poorer fit to the latter points. However, the latter points would be expected to be high since some isomerization to normal ether occurs. At infinite time for example (1260 minutes), the acid concentration found is 0.00024 M instead of zero. Considering this side reaction and the inherent errors in the method of analysis, the agreement obtained is as good as can be expected.

Acknowledgment.—One of the authors (S. H. L.) is indebted to the United States Public Health Service for a fellowship held during the course of this work.

EVANSTON, ILLINOIS RECEIVED DECEMBER 8, 1950

[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Reactions of Benzofurans with Hydrogen[1]

BY JACOB ENTEL, CLARENCE H. RUOF AND H. C. HOWARD

The presence of linear and cyclic ethers has often been postulated to account for the inert character of oxygen in bituminous coals. Little information is available on the behavior of such ethers when subjected to reaction with hydrogen. In this work benzofuran, 2,3-dihydrobenzofuran and 2-methyl-2,3-dihydrobenzofuran have reacted with hydrogen at 200°, 250° and 300° using copper–chromium oxide as catalyst and the products have been separated and identified. The heterocyclic ring is ruptured and at higher temperatures a secondary hydrogenolysis removes the oxygen to form alkyl benzenes and cyclohexanes. A possible mechanism for the reaction, based on yields of the various products and the amenability of possible intermediate products to further reaction, is presented.

Although oxygen is contained in all bituminous coals very little evidence as to its nature has been forthcoming. Even the simple soluble and volatile degradation products from coal often contain more oxygen than can be accounted for in reactive functional groups; as a result, linear and cyclic ether links have been postulated to account for the non-reactive character of the oxygen. Information on reactions of hydrogen with compounds containing cyclic oxygen is therefore of significance in studies on the hydrogenation and hydrogenolyses of coals and their degradation products; and, with the exception of the data on the hydrogenation of diphenylene oxide,[2] such information is limited.

In the present investigation on the reactions of oxygen heterocycles with hydrogen, benzofurans were chosen because of their importance in coal chemistry and their ready synthesis. The following compounds have been synthesized and studied: benzofuran (coumarone) (I), 2,3-dihydrobenzofuran (II) and 2-methyl-2,3-dihydrobenzofuran (III).[3]

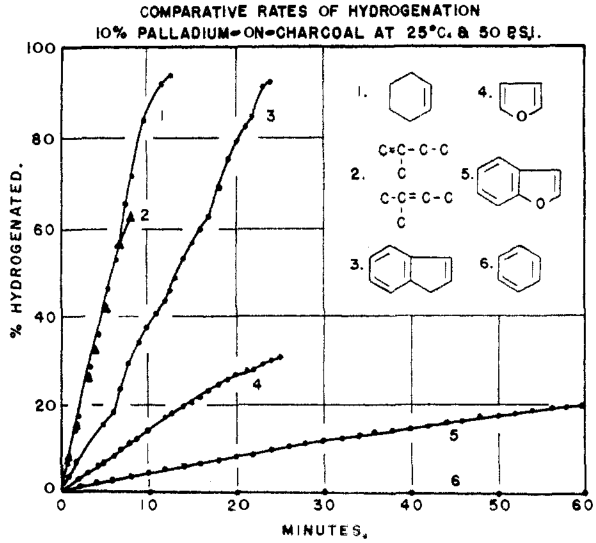

Fig. 1.

Hydrogen Addition.—The simplest reaction of hydrogen with benzofuran is addition to the double bond of the furanoid ring to give 2,3-dihydrobenzofuran. To compare the ease of this addition to the hydrogenation of other unsaturated compounds, a semi-quantitative study (Fig. 1) of the rate of hydrogen absorption was made using palladium as a catalyst at room temperature. The rate of hydrogen absorption by benzofuran is shown to be much slower than that for indene and even furan, but is appreciable in contrast to that of benzene which shows no absorption under these conditions. Cyclohexene and 2-methylbutene show rapid hydrogenation.

A series of experiments was also run to compare the rates of hydrogenation of benzofuran using different catalysts and reaction conditions. While the Raney nickel at 93° gives the fastest reaction, as shown in Fig. 2, the temperature must be rigidly controlled to prevent benzene ring saturation.

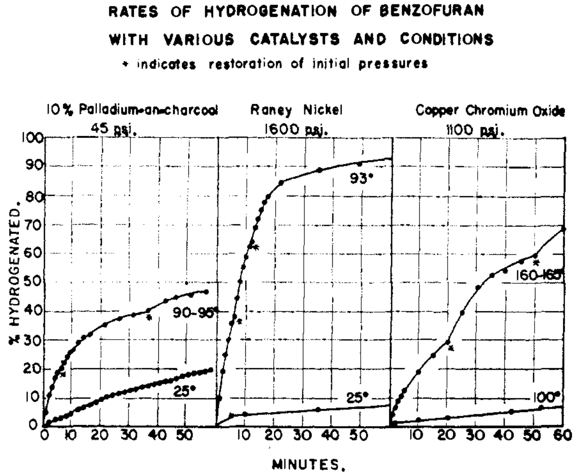

Fig. 2.

Hydrogenolysis Reactions.—In addition to the hydrogenation of the double bond, the reaction of

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[1] Presented before the Gas and Fuel Division, American Chemical Society, 118th National Meeting, September 4–8, 1950, Chicago, Ill.

[2] C. C. Hall and C. M. Cawley, *J. Soc. Chem. Ind.*, **58T**, 7 (1939).

[3] For preparation of III, *cf.* J. Entel, C. H. Ruof and H. C. Howard, THIS JOURNAL, **73**, 2365 (1951).

