

1937

The reduction of furan compounds and biological studies of the products of reduction

Chester Wayne Bradley
Iowa State College

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Organic Chemistry Commons](#)

Recommended Citation

Bradley, Chester Wayne, "The reduction of furan compounds and biological studies of the products of reduction " (1937). *Retrospective Theses and Dissertations*. 13222.
<https://lib.dr.iastate.edu/rtd/13222>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

NOTE TO USERS

This reproduction is the best copy available.

UMI[®]

THE REDUCTION OF FURAN COMPOUNDS AND BIOLOGICAL
STUDIES OF THE PRODUCTS OF REDUCTION

By

Chester Wayne Bradley

124
/ 55-1

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Organic Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1937

UMI Number: DP12591

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform DP12591

Copyright 2005 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

QD405
B728 r

1126-83

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. Henry Gilman for the generous advice and criticism offered during the course of this research.

89

T. 5539 ✓

TABLE OF CONTENTS

	Page
I. FURAN COMPOUNDS	
INTRODUCTION AND HISTORICAL	7
Non-catalytic Reduction	8
Noble Metal Catalysis	10
Vapor Phase Hydrogenation	16
High Pressure, Temperature Hydrogenation	19
EXPERIMENTAL	21
Hydrogenation of Furan	21
Acetic acid solvent, Platinum catalyst	21
Dioxan solvent, Platinum catalyst	23
Dioxan solvent, Raney catalyst	23
Decahydronaphthalene solvent, Raney catalyst	24
No solvent, Raney catalyst	24
The Rates of Hydrogenation of Furan and Dihydrofuran	25
Furan in dioxan, Platinum catalyst	27
Dihydrofuran in dioxan, Platinum catalyst	27
Furan in dioxan, Nickel catalyst	28
Dihydrofuran in dioxan, Nickel catalyst	28
Furan in <u>n</u> -hexane, Nickel catalyst	29
Dihydrofuran in <u>n</u> -hexane, Nickel catalyst	30
Dihydrofuran in <u>n</u> -hexane, Platinum catalyst	30

	Page
Furan in alcohol. Palladium catalyst . . .	31
Hydrogenation of 2-Methylfuran. Raney Catalyst	31
Hydrogenation of 2,5-Dimethylfuran. Raney Catalyst	32
DISCUSSION OF RESULTS	34
SUMMARY	40

II. DIBENZOFURAN COMPOUNDS

INTRODUCTION	41
EXPERIMENTAL	47
Catalytic Hydrogenation	47
Hydrogenation of Dibenzofuran	48
Complete hydrogenation. PtO ₂ catalyst	48
Partial hydrogenation. PtO ₂ catalyst	48
Complete hydrogenation. Raney catalyst	49
Partial hydrogenation. Raney catalyst	49
Partial hydrogenation. Platinum black catalyst	50
Hydrogenation of 2-Hydroxydibenzofuran. PtO ₂ Catalyst	52
Hydrogenation of 4-Hydroxydibenzofuran. PtO ₂ Catalyst	52
Hydrogenation of 4-Hydroxydibenzofuran. Nickel Catalyst	53
Hydrogenation of 4-Methoxydibenzofuran. Nickel Catalyst	54
Hydrogenation of 2-Methoxydibenzofuran. PtO ₂ Catalyst	55
Preparation of 3-Aminodibenzofuran	55
Preparation of 4-Aminodibenzofuran	57

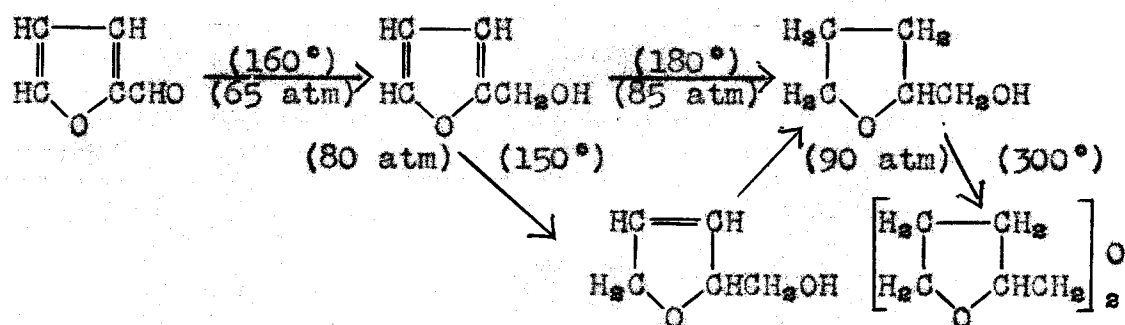
	Page
Preparation of 2-Aminodibenzofuran	58
Attempted Hydrogenation of 3-Aminodibenzo- furan. Nickel Catalyst	59
Attempted Hydrogenation of 4-Aminodibenzo- furan. Nickel Catalyst	59
Hydrogenation of 3-Aminodibenzofuran. Raney Catalyst	59
Action of Lithium on Dibenzofuran in Ether Solutions	61
Reductions in Liquid Ammonia	63
Preparation of Dihydrodibenzofuran	63
Addition of Bromine to Dihydrodibenzofuran .	64
Dehydrogenation of Dihydrodibenzofuran . . .	65
Acetylation of Dihydrodibenzofuran	66
Reduction of Acetyldihydrodibenzofuran Oxime.	68
Metalation of Dihydrodibenzofuran	69
Metalation of 1,4-Dihydronaphthalene	70
Reduction of Dihydrodibenzofuran	71
Attempted Isomerization of Dihydrodibenzofuran with Sodium Ethylate	72
Attempted Isomerization of Dihydrodibenzofuran with Raney Catalyst	72
Ozonization of Dihydrodibenzofuran	73
Action of Lithium on Dihydrodibenzofuran . .	77
Reduction of 4-Hydroxydibenzofuran in Liquid Ammonia	78
Reduction of 4-Methoxydibenzofuran in Liquid Ammonia	79
Attempted Reduction of 3-Aminodibenzofuran, 3-Diethylaminodibenzofuran and 4-Aminodi- benzofuran in Liquid Ammonia	79

	Page
Reduction of Dibenzofuran by Calcium in Liquid Ammonia	80
DISCUSSION OF RESULTS	84
SUMMARY	94

FURAN COMPOUNDS

INTRODUCTION AND HISTORICAL

The production of partially reduced furan compounds from the parent furan compounds by reduction has not been specifically investigated. The single example of such a reaction is the preparation of dihydrodehydromucic acid from dehydromucic acid by reduction with sodium amalgam or electrolytically¹. Komatsu and Masumoto² represent the course of hydrogenation of furfural in the presence of a nickel catalyst by the following scheme:



The support for this scheme comes from curves of the rates of hydrogenation of the compounds investigated except that dihydrofurfuryl alcohol was not independently hydrogenated and it may well have been a mixture of furfuryl alcohol and tetrahydrofurfuryl alcohol. In no other cases have dihydrofurans been shown to occur as products or intermediates.

¹ Hill and Wheeler, Am. Chem. J., 25, 463 (1901).

² Komatsu and Masumoto, Bull. Chem. Soc. Jap., 5, 241 (1930).
 [C. A., 24, 5718 (1930)].

The partial hydrogenation, by Bray and Adams³, of β -furylacrolein ($C_4H_5O-CH=CH-CHO$) in ethyl alcohol solution with platinum oxide catalyst has led to results somewhat different from those obtained by complete hydrogenation. If the hydrogenation was stopped at the addition of three moles of hydrogen, γ -furylpropyl alcohol and some γ -tetrahydrofurylallyl alcohol were formed. No pure products could be isolated when one or two moles of hydrogen were added. The maximum amount of hydrogen absorbed was 4.2 to 4.4 moles, γ -tetrahydrofurylpropyl alcohol and a heptanediol being formed. The authors believed it improbable that dihydrofurans would be isolated.

Other conditions of reduction such as non-catalytic methods, vapor phase catalytic hydrogenation and specific catalytic action are known to lead to partial reduction in some cases. The literature on the reduction of furan compounds was examined with this in mind.

Non-catalytic Reduction.

2-Phenyl-5-methylfuran⁴ and 1-phenyl-3-furylpropane⁵ have been reduced by the use of sodium and alcohol to 2-phenyl-5-methyltetrahydrofuran and 1-phenyl-3-tetrahydro-

³ Bray and Adams, J. Am. Chem. Soc., 49, 2101 (1927).

⁴ Paal, Ber., 17, 2756 (1884).

⁵ Semmler, Ber., 39, 726 (1906).

Table I

Compound	Reducing Agent	Products
Furfural ⁶	Electrolytic-ally	Tars
β -Furylacrylic acid ⁷	Electrolytic-ally	β -Furylprop-ionic acid
β -Furylnitroethylene ⁸	Electrolytic-ally	β -Furylethyl-amine
Ethyl β -furylacrylate ⁹	Na-Hg in C ₂ H ₅ OH	Ethyl β -furyl-propionate
Furfuralacetone ¹⁰	Na-Hg in CH ₃ OH	Furfurylacetone and 4,5-difuryloctadione-2,7
Difurfuralacetone ¹⁰	Na-Hg in CH ₃ OH	Difurylacetone and 3,4-difurylpentanone
Furfurylacetone oxime ¹⁰	Na-Hg in CH ₃ OH	δ -Furylbutane- β -amine
β -Furylacrolein oxime ¹²	Na-Hg in C ₂ H ₅ OH	γ -Furylpropyl-amine
Furylangelic acid ¹³	Na-Hg in H ₂ O	Furylvaleric acid
2-Furoic acid ¹³	Na-Hg in H ₂ O	No reduction
Furfural phenylhydrazone ¹⁴	Na in C ₂ H ₅ OH	Furfurylamine and aniline
Furfural oxime ¹⁴	Na in C ₂ H ₅ OH	Furfurylamine
Furfural oxime ¹⁴	CaH ₂	No reduction

- ⁶ Law, J. Chem. Soc., 89, 1517 (1906).
- ⁷ Ingersoll, "Organic Syntheses", John Wiley and Sons, Inc., New York City, 1932, Coll. Vol. I, p. 306.
- ⁸ Takamoto, J. Pharm. Soc. Japan, 48, 136 (1928). [C. A. 22, 2354 (1928)]
- ⁹ Asahina and Schibata, J. Pharm. Soc. Japan, 423, 391, 400 (1917). [C. A. 11, 2457 (1917)]
- ¹⁰ Fijuta, J. Pharm. Soc. Japan, 519, 456 (1925). [C. A. 20, 412 (1926)]
- ¹¹ Takamoto and Hirohashi, J. Pharm. Soc. Japan, 48, 446 (1928). [C. A. 22, 3409 (1928)]
- ¹² Carter, J. Am. Chem. Soc., 50, 2299 (1928).
- ¹³ Yoder and Tollens, Ber., 34, 3462 (1901).
- ¹⁴ Williams, Compt. rend. acad. sci. U.R.S.S., 1930A, 523. [C. A. 25, 5163 (1931)]

furylpropane respectively. In view of the fact that ethylenic double bonds conjugated with a carbonyl double bond are more susceptible to reduction by metals and metal combinations than are simple or conjugated ethylenic bonds it is surprising to find that some carboxylic acids of furan listed in Table I are not reduced by non-catalytic methods. This may be explained by the diminished aromaticity of the alkyl and aryl substituted furans. None of the compounds of Table I undergoes nuclear reduction with the reducing agent named.

Noble Metal Catalysis.

Noble metal catalysis in the reduction of furans was first employed by Bargellini and Martegiana¹⁵. Furfural- α -acetyl-pyrrole was hydrogenated in alcohol solution in the presence of a palladium black catalyst. One mole of hydrogen was added. No ring reduction occurred. Furoic acid in water solution hydrogenates very slowly with a colloidal palladium catalyst, the product being tetrahydrofuroic acid¹⁶. β -Tetrahydrofurylpropionic acid may be produced in good yields from the hydrogenation of β -furylpropionic acid in glacial acetic acid with a platinum black catalyst⁹. β -Furylacrylic acid dissolved in sodium carbonate and hydrogenated in the presence of palladium sponge

¹⁵ Bargellini and Martegiana, Gazz. chim. ital., 42, (2) 417, 427 (1912). [C.-A. 7, 1713 (1913)].

¹⁶ Wienhaus and Sorge, Ber., 46, 1927 (1913).

yields β -tetrahydrofurylpropionic acid¹⁷. Furfuryl alcohol and furfural have been hydrogenated without a solvent but frequent additions of fresh catalyst (palladium on charcoal) were necessary to complete the hydrogenations in five days¹⁸. Furfural yielded about 50% of tetrahydrofurfuryl alcohol. Also, the hydrogenation of furfuryl alcohol in water suspension with a colloidal palladium catalyst was extremely slow.

Upon the development by Adams¹⁹ of the platinum oxide-platinum black catalyst its use became more general than the more difficultly prepared noble metal catalysts. Kaufmann and Adams²⁰ first employed it in the furan series, the reduction products of furfural being the most extensively studied. It could be almost quantitatively hydrogenated to furfuryl alcohol which in turn was hydrogenated to tetrahydrofurfuryl alcohol, 1,2-pentanediol, 1,5-pentanediol and *n*-amyl alcohol. The yields were in the order given, much the larger fraction being tetrahydrofurfuryl alcohol. Furfuralacetone, furcin, furoic acid, ethyl furoate and β -furylacrylic acid were hydrogenated with much the same results. Furcin and furfural acetone were readily hydrogenated to the corresponding saturated alcohols in good yields. Furoic acid was slowly hydrogenated to tetrahydro-

¹⁷ Windaus and Dalmer, Ber., 53, 2304 (1920).

¹⁸ Wienhaus, Ber., 53, 1656 (1920).

¹⁹ Adams and Shriner, J. Am. Chem. Soc., 45, 2171 (1923).

²⁰ Kaufmann and Adams, J. Am. Chem. Soc., 45, 3029 (1923).

furoic acid and unidentified higher and lower boiling fractions. Ethyl furoate gave good yields of ethyl tetrahydrofuroate but it absorbed hydrogen with extreme slowness. β -Furylacrylic acid has been hydrogenated by Adams' method to give β -tetrahydrofurylpropionic acid, heptolactone and heptylic acids²¹. These results are similar to those already noted in the case of β -furylacrolein. Platinum on charcoal was found to be more effective than platinum or palladium black in the preparation of tetrahydrofurfural from diethyl furfural acetal or furfuraldiacetates. Pierce and Adams²² found that a hydroxyl group on the first carbon atom in the side chain gave rise to ring instability. Ethylfurylcarbinol absorbed from 2.5 to 2.7 moles of hydrogen to give, largely, ethyltetrahydrofurylcarbinol, a little heptane-3-ol and perhaps some heptanediols. *n*-Butylfurylcarbinol acts in a like manner. Furylphenylcarbinol gave no isolable products.

It appears from the work thus far surveyed that the noble metal catalysts are prone to bring about cleavage of the furan ring. Kaufmann and Adams²³ determined that the tetrahydrofuran ring in tetrahydrofurfuryl alcohol is stable to hydrogenation by the platinum oxide catalyst. Ring and chain reduction as well as ring cleavage probably occur at the same time since no products are isolated when but one

²¹ Keimatsu, Kato and Fukushima, *J. Pharm. Soc. Japan*, 50, 653 (1930). C. A., 24, 5022 (1930).
²² Scheibler, Sotscheck and Friese, *Ber.*, 57B, 1443 (1924).
²³ Pierce and Adams, *J. Am. Chem. Soc.*, 47, 1098 (1925).

mole of hydrogen is added. Adkins²⁴ has pointed out that the solvent may alter the course of a hydrogenation. Furfuralacetone hydrogenated by Adams' method undergoes three competing reactions: (1) addition to C=C, (2) addition to $\overset{\text{O}}{\parallel}\text{C}-$, and (3) resinification. One mole of hydrogen was added to furfuralacetone in petroleum ether, in ethyl alcohol, and in ethyl acetate. The largest yield of 4-furylbutanone-2 and the largest recovery of distillate were obtained from hydrogenation in petroleum ether, so the first reaction is favored. Ethyl alcohol favored resinification as indicated by a low yield of 4-furylbutanone-2 and low total recovery. The total recovery from these hydrogenations with one mole of hydrogen was 68 to 87%, and 45 to 65% was identified, indicating that the hydrogenations were complex.

Karyione²⁵ has made a rather extended study of the hydrogenation of furan derivatives which includes some three dozen compounds. The results in a few cases appear to be at variance with the findings already noted. Platinum and palladium catalysts in various forms were employed, usually in acetic acid, acetic anhydride or ethyl ether medium. The rate of hydrogenation of a few compounds was determined. Furylethylene gave a smooth hydrogenation curve which indicated simultaneous hydrogenation of ring and chain whereas

²⁴ Adkins, Diweky and Broderick, J. Am. Chem. Soc., 51, 3418 (1929).

²⁵ Karyione, J. Pharm. Soc. Japan, No. 515, 1 (1925).
[C. A., 20, 412 (1926); Chem. Zentr., 96, I, 2376 (1925)].

the hydrogenation curve for styrene showed a distinct break at the point of addition of one mole of hydrogen, indicating complete chain saturation prior to nuclear reduction. β -Furylacrylic acid gave a quantitative yield of β -furylpropionic acid on the addition of one mole of hydrogen. The compounds studied were grouped into four classes according to their ease of hydrogenation: first, compounds having the CH_2 - or CH= groups in the alpha-position (furyl-ethylene, furfural acetone, furylphenylmethane, and furyl alcohol) were the most readily reduced; second, compounds having the $\overset{\text{O}}{\parallel}{\text{C}}$ - group in the alpha-position (furyl methyl ketone, furyl phenyl ketone, furoin, furil, and ethyl furoylacetate) were somewhat less readily reduced; third, furfural and its derivatives; fourth, furoic acid and its derivatives (ethyl furoate, furamide, β (?)-nitro-furoic acid, and dehydromucic acid and its dimethyl ester) were reduced with difficulty. In each case the main product was the tetrahydro derivative. 2,5-Dimethylfuran-3-carboxylic acid, 2,5-diphenyl-furan-3-carboxylic acid, and 2,5-diphenylfuran-3,4-dicarboxylic acid were not reduced.

