

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, WEST LAFAYETTE, INDIANA]

The Selective Reduction of Aromatic Compounds to Dihydro or Tetrahydro Products by an Electrochemical Method^{1,2}

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A dramatic change in product composition was found to occur when a series of representative aromatic hydrocarbons was reduced electrochemically in a divided and undivided cell. In the undivided cell, dihydro products were formed almost exclusively, while in the divided cell tetrahydro products predominated. An electrolyte consisting of lithium chloride dissolved in methylamine was used in every case. It is shown that the cell divider serves to keep apart the lithium alkylamide produced in the cathode compartment from the methylamine hydrohalide formed in the anode compartment. The unconjugated dihydro products, formed in the cathode compartment initially, are isomerized by the alkylamide to conjugated diene systems, thereby allowing them to be reduced further to tetrahydro products. In the undivided cell, it is suggested that alkylamide is neutralized immediately by the amine hydrohalide so that the unconjugated dihydro products are isolated intact. It is also shown that the aromatic compounds, as well as their intermediate dihydro reduction products, do not undergo any appreciable oxidation at the anode in these cells. Instead, the amine solvent is oxidized, either directly at the anode or through the intermediacy of chlorine atoms resulting from oxidation of chloride ions. Methylamine hydrohalide and 1,3,5-trimethylhexahydro-*s*-triazine have been isolated from the anode compartment. After hydrolysis of the anolyte, *N*-methylformamide has also been found in this compartment.

It is well established that the ring systems of many aromatic compounds are reduced to monoolefins (tetrahydro products) by a solution of lithium metal in certain low molecular weight amines.¹ It has also been established that similar reductions carried out in a solvent mixture consisting of the amine and an alcohol are equally selective, but in these cases the reaction proceeds only to the dihydro stage.³ The latter cases represent a variation of the well known Birch⁴ reduction.

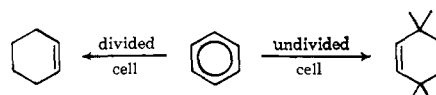
While these lithium-amine reductions are of considerable synthetic utility,⁵⁻⁸ the cost of lithium metal makes them rather expensive for large-scale usage. At the same time, the monoolefins produced in the reductions are often isomer mixtures⁹ of closely related structures which makes separation of any one pure component a rather formidable task. It was thought that perhaps a solution to both of these problems could be achieved by carrying out the reductions electrochemically.

Lithium salts, dissolved in the appropriate amine, might serve as the electrolyte, the lithium ion acting simply as a "current carrier," possibly undergoing reduction to the metal and then oxidation back to the ion as the aromatic compounds present are reduced. In this way the electrolyte would be capable of reuse, thereby helping to offset the cost of lithium metal. At the same time it was hoped that a greater selectivity might be achieved electrochemically, in that variables like electrode potentials and concentration of metal could be conveniently controlled. This paper de-

scribes the results obtained when such electrochemical reductions were carried out.¹⁰

Reduction Products in Divided and Undivided Cells.—It was noted at the very outset¹¹ that there was a marked difference in the aromatic reduction product when the electrolysis was carried out in a simple cell in which the anode and cathode were not separated and when a divided¹² cell was employed.

When aromatic compounds like benzene, dissolved in methylamine containing lithium chloride, were reduced in an undivided cell,¹³ dihydro products resulted almost exclusively. When the same reductions were repeated using a divided cell, tetrahydro products (monoolefins) were produced and dihydro products were eliminated.



Tables I and II summarize the results obtained when several representative aromatic hydrocarbons were reduced in both the divided and undivided cell.

Problems Associated with Cell Divider.—The type of cell divider to be used presented several design problems. The divider had to be chemically inert to both acid and base, since a base was being generated in the cathode compartment and an acid in the anode compartment. It had to be inert to the blue solution of lithium dissolved in the amine and yet permeable enough to permit ion passage. After screening several materials, it was decided that ordinary asbestos met most of the necessary requirements. Unfortunately, even this material had a serious drawback. Often, as a divided cell electrolysis proceeded, a sudden drop in current was noted. This could be overcome occasionally by interrupting the current altogether and then starting it up again. On still other occasions, if the applied voltage was diminished and then gradually

(10) Professor Birch had reported a successful electrolytic reduction of *m*-tolyl methyl ether in liquid ammonia; see *Nature*, **168**, 60 (1946).