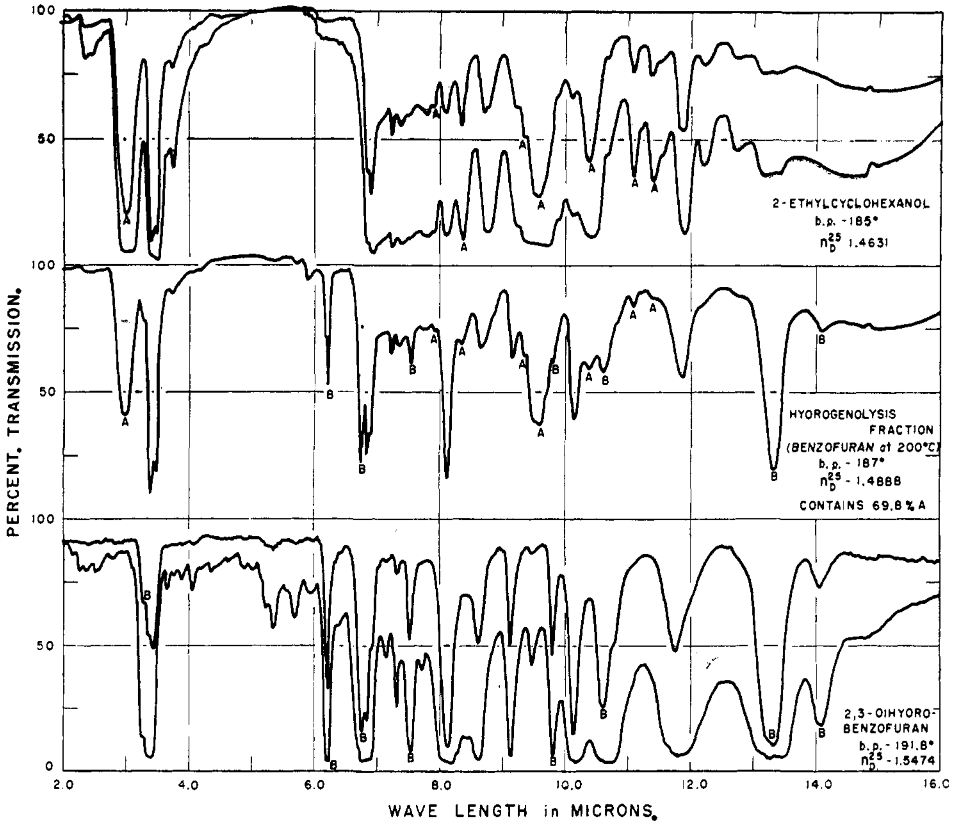

Fig. 3.—Infrared spectra (capillary films).

benzofurans with hydrogen can proceed further with saturation of the benzene ring and hydrogenolytic rupture of the furanoid ring to produce alcohols and phenols; further reaction can result in elimination of oxygen with the formation of alkyl benzenes and cyclohexanes.

In Table I are summarized the effects of several catalysts on the extent of ring opening. Under these conditions, where the removal of the hydroxyl group by a secondary hydrogenolysis is not appreciable, the yield of –OH indicates the amount of ring rupture. The experiment using palladium-on-charcoal produced hydrogenation of the double bond and little hydrogenolysis. The run with Raney nickel, while giving little hydrogenolysis, resulted in a large amount of benzene ring saturation as evidenced by high hydrogen absorption and low refractive index of the product. This emphasizes the necessity of rigid temperature control if selective hydrogenation of the furanoid double bond only is desired as in the preparation of 2,3-dihydrobenzofuran. However, when copper–chromium oxide was used as the catalyst, the amount of hydrogenolytic rupture increased six-fold even with less hydrogen absorption. Adkins[4] has shown that there is a labilizing effect on the carbon-to-oxygen linkage by the presence of carbon-to-carbon double bonds. Since copper chromite is not as active for saturation of double bonds as is palladium or Raney nickel, the hydrogenation is slow. The double bond persists longer and labilizes the carbon-to-oxygen bond in benzofuran longer, thus permitting greater cleavage of the furanoid ring.

TABLE I

EFFECT OF CATALYST ON HYDROGENOLYSIS OF BENZOFURAN

Catalyst	Palladium-on-charcoal	Raney nickel	Copper chromite
Temperature, °C.	100	120	160
Time, hours	16	18	8
Pressure, p.s.i.g.	45	2000	2000
Moles of H_2/mole benzofuran	1.02	1.88	1.36
Weight %, OH	0.14	0.16	0.92
n^{25}D of product	1.5455	1.4840	1.5420
n^{25}D of 2,3-dihydrobenzofuran	1.5474	1.5474	1.5474

In the present work the hydrogenolyses were performed by treating I, II and III with hydrogen at 200, 250 and 300° over copper–chromium oxide for 12 hours. After removal of the phenols by alkaline wash, the products were fractionally distilled; fractionation data are presented graphically in Figs. 7, 8 and 9. The various fractions were characterized by comparison with the boiling points, refractive indices and infrared spectra of the possible products. A typical example of the use of infrared spectra for this analysis is shown in Fig. 3 in which 2-ethylcyclohexanol and 2,3-dihydrobenzofuran are identified in a fraction, b.p. 187°, n^{25}D –1.4888, from the hydrogenolysis of benzofuran at 200°. The absorption maxima characteristic of 2-ethylcyclohexanol are designated as "A" and those of 2,3-dihydrobenzofuran as "B"; all others are common to both, showing that these are the only components present. Calculations from the known re-

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[4] H. Adkins, "Organic Chemistry," edited by H. Gilman, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 822.

