)$$

The equation reduces to (4), that found experimentally to apply provided that $k_{-1} >> k_2[\mathrm{ROH}]$. Were the intermediate formation of a dianion to be involved, the kinetic law would require the concentration of alkali metal to appear as the second power in the rate expression.

If, in fact, $k_{-1} >> k_2[\mathrm{ROH}]$, then $k_{\text{observed}} = k_1k_2/k_{-1} = K_ek_2$, where K_e is the equilibrium constant for the formation of the metal cation–(aromatic anion-radical) ion-pair I from "solvated electrons" and aromatic hydrocarbon. Bulky substituents in general should reduce both K_e and k_2, since in the former case they would lessen the effective stabilization of the ion-pair I by solvation and in the latter could provide some steric hindrance to the approach of the alcohol molecule in step 3. In general, this is seen to be the case, the relative rates falling from 1 for benzene to 0.05 for *t*-butylbenzene and to an undetectably slow rate for *p*-di-*t*-butylbenzene. The importance of this effect is also visible in the relative rates of reduction of *o*-xylene (0.05), tetralin (0.38) and indan (0.94).

At least part of the reason for the effectiveness of lithium in the reduction appears to be the ease with which the solvated ion can form the required ion-pair I. The increase in rate of reduction with sodium and ethanol when lithium bromide is added may be interpreted in terms of the equilibrium

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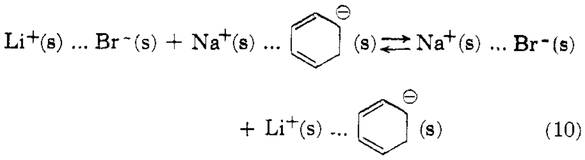
(12) W. Hückel and H. Bretschneider, *Ann.*, **540**, 157 (1939).

(13) T. L. Chu and S. C. Yu, THIS JOURNAL, **76**, 3367 (1954).

(14) D. E. Paul, D. L. Lipkin and S. I. Weissman, *ibid.*, **78**, 116 (1956).

(15) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **26**, 1517 (1957).



(10)

which goes far to the right. The equilibrium may be approached from either side, as is shown by the near equality of the rate constants observed for the lithium reduction with added sodium bromide, and for the sodium reduction with added lithium bromide. The rate of reduction with sodium and ethanol is essentially unaffected by added sodium bromide, as would be expected. The existence of an equilibrium of the type shown in equation 10, and the large effect of the metal ion on the stability of ion-pairs of this nature has previously been observed.[16]

The energy of activation for the lithium–ethanol reduction of benzene in liquid ammonia calculated from the observed rate constants at −34° and −74° is 2.7 kcal./mole. The corresponding quantity for the reduction with lithium and *t*-butyl alcohol is 4.4 kcal./mole. The very low values are in general accord with the proposed mechanism. The main energy barrier to be overcome would be the close approach of the alcohol molecule to the anion, displacing more effective solvating molecules. On this basis the slightly greater energy of activation observed for the bulky *t*-butyl alcohol is expected.

Since the major product in the reduction of monoalkyl benzenes is the 2,5-dihydro derivative, the original addition of a proton in step 3 must occur at a position *ortho* or *meta* to the alkyl group. In this connection it is interesting that the hyperfine splitting in the electron spin resonance spectrum of the toluene radical anion as observed by Tuttle and Weisman,[11] indicates about equal density of the unpaired electron at the *o*- and *m*-positions, but little or none at the *p* position.

Initial addition at the *m*-position seems attractive for a number or reasons. Firstly, the *m*-position is more open to attack, the *o*-position being somewhat shielded by the alkyl substituent. Secondly, the radical produced would have the greatest unpaired electron density at the positions *ortho* and *para* to the alkyl group where it could be most efficiently solvated. Thirdly, in the subsequent addition of the second proton, a bulky substituent would hinder addition at the *o*-position and increase the fraction of the reactants passing by way of step 5′ to produce cyclohexenes. In fact, there is a definite trend toward a greater fraction of cyclohexenes in the product as the steric requirements of the alkyl group are increased (*cf.* Table VI). Thus, the product from *t*-butylbenzene contains more than 10% of assumed cyclohexenes. With this interpretation in mind, it is not surprising that the reduction of *o*-xylene yields a substantial amount of 1,4-dihydro-*o*-xylene in addition to the expected 3,6-dihydro-*o*-xylene.