Furan derivatives containing nitrogen may, arbitrarily, be treated at the same time.

Furylethylamine²⁶ and furylpropylamine²⁷ are reduced

²⁶ Takamoto, J. Pharm. Soc. Japan, 48, 366 (1928). [C. A., 22, 3162 (1928)]

²⁷ Takamoto, ibid, 48, 686 (1928). [C. A., 23, 387 (1929)]

by platinum oxide and hydrogen at atmospheric pressure to the corresponding tetrahydrofuryl derivatives. On further hydrogenation at 1.5 to 2.0 atmospheres pressure the rings are ruptured to form γ -hydroxyhexylamine and γ -hydroxyheptylamine, respectively. This affords a very good example of the effect of pressure on the ease of hydrogenation. Williams^{28, 1*} has hydrogenated furfural oxime, furfurylamine and furonitrile in various solvents and with various platinum and palladium catalysts. Furfural oxime in absolute ether in the presence of palladium on charcoal is hydrogenated to difurfurylamine. In acetic acid solution the product is mostly water soluble resins with some primary furfurylamine. In alcoholic hydrochloric acid solution, 27% of primary furfurylamine and 17% of primary tetrahydrofurfurylamine are isolated along with some unidentified substances. Primary furfurylamine in absolute ether with the same catalyst does not hydrogenate; in glacial acetic acid with platinum oxide catalyst it is reduced in nine hours to 60% primary tetrahydrofurfurylamine with 18% unchanged. In alcoholic hydrochloric acid solution with platinum oxide catalyst 81% of the reduced amine is formed in the same time with 14% unchanged. In alcoholic hydrochloric acid solution with palladium on charcoal catalyst but 45% of the reduced amine is obtained in thirteen hours

²⁸ Williams, Ber., 60B, 2509 (1927).

with a 42% recovery of the original compound. Furonitrile in glacial acetic acid solution with palladium on charcoal catalyst gives 50% resins but in alcoholic hydrochloric acid solution good yields of primary furfurylamine are formed. Alkali destroys the activity of the catalysts. Hydrofufuramide hydrogenated by Adams' method yields 38% of trifurfurylamine²⁹. Ethyl 5-nitro-2-furoate may be catalytically reduced to ethyl 5-acetamino-2-furoate³⁰. The Rosenmund reaction has been applied to the acid chlorides of the furan series with success. 4-Carbomethoxy-2-furoyl chloride in dry xylene is hydrogenated in the presence of palladium on barium sulfate to 4-carbomethoxy-2-furaldehyde³¹.

In contrast to the tendencies already noted with other catalysts a platinum black catalyst activated with palladous chloride produces sylvan from the hydrogenation of furfuryl alcohol in ethyl alcohol solution³², and a palladium oxide-palladium black catalyst causes furan to be hydrogenated nearly quantitatively to tetrahydrofuran³³.

Vapor Phase Hydrogenation.

Padoa and Ponti³⁴ were the first to apply catalytic

²⁹ Gilman and Dickey, Iowa State Coll. J. Sci., 5, 193 (1931).

³⁰ Gilman and Wright, ibid., 5, 87 (1931).

³¹ Gilman, Burtner and Smith, J. Am. Chem. Soc., 55, 403 (1933).

³² Zelinski, Packendorff and Packendorff, Ber., 67B, 300 (1934).

³³ Starr and Nixon, J. Am. Chem. Soc., 56, 1596 (1934).

³⁴ Padoa and Ponti, Atti. r. accad. Lincei, (5), 15, II, 610 (1906).

methods to the hydrogenation of furan derivatives. They passed furfural vapors over a nickel catalyst at 160°. The main product was furfuryl alcohol, which hydrogenated in turn by the same method, gave sylvan, tetrahydrosylvan, α -methyl-n-butyl alcohol and methyl propyl ketone. At higher temperatures (270°) the products were furan and carbon dioxide. Pringsheim and Noth³⁵ hydrogenated furfuryl alcohol over nickel at 170°, finding, besides the higher boiling fraction which contained tetrahydrofurfuryl alcohol, furan and very small amounts of sylvan. Kotake and Fujita³⁶ obtained furfuryl alcohol together with 4 to 5% of n-butyl alcohol from the hydrogenation of furfural over nickel at 130-150°, while Van Peurse³⁷ and Brown, Gilman and Van Peurse³⁸ found only furfuryl alcohol in amounts up to 5% employing reduced copper and nickel catalysts at temperatures of 175 to 275°.

Furylethylcarbinol behaves similarly to give a variety of products. As expected the main product was tetrahydrofurylethylcarbinol accompanied by lesser amounts of dipropyl ketone, a mixture of α -(n-propyl)furan and α -(n-propyl)tetrahydrofuran, and a very small amount of a glycol³⁹.

³⁵ Pringsheim and Noth, Ber., 53, 114 (1920).

³⁶ Kotake and Fujita, J. Chem. Soc. Japan, 51, 354 (1930).
[C. A., 25, 3649 (1931)].

³⁷ Van Peurse, Proc. Iowa Acad. Sci., 37, 225 (1930).

³⁸ Brown, Gilman and Van Peurse, Iowa State Coll. J. Sci., 6, 133 (1932).

³⁹ Douris, Compt. rend., 157, 722 (1913).

From the hydrogenation of furan at 170° Bourguignon⁴⁰ obtained tetrahydrofuran with some n-butyl alcohol and some hydrocarbons, probably a mixture of butane and ethane. Fifty grams of furan yielded 6 grams of tetrahydrofuran from a total recovery of 34 grams of liquid products. A nickel catalyst was employed. The high temperature necessary for the nickel catalyst to become active probably accounts for the hydrogenolysis observed in their use since a smooth hydrogenation of sylvan vapors to tetrahydrosylvan is observed in the following work.

Vapor phase hydrogenations with metals of the platinum group are infrequently employed. Zelinski and Schuikin⁴¹ have employed one of the least active of this group, namely, osmium, in the vapor phase hydrogenation of sylvan and compared its activity to that of a similar platinum catalyst. Below 100°, 20% platinum activated charcoal or 19% platinized asbestos have very little effect upon sylvan vapors. At 160° a four fold repetition over platinum activated charcoal resulted in a mixture of tetrahydrofuran, tetrahydrosylvan, butane-2-ol and pentane-2-ol. Sylvan was vaporized at 80-82° and carried over 25% osmium activated asbestos by a stream of hydrogen. On repetition there was little change of refractive index; therefore the hydrogenation

⁴⁰ Bourguignon, Bull. Soc. Chim. Belg., 22, 89 (1908).

⁴¹ Zelinski and Schuikin, Compt. rend. acad. sci. U.R.S.S., N.S., 60 (1933). [C. A., 28, 2002 (1934)].

tion was specific and complete. The product consisted wholly of tetrahydrosylvan.

High Pressure, Temperature Hydrogenation.

According to patent information furfural may be hydrogenated under pressures of 50 to 100 pounds at temperatures of 50 to 150° employing a nickel catalyst⁴²; and a high yield of tetrahydrofurfuryl alcohol is claimed from the hydrogenation of furfural over a supported nickel catalyst⁴³. Pressures of 40 to 100 atmospheres and temperatures of 100 to 150° are specified. At temperatures higher than 150° mixtures of pentanediols are formed.

A number of furan derivatives have been hydrogenated by Adkins and co-workers. Furfuryl alcohol in the presence of a copper chromite catalyst, at 100 to 150 atmospheres pressure and 150 to 200°, gives 70% pentanediols, 10% n-amyl alcohol, some tetrahydrosylvan and some tetrahydrofurfuryl alcohol⁴⁴. Furoic acid was not attacked under these conditions. Diethyl furfural acetal, under the influence of a supported nickel catalyst and a promoter, gives 75 to 80% of diethyl tetrahydrofurfural acetal⁴⁵.

⁴² E. I. du Pont de Nemours and Co., British patent 337,296. [C. A., 25, 1844 (1931)].

⁴³ Schoeller and Jordan, German patent 555,405. [C. A., 26, 5102 (1932)].

⁴⁴ Adkins and Connor, J. Am. Chem. Soc., 53, 1091 (1931).

⁴⁵ Covert, Connor and Adkins, J. Am. Chem. Soc., 54, 1651 (1932).

Normal primary aliphatic amines were found to be the best promoters. Without a promoter the product was tetrahydrofurfuryl ethyl ether. A molecule which affords the possibilities of ring or chain saturation, reduction of the functional group, and hydrogenolysis of the ring or chain is afforded in β -furylacrolein. This was hydrogenated in the presence of nickel on kieselguhr, Raney nickel, and copper-chromium oxide catalysts. The products depend upon the catalyst employed and the temperature as illustrated by the following table⁴⁶.

Table II

Catalyst	Temperature	Products
Nickel on Kieselguhr	160°	3-Tetrahydrofurylprop- anol 38% and 1,5-Di- oxooctahydroindene 33%
Raney nickel	160°	3-Tetrahydrofurylprop- anol 65%
Raney nickel	23°	β -Furylpropionaldehyde 46%
Copper-chromium oxide	120-175°	3-Furylpropanol 72%
Copper-chromium oxide	200°	Heptanediols 49%

⁴⁶ Burdick and Adkins, J. Am. Chem. Soc., 56, 438 (1934).

EXPERIMENTAL

The partial hydrogenation of furan was attempted, employing Adams' platinum oxide⁴⁹ and Raney nickel⁴⁷ as representatives of the noble metal and iron group catalysts. The hydrogenations were carried out in an Adams type hydrogenation apparatus⁴⁸ at approximately 3 to 6 atmospheres pressure.

The reaction mixtures were fractionated through a distillation apparatus of the total condensation partial take-off type having a column with 33x1.4cm. packed section packed with glass helix⁴⁹. A double jacket with heating coil in the annular space was provided.

The furan used was prepared by the decarboxylation of furoic acid according to the directions of Gilman and Lousinian⁵⁰ and had the following physical constants: b.p. 32°; n_D^{20} 1.4162; d_4^{20} 0.908.

Hydrogenation of Furan.

Acetic acid solvent. Platinum catalyst. Four 50 g. portions of furan, each in 100 cc. of glacial acetic acid,

⁴⁷ Adkins, J. Am. Chem. Soc., 54, 4116 (1932).

⁴⁸ Voorhees and Adams, "Organic Syntheses", John Wiley and Sons, Inc., 1932, Coll. Vol. I, p. 58.

⁴⁹ Wilson, Parker and Laughlin, J. Am. Chem. Soc., 55, 2795 (1933).

⁵⁰ Gilman and Lousinian, Rec. trav. chim., 52, 156 (1933).

were hydrogenated and combined. One-half gram of platinum oxide was employed for all four runs. The hydrogenations were interrupted after one molecular equivalent of hydrogen had been absorbed. Each reduction required about 3 hours with 3 or 4 reactivations of the catalyst. Reactivations were accomplished by evacuation of the container, filling it with oxygen and shaking for 5 minutes²⁰.

The combined solutions were distilled to remove low boiling material. The residue was then cooled and neutralized with sodium hydroxide and extracted with ether. The ether was then removed through the fractionating column and the residue fractionated. By this procedure the following fractions were obtained: (1) 31-35°, 93.5 g.; (2) 35-74°, 28 g.; (3) 75-89°, 17.2 g.; (4) 90-118°, 11 g.; (5) 118-123°, 45 g. The first fraction is almost pure furan and represents 46.8% recovery. The second fraction was refractionated to yield 19 g. of material, b.p. 62-64°; n_D^{20} 1.4050; d_{20}^{20} 0.888, and which did not absorb bromine. The physical constants identify it as tetrahydrofuran, b.p. 63-64°; n_D^{20} 1.4076; d_4^{21} 0.888⁵¹. Fractions (3) and (4) were not resolvable into closer boiling fractions. Fraction (5) was identified as butyl acetate by hydrolysis and preparation of the 3,5-dinitrobenzoate of the butyl alcohol, b.p. 64°. This amount of butyl alcohol represents

⁵¹ Henniger, Ann. chim., (6), 7, 211 (1886).

13.2% of the furan used.

Dioxan solvent. Platinum catalyst. The dioxan solvent was subjected to hydrogenation to remove any unsaturated material and then fractionated through the column, that portion boiling from 99.5° to 101° being retained. Thirty-four grams of furan in 125 cc. of dioxan with 0.5 g. of catalyst required 2 hours to absorb one mole equivalent of hydrogen. One reactivation was necessary. The same catalyst and solvent were used for a second 34 g. portion of furan. The products were fractionated into three fractions: (1) 31-40°, 27.5 g.; (2) 40-64°, 2.5 g.; (3) 64-101°, 35 g. Fraction (3) was refractionated, yielding: (1a) 45-70°, 3 g.; (2a) 70-98°, 68 g.; (3a) 98-101°, 22 g. No considerable amount of reduced furan could be present. The dioxan remaining was fractionated yielding: (1b) 102-108°, dioxan; (2b) 108-112°, 1.5 g.; (3b) 112-113°, 3 g.; residue 10 g. Fraction (3b) was identified as butyl alcohol. The residue, distilled from a small flask, boiled gradually over the range 113° to 210°.

Dioxan solvent. Raney catalyst. Ninety-two grams of furan in 100 cc. of dioxan with 16 g. Raney nickel catalyst was hydrogenated at 3 atmospheres, 1½ hours being required for the addition of one mole equivalent of hydrogen. The following fractions were taken: (1) 30-40°, 32.5 g.; (2) 40-59°, 5.7 g.; (3) 59-95°, 37 g.; (4) 95-100°, dioxan. Fraction (3) was refractionated: (1a)

47-62°, 2 g.; (2a) 62-67°, 32 g. The range of physical constants from the first to the last parts of fraction (2a) were, n_D^{20} 1.4065 to 1.4076; d_4^{20} 0.887 to 0.892; identifying it as nearly pure tetrahydrofuran. Fraction (1) represents a 35% recovery of furan and fraction (2a) represents a 38% recovery of tetrahydrofuran.

Decahydronaphthalene solvent. Raney catalyst. Approximately 15 cc. of the alcohol suspension of Raney nickel catalyst was introduced into the hydrogenation bottle, the alcohol distilled in a stream of nitrogen and then 150 cc. of decahydronaphthalene added. This was shaken with hydrogen for a time but no hydrogen was absorbed. The furan (55.4 g.) was added and the hydrogenation conducted at the temperature of steam to increase the velocity. About 5 hours were required to introduce one mole equivalent of hydrogen. The reaction mixture was then fractionated, yielding two large fractions: (1) 31-42°, 20.3 g.; (2) 42-59°, 3.8 g.; (3) 42-65.5°, 28.9 g. Distillation ceased at this point and resumed at 112.5°. Between 112.5° and 115°, 1 g. was received and identified as butyl alcohol. The temperature then rose rapidly to the boiling point of the solvent. Fraction (3) gave 26.5 g. of pure tetrahydrofuran on refractionation, or 45% of the furan used. Fraction (1) is 36.8% of the original amount of furan.

No solvent, Raney catalyst. Complete hydrogenation.

A small amount of furan (8 g.) was hydrogenated at room

temperature, at 90 pounds pressure, and in the presence of 2 g. of Raney nickel catalyst. Fifteen minutes were required for almost exactly 2 mole equivalents of hydrogen to be absorbed. The hydrogenation stopped suddenly at this point, indicating a smooth hydrogenation to tetrahydrofuran. A larger amount of furan was then hydrogenated with the same catalyst. One hour was required to saturate 45 g. of furan, approximately 1.9 moles being absorbed. Fractionation of this product gave: 42-61°, 2.7 g.; 61-65°, 41.8 g. and 2.3 g. clear residue. The large fraction represented an 88% yield of tetrahydrofuran; n_D^{20} 1.4073; n_D^{25} 0.885.

Partial hydrogenation. A like amount of furan was hydrogenated to the extent of one mole equivalent, obtaining: (1) 31.5-40°, 21.5 g.; (2) 40-56°, 3.4 g.; (3) 56-65°, 18.5 g. Fraction (3) was redistilled to give 17 g. of tetrahydrofuran, n_D^{20} 1.4071. The furan recovered was 47.8% and tetrahydrofuran obtained 36.6% of the furan used.

The Rates of Hydrogenation of Furan and Dihydrofuran.

Furan and dihydrofuran were hydrogenated in the presence of platinum oxide, Raney nickel and colloidal palladium catalysts. Dioxan, n-hexane and ethyl alcohol were used as solvents. The hydrogenations were performed at a constant pressure of approximately two atmospheres, the apparatus used being similar to that described by

Muskat and Knapp⁵². The mercury filled gas burette was graduated in centimeters and calibrated by two independent methods: first, by weighing the water contained by the burette; and second, by hydrogenating a weighed amount of maleic acid in the apparatus and observing the volume of hydrogen absorbed. The two methods checked within 2%.