(11) Ph.D. Thesis of R. F. Lambert, Purdue University, 1958.

(12) H. W. Sternberg, R. Markby, and I. Wender, *J. Electrochem. Soc.*, **110**, 425 (1963), disclose a similar electrochemical reduction of benzene and tetralin.

(13) Either the cell depicted in our preliminary announcement (ref. 2) can be used without the divider or an ordinary three-necked flask containing two platinum electrodes and a condenser.

(1) This is paper IX in a series entitled: "Reduction of Organic Compounds by Lithium in Low Molecular Weight Amines." See *J. Org. Chem.*, **29**, 1313 (1964), for the previous paper.

(2) A preliminary announcement of this work appeared in *J. Am. Chem. Soc.*, **85**, 2858 (1963).

(3) R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *J. Org. Chem.*, **28**, 1094 (1963).

(4) See A. J. Birch, *Quart. Rev. (London)*, **4**, 69 (1950); **12**, 17 (1958), for pertinent references.

(5) A. W. Burgstahler and L. R. Worden, *J. Am. Chem. Soc.*, **83**, 2587 (1961).

(6) A. W. Burgstahler, L. R. Worden, and T. B. Lewis, *J. Org. Chem.*, **28**, 2918 (1963).

(7) R. A. Benkeser and E. M. Kaiser, *ibid.*, **29**, 955 (1964).

(8) A. Patchornik, M. Wilchek, and S. Sarid, *J. Am. Chem. Soc.*, **86**, 1457 (1964).

(9) Recently we have shown that these reductions can be much more selective by carrying them out in solvent mixtures consisting of primary and secondary amines. See paper VIII (ref. 1).

TABLE I
ELECTROLYTIC REDUCTION OF VARIOUS AROMATIC
HYDROCARBONS IN METHYLAMINE-LITHIUM CHLORIDE
SOLUTIONS WITHOUT CELL DIVIDER^{a,b}

Aromatic	Boiling range of product, °C. (g.) ^c	Product composition, %		
		Di- hydro- benzenes	Alkyl- cyclo- hexenes	Re- covered aromatic
Benzene	87-88 (3.8)	95	4	1
Toluene	111-116 (5.9)	95 ^d	5	..
Ethylbenzene	133-142 (7.7)	96 ^d	4	..
Cumene	152-157 (9.8)	81 ^d	6	13
<i>t</i> -Butylbenzene	166-173 (11.4)	75 ^d	5	20

^a In each case the cell contained 0.8 mole of lithium chloride and 0.1 mole of aromatic compound dissolved in 900 ml. of methylamine. ^b A total of 50,000 coulombs in 7 hr. was passed through the solution in each case. ^c The values in parentheses are the number of grams of product obtained after distillation whose composition is listed in the succeeding columns. ^d Over 90% of the dihydro products obtained possessed the 2,5-dihydro structure.

TABLE II
ELECTROLYTIC REDUCTIONS OF VARIOUS HYDROCARBONS
IN METHYLAMINE-LITHIUM CHLORIDE SOLUTIONS WITH
A MODIFIED CELL DIVIDER^{a,b}

Aromatic	Boiling range ^c of product, °C. (g.)	Product composition, %	
		Alkylcyclo- hexenes	Recovered aromatic
Toluene	100-103 (3.5)	83 ^d	17
Ethylbenzene	130-135 (8.0)	89	11
Cumene	146-153 (8.4)	81 ^e	19
<i>t</i> -Butylbenzene	160-169 (10.6)	65 ^f	35

^a In each case 0.4 mole of lithium chloride and 450 ml. of methylamine were placed in *each* of the half cells. The aromatic compound to be reduced (0.1 mole) was placed only in the cathode chamber. ^b A total of 50,000 coulombs (2 amp.) was passed through the cell for 7 hr. in each case. ^c The values in parentheses are the number of grams of product obtained after distillation whose composition is listed in the succeeding columns. ^d Consisted of 53% 1-methylcyclohexene and 30% 3- and 4-methylcyclohexenes. ^e Consisted of 39% 1-isopropylcyclohexene, 22% 3-isopropylcyclohexene, and 19% 4-isopropylcyclohexene. ^f Consisted of 38% 1-*t*-butylcyclohexene, 19% 3-*t*-butylcyclohexene, and 8% 4-*t*-butylcyclohexene.

increased again the original amperage could be restored. The phenomenon was erratic in that it did not occur in every divided cell electrolysis. Its occurrence was frequent enough, however, to cause us to seek a solution.

