[Contribution from the Research Division, Phillips Petroleum Company]

STRUCTURE OF THE CRYSTALLINE LACTONE FROM THE INTERACTION OF BUTADIENE AND AQUEOUS FURFURAL[1]

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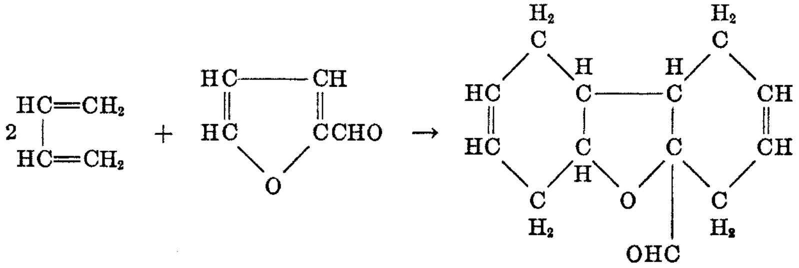
The formation of the trimolecular Diels-Alder condensation product (I) of butadiene and furfural has already been reported (1). It represents the only example known to the authors in which furfural acts as a dieneophile in a diene condensation. The compound is isolated in the purification of the aqueous furfural used in commercial plants which employ this solvent for separation of butadiene from butenes by extractive distillation (2). There is also observed, both in plant wastes and in laboratory synthetic experiments in which water was present with the butadiene and furfural, a crystalline solid, m.p. 135°. The compound partially hydrolyzes in solution with a considerable decrease in *p*H and can be saponified by dilute alkali. Its molecular weight and empirical formula suggest its origin in a condensation of one mole of furfural with one of butadiene with a mole of water probably also taking part in the reaction. The obvious possibility that the compound is the hydrate of the one-to-one adduct of butadiene and furfural is ruled out by its failure to give positive aldehyde reactions. An investigation of its structure has therefore been carried out.



I

The compound is somewhat soluble in cold water, (1.5 g./100 ml.) and alcohol, but may be readily crystallized from hot solutions in either of these solvents, or from benzene, hexane, cyclohexane, and other hydrocarbons. While it distills at 125° at 0.5 mm., slightly above the trimolecular aldehydic adduct, co-distillation occurs and the separation achieved is incomplete. The compound is also present in the steam condensate remaining with the tar residue in commercial plants. It may be isolated from the residue from evaporation of this solution by extraction with acetone, in which it is readily soluble. The properties of the pure crystals obtained after repeated recrystallization from water are tabulated in Table I.

Ultimate analyses correspond with the simple formula $(C_3H_4O)_x$. Cryoscopic

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molecular weights are difficult to obtain with satisfactory precision, but have indicated a value of 158 or slightly more. More satisfactory is the determination of the saponification equivalent, which indicates a molecular weight of approximately 164. The crystals readily absorb hydrogen when treated in alcohol solution over a palladium catalyst; one quantitative hydrogenation indicated 163 as the approximate molecular weight. On this basis a value of 3 was taken for x, giving the empirical formula $C_9H_{12}O_3$, m.w. 168. This corresponds exactly to an adduct of one mole each of butadiene, furfural, and water.

The compound gives negative tests for carbonyl and phenol groups, for water of hydration, and for the furan nucleus. It absorbs bromine and hydrogen readily, and forms an acetate with acetic anhydride, indicating an alcoholic hydroxyl group. A saturated aqueous solution is near *p*H 6.0. On standing, the *p*H is observed to decline and over a period of several days in contact with excess crystals two or three times as much will be in solution as originally. The solid isolated after removing the water *in vacuo* in one instance had m.p. 109–111° and the neutralization equivalent, 178. Recrystallization from hot water yielded only crystals of the original compound, m.p. 134°. A similar result is obtained on acidifying the solution obtained after titrating a hot solution of the compound with NaOH or upon running the saponification equivalent. This behavior suggests that the compound is a readily hydrolyzable ester, probably an inner ester; the absence of any alcohol among the hydrolytic products and the ready reconversion to the ester point strongly toward a *cis*-lactone configuration.