The kinetic data alone do not rule out other possible mechanisms involving one molecule of benzene, one molecule of alcohol and one metal atom (or electron, or ion-pair) before the rate-determining step. Thus, for example, the primary addition of a hydrogen atom as proposed by Hückel, Graf and Münkner,[4e] could satisfy the kinetic criteria provided the concentration of hydrogen atom donors was proportional to the product of the concentrations of the metal and the alcohol. On the other hand, the ammonium ion cannot serve in this role, because much better yields are obtained in the reduction of benzene with alcohols as the proton source than with ammonium chloride as the proton source. That certain added metals and metal ions catalyze the reaction of alkali metals with alcohols in liquid ammonia solution is certainly true; however, addition of such metals to a reduction proceeding under Birch conditions must lower the yield of hydrocarbon reduction product, whatever the reaction mechanism, since it provides an "escape path" for some of the hydrogen which would otherwise be added to the benzene.

While the mechanism of Fig. 4 accounts satisfactorily for the metal–ammonia–alcohol reductions of simple benzenes, it seems likely that the reduction of polynuclear aromatic compounds follows a different path. Attention already has been drawn to the capacity which naphthalene possesses for carrying two electrons in liquid ammonia solution. The fact that addition of ammonium chloride to such a solution affords high yields of reduction products suggests that the reduction may proceed in this and similar cases by the addition of protons to a solvated dianion. The reduction of alkyl benzenes probably proceeds through the radical anion because the equilibrium of step 2 is far to the left, and the further electronation of the radical anion occurs to a vanishingly small extent.

Acknowledgment.—Grateful acknowledgment is made to Research Corporation for a grant in support of this research.

Experimental

Individual Reductions.—The reductions were performed in a flask equipped with a stirrer, soda-lime drying tube, nitrogen inlet and ammonia inlet. After the flask was flushed thoroughly with a slow nitrogen stream, the ammonia was added followed by the addition of the hydrocarbon and, in most cases, ether to effect solution. The metal was added and stirring continued until solution was complete. The proton source was added and on completion of the reaction (as noted by the disappearance of the blue color) ether was added to the ammonia solution. The ammonia was allowed to evaporate partially, water was added, and the ethereal layer was separated. The ethereal layer was washed several times with water and dried over anhydrous potassium carbonate. The dried ethereal solution was utilized directly for the vapor phase chromatographic analysis. For isolation of the reduction product and analysis by ultraviolet spectroscopy and refractometry the ether was removed under reduced pressure.

The instrument utilized for the vapor phase chromatographic analysis was a Perkin–Elmer Vapor-Fractometer model 154B, which could be fitted with a 4-meter "A" or a 4-meter "B" column, the stationary liquid on the columns being didecyl phthalate and di-2-ethylhexyl sebacate, respectively. The component corresponding to each peak in the chromatogram was identified by (1) bubbling the exit gases through 95% ethanol and recording the ultraviolet spectrum of the sample, (2) trapping the exit gases in carbon tetrachloride or carbon disulfide and recording the infrared spectrum, and (3) by comparison of the retention time with that of an independently synthesized sample.

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[16] R. L. Ward and S. I. Weissman, THIS JOURNAL, **79**, 2086 (1957).