The cause for the current drop was traced to a build-up in resistance of the divider. This was caused either by the precipitation of salts in the interstices of the asbestos or by a solvent vapor barrier forming between the asbestos layers.¹⁴ The latter simply had the effect of diminishing the contact area between the two half-cells. The situation could be improved by using asbestos which had been thoroughly wet with water and then allowed to dry or, better still, by using the "modified asbestos" which is described in the Experimental.¹⁵ Such dividers largely circumvented the resistance problem and still provided the barrier between com-

(14) In the interest of brevity, we have not included a rather large body of experimental work which led us to these conclusions. Interested persons can find complete details in the Ph.D. thesis of E. M. Kaiser, Purdue University, 1964.

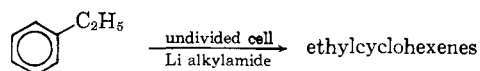
(15) We feel certain that more refined modification for such cell dividers are possible and indeed desirable. It was not in keeping with our intent or interest to dwell on the engineering aspects of cell design. Our chemical curiosities were served by the "modified" asbestos dividers we describe herein.

partments needed to observe the change from dihydro to tetrahydro reduction products.

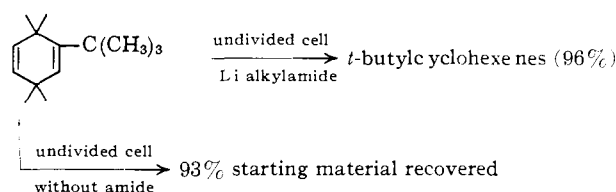
Function of Cell Divider.—The first question which required an answer was the reason for the drastic change in product composition when reductions were carried out in divided and undivided cells. Visually there was a marked difference between reductions carried out in the two types of cells. In reductions carried out in the presence of a cell divider, the amine solution in the cathode compartment became deep blue in color, highly reminiscent of the blue color obtained when lithium metal dissolves in methylamine. This blue color pervaded the entire catholyte solution but stopped abruptly at the asbestos divider. The anode compartment was never blue and usually took on a pale yellow-orange color as the reaction proceeded. In undivided cell reductions, the entire solution never became blue (except perhaps temporarily around the cathode) and, at the end of the reaction, possessed only a slight coloration. These observations strongly hinted that the asbestos divider was serving to keep apart otherwise incompatible anode and cathode products.

From the anode compartment of the divided cell, it was possible to isolate and characterize methylamine hydrohalide which formed in copious quantities. It was obvious that lithium methylamide must be formed in the blue solution of the cathode compartment since methylamine was the only proton source. In the undivided cell, the methylamine hydrohalide could not be detected as a product. It seemed almost certain that the asbestos divider was serving to keep apart the acidic methylamine hydrohalide from the basic lithium alkylamide and hence preventing destruction of the latter material by neutralization.

It was shown previously⁸ that lithium alkylamides cause rapid isomerization of unconjugated dihydro systems to conjugated products which are capable of further 1,4-reductions by the lithium-amine system. Hence, if an aromatic compound were reduced in the undivided cell in the presence of *excess* lithium alkylamide, one might predict that monoolefin products instead of the usual dihydro materials might be produced. When the reduction of ethylbenzene was carried out in the undivided cell in the presence of preformed amide, a deep blue coloration was observed throughout the solution during the course of the reaction and monoolefins, but no diene products, were formed.



Likewise, when pure 2,5-dihydro-*t*-butylbenzene was reduced in the undivided cell in the presence of preformed amide, only monoolefins were obtained. In the absence of the preformed amide, it was shown that passage of the current left the 2,5-dihydro-*t*-butylbenzene virtually unchanged.