Raney nickel is stored suspended in ethyl alcohol. To obtain a sample for hydrogenation the alcohol was removed under reduced pressure in a stream of hydrogen and with a stream of hydrogen flowing through the container, a small flat-bottomed tube of approximately 1 cc. capacity lowered into the container, a sample of catalyst put into it with a long spatula and the tube closed with a rubber stopper stuck onto the end of a wire. The sample thus obtained was weighed and dropped into the hydrogenation bottle. It was impossible to take exactly 1 g. of catalyst in this manner. To make the rates of hydrogenation of different experiments comparable, exactly 0.01 times the amount of catalyst in moles of substance to be hydrogenated was taken for hydrogenation and the amount of hydrogen absorbed, as observed, was reduced to that amount that would have been absorbed by 0.01 mole. These values were plotted against time to obtain the curves of the rates of hydrogenation shown on pages 36 to 39.

⁵² Muskat and Knapp, Ber., 64, 779 (1931).

The dioxan solvent used was the same as that used in previous hydrogenations (p. 23). Commercial n-hexane was subjected to hydrogenation and fractionation, that portion boiling over the range 64-67° being retained for use. Commercial 95% ethyl alcohol was used.

The furan used was described on page 21. Dihydrofuran was prepared from erythritol^{5a}; b.p. 67°; d_{4}^{15} 0.9503.

Furan in dioxan. Platinum catalyst. (Fig. 2). Furan (0.01 mole) in 25 cc. of dioxan with 0.1 g. of platinum oxide catalyst was hydrogenated at an initial pressure of 807 mm. of mercury.

Time (min.)	Burette reading (cm.)	H ₂ absorbed (cc.)
0	0.05	0.0
1	1.0	3.5
3	3.5	20.8
6	9.0	59.0
8	14.5	97.0
11	21.7	147
13	25.7	175
16	30.3	206
19	34.4	236
21	36.8	252
31	45.8	314
36	48.7	334
41	50.9	349
46	52.3	359

Dihydrofuran in dioxan. Platinum catalyst. (Fig. 2).

Dihydrofuran was hydrogenated under the same conditions as in the previous experiment.

Time (min.)	Burette reading (cm.)	H ₂ absorbed (cc.)
0	0.3	0.0
1	0.9	4.16
3	6.7	44.3
5	14.0	95.0
6	17.5	119.2
7	18.1	123.4
8	18.2	124.0
9	18.25	124.5

Furan in dioxan. Nickel catalyst. (Fig. 1). Furan

(0.01067 mole) in 25 cc. dioxan with 1.067 g. of Raney nickel catalyst was hydrogenated at an initial pressure of 819 mm.

Time (min.)	Burette reading (cm.)	H ₂ absorbed (cc.)	cc. H ₂ /0.01 mole
0	10.5	0.0	--
1	11.0	--	--
3	13.5	20.8	19.5
5	15.7	31.0	29.1
8	18.6	56.0	51.7
11	21.2	74.0	69.5
15	24.2	95.0	89.0
18	26.8	113	106
23	29.0	128	120
25	30.0	135	137
26	30.5	139	130
29	31.8	148	139
33	33.4	159	149
37	34.7	168	158
46	37.3	186	175
61	40.4	208	195
72	41.9	218	204
84	43.3	228	214
101	44.7	237	222
112	45.3	241	226
168	47.5	256	240
250	48.8	265	249

Dihydrofuran in dioxan. Nickel catalyst. (Fig. 1).

Dihydrofuran (0.01062 mole) in 25 cc. dioxan with 1.062 g. Raney nickel catalyst was hydrogenated at an initial pres-

sure of 820 mm.

Time (min.)	Burette reading (cm.)	H ₂ absorbed (cc.)	cc. H ₂ /0.01 mole
0	10.0	0.0	0.0
1	10.9	6.3	5.9
3	13.3	23.0	21.3
5	16.7	42.0	40.0
7	20.5	73.0	69.0
8	22.3	85.0	80.0
10	25.5	107	101
12	27.8	123	116
13	28.6	129	121
14	29.1	132	124
15	29.5	135	127
18	30.1	139	131
24	30.7	143	135
32	31.2	147	138
37	31.4	148	139
128	33.9	165	155

Furan in n-hexane. Nickel catalyst. (Fig. 3). Furan (0.01 mole) in 25 cc. n-hexane with 1.007 g. Raney nickel catalyst was hydrogenated at an initial pressure of 820 mm.

Time (min.)	Burette reading (cm.)	H ₂ absorbed (cc.)
0	9.8	0.0
3	10.6	5.5
6	11.9	14.5
10	13.5	25.6
15	15.4	38.8
20	17.0	50.0
26	19.0	64.0
30	20.1	71.0
35	21.5	81.0
45	23.9	98.0
50	25.1	106
52	25.5	109
72	29.3	135
95	32.3	156
148	36.7	186
203	39.1	203
240	39.8	208
293	40.8	212

Dihydrofuran in n-hexane. Nickel catalyst. (Fig. 3).

Dihydrofuran (0.01156 mole) in 25 cc. n-hexane with 1.156 g. Raney nickel catalyst was hydrogenated at an initial pressure of 820 mm.

Time (min.)	Burette reading (cm.)	H ₂ absorbed (cc.)	cc. H ₂ /0.01 mole
0	23.3	0.0	0.0
1	27.5	29.0	25.0
2	31.8	59.0	51.0
3	34.8	80.0	69.0
4	36.5	91.5	79.0
6	37.7	100	86.5
8	38.1	103	89.0
12	38.3	104	89.9
18	38.5	---	---
33	38.6	106	91.7

Dihydrofuran in n-hexane. Platinum catalyst. (Fig. 3).

3). Dihydrofuran (0.0116 mole) in 25 cc. n-hexane with 0.1 g. of platinum oxide catalyst was hydrogenated at an initial pressure of 820 mm.

Time (min.)	Burette reading (cm.)	H ₂ absorbed (cc.)	cc. H ₂ /0.01 mole
0	14.2	0.0	0.0
1	15.7	10.0	8.6
2	17.0	19.0	16.4
4	19.5	37.0	31.9
6	21.9	58.0	50.0
9	25.5	78.0	67.2
13	30.2	111	95.5
17	34.6	149	128
19	36.8	157	135
22	38.7	170	146
27	39.0	172	148
36	39.2	173	149
46	39.4	175	151

Furan in alcohol. Palladium catalyst. (Fig. 4.)

Furan (0.01 mole) in 25 cc. of ethyl alcohol was hydrogenated in the presence of a colloidal palladium catalyst prepared from 2 cc. of 1% palladium chloride and 2 cc. of 1% gum arabic according to the directions of Skita and Meyer⁵³. Initial pressure was 820 mm.

Time (min.)	Burette reading (cm.)	H ₂ absorbed (cc.)
0	10.0	---
1	12.1	14.3
2	14.8	33
3	17.6	53
4	20.3	72
5	22.8	89
6	25.4	107
7.5	29.2	133
8	30.4	142
9	32.8	157
10	35.0	173
11	37.1	188
12	38.8	200
14	41.7	220
15	42.7	227
17	43.5	232
19	43.7	234
22	44.0	236
25	44.2	237
50	45.7	247

Hydrogenation of 2-methylfuran. Raney catalyst.

2-Methylfuran was prepared from furfural hydrazone by the method of Reichstein⁵⁴. The physical constants of this preparation were: b. p. 63-64°; n_D²⁰ 1.4328; d₂₀²⁰.

⁵³ Skita and Meyer, Ber., 45, 3590 (1912).

⁵⁴ Reichstein, Helv. Chim. Acta, 13, 347 (1930).

0.928. According to Hughes and Johnston⁵⁵: b. p. 63.1°; n_D^{20} 1.4335; d_4^{20} 0.9132. Fifty-two and one-half grams of 2-methylfuran was hydrogenated in the presence of 5 g. of Raney nickel catalyst, one half hour being required for the absorption of one mole equivalent of hydrogen. No solvent was used and considerable heat was evolved during the hydrogenation.

The reaction mixture was fractionated, the whole distilling over the range 66-79.1°. Only a partial separation into 2-methylfuran and 2-methyltetrahydrofuran appeared to have been accomplished. 2-Methyltetrahydrofuran has the following physical constants: b. p. 77-78°; d_4^{20} 0.8748⁵⁶; and the only known dihydroderivative, 4,5-dihydro-2-methylfuran: b. p. 82°; d_4^{25} 0.9018⁵⁷. 4,5-Dihydro-2-methylfuran reacts with warm water to form γ -hydroxypropyl methyl ketone⁵⁷. The distillate and residue obtained above were boiled with water for 8 hours and the water layer tested for ketones with phenylhydrazine. No ketone test appeared.

Hydrogenation of 2,5-dimethylfuran. Raney catalyst.

Fifty and one-half grams of 2,5-dimethylfuran (b. p. 92-93°; n_D^{20} 1.4400) was hydrogenated without a solvent

⁵⁵ Hughes and Johnston, J. Am. Chem. Soc., 53, 745 (1931).

⁵⁶ Lipp, Ber., 22, 2569 (1889);

⁵⁷ Marshall and Perkin, J. Chem. Soc., 59, 880 (1891).

⁵⁸ Sabatier and Mailhe, Compt. rend., 144, 1089 (1907).

in the presence of 3.5 g. of Raney nickel catalyst. A temperature of 100° was maintained. Eight hours was required for the absorption of one mole equivalent of hydrogen.

The reaction mixture distilled over the range 88° to 97°, most of it between 91° and 94°. The index of refraction of the distillate was nearly constant, varying between 1.4200 and 1.4220 at 20°. The physical constants of 2,5-dimethyltetrahydrofuran are: b. p. 90-92°; n_D^{20} 1.4051; d_4^{20} 0.833⁵⁹. The boiling point has been reported elsewhere as 92-94° ⁵⁹, 93° ⁶⁰, and 93-95° ⁶¹.

⁵⁹ Duden and Lemme, Ber., 35, 1336 (1902).

⁶⁰ Behal, Ann. chim. phys., (6), 16, 203 (1889).

⁶¹ Wurtz, ibid., (4), 3, 175 (1864).

DISCUSSION OF RESULTS

The partial hydrogenation of furan, 2-methylfuran and 2,5-dimethylfuran in the presence of Raney nickel catalyst results in tetrahydro derivatives. No dihydro derivatives are formed and little or no hydrogenolysis occurs.

Furan, hydrogenated in the presence of Adams' platinum oxide catalyst, yields tetrahydrofuran and butyl alcohol, the latter resulting from ring scission. No dihydrofuran has been detected.

The relative rates of hydrogenation of furan and dihydrofuran determined under various conditions of solvent and catalyst are illustrated graphically in Figures 1 to 4 inclusive. In each case dihydrofuran is hydrogenated more rapidly than is furan; consequently, barring specific catalytic effects, no dihydrofuran would be expected from the catalytic reduction of furan. Additional interesting facts are illustrated by these hydrogenation curves. All of the curves of the hydrogenation of furan are smooth, showing that there are no consecutive reactions. Curve I, Figure 1 and Curve I, Figure 3 show that two moles of hydrogen are absorbed by furan in the presence of Raney nickel catalyst and in either dioxan or n-hexane solvent, whereas, in the presence of platinum oxide cat-

alyst and in dioxan solvent, three moles of hydrogen are absorbed at an even rate (Curve I, Figure 2). In alcohol solution and in the presence of a colloidal palladium catalyst only two moles of hydrogen are absorbed by furan (Figure 4).

No exact conclusion can be drawn concerning the stage in the reduction of furan, in the presence of platinum oxide catalyst, at which ring scission occurs. In dioxan (Curve I, Figure 2), dihydrofuran absorbs only one mole of hydrogen and furan absorbs three moles, indicating the furan ring and not the dihydrofuran ring is opened. However, in n-hexane solvent (Figure 3) dihydrofuran absorbs twice as much hydrogen in the presence of platinum oxide catalyst as in the presence of Raney nickel catalyst, indicating ring opening of dihydrofuran or tetrahydrofuran. Reduction in n-hexane seems not to be complete.

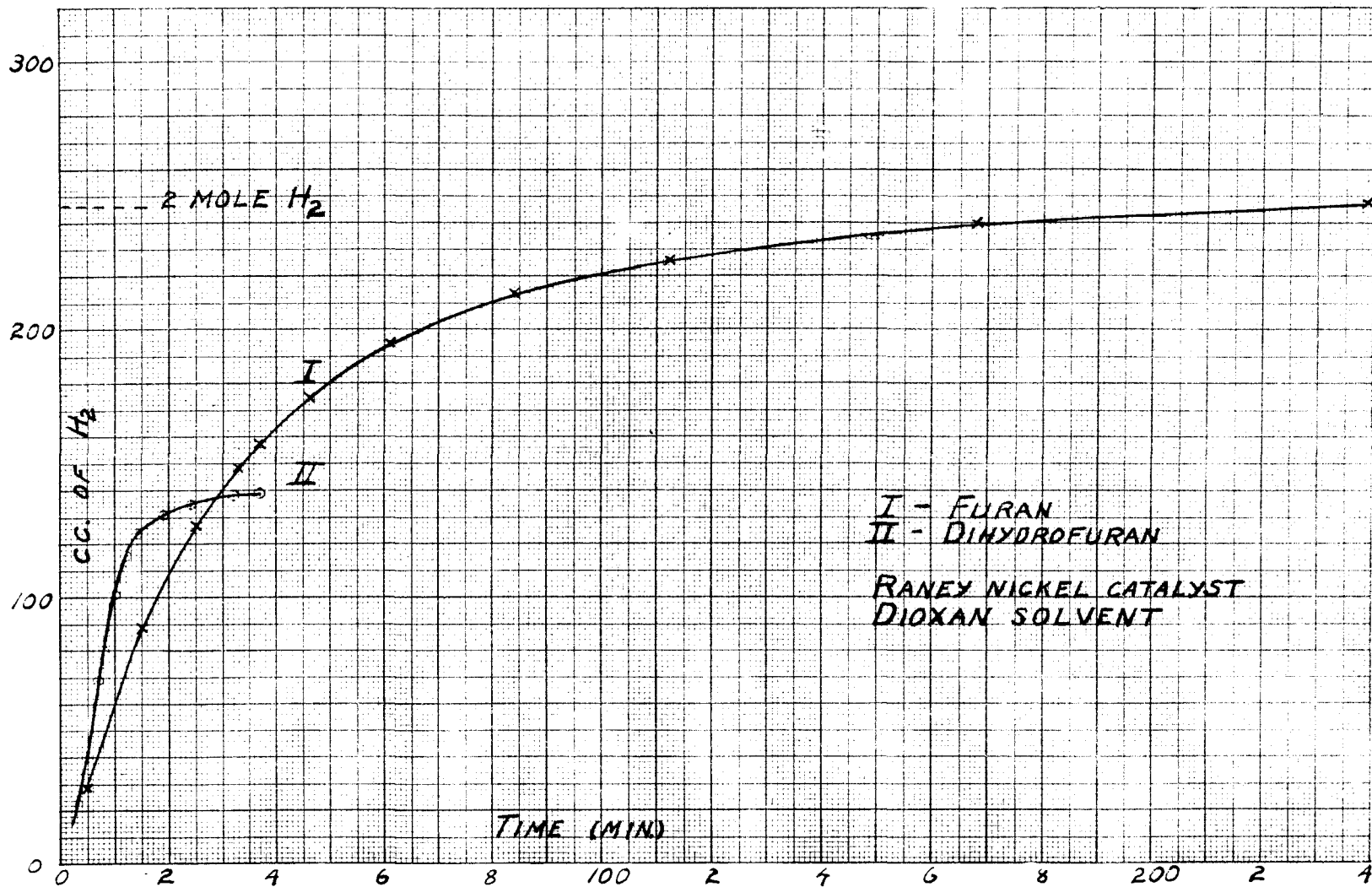


FIG. 1

Rates of hydrogenation of furan and dihydrofuran.

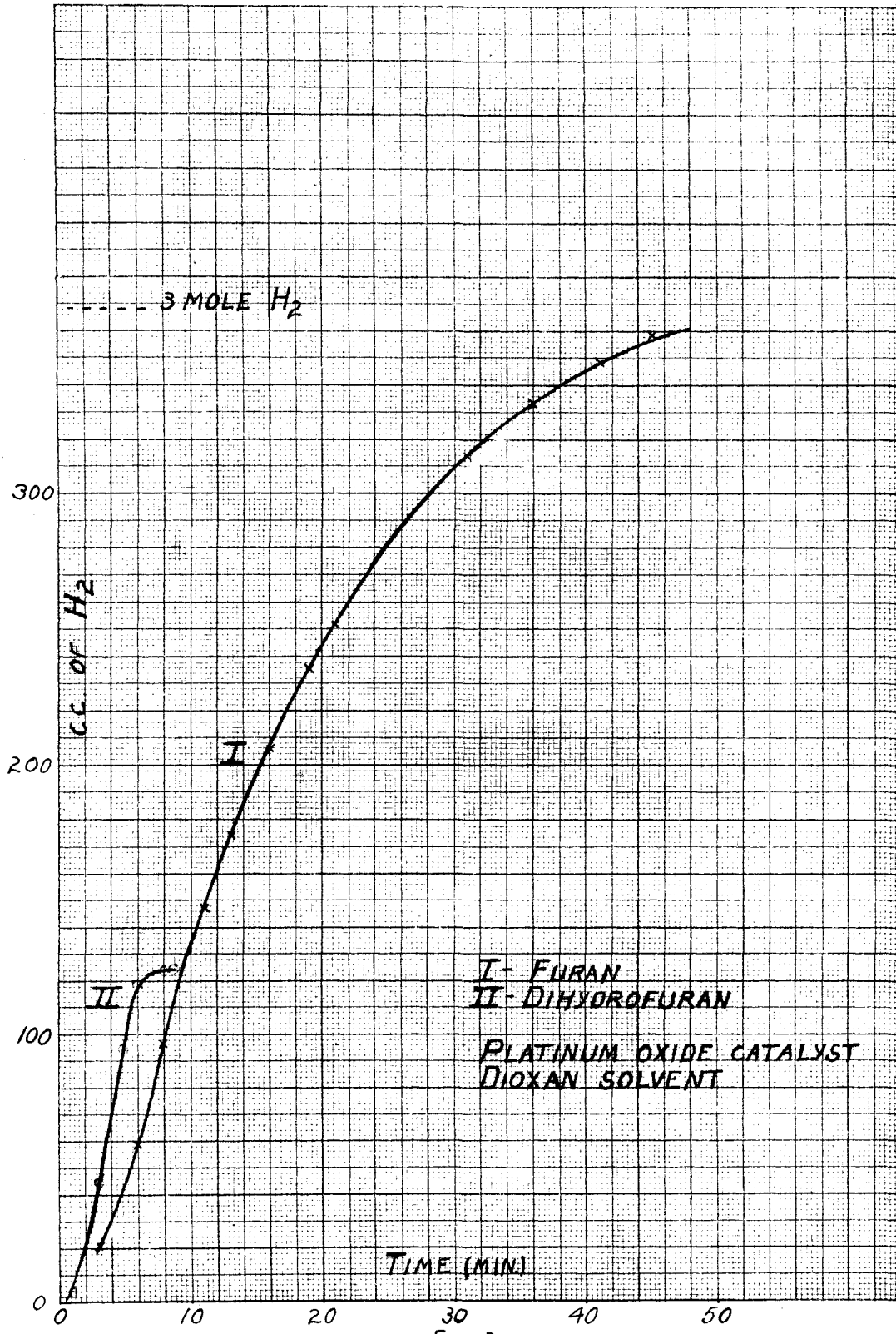


FIG. 2

Rates of hydrogenation of furan and dihydrofuran.