The vapor phase chromatographic analysis for each subsequent run will be found in Table VI (text). In all runs the unreduced hydrocarbon peak on the chromatogram was identified by collection of the sample in 95% ethanol and examination of its ultraviolet absorption spectrum.

a. **Benzene.**—Benzene[17] was reduced in two runs, once using half stoichiometric and once using stoichiometric quantities of lithium and ethanol. The vapor phase chromatographic analysis was performed using a 4-meter "A" column at a temperature of 92°. The cyclohexene was identified by comparison of the retention time and infrared absorption spectrum with that of a commercial sample.[18] The 1,4-dihydrobenzene fraction in 95% ethanol showed only end absorption in the ultraviolet spectrum (about 225 mμ) and deposited black quinhydrone on treatment with quinone in benzene solution.

b. **Toluene.**—In order to ascertain the structure of the major reduction product of toluene[19] a sample of toluene-4-^{2}H was prepared by treatment of *p*-tolylmagnesium bromide with heavy water. The deuterio compound was reduced under the standard conditions. The dihydrotoluene which was isolated showed no ultraviolet absorption in the region 240 to 300 mμ in 95% ethanol and therefore contained no unreduced toluene. The infrared spectrum exhibited an intense absorption peak at 4.46 μ, characteristic of a deuterium substituted on an olefinic carbon.

Toluene[17] was reduced in two runs using half stoichiometric and stoichiometric quantities of lithium and ethanol. The vapor phase chromatographic analysis utilizing a 4-meter "A" column showed the presence of 5 components. The 2,5-dihydrotoluene fraction gave a positive quinhydrone test and showed only end absorption in the ultraviolet absorption spectrum. The minor components were identified as 1-methyl-1-cyclohexene,[20] 3-methyl-1-cyclohexene[21] and 4-methyl-1-cyclohexene[18] by a comparison of the retention times with those of authentic samples.

c. **Ethylbenzene.**—Ethylbenzene[22] was reduced in two runs using stoichiometric and double stoichiometric quantities of lithium and ethanol. The 2,5-dihydroethylbenzene fraction showed only end absorption in the ultraviolet spectrum near the 220 mμ region in 95% ethanol, gave a positive quinhydrone test, and had an infrared spectrum in many respects similar to that of 2,5-dihydrotoluene. The minor component was shown to be 1-ethyl-1-cyclohexene by comparison of the retention time and infrared spectrum of the sample eluted from the column with that of an authentic sample.[23]

d. **Isopropylbenzene.**—Isopropylbenzene[18] was reduced using two moles of lithium and two moles of ethanol. The major product of the reduction was identified as 2,5-dihydroisopropylbenzene by its infrared spectrum, lack of absorption in the ultraviolet spectrum in 95% ethanol, and by a positive quinhydrone test. The minor component was identified as 1-isopropyl-1-cyclohexene by comparison of the retention time on the column with that of a synthetic sample.[24]

e. ***t*-Butylbenzene.**—*t*-Butylbenzene[18] was reduced with two moles of lithium and two moles of ethanol. Vapor phase chromatographic analysis indicated that four components were present. The 2,5-dihydro-*t*-butylbenzene showed only end absorption in the ultraviolet spectrum in 95% ethanol, gave a positive quinhydrone test, and had an infrared spectrum similar to the other 2,5-dihydro systems. The other two minor components were not identified and are assumed to be *t*-butylcyclohexenes.

f. **Anisole.**—Anisole[18] was reduced using stoichiometric and double stoichiometric quantities of lithium and ethanol. The vapor phase chromatographic analysis of the ethereal solution showed the presence of a low-boiling species and several higher boiling fractions. The half-width of the third component was always greater than that of the fourth component, which was identified as anisole by its retention time. This peculiarity in half-width suggested that the component was decomposing on the column. The low-boiling species was identified as cyclohexene by its retention time.