It is attractive to explain the results obtained in the undivided cell by assuming that the lithium alkylamide formed near the cathode is neutralized rapidly by the amine hydrohalide formed near the anode. Under these conditions, the dihydro reduction products (being unconjugated) are stable to further reduction.¹⁶ In the divided cell, the lithium alkylamide in the cathode compartment remains in contact with the initially formed unconjugated dihydro products. The latter undergo isomerization to conjugated systems, which are reduced further to monoolefins.

Fate of Organic Materials in Anode and Cathode Compartment of Divided Cell.—In order to ascertain whether any of the aromatic compounds or their intermediate reduction products were undergoing oxidative changes at the anode, several experiments were carried out in which the material to be reduced was placed in the anode compartment of a divided cell rather than in the cathode compartment. The latter constituted the normal procedure for our reductions.

In one experiment, *t*-butylbenzene was placed in the anode compartment and electrolyzed with "single layer" asbestos as a divider. The experiment was repeated with "double layer" asbestos. The results, as shown in Table III, clearly indicate that the *t*-

TABLE III

DIVIDED CELL ELECTROLYSIS UTILIZING "SINGLE" AND "DOUBLE" LAYER ASBESTOS DIVIDER WITH *t*-BUTYLBENZENE IN ANODE COMPARTMENT^{a,b}

Compounds	Composition after electrolysis, %	
	Anode compartment	Cathode compartment
1- <i>t</i> -Butylcyclohexene	0.8 (—)	22 (30)
3- <i>t</i> -Butylcyclohexene	0.6 (—)	16 (22)
4- <i>t</i> -Butylcyclohexene	.. (—)	7 (9)
<i>t</i> -Butylbenzene	98.6 (100)	55 (38)

^a The first values listed are for the "single" layer asbestos run. The values in parentheses are for the "double" layer run.

^b In each run 13.4 g. (0.1 mole) of *t*-butylbenzene was originally placed in the anode compartment. A total of 43,200 coulombs (2.0 amp.) was passed through the solution in 6 hr. in each case.

butylbenzene was essentially unchanged in the anode compartment. Some of the aromatic had "leaked" into the cathode compartment where it was reduced normally to monoolefins. More leakage had occurred in the case of the single layer asbestos divider as might be expected.

In still another experiment (Table IV), a mixture consisting primarily of 2,5-dihydro-*t*-butylbenzene was placed in the anode compartment. Again, the material recovered from the anode compartment after the current had been passed showed only an insignificant change in chemical composition. The material which "leaked" into the cathode compartment had undergone normal reduction to monoolefin.

In a third experiment, a mixture consisting primarily of conjugated *t*-butylcyclohexadienes was placed in the anode compartment (Table V). After the current had been passed through the mixture, the material recovered from the anode compartment was essentially unchanged

(16) While we strongly favor the above explanation for the undivided cell products, it must be conceded that it has not been rigorously proved. Other explanations might be invoked. It might be conjectured, for example, that it is alkylamide produced in the vicinity of the cathode which is oxidized by some process near or at the anode. Whatever explanation is invoked, it must necessarily involve the rapid destruction of alkylamide since we have clearly demonstrated that the prolonged presence of this material results in monoolefin formation.

TABLE IV
DIVIDED CELL ELECTROLYSIS UTILIZING "DOUBLE" LAYER ASBESTOS DIVIDER WITH UNCONJUGATED *t*-BUTYLCYCLOHEXADIENES^{a,b} IN ANODE COMPARTMENT

Compounds	Composition after electrolysis, %	
	Anode compartment	Cathode compartment
2,5-Dihydro- <i>t</i> -butylbenzene	81	..
1,4-Dihydro- <i>t</i> -butylbenzene	4	..
1- <i>t</i> -Butylcyclohexene	10	62
3- <i>t</i> -Butylcyclohexene	1	24
4- <i>t</i> -Butylcyclohexene	..	7
<i>t</i> -Butylbenzene	4	8

^a The original mixture to be reduced (consisting of 8% 1-*t*-butylcyclohexene, 4% 1,4-dihydro- and 84% 2,5-dihydro-*t*-butylbenzene, and 5% *t*-butylbenzene) was placed in the anode compartment only. ^b A total of 30,000 coulombs in 6.3 hr. was passed through the solution.