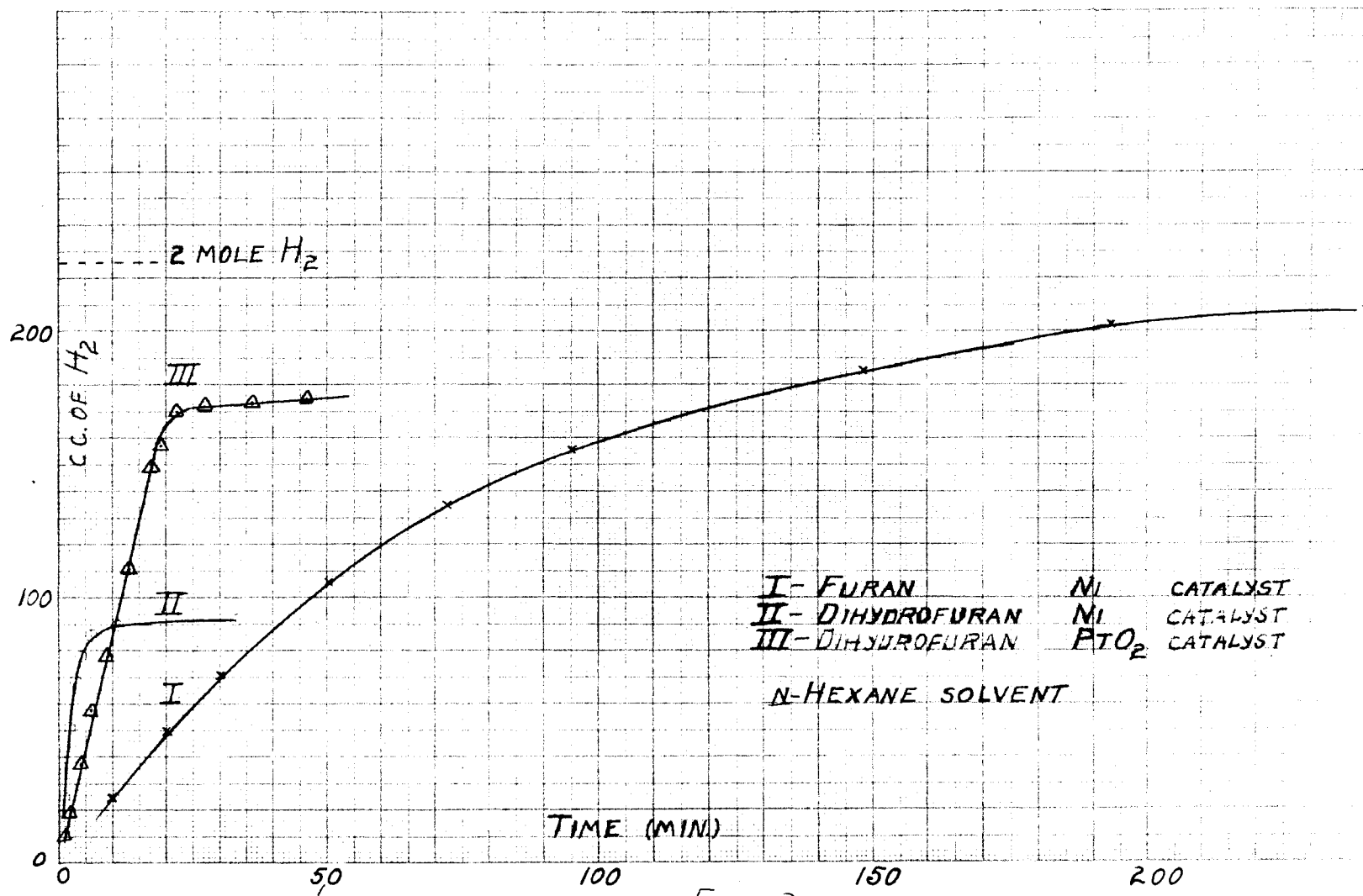


FIG. 3

Rates of hydrogenation of furan and dihydrofuran.

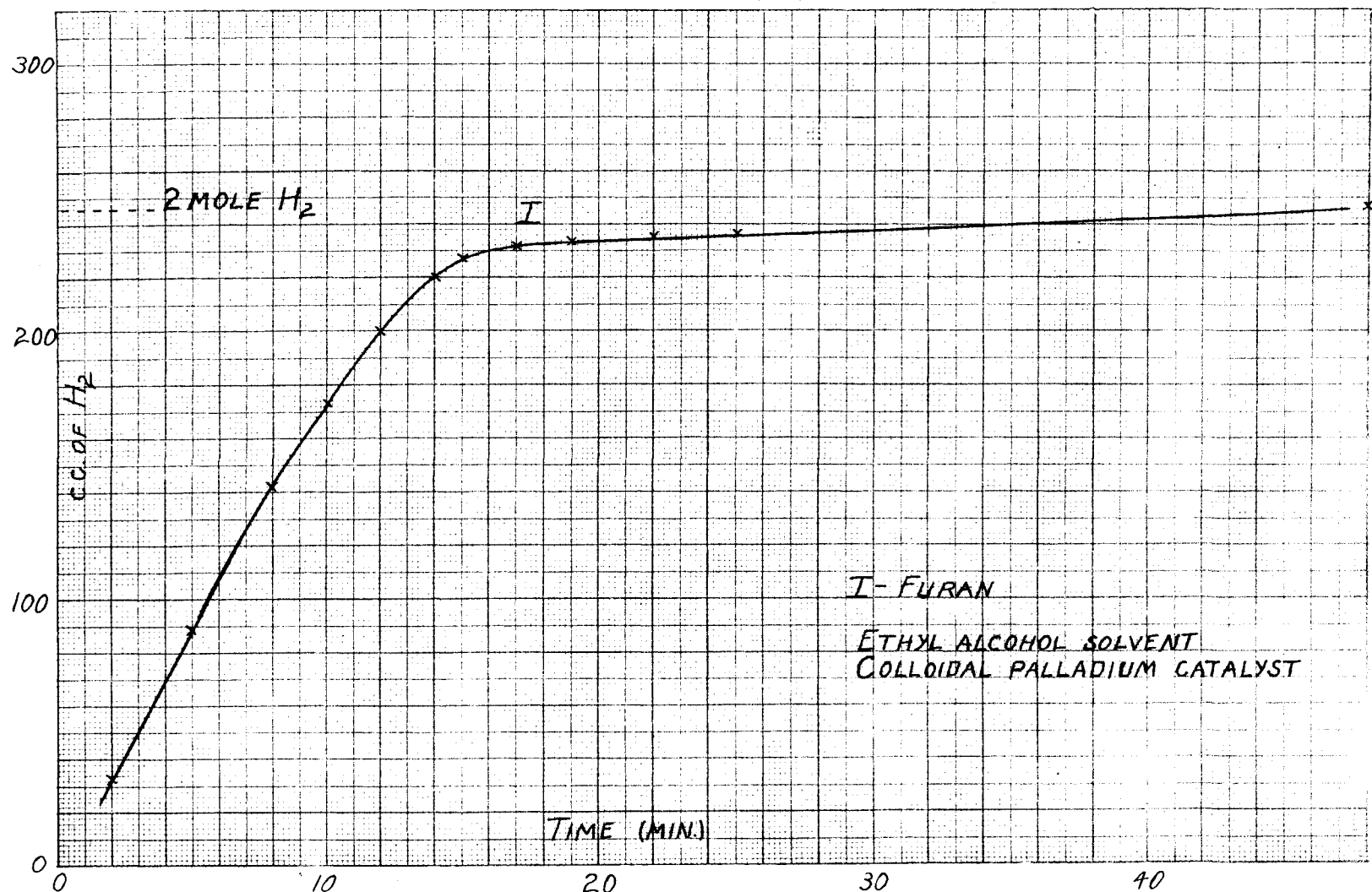


FIG. 4
Rate of hydrogenation of furan.

SUMMARY

The work which has been done on the reduction of furan and furan derivatives has been reviewed, with particular observations on the probability of dihydrofurans being produced.

Furan, 2-methylfuran and 2,5-dimethylfuran have been hydrogenated to yield tetrahydroderivatives and in some cases ring scission products.

The rates of hydrogenation of furan and dihydrofuran have been determined and compared. Under the conditions studied dihydrofuran was hydrogenated more rapidly.

D I B E N Z O F U R A N C O M P O U N D S

INTRODUCTION

The reduction of dibenzofuran and derivatives has not been systematically studied; in fact, no attempt has been made to reduce dibenzofuran derivatives. Dibenzofuran has been reduced non-catalytically to tetrahydrodibenzofuran and catalytically to perhydrodibenzofuran. Since the primary purpose of this research is the production of partially reduced dibenzofurans, previous work concerned with such compounds will be reviewed.

Höntzschmidtee reduced dibenzofuran to tetrahydrodibenzofuran with the aid of sodium and ethyl alcohol. This product could not be further reduced by sodium and amyl alcohol nor was it changed by heating to 250° with hydriodic acid⁵⁵. The same product was obtained by Mayer and Krieger⁶⁴ by employing sodium and cyclohexanol as the reducing agent. Ebel⁵⁵ also synthesized tetrahydrodibenzofuran from sodium phenylate and chlorocyclohexanol by ring closure. He was able to prove it to be 1,2,3,4-tetrahydrodibenzofuran by ozonization and subsequent hydrolysis to *s*-salicylvaleric acid. Gullinane and Padfield⁶⁶ claim to have hydrogenated dibenzofuran

⁵⁵ Höntzschmidt, Monatsh., 22, 561 (1901).

⁶³ Höntzschmidt, Ibid., 23, 829 (1902).

⁶⁴ Mayer and Krieger, Ber., 55B, 1659 (1922).

⁶⁵ Ebel, Helv. Chim. Acta, 12, 3 (1929).

⁶⁶ Gullinane and Padfield, J. Chem. Soc., 1133 (1935).

in dry acetic acid and in the presence of a platinum black catalyst to obtain a 97% yield of tetrahydrodibenzofuran. Different results from a like experiment are reported in the experimental part. Only perhydrodibenzofuran could be obtained.

By using a smaller amount of sodium in the reduction of dibenzofuran Hönigschmidt obtained some material having a higher boiling point than tetrahydrodibenzofuran and which melted at 43°. He advanced the possibility of this being a dihydrodibenzofuran but did not obtain further evidence of its identity. Careful characterization of a similar material, by Gilman, Smith and Cheney⁶⁷, showed it to be impure dibenzofuran.

Hexahydrodibenzofuran is not produced by the reduction of dibenzofuran. J. v. Braun⁶⁸ prepared it by heating *o*-hydroxybiphenyl to 230° with nickel salts and hydrogen under pressure, obtaining 50% yields. Identical material was obtained by Ebel⁶⁸ from tetrahydrodibenzofuran by hydrogenation at atmospheric pressure in the presence of a platinum-palladium black catalyst. Derivatives of v. Braun's hexahydrodibenzofuran have been shown by Gilman, Smith and Cheney to be identical with similar derivatives of tetrahydrodibenzofuran. The latter authors admit the probability of the existence of

⁶⁷ Gilman, Smith and Cheney, *J. Am. Chem. Soc.*, **57**, 2095 (1935).

⁶⁸ J. v. Braun, *Ber.*, **55B**, 3764 (1922).

the parent hexahydrodibenzofuran but believe that it suffers oxidation by the reagents used to prepare the derivatives.

Perhydrodibenzofuran results from the hydrogenation of dibenzofuran at 125-140° and 25-50 atmospheres in the presence of a supported nickel catalyst⁶⁹.

Hydrogenation at higher temperatures and pressures leads to a variety of products. Ogawa⁷⁰ hydrogenated dibenzofuran over nickel at 200-280° and 100 atmospheres of hydrogen to obtain cyclohexylcyclohexanol and bicyclohexyl. At 500° the products were benzene, phenol, *o*-phenylphenol and biphenyl. Hydrogenation at 400-410° with a molybdenum sulfide catalyst yields benzene, cyclohexane, methylcyclopentane and bicyclohexane⁷¹. Ipatiev and Orlov⁷² did not identify the products of Berginization (destructive hydrogenation) of dibenzofuran in the presence of iron, copper and aluminum oxide catalysts. Orlov⁷³ did determine that the dibenzofuran ring was not affected by Berginization.

Passed over calcium hydride at 450° several times, dibenzofuran loses oxygen to give a small yield of di-

⁶⁹ Stenger, German Patent 566,782. [Chem. Zentr., 104, 1, 1686-(1933)-7].

⁷⁰ Ogawa, Bull. Chem. Soc. Japan, 6, 174 (1931). [C. A. 26, 143 (1932)].

⁷¹ Makh and Khadzhinov, Ukrain.-Khem. Zhur., 7, No. 1, -
Sci.-Tech. pt., 32 (1932); [C. A. 27, 1630 (1933)].

⁷² Ipatiev and Orlov, Ber., 62B, 593 (1929).

⁷³ Orlov, Ber., 64B, 2631 (1931).

⁷⁴ Fuchs, Ber., 61B, 2599 (1928).

phenyl⁷⁴.

Reduction by means of alkali or alkaline earth metals dissolved in liquid ammonia has not been previously applied to dibenzofuran nor to its derivatives but has been successfully used in the partial reduction of other aromatic nuclei similar to dibenzofuran. It seemed probable that the method of reduction would be applicable to the dibenzofuran series and it has met with partial success.

Naphthalene reacts with sodium in liquid ammonia to give tetrahydronaphthalene and sodamide. The pioneer work of this type was performed by Lebeau and Picon⁷⁵. By the use of sodium in liquid ammonia as the reducing agent they prepared tetrahydronaphthalene, dihydroanthracene, tetrahydrophenanthrene, tetrahydrodiphenyl and dibenzyl. Amylene, benzene, toluene, cymene and terpinene were not attacked. Fluorene and indene were not reduced but formed sodium substitution products. Wooster and Smith⁷⁶ determined that sodium in liquid ammonia formed a 1,2,3,4-tetrasodium addition product with naphthalene which was 75% ammonolyzed in liquid ammonia solution, at the boiling point of the solvent, to form tetrahydronaphthalene and sodamide. Schlubach⁷⁷ pre-

⁷⁴ Fuchs, Ber., 61B, 2599 (1928).

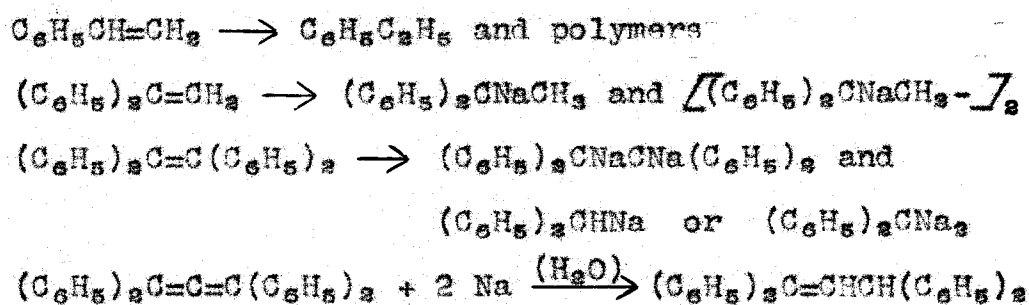
⁷⁵ Lebeau and Picon, Compt. rend., 157, 223 (1913).

⁷⁶ Wooster and Smith, J. Am. Chem. Soc., 53, 179 (1931).

⁷⁷ Schlubach, Ber., 48, 13 (1913).

pared the sodium addition compounds of dimethylpyrone, benzophenone, stilbene and naphthalene and isolated them by evaporation of the ammonia and washing off the excess unsaturated compound with the proper solvent. The reactions were sealed tube reactions taking place mostly at room temperatures. Naphthalene formed a brown addition product unstable at this temperature. It decomposed partly to tetrahydronaphthalene and partly to high molecular weight hydrocarbons.