TABLE I

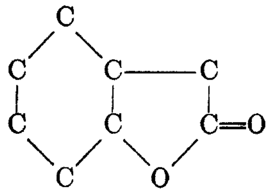
PROPERTIES OF CRYSTALLINE BUTADIENE—FURFURAL CONDENSATE

Melting point	135° (uncorr.)
Boiling point (Approx.)	125° @ 0.5 mm.
Crystal habit	Square prisms. Tetragonal (?)
Refractive index, n_D^{20}	1.565
Specific gravity $\frac{20}{20}$	1.33 ± 0.01
Fluorescence (ultraviolet illumination)	Negative

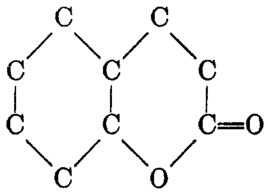
The third oxygen atom is unaccounted for in the lactone structure. The behavior with acetic anhydride gives a further indication of the structure. The resultant product, m.p. 85–86°, is neutral, yet analyzes for the monoacetate, $C_{11}H_{14}O_4$. Saponification, however, required two equivalents of base. This suggests that the anhydride reacts with a hydroxyl group other than the one lactonized, for if the latter were the case, a mixed acid anhydride, $C_{13}H_{18}O_8$, or the free carboxylic acid, $C_{11}H_{16}O_5$, resulting from hydrolysis would be found.

The evidence obtained suggests that the compound is a lactone, probably a *cis-gamma-* or *-delta-*lactone, containing an ethylenic double bond and a free hydroxyl group. Assuming the nucleus is first formed from a Diels-Alder condensation of butadiene and furfural (or a primary hydrolytic product thereof), the four nuclear formulae II to V have been considered as possibilities.

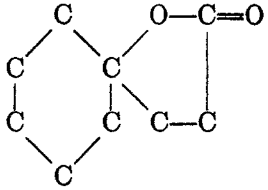
II seemed more probable than III or V because of the usually greater stability and ease of formation of *gamma*-lactone rings. Formula VI is also a *gamma*-lactone, but is a rather unusual *spiro* form.



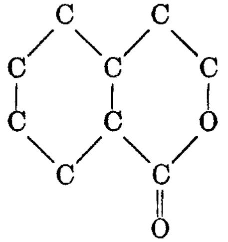
II



III



IV



V

Dehydration with an acid catalyst, especially with phosphoric acid, proceeds smoothly to give a high yield of β-phenylpropionic acid. Since no change in the carbon skeleton or location of the carboxyl group should occur in this reaction, formulae II and V are ruled out. The reaction gives no information on the position of the free hydroxyl group, since the double bond formed by dehydration would be expected to migrate to the ring from any position.

Oxidation with nitric acid yields only oxalic acid; no adipic acid could be found. From the hydrogenated lactone, however, adipic acid is the principal oxidation product recovered. Formation from only the hydrogenated compound indicates that it differs from the unsaturated lactone by the existence of a saturated six carbon chain or ring, and therefore that the double bond is present in the ring as would be expected. Furthermore, if it were adjacent to the lactone ring, a five carbon acid should have been isolated from the oxidation of the original lactone.

In addition to this, however, the presence of the additional alcoholic hydroxyl group in the molecule also affects the possibilities of obtaining adipic acid. If this group were located on the ring in positions 2, 3, 4, or 5 an additional point of attack would be furnished and adipic acid could not be formed even from the hydrogenated product. The arguments are based on the assumption that the intermediate keto acids would not survive under the conditions of the experiment; they are valid for either the *gamma*- or *delta*-lactone structures.