To overcome the difficulty of decomposition on the column the analysis was accomplished as follows: A 1-g. sample of the reduction product was warmed with 10 cc. of 5% hydrochloric acid on the steam-bath for 20 minutes. The mixture was cooled and extracted with ether. The ethereal extract was washed with sodium bicarbonate solution, then with water, and finally dried over potassium carbonate. Vapor phase chromatographic analysis of the dried ethereal extract showed the presence of cyclohexanone, cyclohexenone[21] and anisole. These components were identified by comparison of the infrared spectra of the collected fractions with those of authentic samples. The vapor phase chromatographic analysis was

	2 Li	4 Li
Cyclohexene, %	2.7	4.7
Cyclohexanone, %	7.1	8.8
Cyclohexenone, %	52.0	86.6
Anisole, %	38.2	. .

1. **Conjugated isomer of 2,5-dihydroanisole** was prepared as described by Birch.[25]

2. **Thermal Isomerization of 2,5-Dihydroanisole.**—A 1-g. sample of the anisole reduction product was refluxed for 20 minutes exposed to the air. A sample treated with benzoquinone immediately developed a red coloration indicative of the presence of the conjugated system. Comparison of the infrared absorption spectra of the thermally isomerized dihydroanisole and of the conjugated isomer produced by treatment with sodamide according to Birch[25] showed that the same compound is produced in both cases. In the thermal isomerization, some anisole is also produced (VPC).

3. **Reduction of the Conjugated Isomer.**—A sample prepared according to Birch[25] was reduced under standard conditions with two moles of lithium and two moles of ethanol. Product analysis by VPC indicated the composition: 1-methoxycyclohexene, 65%; cyclohexene, 35%. The 1-methoxycyclohexene was identified by its strong infrared absorption at 6.00 μ and by its acid hydrolysis to yield cyclohexanone.

g. ***p*-Xylene.**—Reduction of *p*-xylene[18] in two runs was performed with stoichiometric and double stoichiometric quantities of ethanol and lithium. The vapor phase chromatogram of the reduction product showed the presence of two components. On addition of *p*-xylene to the reduction mixture the area of the major component was increased thus showing that *p*-xylene was not being separated from its reduction product. The ratio of the amount of major reduction product to the amount of minor reduction product, as determined for the run using four moles of lithium, was found to be 23 (unreduced *p*-xylene was demonstrated to be absent by the lack of ultraviolet absorption). Assuming this ratio to be constant the composition of the mixtures obtained by partial reduction could be calculated from the areas of the peaks in the vapor phase chromatogram. The minor reduction product was identified as 1,4-dimethyl-1-cyclohexene by comparison of the retention time and infrared spectrum with that of a synthetic sample.[26] The major reduction product was identified as 2,5-dihydro-*p*-xylene by its infrared spectrum, positive quinhydrone test and lack of absorption in the ultraviolet spectrum. Reduction of *p*-xylene-2-^{2}H[27] in the standard manner gave a compound showing only end absorption in its ultraviolet spectrum. The infrared spectrum contained two bands of equal intensity at 4.47 μ (deuterium on olefinic carbon) and 4.74 μ (deuterium on saturated carbon).

h. ***o*-Xylene.**—Reduction of *o*-xylene[18] in two runs was performed using stoichiometric and double stoichiometric quantities of lithium and ethanol. The major reduction product has been assigned the structure 3,6-dihydro-*o*-xylene by Hückel, *et al.*[4b(1)] The minor reduction product was identified by a comparison of its retention time with those of the substituted cyclohexenes obtained from the

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[17] Merck and Co., Inc., reagent grade, assay by VPC of greater than 99.9% purity.

[18] Eastman Kodak Co., white label.

[19] An independent demonstration of the structure has been reported by Hückel, *et al.*, ref. 4e.

[20] S. Nametkin and A. Jarzewa, *Ber.*, **56**, 1803 (1923).

[21] Research Stores, Harvard University.

[22] Koppers Co., purity greater than 99.6% as assayed by VPC.

[23] D. Wallach and P. Mendelsohn-Bartholdy, *Ann.*, **360**, 50 (1908).

[24] From the dehydration of 1-isopropylcyclohexanol: K. Auwers and P. Ellinger, *ibid.*, **387**, 223 (1912).

[25] A. J. Birch, *J. Chem. Soc.*, 1551 (1950).

[26] N. Zelinsky and A. Gorsky, *Ber.*, **41**, 2632 (1908).