A better picture of the type of reactions to be expected from the action of metals in liquid ammonia solution on certain unsaturated compounds, and probably aromatic compounds as well, can be had from the reaction with phenylated olefins. This has received much attention and has been summarized by Wooster and Ryan⁷⁸. The usual reaction is reduction; but polymerization, cleavage and partial addition have been noted as shown by the following examples:



Reduction and polymerization both occur in the reaction of

⁷⁸ Wooster and Ryan, J. Am. Chem. Soc., 56, 1133 (1934).

naphthalene with sodium in liquid ammonia. When the reaction of aromatic compounds with metals in liquid ammonia receives greater attention the other types of reaction may be noted as, for example, the partial addition of sodium to dibenzofuran to give a dihydrodibenzofuran.

Alkali metals are frequently of service in the reduction of aromatic compounds, the reduction occurring by hydrolysis of the intermediate alkali metal addition compound⁷⁰. A trial experiment of this kind with dibenzofuran and lithium in boiling dioxan resulted in cleavage of the ether bridge. This type of reduction was not, therefore, pursued further.

⁷⁰ Schlenk and Bergmann, Ann., 453, 1-97 (1928).

EXPERIMENTAL

Catalytic Reductions

The low pressure hydrogenation experiments were carried out in the Adams hydrogenation apparatus already mentioned. The high pressure, high temperature hydrogenations were performed in an Adkins⁸⁰ type of apparatus manufactured by the Parr Instrument Company of Moline, Illinois.

A 500 cc. bomb of stainless steel was used without a liner. It was standardized by hydrogenating in it a known amount of acetone in the presence of Raney nickel catalyst⁸⁰. It was found that the amount of hydrogen absorbed by the acetone could be calculated to agree with the experimental value within one per cent.

The fractional distillation apparatus previously used was found to be unsatisfactory for the distillation of viscous high boiling materials under reduced pressure. A column designed to handle small amounts of such materials was constructed from a one meter glass tube of 6 mm. bore. This was packed with a single wire spiral of No. 22 nichrome wire wound 6 turns to the inch. The column was encased in an electrically heated, double walled glass case.

⁸⁰ Adkins and Cramer, J. Am. Chem. Soc., 52, 4349 (1930).

Hydrogenation of Dibenzofuran.

It was found necessary to free commercial dibenzofuran of catalytic poisons before employing it in hydrogenation experiments. This was accomplished by distilling it from sodium, either at atmospheric pressure or under reduced pressure. It was then recrystallized from alcohol and dried; m.p., 84°.

Complete hydrogenation. PtO₂ catalyst. Eight and four-tenths grams (0.05 mole) of dibenzofuran dissolved in 500 cc. of glacial acetic acid was hydrogenated at 3 atmospheres pressure, employing 0.4 g. of platinum oxide catalyst. Several reactivations were necessary to complete the hydrogenation in 12 hours. Approximately 12 atoms of hydrogen were absorbed. The solvent was neutralized with sodium hydroxide and then extracted with ether. The residue from the dried ether extract was distilled from a Claisen flask at 3 mm. The distillate weighed 6.6 g.; b. p. 92-4°; n_D²⁰ 1.5023; d₄²⁰ 1.035. These constants identify it as nearly pure perhydrodibenzofuran⁶⁷.

Partial hydrogenation. PtO₂ catalyst. Fifty grams of dibenzofuran was hydrogenated under the same conditions as above, employing 1.2 g. of catalyst. With 2 reactivations 6.5 atoms of hydrogen were absorbed in 3.5 hours, the temperature being maintained at 100° by surrounding the hydrogenation bottle with steam.

The solvent was removed through the fractionation column and the residue fractionated at 10 mm. The following fractions were taken: (1) 123-5°, 16 g. (n_D^{20} 1.5018; d_4^{20} 1.012); (2) 125-6°, 5.5 g. (n_D^{20} 1.5095); (3) 126-32°, 6.5 g. (n_D^{20} 1.5182). At this point the distillate began to solidify in the condenser. This solid and the solid residue were identified as dibenzofuran, a total of 44% being recovered. Fractions (2) and (3) were combined and refractionated to yield 8.0 g. of distillate; n_D^{20} 1.5023. The yield of perhydrodibenzofuran was 50%.

Complete hydrogenation. Raney catalyst. Thirty-three grams (0.196 mole) of dibenzofuran was hydrogenated at 150 atmospheres in the presence of 2.5 g. of Raney nickel⁴⁷ catalyst. No solvent was used. The hydrogenation required 5 hours at 200° for completion, 12.2 atoms of hydrogen being absorbed. The reduction product was fractionated at atmospheric pressure, obtaining 1.5 g. of material distilling below 258°, the remainder (28.5 g.) distilling between 258-9°; n_D^{20} 1.5015. There remained an oily residue of 3.0 g. The yield of perhydrodibenzofuran from the distillate was 86%.

Partial hydrogenation. Raney catalyst. Eighty-four grams of dibenzofuran was introduced into the hydrogenation bomb with 6.0 g. of Raney nickel catalyst and hydrogen at 1770 pounds. The temperature was raised slowly to observe the temperature at which hydrogenation began. The pressure

first began to drop noticeably at 175-80°, at which temperature the hydrogenation was conducted until 4.7 atoms of hydrogen had been absorbed; 4 hours were required.

The liquid product was decanted from the catalyst and fractionated at 10 mm. The following fractions were obtained:

(1) 112-21°, 2.5 g. (n_D^{20} 1.5200); (2) 121-8°, 27.8 g. (n_D^{20} 1.5320; d_4^{25} 1.5425); (3) 128-32°, 16.7 g. (n_D^{20} 1.5563).

At this point the distillate began solidifying in the condenser. Fraction (2) was refractionated at atmospheric pressure; (1a) 258-9°, 22.0 g. (n_D^{20} 1.5233 to 1.5342). The residue (5.8 g.) solidified. Fraction (1a) was then refractionated at atmospheric pressure; 258-9°, 13.0 g. (n_D^{20} 1.5230 to 1.5295). This is apparently impure perhydrodibenzofuran, not all of the impurity being dibenzofuran since previous experience showed that a good separation of dibenzofuran and perhydrodibenzofuran could be obtained by use of the fractionation column. The solid residues were combined and recrystallized from alcohol, m. p. 84°. The recovered dibenzofuran was 50% of the original amount used.

Hydrogenation with platinum black catalyst. After observation of the above results on the hydrogenation of dibenzofuran with two types of catalysts it was deemed advisable to repeat the work of Cullinane and Padfield⁵ in which they hydrogenated dibenzofuran in dry acetic acid solution in the presence of a platinum black catalyst to obtain good yields of tetrahydrodibenzofuran.

The platinum black catalyst was prepared according to the directions of Feulgen⁸¹. Dry acetic acid was prepared by four times fractional freezing of glacial acetic acid and then distilling from the calculated amount of phosphorus pentoxide to completely dry it. The amount of water present was calculated from the freezing point⁸².

Dibenzofuran (8.4 g.) dissolved in 50 cc. of dry acetic acid was hydrogenated in the presence of 2.0 g. of platinum black catalyst. The absorption of 4.2 atoms of hydrogen required 12 hours. The warm acetic acid solution was diluted with water until precipitation began and then cooled. After filtration the acid was neutralized and then extracted with ether. The ether was evaporated and the residue taken up in hot dilute alcohol. On cooling more dibenzofuran separated and was filtered. Picric acid was added to the filtrate and allowed to stand for 2 days, obtaining 1.2 g. of picrate identified as the picrate of dibenzofuran by mixed melting point. The total recovery of dibenzofuran was 62%.

The alcohol residue was evaporated under reduced pressure and the remaining oil distilled from a small flask, distilling over the range 259-65°; n_D^{20} 1.5224. This was evidently impure perhydrodibenzofuran. It was not further purified because of the small amount. From the

⁸¹ Feulgen, Ber., 44, 360 (1921).

⁸² Brousfield and Lowry, J. Chem. Soc., 99, 1432 (1911);
Orton et al, ibid., 99, 1432 (1911).

amount of dibenzofuran recovered it is evident that the 4.2 atoms of hydrogen consumed would saturate the remaining dibenzofuran.

Hydrogenation of 2-Hydroxydibenzofuran. PtO₂ Catalyst.

Hydrogenation was performed in glacial acetic acid solution at 3 atmospheres and 100° in the presence of 0.8 g. of platinum oxide catalyst. With 8.4 g. of material 2.5 hours were required to absorb 6 atoms of hydrogen. No reactivation was necessary.

The solvent was neutralized with sodium carbonate and extracted with ether. The ether extract was extracted with 10% sodium hydroxide. Acidification of this alkaline extract yielded 3.5 g. of white solid, m. p. 133°. Mixed melting point with the original, 133-4°. This is a 42% recovery. The alkali insoluble, ether soluble portion was dried and the ether evaporated, obtaining 4.3 g. of oil. This was distilled from a small Claisen flask, yielding 3.5 g. of distillate, b. p. 108-110° (7 mm.); n_{20}^{20} 1.5012; d_{20}^{20} 1.017. This identifies it as perhydrodibenzofuran, the yield being 42%.

Hydrogenation of 4-Hydroxydibenzofuran. PtO₂ Catalyst.

This hydrogenation was carried out in a manner similar to the previous hydrogenation, 15.0 g. of material with 0.7 g. of catalyst requiring two hours, with one reactivation, for

the absorption of 6 atoms of hydrogen. The product was manipulated in the same manner as the product of the previous hydrogenation to obtain 7.0 g. of alkali insoluble material from which was obtained 4.5 g. (31%) of pure perhydrodibenzofuran by distillation. From the alkali soluble fraction 51% of reasonably pure starting material was obtained.

Hydrogenation of 4-Hydroxydibenzofuran. Nickel Catalyst.

A supported nickel catalyst was prepared by depositing nickel hydroxide on kieselguhr by the action of ammonium carbonate on nickel nitrate. The directions of Adkins⁸³ were followed except that the reduction of the hydroxide was carried out at 380° for one hour.

Eight and one-half grams of 4-hydroxydibenzofuran was introduced into the bomb with 4.0 g. of catalyst and hydrogen at 700 pounds pressure. Hydrogenation began slowly at 140° and required 3 hours for the absorption of approximately 6 atoms of hydrogen. The liquid reaction product was washed out with ether, filtered from the catalyst and extracted with 10% sodium hydroxide. The ether soluble material weighed 2.7 g. and was shown to be perhydrodibenzofuran; yield, 32%. The alkali soluble portion came out as an oil on acidification and could not be resolved into a pure product.

⁸³ Adkins, J. Am. Chem. Soc., 54, 1651 (1932).

Hydrogenation of 4-Methoxydibenzofuran. Nickel Catalyst.

This hydrogenation was performed in dioxan solvent with 4.0 g. of supported nickel catalyst which had been reduced at 380-390° for 1 hour. The hydrogenation began at 135° at 160 atmospheres pressure. Twenty grams required $3\frac{1}{2}$ hours for the absorption of 4 atoms of hydrogen.

The reduced solution was freed of the catalyst by filtration, the dioxan removed under reduced pressure and the residue fractionated into 3 fractions: (1) to 110° (3 mm.), 2.2 g. (n_D^{20} 1.5028); (2) 110-119°, 8.2 g.; (3) 119-131°, 4.2 g. The rate of distillation became slower between fractions. The physical constants of the first fraction indicate it to be perhydrodibenzofuran; the third fraction and the residue were found to be unchanged 4-methoxydibenzofuran. The second fraction solidified on strong cooling and agitating with 30-40° petroleum ether. The solid was recrystallized from this solvent and melted constantly at 39-39.5°. It was shown to be methoxotetrahydrodibenzofuran by analysis for carbon, hydrogen and methoxyl; the yield was 41%.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.19; H, 6.99; OCH_3 , 15.4. Found: C, 76.81; H, 6.91; OCH_3 , 15.6.

1,2,3,4-Tetrahydro-6-methoxydibenzofuran has been prepared by Ebel⁴ by ring closure, melting at 39.5°. The mixed melting point of this compound with the methoxytetrahydrodibenzofuran prepared by the above reduction is below 25°.

Hydrogenation of 2-Methoxydibenzofuran. PtO₂ Catalyst.

It was found necessary to free 2-methoxydibenzofuran of catalytic poisons by heating it with a small amount of Raney nickel at 200° for 1 hour -- a treatment also found effective in the purification of dibenzofuran. Fourteen grams of this material in glacial acetic acid was hydrogenated at 100° and 3 atmospheres in the presence of an initial amount of 0.65 g. of platinum oxide catalyst. The hydrogenation was very slow, 20 hours being required for the addition of 6 atoms of hydrogen. Two additions of fresh catalyst were made. After the product had been separated from the catalyst and solvent an attempt was made to fractionate it. It distilled over the range 120-177° (10 mm.) with no discernible fractionation.

Preparation of 3-Aminodibenzofuran.

A catalytic method of reduction of 3-nitrodibenzofuran to 3-aminodibenzofuran was developed. A modification of the method employing platinum oxide catalyst has been employed by Kirkpatrick and Parker³⁴. Raney nickel catalyst is to be preferred because of its ease of preparation and the elimination of the troublesome recovery.

3-Nitrodibenzofuran is best purified by recrystallization from acetic acid. It was found necessary to wash it thoroughly with water and finally with dilute ammonium hy-

³⁴ Kirkpatrick and Parker, J. Am. Chem. Soc., 57, 1123 (1935).

dioxide to remove all of the acetic acid which poisons the catalyst. It was then dried until the odor of ammonia disappeared. Fifty grams of this purified material was introduced into the hydrogenation bottle of 350 cc. capacity, 150 cc. of ethyl alcohol and 15 cc. of an ethyl alcohol suspension of Raney nickel catalyst added. The reduction starts slowly unless the hydrogenation bottle is heated with steam. The hydrogenation was initiated at 45 pounds and was kept above 20 pounds by refilling. This was required to prevent the alcohol from boiling. The theoretical amount of hydrogen was absorbed in 1 hour.

When the reduction was complete the alcohol solution was cooled below its boiling point before releasing the pressure, was then removed, reheated to bring the amine into solution and the solution decanted from the catalyst through a heated filter. The solution was clear and colorless, all of the yellow color of the 3-nitrodibenzofuran having disappeared. On cooling the alcohol solution to about 10° much of the amine crystallizes out, 35 g. being obtained melting at 98-9°. The residue remaining after the removal of the alcohol melted at 87°. It was purified by precipitating it from ether solution as the hydrochloride. Decomposition of a water solution of the hydrochloride with ammonium hydroxide yielded 6.2 g. of amine, m. p. 98-9°. The total yield was 96%.

The catalyst, from which the amine was decanted, was

used repeatedly. Fifty or sixty grams of 3-nitrodibenzofuran was found to be the maximum amount that could be used in the hydrogenation bottle of 350 cc. capacity because a greater amount produced a suspension too viscous to be shaken effectively. Yields of 85-90% of amine melting at 97-9° were generally obtained from the original alcohol solution by dilution and cooling.

Mr. Jacob Swislowsky, in this laboratory, has employed isopropyl alcohol as the solvent in place of ethyl alcohol. The advantage in its use lies in its higher boiling point, obviating some of the cautions mentioned above concerning the use of ethyl alcohol.

Preparation of 4-Aminodibenzofuran.

This substance has been prepared from 4-bromodibenzofuran and 4-hydroxydibenzofuran by several methods, none of which is quite satisfactory⁸⁵. The procedure in greatest use in this laboratory has been the reaction of ammonium hydroxide and cuprous bromide on 4-bromodibenzofuran at 200°, the reaction being carried out in a glass lined steel bomb⁸⁵. Ordinarily the 4-bromodibenzofuran is admixed with dibenzofuran as it is obtained from its preparation by the metalation of dibenzofuran with butyllithium and subsequent bromination,

⁸⁵ P. R. VanEss, in his Doctoral Dissertation, Iowa State College, 1936, page 46, discusses the methods that have been employed in the preparation of 4-aminodibenzofuran.

and this mixture is employed in the amination. The preparation of 4-bromodibenzofuran from this material by the reaction of sodamide in liquid ammonia was attempted.

Thirty-five grams of crude 4-bromodibenzofuran in 60 cc. of dry benzene was added dropwise to a solution of sodamide in 400 cc. of liquid ammonia. Rapid stirring was maintained. The sodamide was prepared in solution from 5.6 g. of sodium by the method of Vaughn, Voght and Nieuwland⁸⁸. The reaction was not vigorous. One hour was allowed for the reaction. Excess ammonium chloride was then added and the product recovered in the usual manner. The amine was precipitated from ether solution as the hydrochloride and recrystallized from water as such. It was then decomposed in water solution with sodium acetate. Eight grams (31%) of amine was obtained. A like amount of the same preparation of crude 4-bromodibenzofuran was aminated by the bomb method just described to yield 4.5 g. (17%) of amine.

Preparation of 2-Aminodibenzofuran.

Thirty-eight grams (0.154 mole) of pure 2-bromodibenzofuran dissolved in 70 cc. of dry benzene was added to a solution of 0.26 mole of sodamide in 400 cc. of liquid ammonia. The sodamide was prepared in solution from 6.0 g. of sodium in the same manner as in the previous experiment. One hour

⁸⁸ Vaughn, Voght and Nieuwland, J. Am. Chem. Soc., 56, 2120 (1934).

was allowed to complete the reaction. The product was recovered and purified to yield 19.7 g. (60%) of pure amine.

This is a lower yield than that obtained by W. G. Bywater⁸⁷ by the bomb method.

Attempted Hydrogenation of 3-Aminodibenzofuran. Nickel Catalyst.