Strong acid dichromate solutions similarly produce adipic acid, but a controlled chromate oxidation of the hydrogenated lactone under mild conditions yields a liquid oxidation product $C_8H_{12}O_2$ which has been identified as the *cis*-lactone of 2-cyclohexanol acetic acid (3, 4). One carbon and one oxygen atom are eliminated from the molecule. This conversion places the hydroxyl group which lactonizes in the 2-position in a cyclohexyl ring, whose presence is itself confirmed. The *spiro* form of a *gamma*-lactone (IV) is eliminated.

Further than this, however, the free hydroxyl group disappears during the reaction without formation of a carbonyl group. The carbon atom eliminated was originally a carboxyl carbon. Since a carboxyl group remains (lactonized) at the next atom in the original chain, it follows that an *alpha*-hydroxy group was present, which oxidizes to carboxyl in this reaction. *Alpha*-hydroxy acids sometimes give a periodic acid test; in this case a weak test was obtained. Carbon monoxide is given off from the compound on treatment with concentrated sulfuric acid, also characteristic of *alpha*-hydroxy acids.

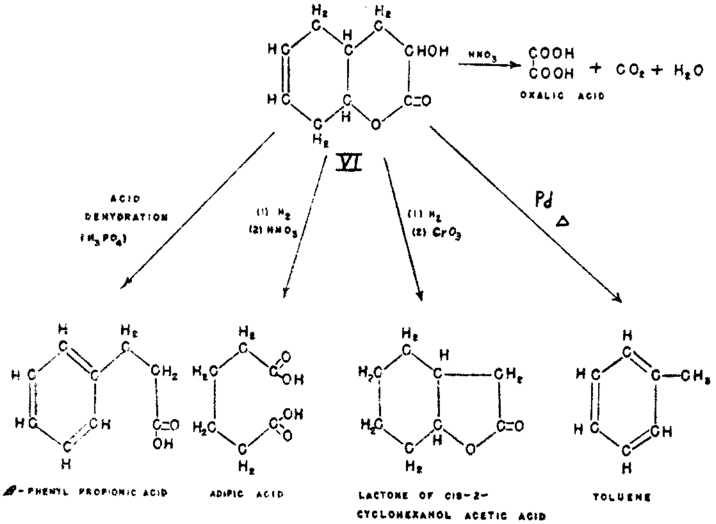


FIG. 1. Reactions of the Lactone from Furfural Residues indicating its structure

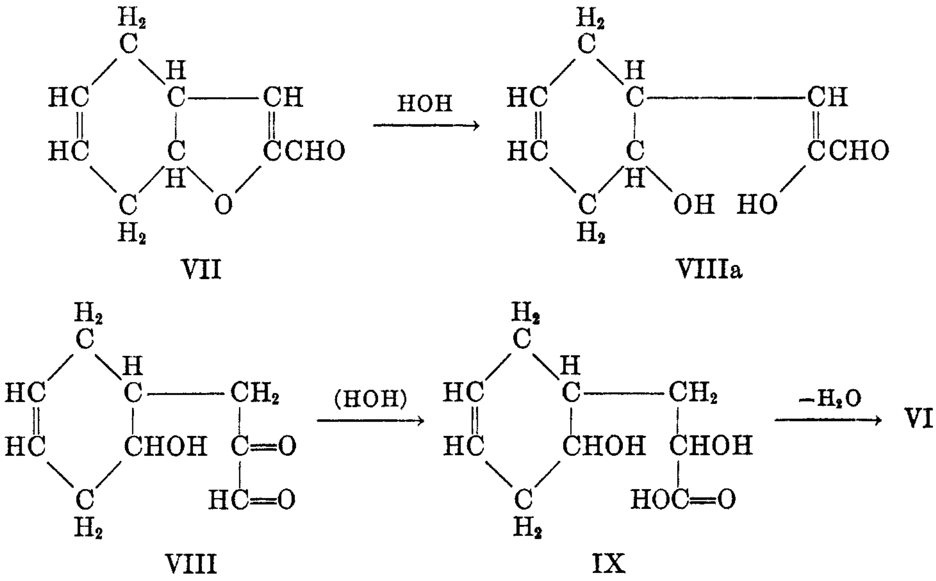
No direct chemical evidence to locate the double bond with certainty between carbon atoms 6 and 7, in preference to the possible alternate 5–6 or 7–8 positions, is at hand. The compound is a *cis*-isomer, however, and *cis*-isomers are always associated with diene additions. Thus, the strong probability that the cyclohexene ring is the result of 1,4-addition of butadiene, would certainly place the unsaturation between carbon atoms at positions 6 and 7 in the structure.