[27] Prepared from the Grignard reagent by reaction with deuterium oxide.

phosphoric acid dehydration of the alcohol produced by the reaction of methylmagnesium iodide with 2-methylcyclohexanone.[28] The major product in this dehydration in the ratio of 3 to 1 was 1,2-dimethyl-1-cyclohexene; the minor product was 2,3-dimethyl-1-cyclohexene.[28] The minor reduction product corresponded in retention time to 2,3-dimethyl-1-cyclohexene. That the major product of the dehydration of 1,2-dimethylcyclohexanol-1 was 1,2-dimethyl-1-cyclohexene was also shown by the nuclear magnetic resonance spectrum, which indicated the absence of hydrogen atoms situated on doubly bonded carbons.

The 1,4-dihydro-*o*-xylene was identified by its infrared spectrum, positive quinhydrone test and lack of absorption in the ultraviolet.

i. ***m*-Xylene.**—Reduction of *m*-xylene[18] in two runs was performed using stoichiometric and triple stoichiometric quantities of lithium and ethanol. The low retention time species on the chromatogram were shown to be identical to the two substituted cyclohexenes obtained from the phosphoric acid dehydration of 1,3-dimethyl-1-cyclohexanol.[26,28,29] By vapor phase chromatography it was shown that in the dehydration the products were produced in the ratio of two to one. Dehydration of the alcohol produced by the lithium aluminum hydride reduction of *cis*-3,5-dimethyl-1-cyclohexanone[30] produced three olefins in the ratio of 30:26:44. Two of these compounds were identical with the products of dehydration of 1,3-dimethyl-1-cyclohexanol. The species not appearing in the dehydration of 1,3-dimethyl-1-cyclohexanol was probably *cis*-1,3-dimethyl-4-cyclohexene. The structures 1,3-dimethyl-1-cyclohexene and 2,4-dimethyl-1-cyclohexene then could be assigned to the minor components in the reduction product.[29] The major component was 2,5-dihydro-*m*-xylene as was shown by a positive quinhydrone test, lack of absorption in the ultraviolet spectrum and an infrared spectrum in accordance with this structure. The additional minor component was similarly identified as 1,4-dihydro-*m*-xylene.

j. **Mesitylene.**—Mesitylene[18] was reduced in two runs using stoichiometric and one and one-half times stoichiometric quantities of lithium and ethanol. The *cis*-tetrahydromesitylene was identified by comparison of the retention time and infrared absorption spectrum with that of an independently synthesized sample.[31] The 1,4-dihydromesitylene showed a positive quinhydrone test, exhibited only end absorption in the ultraviolet spectrum, and had an infrared spectrum similar to that of the *m*-xylene reduction product.

k. **1-Methoxy-2-cyclohexene.**—Treatment of 1-methoxy-2-cyclohexene[32] with two moles of lithium produced no blue coloration as the color was immediately discharged. The only low-boiling species present in the reduction product was cyclohexene which was identified by its infrared spectrum.

Determination of the Kinetic Order of the Reaction.—The reductions were usually performed at the boiling point of the liquid ammonia. Since reaction times were generally short, no difficulty was encountered in temperature variation. The low energy of activation for the reduction obviated the necessity for very close temperature control. The reductions were performed as described above. A calibrated reaction vessel equipped with a stopcock on the bottom was utilized. Zero time was taken as the time at which the proton source was added. The reaction was quenched by draining an aliquot into an ethereal suspension of sodium benzoate. The ethereal suspension was washed with water, dried over anhydrous potassium carbonate, and the dried ethereal solution analyzed directly by vapor phase chromatography.

Reduction of Benzene–Sodium Benzoate.—To 150 cc. of liquid ammonia was added 2.0 g. (0.026 mole) of benzene, 3.7 g. (0.026 mole) of sodium benzoate and 50 cc. of ether. To this mixture was added 0.18 g. (0.052 mole) of lithium. The initial blue color changed to yellow, then brownish-yellow. Three grams (0.065 mole) of ethanol was added to discharge the color. After standard workup the vapor phase chromatogram showed that none of the benzene had been reduced.