TABLE II

SUMMARY OF HYDROGENOLYSES OF BENZOFURAN AND 2,3-DIHYDROBENZOFURAN

(Copper–chromium oxide catalyst; 12 hr.)

	Benzofuran			2,3-Dihydrobenzofuran		
	200°	250°	300°	200°	250°	300°
Mole of heterocycle used	0.457	0.457	0.457	0.450	0.450	0.450
Moles of H_2 absorbed	1.285	2.500	2.740	0.357	1.93	2.36
Gram of phenols	0.5	0	0	Trace	0	0
Weight % -OH in products	2.74	9.74	3.78	1.35	9.21	2.52
Weight %[a] yields of non-phenolic products						
2,3-Dihydrobenzofuran (II)	45	....	....	69	....	..
Octahydrobenzofuran (IV)	27	18	4	14	15	4
Phenethyl alcohol (V)	2	....	..	2	....	....
2-Ethylcyclohexanol (VI)	23	68	29	12	75	19
Cyclohexane-ethanol (VII)	2.5	3	1	2.5	2	2
Ethylbenzene (VIII)	0.5	2	1	0.5	2	1
Ethylcyclohexane (X)	....	9	65	....	6	74

[a] Mole % is identical with weight % within the precision of these experiments.

TABLE III

SUMMARY OF HYDROGENOLYSES OF 2-METHYL-2,3-DIHYDROBENZOFURAN

(Copper–chromium oxide catalyst; 12 hr.)

	200°	250°	300°
Mole of heterocycle	0.377	0.377	0.377
Moles of H_2 absorbed	0.357	1.79	2.07
Gram of phenols	0	0	0
Weight % -OH in products	1.61	5.85	0
Weight %[a] yields of products			
2-Methyl-2,3-dihydrobenzofuran (III)	73	....	....
2-Methyloctahydrobenzofuran (XI)	14	13	....
α-Methylcyclohexane-ethanol (XIV)	13	5	....
2-Propylcyclohexanol (XV)	....	47	4
Propylbenzene (XVI)	....	0.5	....
Propylcyclohexane (XVII)	....	34.5	96

[a] Mole % is identical to weight % within the precision of these experiments.

fractive indices show that the fraction contains 69.8% of 2-ethylcyclohexanol, while that from the acetylation value is 60.5%, which, as expected for cyclohexanols, is somewhat low (*cf.* Experimental).

The yields of the various hydrogenolysis products are summarized in Tables II and III.

From these data and hydrogenolysis experiments on several of the possible products it can be concluded that the reaction probably proceeds as follows: benzofuran can be readily hydrogenated to 2,3-dihydrobenzofuran over copper–chromium oxide at 160°; this reaction is the first step. At 200° only *ca.* 1% ethylphenol and 2% phenethyl alcohol appear as products of the ring opening of the dihydro compound. Simultaneous hydrogenation of the phenyl ring produces the octahydro compound which undergoes ring rupture to give 2-ethylcyclohexanol and cyclohexane-ethanol. The small amount of ethylbenzene is derived from the phenethyl alcohol; thus, phenethyl alcohol is converted in 95% yield to ethylbenzene at 250° over CuCrO. It is improbable that the 2-ethylcyclohexanol comes from the 2-ethylphenol since the analogous *m*-ethylphenol undergoes only 4 and 13% hydrogenation at 250° and 300°, respectively, while *o*-cresol likewise undergoes 4% hydrogenation at 250°. The ethylcyclohexane is probably derived from several sources; for example, using CuCrO as catalyst for the hydrogenolysis, 2-ethylcyclohexanol at 300° yields 50%, phenethyl alcohol at 250° yields 3%, and cyclohexane-ethanol at 300° yields 28% of ethylcyclohexane. These reactions are summarized in Fig. 4; the solid arrows represent the most plausible methods for the formation of each of the products while the dotted arrows indicate improbable—although possible—reactions. The hydrogenolysis products of 2-methyl-2,3-dihydrobenzofuran are formed essentially in the same manner as those of benzofuran and 2,3-dihydrobenzofuran.

Possible mechanism of reaction of benzofuran and 2,3-dihydrobenzofuran with hydrogen

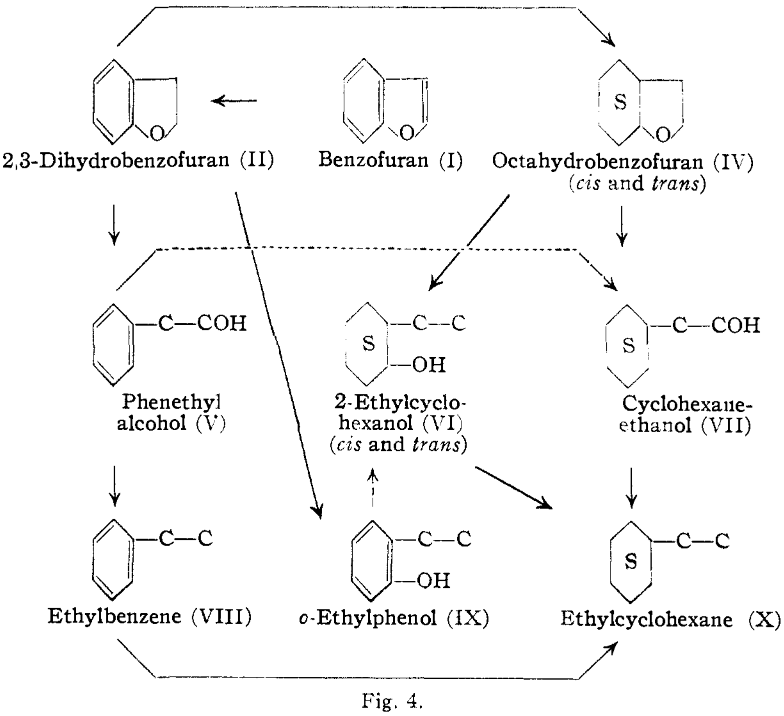

Fig. 4.