The final structure shown by this work thus is that of *cis*-3-hydroxy-3, 4, 4a, 5, 8, 8a-hexahydro-1,2-benzopyrone (VI) or the lactone of *cis*-α-hydroxy-β-(4-cyclohexene-2-ol)propionic acid (See Fig. 1.).

Dehydrogenation of the compound with a palladium catalyst yields toluene and carbon monoxide together with a very viscous, light colored and very pleasant-smelling polymer residue. Sodium hydroxide fusion of the hydrogenated lactone results in liberation of hydrogen and carbon dioxide. From the residue, liquid products can be distilled, in which small amounts of cyclohexanone and 2-methylcyclohexanone have been identified.

The reactions important in determining the structure are shown in the chart, Fig. 1.

A possible series of reactions by which this benzopyrone structure is formed from a diene condensation of butadiene and furfural involves hydrolysis of the oxygenated ring in the original adduct (VII), to the enol form (VIIIa) of an *alpha*-keto aldehyde (VIII) which undergoes intramolecular oxidation and reduction to the hydroxy acid (IX) corresponding to the final lactone. No direct proof of this course of reaction is at hand, but all the reactions are well known and would be expected under the reaction conditions employed. It is believed the one-to-one mole adduct (VII) which is first formed in the reaction then reacts very rapidly with a second mole of butadiene, to form the ternary adduct, so that it is never isolated itself. In the presence of water, the hydrolytic reaction postulated above competes with the second diene condensation for part of the original adduct.



VII VIIIa

VIII IX

Acknowledgement. The authors wish to express their appreciation to Mr. D. A. Nicewander and Mr. Clark Ice both formerly with Phillips Petroleum Company, Research Division, for their part in the first isolations and structural studies; to Mr. L. A. Webber and his associates at the Plains Butadiene Plant for generous supplies of the raw materials and the close cooperative work of his laboratory on the isolation; and to Drs. H. R. Snyder, and N. J. Leonard of the University of Illinois and to various members of the staff of Phillips Research Division for consultations and advice during the structural determinations. The authors wish to thank Phillips Petroleum Company and the Synthetic Rubber Division, Reconstruction Finance Corporation for permission to publish this paper.

EXPERIMENTAL PART

A. Isolation of lactone crystals from plant wastes. A sample of the crude tar phase from the furfural purification unit at the Plains Butadiene Plant weighing 1435.5 g. was placed in a large flask and distilled through a short column at a pressure of 1 to 2 mm. The pot was heated by an oil-bath, and was controlled at a set temperature, which was 204° after the lighter components had distilled off. The condensed overhead fraction comprised two phases, a water phase arising from the considerable amount of condensed steam emulsified and mechanically trapped in the crude tar, and an oil layer. The water layer weighed 365 g., the oil layer 267.4 g. On cooling, crystals separated from the oil layer. These were removed, washed, and dried. A yield of 43.5 g. or 3.03% of the crude tar was obtained in the form of cream-colored crystals. In this case no effort was made to recover any lactone which may have redissolved in the water layer. Additional quantities are also known to remain dissolved in the oil layer after the separated crystals are removed. Repeated recrystallization from water, using decolorizing charcoal, yields the product in the form of pure white needles, m.p. 134–135°. From three to ten crystallizations are usually required to produce material of this quality.