TABLE V

DIVIDED CELL ELECTROLYSIS UTILIZING "DOUBLE" LAYER ASBESTOS DIVIDER WITH CONJUGATED *t*-BUTYLCYCLOHEXADIENES^{a,b} IN ANODE COMPARTMENT

Compounds	Composition after electrolysis, %	
	Anode compartment	Cathode compartment
2,3-Dihydro- <i>t</i> -butylbenzene	52	..
3,4-Dihydro- <i>t</i> -butylbenzene	18	..
2,5-Dihydro- <i>t</i> -butylbenzene	7	..
1- <i>t</i> -Butylcyclohexene	10	77
3- <i>t</i> -Butylcyclohexene	..	17
4- <i>t</i> -Butylcyclohexene	..	6
<i>t</i> -Butylbenzene	13	..

^a The original mixture to be reduced (consisting of 9% 1-*t*-butylcyclohexene, 19% 3,4-dihydro- and 51% 2,3-dihydro-*t*-butylbenzene, 7% 2,5 dihydro-*t*-butylbenzene, and 13% *t*-butylbenzene) was placed in anode compartment only. ^b A total of 30,000 coulombs in 4.5 hr. was passed through the solution.

in chemical composition. The material which "leaked" to the cathode compartment was reduced to monoolefins.

Several conclusions become immediately apparent from these results (Tables III, IV, V): (1) Whatever material finds its way from the cathode to the anode compartment will remain essentially unchanged. (2) Whatever oxidation processes are occurring at the anode do not involve the initial aromatic compound or its intermediate reduction products. We will return to this latter point momentarily.

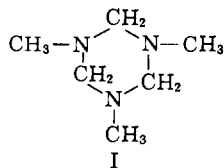
Gaseous Products of Electrolysis.—It was determined that small amounts of hydrogen were evolved during electrolysis in an undivided cell. The amount of hydrogen did not seem to vary appreciably with time.

In a divided cell electrolysis, no anode gases of any consequence could be collected. From the cathode compartment, however, appreciable quantities of hydrogen could be detected which increased with time. Apparently as the reduction progresses and the lithium alkylamide concentration increases in the cathode compartment, so does the tendency for the metal being liberated to react with solvent to yield hydrogen. The reaction between sodium and ammonia to form hydrogen and sodium amide is also known to be catalyzed¹⁷ by amide ion.

Anode Oxidation Products.—While most attention was centered in the study on the reduction process occurring at the cathode, some attempt was made to

(17) C. A. Kraus, *J. Am. Chem. Soc.*, **29**, 1557 (1907).

isolate anode oxidation products. Amine hydrohalide could always be detected in the anode compartment. This product pointed to the loss of hydrogen atoms by some substance as one of the primary oxidation steps. Since we had already demonstrated that the aromatic compounds and their intermediate reduction products were not being oxidized at the anode, this left the methylamine solvent as the principal suspect. The isolation of two other products from the anode compartment, namely N-methylformamide and 1,3,5-trimethylhexahydro-*s*-triazine (I), tended to substantiate the idea that it was the methylamine solvent



which was being oxidized, either directly at the anode or through the intermediacy of chlorine atoms derived from chloride ions.

It was shown that N-methylformamide appeared in the anolyte only *after* hydrolysis, while the triazine could be detected both before and after hydrolysis. Both the N-methylformamide and the triazine were characterized by isolating them from the anolyte and comparing their properties (n.m.r., infrared, and mass spectra) with authentic samples. An authentic sample of 1,3,5-trimethylhexahydro-*s*-triazine was synthesized from methylamine hydrochloride and formalin.¹⁸

Electrode Reactions.—Since it was not the intent of this work to establish the electrode reactions precisely, carefully controlled electrode potentials were not maintained nor quantitative product analyses made. However, the numerous qualitative observations made enable one to set forth a fairly satisfactory quantitative picture to explain the results obtained.