The infrared and ultraviolet absorption spectra of the starting compounds are shown in Figs. 5 and 6. The effect of the presence of the double bond on the ultraviolet spectra is very striking and would be valuable for analytical purposes; the log ε reaches a maximum

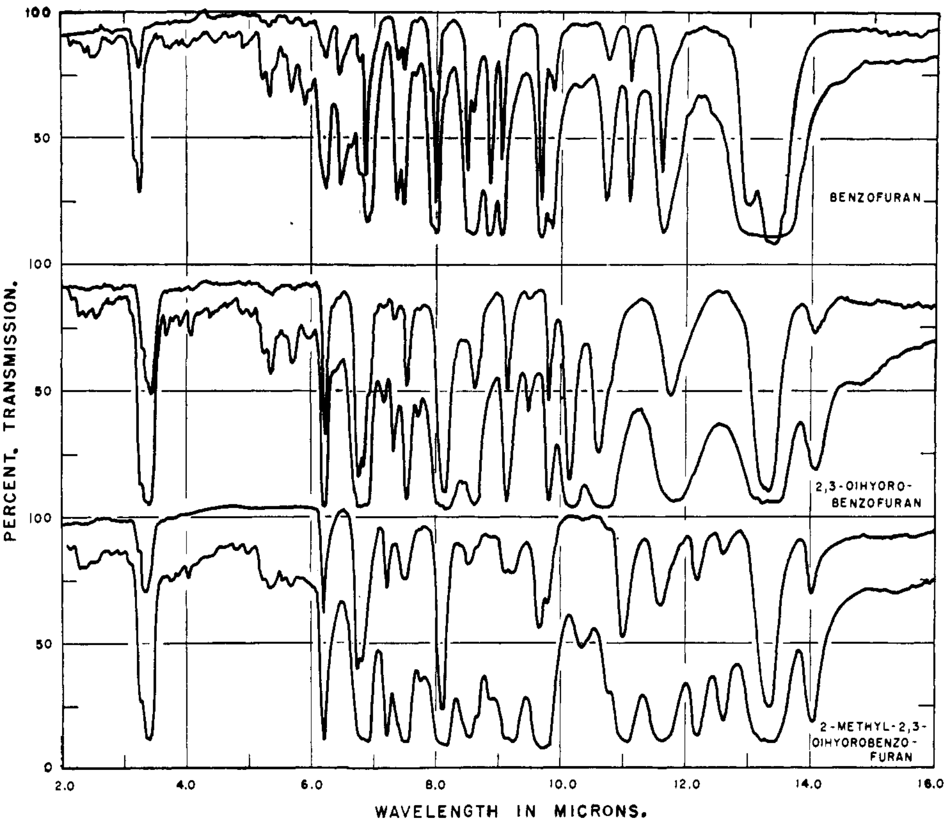

Fig. 5.—Infrared spectra (capillary films).

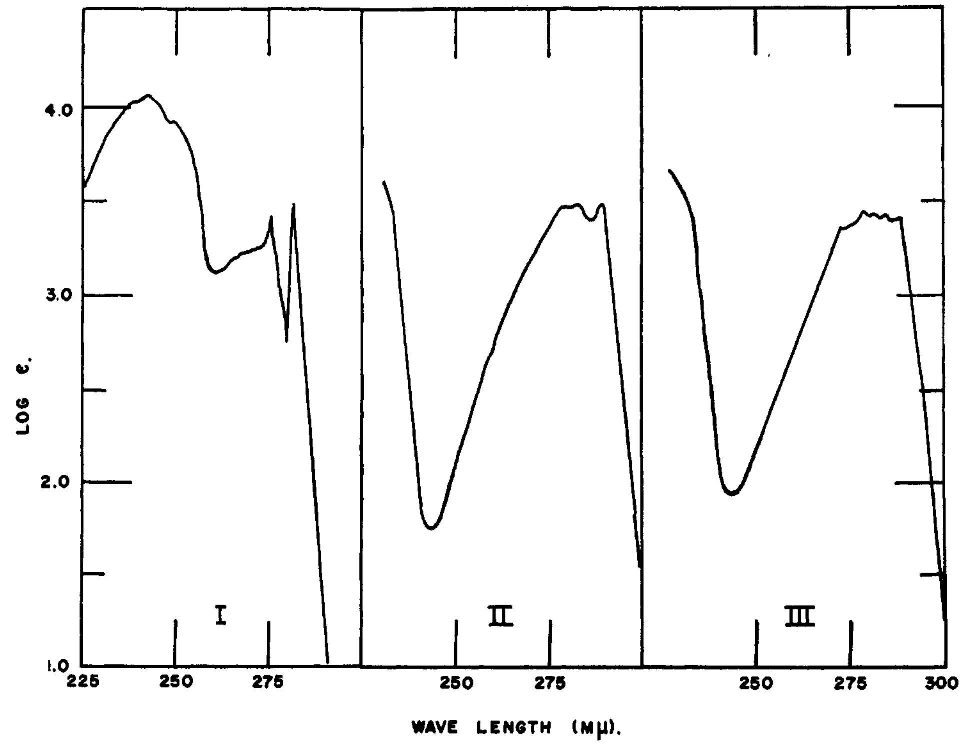

Fig. 6.—Ultraviolet spectra in isoöctane of (I) benzofuran, (II) 2,3-dihydrobenzofuran and (III) of 2-methyl-2,3-dihydrobenzofuran.

in the ultraviolet spectrum at 245 mμ for benzofuran, and a minimum at the same wave length for the dihydro compound.