Accompanying the tar discharged from the furfural rerun unit is an aqueous phase comprising that portion of the open steam injected which condenses in the third vessel (2).

Evaporation of this aqueous phase yields a solid, dark brown residue, generally consisting of sticky crystals, and some dry brown powder. Recrystallization of this material also yields the white crystals, m.p. 135°.

B. Synthesis from furfural, butadiene, and water. Pure fractionated furfural (760 g.), 50 g. of distilled water, and 186 g. of butadiene were placed in a steel bomb and heated from 149° to 204° for 40 minutes and at 204° for 2 hours. The water, butadiene dimer, and furfural were removed from the reaction mixture by distillation under a vacuum. The residue amounted to 90 g.

Distillation of this 90-g. residue gave 32 g. overhead at 100° to 130° at 0.5 mm. The overhead product contained 2,3,4,5-bis(Δ^2-butenylene)tetrahydrofurfural and white crystals. The crystals were recovered by filtration and washing with cold ethyl ether. The 3.6 g. recovered melted at 132–133° and had a saponification equivalent of 160. Analysis of the filtrate indicated an additional 3.5 g. of the crystalline material in solution.

C. Properties of the lactone. The compound, when highly purified, occurs as long white needles melting sharply at 135°, which appear to be square prisms, probably belonging to the tetragonal system. The compound is readily soluble in acetone, and quite soluble in alcohol and hot water, from either of which it may be crystallized. Its solubility in cold (25°) water is about 1.5–2.0 g. per 100 ml. It is sparingly soluble in benzene, ether, and hydrocarbons such as hexane, isooctane and cyclohexane. It may be distilled under a vacuum although considerable difficulty is experienced with sublimation; b.p. about 125° at 0.5 to 1.0 mm. Sublimation has also been employed on a small scale as a method of purification. Some very pure crystals have been obtained by this means, but when employed on a large scale the apparatus used was inadequate to prevent contamination by volatile oils, spattering, etc.

Sodium fusion of the compound resulted in negative tests for nitrogen, sulfur, halogens, and phosphorus and there was no metallic ash left after combustion. It dissolves in sulfuric acid forming a dark red solution. Ultimate analyses showed: C, 63.66; H, 7.23; O, 29.11 (by difference). This corresponds closely to the empirical formula $(C_3H_4O)n$. Molecular weight determination, by the cryoscopic method in benzene and water as solvents proved to be difficult due to the low solubility and gave somewhat erratic results. The results in which most reliance was placed gave a value of 158. The compound was acidic, but could not readily be titrated in cold water solution. The saponification equivalent could be determined in the usual manner, however, by adding excess standard base, heating, and back titrating. The value obtained, assuming a monobasic acid, indicated a molecular weight of 164.

Unsaturation was detected in the molecule by a bromine water test. Hydrogenation proceeded readily in a Parr hydrogenator using a supported palladium catalyst. From a quantitative run, the volume of hydrogen consumed (0.092 mole by a 15.0-g. sample) indicated a molecular weight of 163 on the basis of one double bond per molecule.

The compound gave a negative aniline acetate test, developed no color with ferric chloride solution, gave a negative test with Schiff's reagent and with 2,4-dinitrophenylhydrazine, but did give a derivative with acetic anhydride. No acetylene was evolved when 5.0 g. of the compound was heated with 1.5 g. of calcium carbide in a closed system to 170°.

The specific gravity was determined in a series of ethylene chloride-carbon tetrachloride mixtures, and the refractive index by microscopic observation of the crystals suspended in a series of brominated solvents.