3-Aminodibenzofuran was prepared for hydrogenation by reduced pressure distillation from Raney nickel. Hydrogenation was then attempted in dioxan solution employing nickel on kieselguhr as catalyst. No hydrogenation had taken place after shaking for 3 hours at 235° and 170 atmospheres.

Attempted Hydrogenation of 4-Aminodibenzofuran. Nickel Catalyst.

4-Aminodibenzofuran was subjected to hydrogenation under the conditions of the previous experiment. No hydrogen was absorbed and the 4-aminodibenzofuran was recovered.

Hydrogenation of 3-Aminodibenzofuran. Raney Catalyst.

Four and one-half grams of 3-aminodibenzofuran, which had been distilled from Raney nickel, was hydrogenated in ethanol solution at 100° and 3 atmospheres. Approximately 2 g. of Raney catalyst was employed. The hydrogenation was

⁸⁷ W. G. Bywater, Doctoral Dissertation, Iowa State College, 1934, page 30.

slow, 3 hours being required for the absorption of the first atom of hydrogen and 14 hours for 1.9 atoms.

The resulting solution was filtered from the catalyst, warmed, diluted, and then cooled to precipitate 3.6 g. (80%) of a crystalline amine melting at 72°; recrystallized from the same solvent, it melted at 72°.

Anal. Calcd. for $C_{13}H_{11}ON$: C, 77.80; H, 5.99. Found: C, 77.38; H, 6.01.

The amine absorbed bromine without the loss of hydrogen bromide. To 0.5 g. (0.0027 mole) of dihydro-3-aminodibenzofuran in 20 cc. of dry chloroform at 0° was added 0.0432 g. (0.00054 mole) of bromine in 20 cc. of cold chloroform. The bromine was decolorized immediately without the formation of a precipitate. Had hydrogen bromide been evolved the amine would have been precipitated as the hydrobromide. One-half of the chloroform was evaporated and the remainder diluted with 60-8° petroleum ether. On cooling, a white crystalline solid separated, melting at 185-6° with decomposition. It was recrystallized from the same solvent, m. p. 186°, with decomposition. The amount obtained was 0.68 g. or 71%. Analysis for bromine showed it to be a dibromide.

Anal. Calcd. for $C_{13}H_{11}ONBr_2$: Br, 46.32. Found: Br, 46.71.

Three-tenths gram of this dibromide was refluxed for 2 hours in an absolute ethanol solution of sodium hydroxide. The cooled solution was filtered to remove precipitated

sodium bromide and the filtrate diluted. One-tenth gram (62%) of crystalline material which melted at 90-2° was obtained. This was recrystallized from dilute ethanol; m. p. 97-8°. It was found to be 3-aminodibenzobenzofuran by the method of mixed melting points.

Action of Lithium on Dibenzofuran in Ether Solutions.

One-tenth mole (16.8 g.) of dibenzofuran which had been well desiccated over sulfuric acid, 0.22 mole (1.5 g.) of lithium and 200 cc. of sodium dried dioxan were placed in a 3-necked flask equipped with an efficient stirrer and reflux condenser which was closed with a drying tube. The dioxan was heated to slow reflux and rapid stirring was maintained. The solution turned a brick red in color immediately on heating and as the reaction proceeded a chocolate brown solid appeared. Rapid stirring was necessary to keep the surface of the lithium clean. Most of the lithium had been consumed at the end of 4 hours. At the end of 12 hours the reaction mixture was cooled and water-dioxan mixture carefully added to hydrolyze the reaction product. Most of the solvent was withdrawn by means of the water pump, the residue acidified and extracted with ether. The ether solution was dried and the ether evaporated. The residual oil distilled at 137-141° (6 mm.). The distillate solidified on standing and was found to melt at 55-6°. It was

recrystallized from 60-68° petroleum ether, melting at 57°. The melting point was not depressed by mixing it with o-hydroxybiphenyl which melted at 57°. The yield was 13.1 g. or 78%.

The same reaction takes place in diethyl ether but at a much slower rate.

Eight and four-tenths grams of dibenzofuran (0.05 mole) was dissolved in 75 cc. of dry ether and introduced into a Schlenk tube in which an atmosphere of nitrogen was maintained. To this was added 0.75 g. (0.107 mole) of lithium which had been cut into small pieces. The tube was closed and placed in a mechanical shaker to maintain constant and vigorous shaking. This was necessary to keep the surface of the lithium free of the brown solid which began to form in about one-half hour. The shaking was discontinued in 36 hours and the contents of the tube drained from the small amount of lithium which remained. Water was carefully added to hydrolyze the product. The mixture was acidified and the ether layer separated and dried. The ether was evaporated and the remaining oil distilled at atmospheric pressure; b. p. 283-5° (740 mm.). The distillate solidified on cooling; m. p. 50-5°. It was twice recrystallized from 60-8° petroleum ether to yield 5.1 g. (60%) of o-hydroxybiphenyl melting at 56-7°.

Reductions in Liquid Ammonia

Preparation of Dihydrodibenzofuran.

Typical of experiments on reductions in liquid ammonia is the following reduction of dibenzofuran in liquid ammonia.

Liquid ammonia (400 cc.) was run into a pint Dewar flask from a commercial ammonia tank or from a small auxiliary tank. The Dewar flask was equipped with a motor driven stirrer. To the liquid ammonia was added 12.0 g. (0.54 mole) of sodium cut into small slices. This dissolved on stirring for a few minutes after which the dry solid dibenzofuran was slowly added. It was found to be essential to complete reduction that the dibenzofuran be finely divided. After the addition of 30.0 g. (0.18 mole) of dibenzofuran, which required 20 to 30 minutes, stirring was continued for 30 minutes. Excess^o ammonium chloride was then added, carefully to prevent too rapid reaction. The resulting mixture was poured into a beaker and the ammonia evaporated from a steam bath. It was found unnecessary to trap the ammonia vapors if the work was performed under an efficient hood. An ordinary three-necked flask serves quite as well as the Dewar

^oNote: The amount of ammonium chloride added should be equivalent to the total amount of sodium used. Sodamide is formed by the ammonolysis of the organosodium compound and may exist in solution after the decomposition of the dissolved sodium and organosodium compound. The latter two are detected by the respective blue and red colors which they impart to the solution. Sodamide is very explosive in contact with moisture.

flask except that additional liquid ammonia had to be added to replace that lost by evaporation.

The reduction mixture, freed of ammonia, was dissolved in ether and water, the ether layer separated, dried over calcium chloride and the ether evaporated. The residual material was distilled under reduced pressure, b. p. 110° (5 mm.). The distillate solidified on cooling, m. p. $40-1^{\circ}$. The yield was 82%. Recrystallization from methanol or $60-68^{\circ}$ petroleum ether raised the melting point to 42° .

Anal. Calcd. for $C_{12}H_{10}O$: C, 84.65; H, 5.93; found: C, 84.40; H, 5.87.

Addition of Bromine to Dihydrodibenzofuran.

To 8.5 g. of 1,4-dihydrodibenzofuran in 50 cc. of dry chloroform, cooled to -10° , was added a solution of 8.0 g. of bromine in dry chloroform at such a rate that the temperature did not rise above 0° . Not all of the bromine was absorbed and some hydrogen bromide was evolved toward the end of the addition. The reaction was allowed to stand 12 hours at 10° . The chloroform and excess bromine were then evaporated under diminished pressure and the residue recrystallized twice from chloroform-methyl alcohol solution to yield 64% of dibromotetrahydrodibenzofuran, m. p. 79° .

Anal. Calcd. for $C_{12}H_{10}OBr_2$: Br, 48.45; found: Br, 48.22.

One gram of dibromotetrahydrodibenzofuran was added

to 1.0 g. of potassium hydroxide in 25 cc. of absolute ethanol and the solution refluxed for 12 hours. After cooling, the potassium bromide which separated was filtered from the solution and the filtrate warmed and diluted. On cooling there was obtained 0.33 g. (64%) of solid, m. p. 78-9°. After two recrystallizations from alcohol it melted at 83° and mixed with dibenzofuran it melted at 83-4°.

Dehydrogenation of Dihydrodibenzofuran.

A mixture of 1.0 g. each of dihydrodibenzofuran and sulfur was placed in a test tube fitted with a cold spot condenser and the tube heated in a metal bath to 250° for 90 minutes. Hydrogen sulfide was rapidly evolved when the temperature first approached 250°. The cooled reaction mass was extracted with hot absolute ethanol. From this extract there was obtained, by dilution and cooling, a 70% yield of dibenzofuran.

Dihydrodibenzofuran is also oxidized to dibenzofuran in very good yields by 5% alkaline permanganate and by chromic oxide in glacial acetic acid.

Treated with hypochlorous acid in the same manner that Bamberger and Lodter⁸⁸ treated 1,4-dihydronaphthalene to obtain tetrahydronaphthalenechlorhydrin, dihydrodibenzofuran yields 70% of pure dibenzofuran.

⁸⁸ Bamberger and Lodter, Ann., 288, 81 (1895).

Oxidation also occurred when an attempt was made to nitrate dihydrodibenzofuran by treating an acetic anhydride solution at -10° with fuming nitric acid, conditions under which tetrahydrodibenzofuran is nitrated⁸⁸. The only product was a small amount of impure dibenzofuran.

Acetylation of Dihydrodibenzofuran.

The method found favorable for the acetylation of tetrahydrodibenzofuran was found to acetylate dihydrodibenzofuran in good yields. Thirteen grams of dihydrodibenzofuran, 7.7 g. of acetic anhydride, 40.0 g. of anhydrous stannic chloride and 150 cc. of dry benzene were placed in a 3-necked flask equipped with a stirrer and condenser closed with a drying tube. This mixture was refluxed for 16 hours, hydrolyzed with ice and then extracted with ether. A relatively large amount of ether was found to be necessary since the product was not highly soluble in ether. Chloroform was found to be a better solvent. The ether solution was washed with dilute sodium hydroxide and with water and dried over anhydrous sodium sulfate. Evaporation of the solvent left 15.5 g. of solid; m. p. $107-12^{\circ}$. This was recrystallized from acetic acid to yield 14.3 g., or 89%, of acetyldihydrodibenzofuran melting constantly at 117° .

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.21; H, 5.71. Found: C, 79.65; H, 5.68.

Five grams of this acetyldihydrodibenzofuran was

suspended in 500 cc. of water and 25 g. of calcium hypochlorite and 40 g. of sodium carbonate were added. This was heated on a steam bath with stirring for 10 hours. It was then filtered and the filtrate acidified with hydrochloric acid. One gram of precipitate was obtained, which was recrystallized once from ethanol and twice from dilute acetic acid to melt at 270°; yield, 20%. 3-Dibenzofuran-carboxylic acid melts at 271°. A mixed melting point of these two melted at 270-1°.

One-half gram of the acid from the oxidation of the acetyldihydrodibenzofuran was methylated by passing dry hydrogen chloride into a boiling absolute methanol solution. Reflux was maintained for 3 hours. The ester was crystallized from the diluted solution to obtain 0.4 g. of ester, m. p. 137°. Recrystallized once from petroleum ether it melted at 138°; mixed melting point with 3-carbomethoxydibenzofuran, 138°.

To establish the structure of this acetyldihydrodibenzofuran to be 7-acetyldihydrodibenzofuran it was reduced to the known 7-acetyl-1,2,3,4-tetrahydrodibenzofuran. This was accomplished by hydrogenation with Raney nickel catalyst at room temperature and 2 atmospheres pressure in ethyl alcohol solution. Forty minutes was required to hydrogenate 5.0 g. of substance employing approximately 2.5 to 3.0 g. of catalyst. The product melted at 65°. The melting point was raised to 67° by one recrystallization from 60-8° pe-

troleum ether. Mixed melting point with authentic 7-acetyl-1,2,3,4-tetrahydrodibenzofuran, 67°. The yield of purified material was 1.6 g. (^{31%}80%). It was found necessary to purify the material to be reduced by distillation from a small amount on the nickel catalyst. The reduction was first attempted at 100°. An oily product was obtained which undoubtedly resulted from the reduction of the carbonyl group as well as reduction of the ring. This oil was not investigated further.

The oxime of acetyldihydrodibenzofuran was prepared by the usual method; m. p. 166°.

Anal. Calcd. for $C_{14}H_{13}O_2N$: N, 6.17. Found: N, 6.27.

Reduction of Acetyldihydrodibenzofuran Oxime.

A zinc dust and acetic acid reduction was carried out on this oxime in order to obtain the corresponding amine. To 7.0 g. of oxime in 100 cc. of absolute ethanol was added 20 cc. of glacial acetic acid, 10 g. of zinc dust and 5 cc. of water. This was refluxed for 4 hours. The hot solution was filtered from the zinc sludge and the alcohol removed with steam. The residue was taken up in ether, the ether solution dried, and dry hydrogen chloride added. The hydrochloride which separated melted at 248°; amount, 1.4 g. It melted at the same point after recrystallization from water strongly acidified with hydrochloric acid. The analysis indicates 7, α -aminoethyl-dihydrodibenzofuran. No test was made for a primary amine.

Anal. Calcd. for $C_{14}H_{15}ONCl$: N, 5.58. Found: N, 5.60.

Metalation of Dihydrodibenzofuran.

n-Butyllithium was prepared by the action of excess lithium on 10.6 g. (0.077 mole) of n-butyl bromide in 200 cc. of dry ether. An atmosphere of nitrogen was maintained during this and subsequent operations. The reaction mixture was cooled in an ice-salt bath and filtered from the excess lithium into a cooled ether solution of 8.5 g. (0.05 mole) of dihydrodibenzofuran. A slight yellow color developed immediately and deepened to a red color in a few minutes. The reaction was allowed to proceed at -15° for 35 minutes and was then carbonated by pouring it into an ether-solid carbon dioxide mixture.

Acidification of a water extract of the carbonated product yielded 3.6 g. (34%) of acidic material which was recrystallized twice from ethanol and once from acetic acid; m. p. $278-9^{\circ}$. Analysis, molecular weight and neutral equivalent showed it to be a monocarboxylic acid of dihydrodibenzofuran.

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 72.70; H, 4.70; neut. equiv., 214; mol. wt., 214. Found: C, 72.58; H, 4.84; neut. equiv., 216; mol. wt. (Rast), 210.

From the above ether extract there was recovered 5.0 g. (59%) of dihydrodibenzofuran.

Fifteen-hundredths grams of dihydrodibenzofurancarboxylic acid was dehydrogenated by heating it with an equal

weight of sulfur for 45 minutes at 250°. The dehydrogenated product was extracted with hot absolute ethanol and crystallized by dilution and cooling. After two recrystallizations from dilute acetic acid it melted constantly at 248-9°; yield, 0.1 g. (66%). A mixed melting point with 2-dibenzofurancarboxylic acid which melts at 248-9° was not depressed. The methyl ester was prepared and found to have the same, and not to depress, the melting point of 2-carbomethoxydibenzofuran, m. p. 73-4°.

Metalation of 1,4-Dihydronaphthalene.

1,4-Dihydronaphthalene was prepared by the sodium and alcohol reduction of naphthalene⁸⁸ and purified by the method of Sand⁸⁹. Five grams (0.038 mole) was metalated in the same manner as was dihydrodibenzofuran except that the reaction was allowed to proceed for 7 hours before carbonation. Sixty-four per cent of the 1,4-dihydronaphthalene was recovered. From the alkaline extract there was obtained 1.7 g. of acidic material which was recrystallized twice from 50% acetic acid to melt at 105-6°. One-tenth gram of this acid was digested for 2 hours with alkaline potassium ferricyanide. On acidification an acid was precipitated which, after one recrystallization from dilute acetic acid, melted at 182°. β -Naphthoic acid melts at this same temperature and a mixed melting point

⁸⁸Bamberger and Lodter, Ann., 288, 75 (1895).
⁸⁹Sand, Ber., 36, 3705 (1905).

showed them to be the same. 1,2-Dihydro-2-naphthoic acid is described by Bayer⁹¹ as melting at 104° and to be easily oxidized to β -naphthoic acid with alkaline potassium ferricyanide. The 1.7 g. of 1,2-dihydro-2-naphthoic acid obtained from the metalation represented a 26% yield.

Reduction of Dihydrodibenzofuran.

Eight and four-tenths grams (0.05 mole) of dihydrodibenzofuran was hydrogenated in ethanol solvent at 2.5 atmospheres pressure and in the presence of platinum oxide catalyst. The absorption of hydrogen stopped at 2 atoms. With one reactivation 4 hours were required for the reduction. The alcohol solution was filtered from the catalyst, the alcohol removed under reduced pressure, and the residual oil distilled. All of it distilled over the range 107-9° (4 mm.); n_D^{20} 1.5798. These constants indicate pure tetrahydrodibenzofuran; n_D^{20} 1.5795, b. p. 135° (9 mm.)⁶⁷. The picrate was prepared, melting at 97°. The picrate of tetrahydrodibenzofuran melts at 97°; mixed melting point, 97°.

Reduction to tetrahydrodibenzofuran was also accomplished by employing Raney nickel as the catalyst under conditions similar to the above and by reducing with sodium and alcohol. In neither case was the product as pure as

⁹¹ Bayer, Ann., 266, 202 (1891).

that produced by reduction with platinum oxide, apparently because of incomplete reduction.

Attempted Isomerization of Dihydrodibenzofuran with Sodium Ethylate.

Dihydrodibenzofuran was heated with 5 times its weight of 5% sodium ethylate in a sealed tube at 120° for 5 hours. The starting material was recovered with only a slight depression in melting point. The experiment was repeated, heating to 180° for 9 hours. The reaction product was an oil which was distilled from a small Claisen flask. Three grams of distillate was obtained [b. p. 112-18° (5 mm.)] from 7.0 g. of starting material. The remainder became a glassy solid on cooling.