Experimental

Preparation of Benzofuran.—A mixture of 139 g. of coumarilic acid prepared as described,[5] 139 g. of barium oxide and 30 g. of copper–bronze catalyst[6] was heated in a modified iron "cresol still." Decarboxylation started at 250–285° and proceeded slowly to *ca.* 370° where it became extremely exothermic with an instantaneous rise to 475–500° and vigorous gas evolution. A total of 765 g. of crude benzofuran was prepared by this method; yield 57.5%. After washing twice with 20% aqueous potassium hydroxide, the product was steam distilled, dried over anhydrous potassium carbonate, and fractionated through a column of maximum efficiency of 50 theoretical plates to give 577 g. of benzofuran, b.p. 171° (743 mm.), n^{24}D 1.5639.

Hydrogenation of Benzofuran (a) Rate Comparison with Other Unsaturates.—To demonstrate the type of unsaturation exhibited by the furanoid double bond of benzofuran a semi-quantitative hydrogenation rate comparison was made. Cyclohexene and 2-methylbutene-1 and -2 were prepared by dehydrating cyclohexanol and *t*-amyl alcohol, respectively, followed by fractionation; "Elchem 655" furan was secured from the E. I. du Pont de Nemours Company, Inc.; "Rein Indene" was obtained from Gesellschaft für Teerverwertung m.b.H., Duisberg-Meiderich, Germany; and the benzene was Mallinckrodt thiophene-free reagent grade. Each of these unsaturated compounds (25 ml.) was charged to the 370-ml. glass bottle of the standard Parr apparatus without solvent along with 1 g. of 10% palladium-on-charcoal and shaken at room temperature with an initial hydrogen pressure of 50 p.s.i.g. The apparatus was repressured to 50 p.s.i.g. each time the pressure dropped to 10 p.s.i.g. The percentage hydrogenated was calculated from the observed *vs.* the theoretical pressure drop. Results are shown in Fig. 1.

For a comparison of the effect of Raney nickel with that of copper chromite on the rate of hydrogenation of the double bond, 20.5 ml. of benzofuran was hydrogenated over 3 g. of the catalyst in a 44-ml. stainless steel autoclave. Agitation was started when reaction temperature was reached. Results are shown in Fig. 2.

(b) Hydrogenation of the Furanoid Double Bond.—Benzofuran, 200 ml., was hydrogenated over 10 ml. of Raney nickel catalyst at 90° and 1200 p.s.i.g. for four hours. The resulting 2,3-dihydrobenzofuran was fractionated in a column of 50 theoretical plates, b.p. 191.8° (745 mm.), n^{25}D 1.5474.

Anal. Calcd. for C_8H_8O: C, 79.97; H, 6.71. Found: C, 80.00; H, 6.76.

Although benzofuran has previously been hydrogenated with sodium and alcohol[7] and catalytically[8,9,10] the resulting 2,3-dihydrobenzofuran was not separated from the inevitable hydrogenolysis products; consequently, the physical properties reported herein differ from those reported previously for unfractionated products but agree with those obtained for 2,3-dihydrobenzofuran prepared by reaction and cyclization of *o*-methoxyphenylethyl alcohol with HBr.[11]

(c) Hydrogenation of the Benzene Ring.—Benzofuran, 27.5 g., was hydrogenated over 2 ml. of Raney nickel at 190° and 1700 p.s.i. for 12 hours. After filtering, washing with 20% potassium hydroxide and water, and drying over anhydrous potassium carbonate, the products were fractionated through the 50-plate column. While 2-ethylcyclohexanol was readily isolated in 32% yield, the octahydrobenzofuran still contained cyclohexane-ethanol as detected by acetylation and infrared spectrum. The peaks in the spectrum at 8.95, 10.80, 11.70, 12.40 and 12.90 microns are characteristic of the octahydro compound and were used in its identification.

2-Methyl-2,3-dihydrobenzofuran, 25.5 g., was hydrogenated over 2 ml. of Raney nickel at 214° and 1500 p.s.i.g. until absorption ceased. The filtrate after catalyst removal was washed with 10% potassium hydroxide and then water and fractionated through a 20-plate column to give the octahydro compound, b.p. 174° (740 mm.), n^{25}D −1.4562. *cis* and *trans* forms were not separated. A small amount of 2-propylcyclohexanol was identified in the still residue by infrared spectrum.

Hydrogenolyses.—All hydrogenolyses were run in a 1080-ml. stainless steel (Type 347) rocking autoclave which was heated by an external electric furnace. The rocking was automatically maintained for 12 hours at the recorded values ±5°. In all cases 3 g. of the same preparation of copper–chromium oxide catalyst,[12] 50 ml. of heterocycle and 1400–1500 p.s.i.g. of hydrogen pressure were charged to the autoclave. The bomb was cooled to room temperature after reaction and the gaseous products were bled off, but not further analyzed. After filtration, a sample of the liquid products was analyzed for –OH.

Pentane, 125 ml., was used in three portions to rinse the bomb and catalyst. The filtered washings were combined with the filtered reaction products and the composite washed twice with 50 ml. of 20% aqueous potassium hydroxide and once with 50 ml. of water. The alkaline extract was acidified with hydrochloric acid and extracted twice with 50 ml. of ether; the ether was evaporated to obtain the phenols. Data on the various runs are summarized in Tables II and III.