Hydrolysis of the lactone. The lactone (3 g.) was dissolved in 100 ml. of hot water and rapidly cooled. About one-half of the material separated as the typical needle-shaped crystals on cooling, since the solubility was exceeded. The solution was allowed to stand at room temperature. The quantity of crystals gradually decreased. At the end of 10 days, no more insoluble crystals were present. The solution was then evaporated to dryness *in vacuo*. The solid residue was washed with alcohol and ether and dried. It melted at 109–111°, being still contaminated with some unhydrolyzed lactone. A dilute aqueous solution had *p*H 2.9, and the neutralization equivalent was found to be 178. (Calculated for $C_9H_{12}O_3 + H_2O$, 186). The ultimate analysis gave: C, 61.62; H, 8.11. Calculated values for $C_9H_{14}O_4$ are: C, 58.1; H, 7.53. When dissolved in hot water, acidified with a few drops of sulfuric acid, a solution is formed which deposits white needles on cooling. These had m.p. 133–134° and were identical with the original compound. Solutions refluxed for several hours underwent a similar change. The solid isolated from such solution generally had a melting point range from 90 to 115°.

Preparation of the monoacetate. The lactone (6 g.) and 20 ml. of acetic anhydride were refluxed for one hour and then poured into 200 ml. of water. The crystals which separated were removed and recrystallized from hexane; m.p. 85–86°.

Anal. Calc'd for monoacetate ($C_{11}H_{14}O_4$): C, 62.8; H, 6.67; Sapon. equiv. (one ester and one lactone), 210.

Found: C, 62.35; H, 6.83; Sapon. equiv., 211.

An aqueous solution of the acetate was found to be neutral.

Hydrogenation. The lactone (15 g.) was dissolved in 100 ml. of ethyl alcohol and approximately 0.5–1.0 g. of 10% palladium-on-charcoal catalyst was added. The hydrogenation was carried out on a Parr hydrogenator at 25°. Hydrogen absorbed was 0.0925 mole. Three duplicate runs were made with identical results. On the basis of one double bond, the calculated molecular weight is 162.5. The average of seven other runs on a total of 135 g. was 163.3. The product from this test was recrystallized from ethanol. The resulting crystals melted at 140–141°, did not decolorize bromine water, and had a saponification equivalent of 169.

Anal. Calc'd for $C_9H_{14}O_3$: C, 63.51; H, 8.24.

Found: C, 63.56; H, 8.71.

The hydrogenated product (10 g.) was refluxed one hour with 20 ml. of acetic anhydride, and then poured into 200 ml. of water. The crystals which separated were recrystallized from hexane, m.p. 86–87°. A mixture melting point with the acetate of the unsaturated compound was 72–79°.

Dehydration to β-phenylpropionic acid. In a typical experiment 40 g. of the pure lactone was mixed with 130 ml. of 80% phosphoric acid and 30 ml. of water was added. This mixture was heated on an oil-bath at 160° for 24 hours, then cooled to room temperature, when two layers separated. The top layer crystallized on cooling in an ice-bath and was removed. Recrystallization from ethyl alcohol-water gave 27 g. (75.5%) of material which melted at 47–48°.

This material was identified as β-phenylpropionic acid, (hydrocinnamic acid) by mixture melting point with a known sample of m.p. 46–47°, preparation of the amide (m.p., found 100°, reported 105°), oxidation to benzoic acid (m.p. 121°), and by formation of 1-indanone, m.p. 42°. The dinitrophenylhydrazone of the latter was prepared, m.p. found 260°, reported 258°. Neutralization equivalent of the β-phenylpropionic acid was 151.

The dehydration was also accomplished with sulfuric acid but with less satisfactory results. Excessive charring occurred, and yields were only 30–40%. Aromatic sulfonic acids used in boiling xylene were also successful reagents.

Oxidation of hydrogenated lactone with nitric acid. A 10-g. sample of the lactone which had been reduced with hydrogen in a Parr hydrogenator was added slowly to 50 ml. of concentrated nitric acid containing a small amount of a vanadium pentoxide catalyst. The temperature was maintained at 50–60° during the addition. After one hour the reaction mixture was cooled and filtered. The solid product, when recrystallized from nitric acid, weighed 3.0 g. The melting point was 150° and a mixture melting point with a known sample of adipic acid was 150°.