The distillate became a mushy solid on cooling. Repeated recrystallization from methyl alcohol yielded one-half gram of pure dibenzofuran.

Attempted Isomerization of Dihydrodibenzofuran with Raney Catalyst.

Three grams of dihydrodibenzofuran was heated to 230° in a sealed tube with Raney nickel for 4 hours. The product melted at 76-9°. It was dissolved in hot alcohol, filtered from the catalyst and cooled. The solid which separated was recrystallized to yield 1.1 g. of pure dibenzofuran. The alcohol filtrates were combined and 2.0 g. of picric

acid added. The picrate which separated was found to be the picrate of dibenzofuran. A total of 2.5 g. (83%) of pure dibenzofuran was recovered. Not all of the residual dibenzofuran was removed by treatment with picric acid as a crystalline solid and droplets of oil separated from the alcoholic picric acid solution on dilution and neutralization with sodium hydroxide. The alcohol was removed from this residue and the latter distilled from a small flask. A few drops of distillate was obtained, boiling at 259-61°; n_D^{20} , 1.5121. These physical constants are near those of perhydrodibenzofuran and the odor was characteristic of perhydrodibenzofuran. It did not form a picrate.

Ozonization of Dihydrodibenzofuran.

Several attempts were made, under a variety of conditions, to obtain ozonization products of dihydrodibenzofuran which would be of value in elucidating its structure. The only products obtained were dibenzofuran and salicylic acid.

Experiment No. 1. Nine grams (0.053 mole) of dihydrodibenzofuran in 200 cc. of dry chloroform was ozonized at room temperature for 12 hours. A gummy ozonide precipitated. A sample of the supernatant liquid was found not to absorb bromine. The stability of the ozonide was tested by placing a small sample on a spatula and warming over a flame. It was found to be quite stable, as it exploded only after

considerable warming.

The chloroform was removed by means of the water pump and the remaining ozonide covered with 100 cc. of water. No reaction was apparent until the water was heated, when the ozonide gradually became liquid. After 3 hours of heating the whole was cooled. The oily material became sufficiently solid to be filtered. The residue was dissolved in alcohol and diluted. On cooling there was obtained 0.9 g. of dibenzofuran. Further dilution yielded an oily precipitate. Steam distillation was then attempted. The only product obtained was 1.2 g. of dibenzofuran from the distillate. The residue was tarry.

Experiment No. 2. Thirteen grams of dihydrodibenzofuran in 100 cc. of dry chloroform was ozonized for 12 hours. The chloroform was decanted from the ozonide and the latter suspended in 50 cc. of acetic acid. Seventy cubic centimeters of 30% hydrogen peroxide was added and the mixture warmed on the steam bath for 1 hour, when all of the ozonide was decomposed. The solution was filtered to free it of a small amount of suspended material and then diluted. A small amount (0.2 g.) of dibenzofuran separated and was filtered from the solution. Further dilution precipitated an amorphous brown solid. The acetic acid was neutralized with sodium carbonate and then made slightly acid with hydrochloric acid. The solid material was extracted with ether from which extract there was obtained only 1.2 g. of salicylic acid, identified

by melting point and mixed melting point.

The chloroform was evaporated and the remaining oil distilled, obtaining 3.2 g. of dibenzofuran. The yield of dibenzofuran was 26% and of salicylic acid 11%.

Experiment No. 3. A solution of 10.0 g. of dihydrodibenzofuran in 100 cc. of glacial acetic acid was ozonized at room temperature for 36 hours. The acetic acid solution was diluted to 200 cc. with ether and zinc dust added in small quantities. It was necessary to add a little water to start the reaction, which then became vigorous. When the reaction had ceased the excess zinc was removed by filtration and most of the solvent evaporated. The remaining solvent was diluted slightly with water to precipitate 2.0 g. of dibenzofuran. Further dilution precipitated a small amount (0.2 g.) of amorphous solid which could not be purified.

Experiment No. 4. Eight grams of dihydrodibenzofuran was ozonized in 125 cc. of carbon tetrachloride to which had been added 0.008 g. of bromine. Such a medium was found by Ebel⁶⁵ to be effective in the ozonization of tetrahydrodibenzofuran. After 8 hours of ozonization the carbon tetrachloride solution was found not to absorb bromine. The ozonide which separated was a granular solid, quite different in this respect from the ozonides obtained without the use of bromine. The ozonide was filtered from the solvent and air dried for an hour, obtaining 11.0 g. It was subjected to steam distillation to yield 1.6 g. of dibenzofuran.

Evaporation of the carbon tetrachloride filtrate yielded an additional 0.6 g. of dibenzofuran, making a total yield of 28% of this material.

The residue from the steam distillation hardened on cooling and was filtered from the water. It could not be made to crystallize from acetic acid, alcohol, petroleum ether, acetone or benzene. An attempt was made to distill it at 4 mm. pressure. There was obtained only 0.8 g. of salicylic acid, the remainder decomposing before distilling.

Experiment No. 5. Five grams of ozonide obtained as in Experiment No. 4 was suspended in 75 cc. of 5% sodium carbonate solution and shaken for 12 hours. At the end of this time the sodium carbonate solution had turned brown but much solid remained. This was filtered and the solution acidified. An oil was precipitated which coagulated to a gummy mass of approximately one-half gram. It seemed resinous and could not be made to crystallize.

Experiment No. 6. The ozonide as obtained in the last experiments was purified for catalytic hydrogenation by washing it 3 times with anhydrous ether and then drying it in a vacuum desiccator at 4 mm. for 4 hours. Five grams of this ozonide was dissolved in 25 cc. of glacial acetic acid and hydrogenated at atmospheric pressure and temperature in the presence of 0.3 g. of platinum oxide catalyst. After an induction period of 15 minutes hydrogen was absorbed rapidly, 2.2 atoms being absorbed in 40 minutes. The solvent

was removed under reduced pressure, leaving a viscous brown oil. As in the previous experiments, attempts to purify it failed.

Action of Lithium on Dihydrodibenzofuran.

Eight and one-half grams (0.05 mole) of dihydrodibenzofuran, 0.8 g. (0.11 atom) of lithium and 100 cc. of sodium dried dioxan were introduced into a three-necked flask and kept under an atmosphere of nitrogen. The solution was heated to gentle reflux and stirred vigorously for 24 hours. The solution began to turn brown as soon as it became hot and the color deepened rapidly. At the end of the period of reaction the brown color had all disappeared and a white precipitate had appeared.

Water-dioxan solution was added to the cooled reaction mixture to hydrolyze any organometallic compound which might have remained undecomposed. The water and dioxan were removed under reduced pressure and the residue treated with 5% sodium hydroxide. Most of it dissolved in this solvent. This was washed once with ether, acidified, and extracted with ether. The ether extract was dried and the ether removed. The resulting oil was distilled; b. p. 120-5° (7 mm.). The distillate solidified on cooling; m. p. 56-7°. This was recrystallized from 60-8° petroleum ether and melted at 58°. This corresponds to the melting point of o-hydroxybiphenyl and a mixed melting point was not depressed. The yield of

purified material was 6.0 g. or 70%. A second experiment one-half the size of the one just described yielded 60% of o-hydroxybiphenyl.

Reduction of 4-Hydroxydibenzofuran in Liquid Ammonia.

Ten grams (0.054 mole) of solid 4-hydroxydibenzofuran was added slowly to a solution of 5.5 g. of sodium in 300 cc. of liquid ammonia. To maintain a blue color for 40 minutes after the addition of all of the 4-hydroxydibenzofuran it was necessary to add an additional 1.5 g. of sodium. Excess ammonium chloride was added and the ammonia evaporated. The residue was taken up in water and ether. The ether solution was extracted with 5% sodium hydroxide. Acidification of this alkaline solution yielded 5.1 g. of impure solid which was recrystallized first from 77-110° petroleum ether and then from methanol, the latter being decolorized with norite. The 4.5 g. (45%) of pure material melted at 116-117°. Analysis showed it to be a dihydrohydroxydibenzofuran.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.39; H, 5.42. Found: C, 77.62; H, 5.41.

Its phenolic properties indicate that it is 1,4-dihydro-6-hydroxydibenzofuran. It was dehydrogenated by heating with sulfur at 230° for an hour. The product was extracted from the sulfur by means of hot alcohol and crystallized by dilution and cooling. From 0.8 g. of material there was obtained 0.52 g. (65%) of 4-hydroxydibenzofuran

identified by mixed melting point.

One gram of this was methylated with methyl sulfate to yield 0.75 g. (70%) of methyl ether melting at 54°.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.97; H, 6.04; found: C, 77.71; H, 6.02.

Reduction of 4-Methoxydibenzofuran in Liquid Ammonia.

Twelve grams of solid 4-methoxydibenzofuran was added slowly to a solution of 9.0 g. of sodium in liquid ammonia. The reduction product was isolated and distilled at 7 mm. pressure, obtaining two considerable fractions: (1) to 112°, 0.5 g.; (2) 112-14°, 5.1 g.; (3) 114-35°, 0.6 g.; (4) 135-42°, 4.0 g. By treatment with 5% sodium hydroxide the second fraction was made to solidify. This solid proved to be dihydrodibenzofuran. Three and one-tenth grams (26%) was obtained. The alkali soluble portion was an oil and could not be made to solidify. The higher boiling material and the residue also seemed to be mixtures and were not resolved into pure substances.

Attempted Reduction of 3-Aminodibenzofuran, 3-Diethylamino-dibenzofuran and 4-Aminodibenzofuran in Liquid Ammonia.

These three compounds were subjected to reduction in liquid ammonia in the usual manner. There was recovered 64% of the 3-aminodibenzofuran, 80% of the 3-diethylaminodibenzofuran, and 80% of the 4-aminodibenzofuran. The other products

were tars and humus-like products. The amount of sodium consumed in the reductions was roughly in inverse proportion to the amount of amine recovered.

Reduction of Dibenzofuran by Calcium in Liquid Ammonia.

Dibenzofuran is reduced to a greater extent by calcium in liquid ammonia than by sodium in liquid ammonia. The stage at which the reduction stops is, however, not so specific as in the case of reduction with sodium because the product always seems to be a mixture, and if the reduction product is subjected to a second reduction under the same conditions greater reduction occurs, the product being still a mixture.

Run 1. Twenty grams of dibenzofuran (0.12 mole) was added to 500 cc. of liquid ammonia. Calcium was then added, three-fourths of an hour being required for the addition of 17 g. That amount was required to maintain the blue color of unused calcium for 20 minutes. The product was fractionated at 9 mm. pressure, obtaining: (1) to 110°, 2.0 g.; (2) 110-13°, 11.2 g., n_{D}^{20} , 1.5680, d_{4}^{20} , 1.1062. The remainder of the material was resinous. The molecular refractivity was calculated to be 50.88 as compared to 51.58 required by theory for 1,2,3,4-tetrahydrodibenzofuran²². Ebel⁶⁵ deter-

²² Refractivity constants taken from Cohen's Organic Chemistry, Longmans, Green and Co., 1918, New York, pages 19-35.

mined the physical constants of 1,2,3,4-tetrahydrodibenzofuran to be: n_D^{25} 1.56955; n_D^{17} 1.0962; and found the molecular refractivity to 51.45 as compared to a theoretical value of 51.14.

Run 2. Two like experiments were performed with the one difference that the dibenzofuran was added to a solution of the calcium in liquid ammonia. Each 20.0 g. run of dibenzofuran required approximately 17-18 g. of calcium to maintain a blue color for 1 hour. The products of the two experiments were combined and distilled from a Claisen flask at 5 mm. pressure. After a 4 cc. fore-run there was collected 28 g. of material boiling over the range 115-34°. The residue became resinous on cooling. The 28 g. of material was then fractionated. It distilled constantly at 112-112.5° (7 mm.). Four fractions were taken and the index of refraction each fraction determined: (1) 4.5 g., n_D^{25} , 1.5665; (2) 7.0 g., n_D^{25} , 1.5672; (3) 3.3 g., n_D^{25} , 1.5685; (4) 2.2 g., n_D^{25} , 1.5690. The middle fractions were combined and used in the following analysis and bromine addition experiment.

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.67; H, 7.04. Found: C, 83.32; H, 7.02.

Bromine was rapidly decolorized by this material; 1.72 g. (0.01 mole) was dissolved in 20 cc. of dry chloroform and cooled to -5°. To this was added 1.0 cc. (0.011 mole) of bromine in 20 cc. of cold chloroform. The bromine was absorbed instantly at first with little evolution of hydrogen

bromide, slowly toward the last of the addition with the evolution of considerable hydrogen bromide. The mixture was allowed to stand at -5° for 1 hour and then the chloroform and excess bromine removed by means of the water pump. The remaining white solid was recrystallized from chloroform-methanol solution to yield 3.1 g. of material melting at $140-5^{\circ}$. This was again recrystallized from chloroform-methanol solution and once from chloroform-petroleum ether ($60-8^{\circ}$) solution to yield 2.2 g. (45%) of tribromotetrahydrodibenzofuran, melting at 148° .

Anal. Calcd. for $C_{12}H_{11}OBr_3$: C, 35.13; H, 2.70; Br, 58.35. Found: C, 34.95; H, 2.84; Br, 58.56.

The product of the first reduction (n_D^{20} 1.5680) was reduced catalytically in the presence of platinum oxide catalyst. The reduction was done at room temperature and at atmospheric pressure. The volume of hydrogen absorbed was measured, 630 cc. or 2.08 atoms being absorbed in 20 minutes by 4.3 g. (0.025 mole) of material. The product was distilled from a small Claisen flask; b. p., $114-17^{\circ}$ (8 mm.); n_D^{20} 1.5509; d_{20}^{20} 1.066.

Run 3. In a fourth reduction of a 20.0 g. portion of dibenzofuran 24 g. of calcium was required to maintain a blue color in the liquid ammonia for 1 hour after all of the dibenzofuran had been added. Fractionation of the product at 4 mm. pressure yielded: (1) to 90° , 3.0 g.; $90-8^{\circ}$, 10.5 g., n_D^{20} 1.5480. The residue became resinous on cooling.

Run 4. Twelve grams of reduced material, n_D^{20} 1.5680, was again subjected to reduction by calcium in liquid ammonia to obtain, on fractionation at 4 mm. pressure: (1) 80-92°, 2.0 g.; (2) 92-4°, 6.3 g., n_D^{20} 1.5494. This product has about the same physical constants as the product of Run 3.

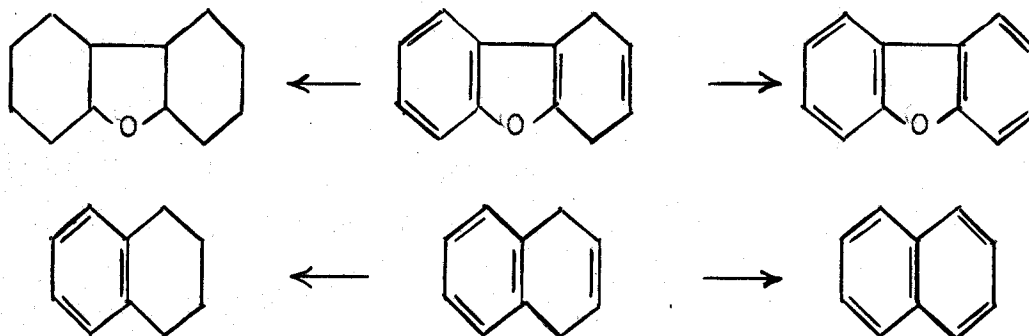
Run 5. The products of Runs 3 and 4 were combined and again subjected to reduction by calcium in liquid ammonia. The product was fractionated at atmospheric pressure: (1) to 258°, 1.2 g.; (2) 258-64°, 3.5 g., n_D^{20} 1.5380; (3) 264-6°, 4.1 g., n_D^{20} 1.5494; (4) 266-7°, 0.8 g., n_D^{20} 1.5518. Some additional reduction appears to have taken place.

DISCUSSION OF RESULTS

The hydrogenation of dibenzofuran with insufficient hydrogen to saturate it has not led to a partially reduced dibenzofuran but to a mixture of perhydrodibenzofuran and unreduced dibenzofuran. Adams' platinum oxide catalyst was used at low temperature and pressure, Raney nickel catalyst at 175° and 200 atmospheres, and a platinum black catalyst at low pressure and temperature. The results were the same in each case. The last named catalyst was used in an attempt to duplicate the work of Cullinane and Padfield⁶⁶, who obtained tetrahydrodibenzofuran by reduction in dry acetic acid.

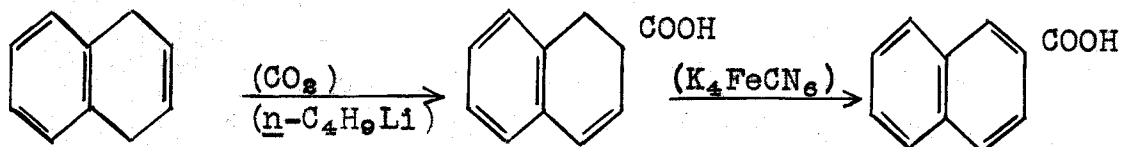
In this connection it is noteworthy that 1,4-dihydrodibenzofuran heated to 230° in the presence of a nickel catalyst undergoes simultaneous hydrogenation and dehydrogenation to produce dibenzofuran and perhydrodibenzofuran. In comparison, 1,4-dihydronaphthalene heated to 130° in the presence of a palladium catalyst yields a mixture of naphthalene and tetrahydronaphthalene⁶³. This difference is in agreement with the fact that naphthalene is readily hydrogenated to tetrahydronaphthalene, whereas dibenzofuran is not partially hydrogenated.