The neutral material was then fractionated in a 10-plate column packed with $^1/_{16}''$ glass helices. Distillation data are presented in Figs. 7, 8 and 9. The fractions were analyzed as previously described and the yields of products summarized in Tables II and III.

Hydroxyl Determinations.—Since the method of Freed and Wynne[13] for –OH acetylation gives low results for various cyclohexanols, their acetylation procedure was altered. In this modification 3 ml. of reagent—8 ml. of acetic anhydride in 20 ml. of dry pyridine—was boiled for one hour in a 100-ml. acetylation flask with 0.3 to 0.35 g. of sample. The reaction mixture was transferred to a beaker with thorough rinsing of the condenser and flask with distilled water, diluted to *ca.* 100 ml., and titrated with 0.4 *N* sodium hydroxide to the phenolphthalein end-point. To avoid tar formation,[14] which causes discrepancies in the original titer, the blank was not heated. Results obtained for various cyclohexanols by the Freed and Wynne method and the modification are compared in Table IV.

TABLE IV

Compound	Per cent. of theoretical –OH acetylated Method of Freed and Wynne	Modification
Cyclohexanol	58.7	94.0
		89.0
2-Propylcyclohexanol	63.8	96.9
	61.3	95.0
		97.9
		99.5
3-Ethylcyclohexanol	90.7	95.5
	91.7	96.4

Reference Infrared Spectra.—For analysis the infrared spectra of the hydrogenolysis products were compared with those of authentic reference compounds (Fig. 10).

2-Ethylcyclohexanol, b.p. 185° (740 mm.), n^{25}D 1.4631, and cyclohexane-ethanol, b.p. 204° (740 mm.), n^{25}D 1.4630, were prepared by hydrogenation over U.O.P. nickel catalyst at 200° of *o*-ethylphenol and phenethyl alcohol, respectively; and *o*-propylphenol, b.p. 218° (734 mm.), n^{25}D 1.5238 and 2-propylcyclohexanol, 204° (740 mm.), n^{25}D 1.4620, by the hydrogenation of *o*-allylphenol over palladium-on-charcoal (10%) at 25° and over Raney nickel at 180°, respectively. *cis* and *trans* forms of the cyclohexanols were not separated.

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(5) R. C. Fuson, J. W. Kneisley and E. W. Kaiser, *Org. Syntheses*, **24**, 33 (1944).

(6) E. C. Kleiderer and R. Adams, THIS JOURNAL, **55**, 4225 (1933).

(7) H. Alexander, *Ber.*, **25**, 2409 (1892).

(8) E. W. Smith, Doctoral Dissertation, Iowa State College, 1936.

(9) N. I. Shuĭkin, I. I. Dmitriev and T. P. Dobrynina, *J. Gen. Chem. U. S. S. R.*, **10**, 967 (1940); *C. A.*, **35**, 2508 (1941).

(10) G. M. Bennett and M. M. Hafez, *J. Chem. Soc.*, 287 (1941).

(11) G. Chatelus and P. Cagniant, *Compt. rend.*, **224**, 1777 (1947).

(12) C. H. Ruof, T. R. Savich and H. C. Howard, THIS JOURNAL, **73**, 3873 (1951).

(13) M. Freed and A. M. Wynne, *Ind. Eng. Chem., Anal. Ed.*, **8**, 278 (1936).

(14) P. A. Nelson and A. E. Markham, THIS JOURNAL, **72**, 2417 (1950).

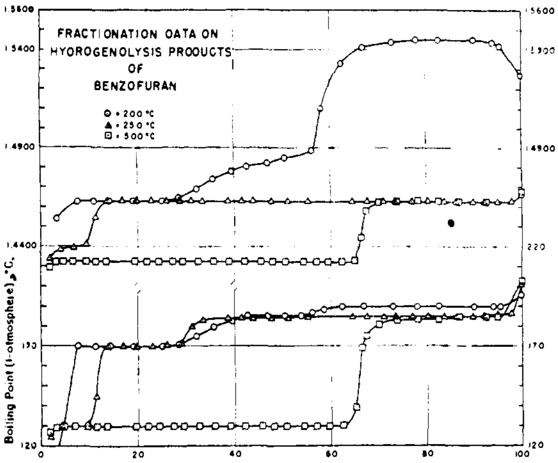


Fig. 7.

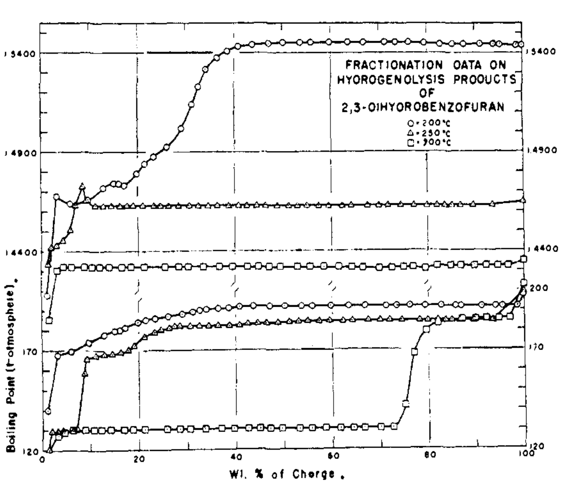


Fig. 8.