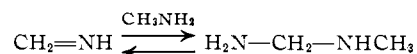
At the cathode, electrons are pumped into solution in the presence of lithium ions to form the well known blue solution which constitutes the active reducing agent. The mobile electrons in solution¹⁹ are transferred to the aromatic species present, forming anion-radicals or possibly dianions. The anionic species²⁰ are protonated by solvent to form unconjugated dihydro products and lithium alkylamide. In the undivided cell, the latter material is immediately neutralized¹⁶ by the amine hydrohalide forming at the anode and dihydro products are isolated. In the divided cell, the unconjugated dihydro materials are quickly isomerized to conjugated dienes by the alkylamides and are reduced further to monoolefins.

At the anode, methylamine is being oxidized either directly or through the intermediacy of chlorine atoms (by anode oxidation of chloride ion) to form hydrogen chloride and possibly methylenimine (CH₂=NH). The hydrogen chloride would react with solvent accounting for the methylamine hydrohalide detected. The methylenimine could certainly react reversibly with solvent

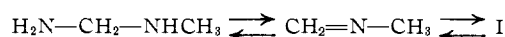
(18) J. Graymore, *J. Chem. Soc.*, **125**, 2284 (1924).

(19) At the present time we are of the belief that our electrolytic reductions are occurring in solution, although it is conceivable that they are taking place directly on the electrode surface. We are in the process of checking this point.

(20) See A. J. Birch and D. Nasipuri, *Tetrahedron*, **6**, 148 (1959), for an excellent discussion of the probable mechanism for such reductions.



The aminomethyl-N-methylamine could just as easily lose ammonia and the N-methylmethylenimine formed then trimerize²¹⁻²³



The N-methylformamide could arise from hydrolysis²⁴ of the triazine I and/or its precursors.

Experimental

General Directions for the Electroreduction of Alkylbenzenes in Methylamine in an Undivided Electrolysis Cell.—Alkylbenzenes were reduced in an undivided electrolysis cell previously described.² The cell was charged with 34.0 g. (0.8 mole) of lithium chloride, 900 ml. of anhydrous methylamine, and 0.1 mole of the aromatic compound to be reduced. A total of 50,000 coulombs was passed through the solution in 7 hr. (2.0 amp., 85 v.). At the end of this time, solvent was allowed to evaporate. The residue was hydrolyzed by the slow addition of water and the organic materials were extracted by ether. The ethereal extract was dried by calcium sulfate and the solvent removed. The product was distilled and the distillate analyzed by v.p.c. (Aerograph; 14 ft. β,β' -oxydipropionitrile column at 75°, 16 p.s.i. helium). Table I summarizes the results obtained by this procedure.

General Directions for the Divided Cell Reductions of Alkylbenzenes in Methylamine Using Modified Asbestos Dividers.—These reductions were accomplished in the electrolysis cell previously described. The cell was divided into two chambers by asbestos modified as follows. A 11 × 11 cm. piece of asbestos was moistened and all but 6–6.5 cm. separated into two layers. The thinner of the single layers was torn off and discarded. The resulting divider, after it was dried, was placed in the electrolysis cell such that 1 cm. in depth of the electrolyte solution was exposed to “single layer” asbestos, while 6 cm. of the solution was exposed to “double layer” asbestos. This type of asbestos did not cause a sudden current drop as the reductions proceeded.

Lithium chloride (17.0 g., 0.4 mole) and 450 ml. of methylamine were placed in *both* half cells and 0.1 mole of aromatic hydrocarbon was placed in the cathode compartment. Current was then passed through the cell for 7 hr. (50,000 coulombs, 2 amp.). The amine was allowed to evaporate through water condensers and the residue in each half cell was hydrolyzed by the slow addition of water. The aqueous solutions were combined at this point. Product isolation and identification were identical with that described under the directions for the undivided cell. The results of the divided cell reductions are listed in Table II.