⁶³ Zelinskii and Pavlov, Ber., 57B, 1066 (1924).

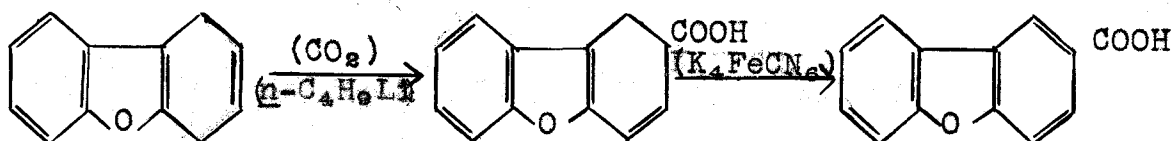


The dihydrodibenzofuran used in the above mentioned hydrogenation-dehydrogenation experiment was obtained by the reduction of dibenzofuran with sodium in liquid ammonia. Experiments to determine its structure by oxidation with chromic acid or permanganate resulted only in the formation of dibenzofuran. Ozonization also produced some dibenzofuran, a little salicylic acid and much amorphous material which could not be identified. The evidence for the 1,4-dihydro structure comes from metalation experiments.

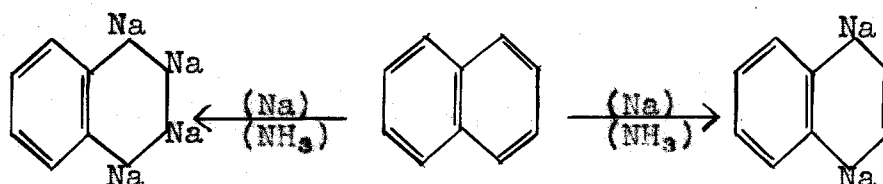
1,4-Dihydronaphthalene was metalated with n-butyllithium and subsequently carbonated to yield 1,2-dihydro-2-naphthoic acid. This acid was readily oxidized by potassium ferri-



cyanide to β -naphthoic acid. A similar metalation of 1,4-dihydrodibenzofuran yielded a dihydrodibenzofurancarboxylic acid melting at 278-9° and which was oxidized readily by potassium ferricyanide to 2-dibenzofurancarboxylic acid.



Additional evidence for the structure of 1,4-dihydrodibenzofuran comes from its mode of formation and analogous reductions. The action of alkali metals on unsaturated compounds in ether solution is similar to that in liquid ammonia solution. Compounds found by Lebeau and Picon⁷⁵ to give hydro derivatives with sodium in liquid ammonia yield sodium addition products in ether solution. By reduction in liquid ammonia anthracene and stilbene yield dihydro derivatives; phenanthrene and biphenyl yield tetrahydro derivatives. By the action of sodium on ether solutions, anthracene⁷⁴, stilbene⁷⁴, phenanthrene⁷⁹ and biphenyl⁷⁹ all yield disodium addition products; and dihydro derivatives by hydrolysis. Naphthalene in ether solution yields a 1,4-disodium addition product⁷⁹ and in liquid ammonia a 1,2,3,4-tetrasodium addition product⁷⁵.

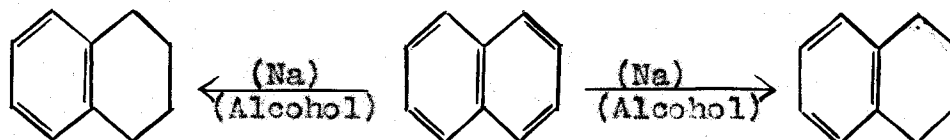


The mechanism of sodium amalgam reduction has been postulated by Willstätter, Seitz and Bumm⁷⁵ to be the inter-

⁷⁴ Schlenk, et al, Ber., 47, 473 (1914).

⁷⁵ Willstätter, Seitz and Bumm, Ber., 61, 871 (1928).

mediate formation of a sodium addition compound followed by solvolysis. This undoubtedly can be extended to sodium and alcohol reduction. By sodium and alcohol reduction naphthalene can be made to yield either 1,4-dihydronaphthalene or 1,2,3,4-tetrahydronaphthalene, depending upon the temperature of the reduction⁶⁶.



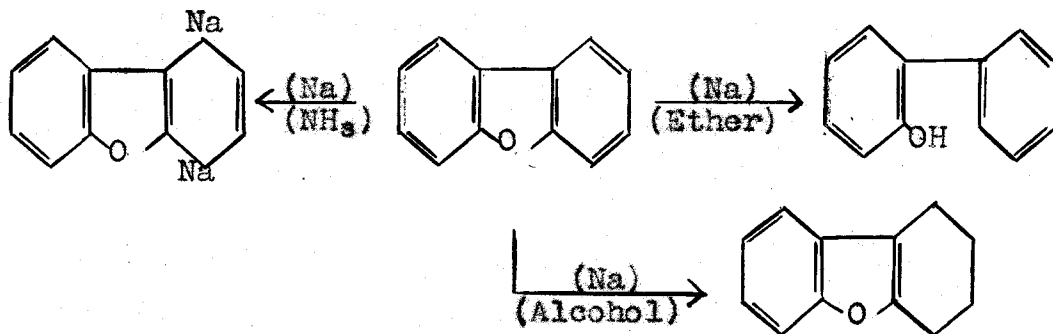
Similarly, phenanthrene may be made to yield either a dihydro or tetrahydro derivative by reduction with sodium and alcohol⁶⁷. It appears that the action of sodium on unsaturated compounds under the various conditions discussed differs only in degree and not in kind.

It might be predicted that dibenzofuran would undergo similar reactions. In the introductory part it was pointed out that sodium and alcohol reduction leads to the formation of tetrahydrodibenzofuran. In this investigation it has been found that sodium in liquid ammonia, followed by solvolysis, gives good yields of dihydrodibenzofuran. By analogy to the addition of sodium to naphthalene it would be expected to be 1,4-dihydrodibenzofuran. The presence of the oxygen bridge in dibenzofuran gave rise to anomalous results when an attempt was made to add sodium to dibenzofuran in

⁶⁶ Bamberger and Lodter, Ber., 20, 1703 (1887).

⁶⁷ Schmidt and Mezger, Ber., 40, 4240 (1907).

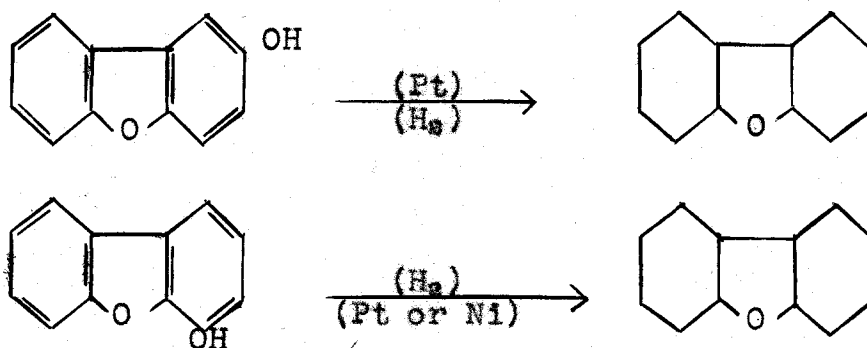
ether solution. The oxygen bridge was cleaved to give, on hydrolysis, *o*-hydroxybiphenyl.



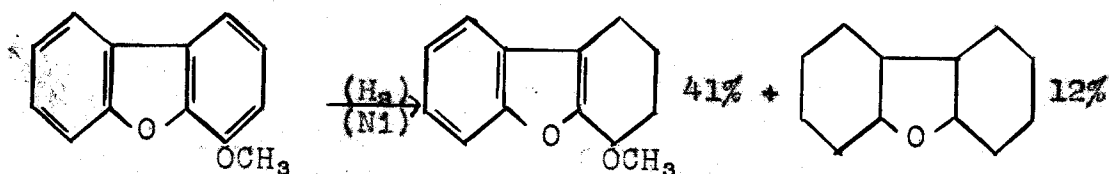
The reduction of dibenzofuran by means of calcium in liquid ammonia does not stop at a definite stage as does the reduction with sodium. Fractional distillation of the mixture yielded a fraction, though not quite pure, having the average composition of tetrahydrodibenzofuran and physical constants (n_D^{20} 1.5680; d_4^{20} 1.1062) near those reported by Ebel⁶⁵ for 1,2,3,4-tetrahydrodibenzofuran (n_D^{20} 1.5696; d_{17}^{20} 1.0962). A considerable amount of polymeric product was left from the distillation.

The incomplete hydrogenation of 2-hydroxydibenzofuran resulted in the formation of 31% of perhydrodibenzofuran and the recovery of 42% of the 2-hydroxydibenzofuran when the reduction was carried out in the presence of platinum oxide catalyst. Similarly, 4-hydroxydibenzofuran yielded 32% of perhydrodibenzofuran and 51% was recovered. Approximately six atoms of hydrogen were absorbed in each case. 4-Hydroxydibenzofuran was also hydrogenated at high pressure and temperature in the presence of a supported nickel catalyst to yield 32% of perhydrodibenzofuran. In this case the

remainder of the material was alkali soluble but could not be purified.



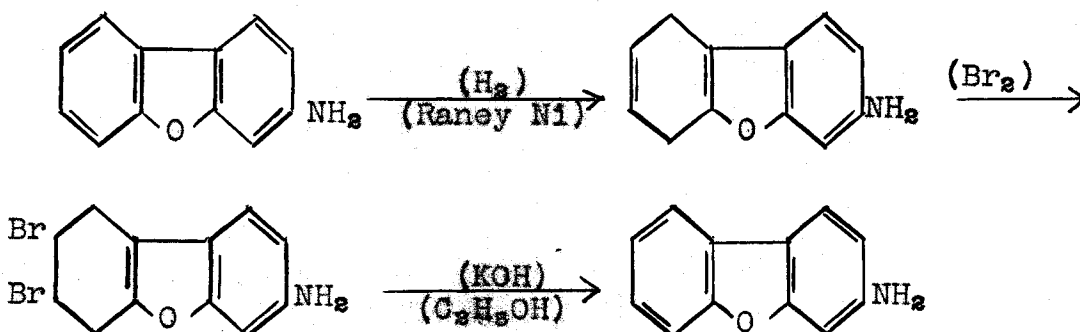
The products of the hydrogenation of 2-methoxydibenzofuran in the presence of platinum oxide catalyst could not be separated and purified. 4-Methoxydibenzofuran hydrogenated in the presence of a supported nickel catalyst and in dioxan solvent yielded 12% of perhydrodibenzofuran and 41% of a tetrahydromethoxydibenzofuran. This was shown, by the method of mixed melting points, to be different from the 1,2,3,4-tetrahydro-6-methoxydibenzofuran prepared by Ebel⁶⁸. It must, therefore, be 1,2,3,4-tetrahydro-4-methoxydibenzofuran.



Some new methods were applied to the preparation of aminodibenzofurans. Distinct advantages over the methods previously employed were noted in some instances. 3-Nitrodibenzofuran was reduced catalytically to 3-aminodibenzofuran employing Raney catalyst and ethanol solvent. The reduction

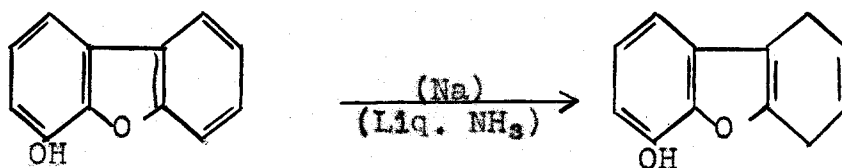
was rapid when carried out at 100° and yields of 90-95% of high purity could be obtained. 2-Aminodibenzofuran and 4-aminodibenzofuran were prepared from the corresponding bromodibenzofurans by the action of sodamide in liquid ammonia. The yield of 2-aminodibenzofuran was 60%, which is somewhat lower than that of the best method previously employed -- the action of ammonium hydroxide in a steel bomb at 225° and with cuprous bromide catalyst⁸⁷. The yield of 4-aminodibenzofuran was 31% as compared to 17% obtained by the bomb method. The preparation of the amines in liquid ammonia has the advantage that a special bomb is not required.

Attempts were made to reduce 3-aminodibenzofuran and 4-aminodibenzofuran in dioxan solution and in the presence of the supported nickel catalyst. No reduction had occurred up to a temperature of 235° and at 160 atmospheres pressure. Unexpected results were obtained by subjecting 3-aminodibenzofuran to reduction at 100° and 3 atmospheres in the presence of Raney catalyst. A dihydroaminodibenzofuran was obtained. This could be precipitated from ether solution as the amine hydrochloride but not by moist carbon dioxide, indicating that the non-substituted ring was reduced. A dibromo addition product was obtained which was decomposed with alcoholic potassium hydroxide to yield 3-aminodibenzofuran.



Some derivatives of dibenzofuran were subjected to reduction by sodium in liquid ammonia. 3-Aminodibenzofuran, 3-diethylaminodibenzofuran and 4-aminodibenzofuran were tried. In each case considerable sodium was consumed with the production of tars and humus like material. Approximately three-fourths of the starting materials were recovered.

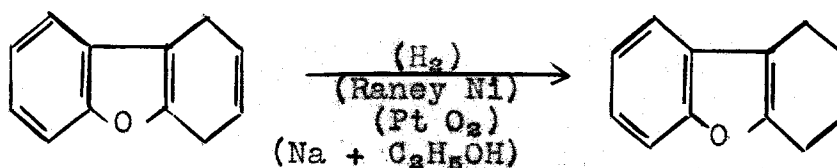
4-Hydroxydibenzofuran was reduced by sodium in liquid ammonia to yield 45% of 1,4-dihydro-6-hydroxydibenzofuran. This structure was assigned on the basis that the material was phenolic, being soluble in dilute alkali.



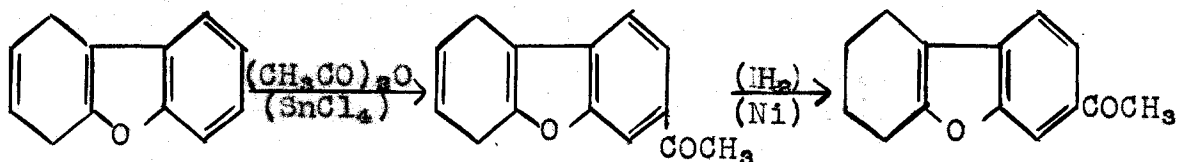
4-Methoxydibenzofuran was also reduced in liquid ammonia but the reaction was more complex, as 26% of dihydrodibenzofuran was obtained and the remainder of the reduction product could not be purified and characterized.

Dihydrodibenzofuran was subjected to the action of several reagents. Reduction by means of sodium and alcohol

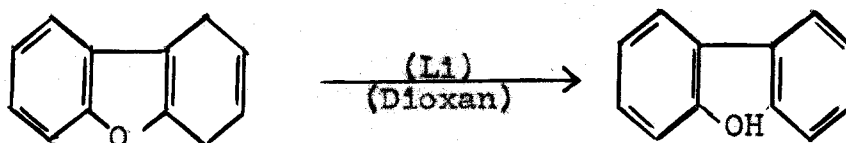
or catalytically at low pressure and temperature in the presence of either Raney nickel or platinum oxide yielded tetrahydrodibenzofuran, identified by means of its picrate. Undoubtedly dihydrodibenzofuran or tetrahydrodibenzofuran would be hydrogenated to perhydrodibenzofuran under conditions milder than those necessary to hydrogenate dibenzofuran. Acetylation with acetic anhydride and stannic chlor-



ide yielded 7-acetyldihydrodibenzofuran. This compound was characterized by oxidizing it to 3-dibenzofurancarboxylic acid by means of hypochlorous acid. It was also reduced in the presence of Raney catalyst to the known 7-acetyl-1,2,3,4-tetrahydrodibenzofuran⁶⁷. The action of lithium



on dihydrodibenzofuran in dioxan solution was similar to its action on dibenzofuran. A subsequent decomposition of the reaction product took place yielding *o*-hydroxybiphenyl instead of the expected dihydroxybiphenyl. The attempt to isomerize dihydrodibenzofuran by heating in the presence



of a catalyst has been discussed. An additional attempt was made to isomerize under the conditions that 1,4-dihydronaphthalene is isomerized to 1,2-dihydronaphthalene⁸⁸. No reaction took place by heating with 5% sodium ethylate at 120°. By heating to 180° polymeric products were obtained along with a small amount of dibenzofuran.

⁸⁸ Strauss and Lemmel, Ber., 46, 232 (1913).

SUMMARY

Previous work on the reduction of dibenzofuran and derivatives has been discussed.

Dibenzofuran and some amino and hydroxy derivatives have been subjected to reduction catalytically and by means of sodium in liquid ammonia.

Catalytically, dibenzofuran has been reduced to perhydrodibenzofuran; 4-methoxydibenzofuran to 1,2,3,4-tetrahydro-4-methoxydibenzofuran; and 3-aminodibenzofuran to 1,4-dihydro-7-aminodibenzofuran.

In liquid ammonia, dibenzofuran has been reduced to 1,4-dihydrodibenzofuran, and 4-hydroxydibenzofuran to 1,4-dihydro-6-methoxydibenzofuran.

Evidence has been offered for the structures assigned.

Improved syntheses for aminodibenzofurans have been described.

Dihydrodibenzofuran has been subjected to reduction, oxidation, dehydrogenation, acetylation, metalation and the addition of bromine.

Lithium reacts with dibenzofuran and dihydrodibenzofuran in ether solutions to cleave the oxygen bridge.