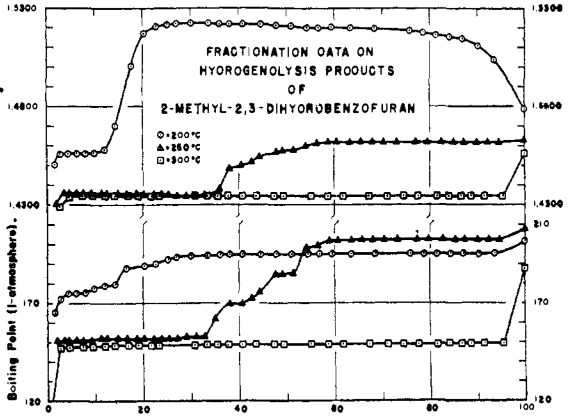


Fig. 9.

Phenethyl alcohol, Eastman Kodak Co. No. 313, was used without further purification.

Amenability of Possible Intermediates to Further Hydrogenolysis.—All of the following runs were made in a 1-liter autoclave at 1500–1700 p.s.i.g. of hydrogen over copper-chromium oxide catalyst for 12 hours at the reaction temperature indicated. *m*-Ethylphenol, *o*-cresol and 3-ethylcyclohexanol were used for these experiments since *o*-ethylphenol and 2-ethylcyclohexanol were unavailable; toluene was used to test the effect of this catalyst on the benzene ring.

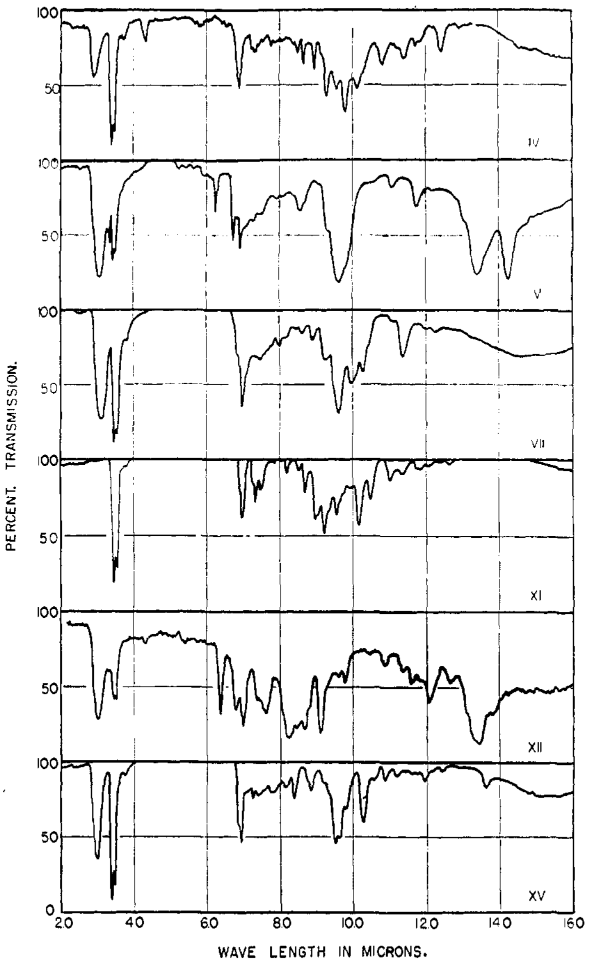


Fig. 10.—Infrared spectra (capillary films) of (IV) octahydrobenzofuran (*cf.* text), (V) phenethyl alcohol, (VII) cyclohexane-ethanol, (XI) 2-methyloctahydrobenzofuran, (XII) 2-propylphenol, (XV) 2-propylcyclohexanol.

Toluene.—Toluene, 0.90 mole, and 5 g. of catalyst at 300° showed a quantitative absorption of hydrogen to form methylcyclohexane.

Ethylbenzene.—Ethylbenzene, 0.87 mole, and 6 g. of catalyst at 300° absorbed 83.5% of the theoretical hydrogen; the hydrogenation was 80.5% based on the refractive index of the product, $n^{25}D$ 1.4430, *vs.* that of ethylbenzene, $n^{25}D$ 1.4932 and ethylcyclohexane, $n^{25}D$ 1.4308.

***m*-Ethylphenol.**—This compound, 0.81 mole, and 5 g. of catalyst at 250° showed 5.7% hydrogenation based on pressure drop and 4.2% based on the $n^{25}D$ of the product, 1.5255, *vs.* that of *m*-ethylphenol, $n^{25}D$ 1.5284, and of 3-ethylcyclohexanol, $n^{25}D$ 1.4594. At 300° the per cent. hydrogenation increased to 12.4 and 12.9% based on pressure drop and $n^{25}D$ of product, respectively.

***o*-Cresol.**—This material, 0.93 mole, and 5 g. of catalyst at 250° shows only 3.5% hydrogenation based on pressure drop. Consequently, it is highly improbable that the alkyl cyclohexanols were produced by the hydrogenation of the alkyl phenols in the hydrogenolyses of the benzofurans.

3-Ethylcyclohexanol.—*m*-Ethylphenol, 0.81 mole, was hydrogenated over 5 g. of Raney nickel catalyst at 160–180°. After filtering to remove the catalyst, the product was washed twice with 100 ml. of 20% aqueous KOH and twice with 100 ml. of cold water. The 3-ethylcyclohexanol was dried over anhydrous K_2CO_3 and distilled, b.p. 193° (740 mm.), $n^{25}D$ 1.4594. 3-Ethylcyclohexanol, 0.5 mole and 3 g. copper-chromium oxide catalyst at 300° showed 50.6% hydrogenolysis based on pressure drop and 48.6% based on $n^{25}D$ of product, 1.4455, *vs.* that of the starting material, $n^{25}D$ 1.4594 and that of ethylcyclohexane, $n^{25}D$ 1.4308. Hence, the alkyl cyclohexanes can be derived from the alkyl cyclohexanol.