Reactions of Hydrocarbons Occurring in Anode and Cathode Compartments of Divided Cell. Permeability of Asbestos Dividers.—The following experiments were carried out in the usual electrolysis cell in which the two compartments were separated by either “single” or “double” layer asbestos. The “double” layer asbestos refers to ordinary asbestos which had been first moistened and then allowed to dry. The moistened asbestos could be separated gently into two layers—the thicker layer of which, after drying, was used as “single” layer. In each reduction, *t*-butylbenzene or its intermediate reduction products were placed in the *anode* compartment. Lithium chloride (17 g., 0.4 mole) in 450 ml. of methylamine was placed in *each* half cell. When the reduction was completed, the contents of each half cell was hydrolyzed and worked up separately in the usual manner. Analysis was by v.p.c. (14 ft., β,β' -oxydipropionitrile, 80°, Aerograph). In all runs where “double” layer asbestos was used, 85–93% of the hydrocarbon materials isolated was found still in the anode compartment. In the case where “single” layer asbestos had been used, only 82% of the hydrocarbon material was still located in the anode. Tables III to V summarize these results.

Reduction of 2,5-Dihydro-*t*-butylbenzene in Undivided Cell. (A) In the Absence of Lithium Alkylamide.—The reduction of

(21) O. C. Wetmore and H. A. Taylor, *J. Chem. Phys.*, **12**, 61 (1944).

(22) G. W. Meadows and J. J. Kirkland, *J. Phys. Chem.*, **65**, 2139 (1961).

(23) C. Schopf, A. Komzak, F. Braun, and E. Jacobi, *Ann.*, **559**, 1 (1948).

(24) E. E. van Tamelen and G. C. Knapp, *J. Am. Chem. Soc.*, **77**, 1860 (1955). We are grateful to Dr. Knapp for bringing this reference to our attention.

13.0 g. (0.095 mole) of pure 2,5-dihydro-*t*-butylbenzene²⁵ was accomplished by passing 22,800 coulombs (1.3–1.7 amp.) in 4.5 hr. through an electrolyte composed of 10.2 g. (0.24 mole) of lithium chloride in 500 ml. of methylamine. The general procedure and work-up were identical with that described under the heading of "General Directions." Distillation at 165–172° gave 9.25 g. of product. Analysis by v.p.c. under the usual conditions showed: 4% 1-*t*-butylcyclohexene, 2% 3-*t*-butylcyclohexene, 1% 4-*t*-butylcyclohexene, and a 93% recovery of 2,5-dihydro-*t*-butylbenzene.

(B) **In the Presence of Lithium Alkylamide.**—Lithium methylamide was prepared *in situ* by the interaction of 3.9 g. (0.05 mole) of benzene and 1.55 g. (0.25 g.-atom) of lithium metal in 500 ml. of methylamine. Lithium chloride (10.2 g., 0.24 mole) was present in the mixture at this time. After the lithium metal was entirely consumed, 13.0 g. (0.095 mole) of pure 2,5-dihydro-*t*-butylbenzene was added and the mixture electrolyzed by the passage of 22,650 coulombs (1.6–1.9 amp.) in 3.5 hr. Distillation gave 9.8 g. of product boiling at 163–168°. Analysis by v.p.c. under the usual conditions showed: 80% 1-*t*-butylcyclohexene, 13% 3-*t*-butylcyclohexene, 3% 4-*t*-butylcyclohexene, and 3% *t*-butylbenzene.

Reduction of Ethylbenzene in Undivided Cell in the Presence of Lithium Methylamide.—Lithium methylamide was performed in the presence of 34.0 g. (0.8 mole) of lithium chloride dissolved in 1 l. of methylamine in a manner similar to that described in the previous experiment.²⁶ Ethylbenzene (10.6 g., 0.1 mole) was added and a total of 50,100 coulombs was passed through the mixture in 7.3 hr. In contrast to the usual undivided cell electrolyses, the entire amine solution exhibited a deep blue coloration. Distillation of the product yielded 7.7 g. boiling at 133–135°. Analysis by v.p.c. under the usual conditions showed 5% ethylcyclohexane, 38% ethylcyclohexenes, and 57% ethylbenzene. Dienes were completely absent.

Analysis for Possible Gaseous Products Generated during Electrolysis. (A) **Divided Cell.**—The usual divided cell was used with a modified asbestos divider. Either the anolyte or catholyte condenser was attached to a Dry Ice trap which led to a gas collection bulb fitted with a standard taper joint suitable for connection to a Bendix Time of Flight Mass Spectrometer. In all runs, both half cells were charged with 17.0 g. (0.4 mole) of lithium chloride and 450 ml. of methylamine. The entire system was flushed with helium, and then current (2 amp.) was passed through the cell. Air was prevented from diffusing back into the collection bulb by a trap containing di-*n*-butyl phthalate.