Order Determination.—Data on the reduction of benzene by lithium and *t*-butyl alcohol are given in Table III (text). Reduction of benzene at 0.061 *M* with 0.122 *M* lithium and 0.122 *M* *t*-butyl alcohol proceeded initially at the rate of 0.000049 mole/liter sec. Doubling the concentration of lithium raised the initial rate to 0.000098 mole/liter sec., while doubling the concentration of *t*-butyl alcohol raised the rate to 0.00011 mole/liter sec. The order with respect to each is therefore one.

Data on the reduction of benzene with lithium and ethanol are given in Table II and plotted on a third-order rate plot in Fig. 1. Plots assuming other kinetic orders show pronounced curvatures.

Competitive Reductions (Benzene–Toluene).—In a one-liter three-necked flask fitted with a mechanical stirrer, soda-lime drying tube, nitrogen inlet and dropping funnel, were placed 500 cc. of liquid ammonia, 7.85 g. (0.1005 mole) of benzene and 9.27 g. (0.1006 mole) of toluene. To this mixture was added 1.39 g. (0.2000 mole) of lithium metal. The mixture was stirred for 1400 seconds under a slow nitrogen stream. To the resulting blue solution was added 13.77 g. (0.3000 mole) of absolute ethanol. The time required to discharge the blue coloration was 230 seconds. The ammonia was partially evaporated, ether was added, and the residual ammonia decomposed by the addition of ice. The ethereal layer was separated, washed thoroughly with water, and dried over potassium carbonate. Vapor phase chromatographic analysis was carried out directly on the ethereal solution. The following analysis was obtained in a typical experiment using a 4-meter "A" column.

Benzene reduction		Toluene reduction	
Benzene, %	45.0	Toluene, %	60.9
1,4-Dihydrobenzene, %	55.0	2,5-Dihydrotoluene, %	39.1

Other Pairs of Hydrocarbons.—Using the same experimental procedure the observations summarized in Table VII were made.

Table VII

Benzene and hydrocarbons	Reduction of benzene, %	Reduction of hydrocarbon, %	Molar ratio benzene/ hydrocarbon/Li
t-Butylbenzene	89.2	10.9	1/1/2
	79.8	7.6	1/2/2
o-Xylene	77.0	7.3	1/1/2
i-Propylbenzene	82.5	15.0	1/1/2
	63.0	10.3	1/2/2
Aniline	82.5[a]	17.7[c]	1/1/2
Ethylbenzene	73.9	28.0	1/1/2
	59.3	19.8	1/2/2
m-Xylene	72.8	33	1/1/2
	60.8	21	1/2/2
p-Xylene	66.3	29.3	1/1/2
	44.9	14.6	1/2/2
	65.9	29.3	1/1/2
Dimethylaniline	70.0[a]	30[c]	1/1/2
Tetralin	43.8	19.0	1/1/2
	30.2	12.6	1/1/1.5
Toluene	55.7	42.2	1/1/2
	38.3	25.2	1/2/2
Indane	48.4	46.4	1/1/2
Anisole	20.8	50[b]	1/1/2
	21.3	52	1/1/2
n-Butylbenzene	70.4	23	1/1/2
	52.1	14	1/1/1
Mesitylene	87.2	3.4	1/1/2

[a] Washed with hydrochloric acid to remove amines, then analyzed by VPC. The percentage reduction of the amine was calculated by assuming complete reaction of all the lithium. [b] Hydrolyzed, then analyzed by VPC. [c] Calcd.

Pittsburgh, Penna.

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[28] P. Sabatier and A. Mailhe, *Compt. rend.*, **141**, 21 (1905).

[29] N. Zelinsky and S. Zelikow, *Ber.*, **34**, 3255 (1901).

[30] Prepared by catalytic hydrogenation of 3,5-dimethylcyclohexene-2-one-1 ("Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 317).

[31] Synthesized by reaction of methylmagnesium iodide with *cis*-3,5-dimethyl-1-cyclohexanone[30] and dehydration of this alcohol.

[32] A. Berlande, *Bull. soc. chim.*, 649 (1942).