Cyclohexane-ethanol.—This compound, 0.45 mole, with 3 g. of catalyst at 250° absorbed no hydrogen, but at 300° showed 24.2% hydrogenolysis based on pressure drop and 28% based on refractive index of the product, $n^{25}D$ −1.4540, *vs.* that of the starting material, $n^{25}D$ −1.4630, and that of ethylcyclohexane, $n^{25}D$ −1.4308.

Phenethyl Alcohol.—At 250° with 4 g. of catalyst, phenethyl alcohol, 0.66 mole, absorbed 27.6% of the hydrogen required for four double bonds. The product was separated from the several ml. of water, dried over "Drierite" and fractionated through a 50-plate column to give 95% ethylbenzene, 3% ethylcyclohexane and 2% cyclohexaneëthanol.

Acknowledgment.—We wish to express our appreciation to Dr. Robert B. Carlin of the Department of Chemistry of Carnegie Institute of Technology and to Dr. H. H. Lowry for their suggestions, to Mrs. Matilda Fine and Mr. Joseph B. Simsic for assistance in the analytical work and Mr. Daniel Muth for help in several of the autoclave experiments. The ultimate analysis was performed by the Huffman Microanalytical Laboratories, Denver, Colorado, and the infrared spectra were determined on a Baird Recording Spectrophotometer at the Mellon Institute.

PITTSBURGH 13, PENNA. RECEIVED FEBRUARY 1, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XVIII. Rearrangement of Cycloöctatetraene Oxide to 1,3,5-Cycloöctatrien-7-one[1]

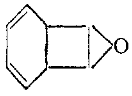
BY ARTHUR C. COPE AND BURRIS D. TIFFANY[2]

Cycloöctatetraene oxide (I) has been prepared by the oxidation of cycloöctatetraene with peracetic acid, a more convenient preparation than the oxidation with perbenzoic acid previously employed. The reaction of I with phenyllithium formed as one product 8% of a yellow liquid with the empirical formula C_8H_8O. This compound is formed by a base-catalyzed rearrangement of cycloöctatetraene oxide, and was obtained in a yield of 39% with mesityllithium as the base and 71% or more with lithium diethylamide. The isomer was proved to be 1,3,5-cycloöctatriene-7-one (II) by the preparation of ketonic derivatives and by quantitative hydrogenation to cycloöctanone and cycloöctanol.

This paper reports the base-catalyzed isomerization of cycloöctatetraene oxide (I) to 1,3,5-cyclooctatrien-7-one (II), which was discovered during an investigation of I as an intermediate in the preparation of substituted cycloöctatetraenes from the parent hydrocarbon.


I II

Cycloöctatraene oxide (I) originally was prepared from cycloöctatetraene and perbenzoic acid, by the method described by Reppe, Schlichting, Klager and Toepel.[3] It was found that I could be prepared more conveniently and in slightly better yield (55%) by oxidation with the commercially available 40% solution of peracetic acid in acetic acid by careful control of the temperature of the exothermic reaction. Friess and Boekelheide[4] have interpreted the ultraviolet absorption spectrum of the epoxide I, its behavior on hydrogenation, and the fact that it forms a maleic anhydride adduct containing one double bond as indicating that the compound has the fused-ring structure Ia. The evidence concerning the structure of I appears to us to be inconclusive. Bridging as well as addition could occur in the reaction of I with maleic anhydride, causing the disappearance of two double bonds, as is the case in the reaction of cycloöctatetraene with maleic anhydride.[3] A choice between structures I and Ia cannot be made with certainty at present on the basis of the ultraviolet absorption spectrum of the compound, for the spectra of models with structures related to I and Ia are too similar; 1,3,5-cycloöctatriene has $\lambda_{max.}$ 265 mμ (ε 3600)[5] and 1,3-cyclohexadiene has $\lambda_{max.}$ 258 mμ (ε 3980)[6] (both in cyclohexane). The fact that cyclooctanol is formed by the hydrogenation of cyclooctatetraene oxide[3,4] provides evidence supporting structure I rather than Ia, for cycloöctatetraene dichloride (which has a bridged ring structure analogous to Ia) yields bicyclo[4.2.0]octane rather than cycloöctane on hydrogenation.[3]


Ia

The reaction of cycloöctatetraene oxide with phenyllithium was investigated in order to determine whether cleavage of the epoxide ring would result in the formation of a phenylcycloöctatrienol that could be dehydrated to obtain phenylcyclooctatetraene. The reaction took an entirely different course. The principal product was an unsaturated ketone $C_{14}H_{14}O$, which was characterized as the 2,4-dinitrophenylhydrazone but not investigated further. Of greater interest was a small amount (8%) of a yellow liquid product, C_8H_8O, formed by the isomerization of cycloöctatetraene oxide. This liquid reduced permanganate, gave a negative fuchsin aldehyde test, and formed a crystalline 2,4-dinitrophenylhydrazone, semicarbazone and oxime. Evidence establishing the structure of this product as 1,3,5-cycloöctatrien-7-one (II) was obtained by its quantitative hydrogenation, which in the presence of palladium-on-calcium carbonate in methanol resulted in the absorption of 95% of

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[2] du Pont Postdoctorate Fellow, 1949–1950.

[3] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[4] S. L. Friess and V. Boekelheide, THIS JOURNAL, **71**, 4145 (1949).

[5] A. C. Cope and F. A. Hochstein, *ibid.*, **72**, 2515 (1950).

[6] We are indebted to Dr. Floyd L. Ramp for these data.