Under a variety of conditions (*e.g.*, in the presence and absence of *t*-butylbenzene) no appreciable gas evolution could be detected from the anode chamber by this method.

On the other hand, the evolution of hydrogen could easily be detected from the cathode. It could be shown that the amount of hydrogen evolved during the first hour was distinctly less than given off during the sixth hour. Hence, hydrogen evolution increased with time.

(25) This material was prepared by the Birch reduction of *t*-butylbenzene as described in paper VII, ref. 1. The crude reduction product was distilled through a spinning-band column and pure material boiling at 175–176° was collected.

(26) The results of this experiment were essentially the same when the lithium methylamide was generated directly by the reaction of lithium with methylamine.

(B) **Undivided Cell.**—When gas samples from reactions carried out in an undivided cell were analyzed, only small amounts of hydrogen could be detected which did not seem to vary appreciably with time.

Anode Oxidation Products. (A) **Isolation of Amine Hydrohalide.**—After a typical divided cell type reduction of ethylbenzene of the kind described above, the solvent was evaporated from the anolyte leaving a solid, orange residue. This was recrystallized from an absolute ethanol-petroleum ether (60–70°) solution and 9.6 g. of pure methylamine hydrochloride (m.p. and m.m.p. 232–233°) was obtained.

(B) **Identification of N-Methylformamide.**—Benzene (0.1 mole) was reduced in the divided cell in the usual way. Current (50,000 coulombs, 2 amp.) was passed for 7 hr. through half-cell solutions of 17.0 g. (0.4 mole) of lithium chloride and 450 ml. of dried²⁷ methylamine. The half-cell solutions were poured into separate 1-l. flasks and the solvent was allowed to evaporate. Analysis by v.p.c. (10 ft., Carbowax 1540, 135°, 20 p.s.i.) at this point indicated the absence of a peak which made its appearance in the chromatogram *only* after the residue had been hydrolyzed. Hydrolysis was achieved by the addition of water, followed by ether extraction in a continuous extractor for 23 hr. The ethereal solution was dried over calcium sulfate and the solvent removed. The residue was distilled at 42–79° (10 mm.). When this material was subjected to v.p.c. analysis several peaks were observed, one of which (see above) did not appear prior to the hydrolysis step. The material responsible for this peak was isolated by v.p.c. and was positively identified as N-methylformamide by a comparison of its retention time, infrared and n.m.r. spectrum with an authentic sample (Eastman Kodak).

Anal. Calcd. for C₂H₅NO: C, 40.68; H, 8.47; N, 23.73. Found: C, 41.01; H, 8.86; N, 24.00.

(C) **Identification of 1,3,5-Trimethylhexahydro-*s*-triazine.**—The anolyte from two separate reductions of benzene as described in (B) above were combined, hydrolyzed, and worked up as before. Distillation gave 4.0 g. of product boiling at 32–42° (4 mm.). The compound responsible for the largest peak obtained when this material was injected onto a 6-ft. Carbowax 400 column (49°, 20 p.s.i. He) was collected.²⁸ This was shown by a comparison of its retention time, infrared, n.m.r., and mass spectra with an authentic sample to be 1,3,5-trimethylhexahydro-*s*-triazine.

Anal. Calcd. for C₆H₁₅N₃: C, 40.67; H, 8.53; N, 23.71. Found: C, 41.01; H, 8.86; N, 24.00.

Authentic 1,3,5-Trimethylhexahydro-*s*-triazine.—A 46% yield of this compound was realized by using the preparative procedure of Graymore.¹⁸

The n.m.r. spectrum of this compound showed a singlet at 7.81 and a second singlet at 6.95 τ . The ratio was 3:2. The mass spectrum showed a parent peak at 129. The largest mass peak was at 42.

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(27) The amine was dried by refluxing it over lithium metal.

(28) Under these conditions, N-methylformamide remains unvaporized.