A similar experiment carried out on the original unreduced lactone resulted in a good yield of oxalic acid. No adipic acid, or other acids could be found in the reaction product.

Chromate oxidation of hydrogenated lactone. The hydrogenated lactone (46 g.) and 50 ml. of water was placed in a 1-liter 3-necked flask, fitted with a stirrer. A solution of 81.6 g. of sodium dichromate monohydrate in 100 g. of concentrated sulfuric acid and 200 ml. of water was slowly added over a period of five hours. The reaction mixture warmed up and the rate of addition was controlled to maintain the temperature at 50°. The mixture was then stirred for one hour, and then extracted with benzene. The benzene solution was neutralized with sodium bicarbonate, filtered, and dried over sodium sulfate. Distillation of the benzene left a clear liquid, which distilled at 124° at 8 mm. Yield, 13.0 g.; *sp. gr.* 1.0912, n_D^{20} 1.4790. It had a strong pleasant odor, distinctive of certain cyclohexanone or hydrobenzofuran compounds. The compound froze in ice-water, and a time-temperature cooling curve gave a long flat at 12.8°. It was acidic, and had a saponification equivalent of 142.

Ultimate analysis gave: C, 68.71; H, 8.75. On this basis the empirical formula is $C_8H_{12}O_2$. Nitric acid oxidation of this compound gave adipic acid.

A sample of this material, prepared some 20 years ago by Dr. E. C. Kendall at the Mayo Foundation was on hand, sealed under inert gas. The odor and constants of this material corresponded with our material except in freezing point. Newman and VanderWerf (4) have reported both the *cis-* and *trans-*forms of this compound. Correspondence of our product with the *cis-*form of this lactone is good as shown below:

	REPORTED	FOUND
B.p.	112° @ 6 mm.	124° @ 8 mm.
M.p.	14.8°	12.8°
n_D^{20}	1.4773	1.4790
d_4^{20}	1.0923	1.0912

The *trans-*lactone melts at −1.2°, which value was exhibited by the old sample in our possession. Unfortunately, a sample of the authentic *cis-*form could not be obtained for comparison.

Tests for α-hydroxy group. The compound (5 g.) and 6.8 g. of potassium periodate were allowed to stand overnight in 600 ml. of water. Then 10 ml. of concentrated sulfuric acid was added and the solution was heated to boiling. The odor of benzaldehyde was evident. From a small aqueous distillate taken off of the reaction mixture, the 2,4-dinitrophenylhydrazine derivative of benzaldehyde was prepared and isolated. No test for a derivative of formaldehyde or other aliphatic aldehyde could be obtained. An 0.8624-g. sample of the compound was treated with 10.0 ml. of concentrated sulfuric acid at 95° for 30 min. The temperature was raised to 140° for 5 minutes. The volume of gas (CO) collected was 15.6 ml.; the theoretical volume was 114.2 ml.

Dehydrogenation to toluene. The lactone (33 g.) was heated at 204° with 1 g. of 10% palladium-on-charcoal catalyst. A light material was observed to reflux, and was then allowed to distill off. There was collected 2.2 ml. of water and 3.7 g. of a light liquid boiling at 110°. This appeared to be toluene. It was positively identified by conversion to the dinitro derivative, m.p. 70°. The mixture melting point with a known sample of 2,4-dinitrotoluene was 70–70.5°.

The pot residue was 20.5 g. of an amber-colored, viscous polymer, undistillable at 300° at 0.5 mm.; other constants were: n_D^{20} 1.5300, density 1.152, and cryoscopic molecular weight, 491. It was oxidized by permanganate to benzoic acid.

A second test was carried out under modified conditions. Here 30 g. of the compound was heated 5 hours at 316° with 1 g. of the palladium catalyst. A 40 mole-% yield of toluene was collected. In addition, 8 l. of gas was collected, which analyzed (by mass spectrometer) 18.2% hydrogen, 61.0% carbon monoxide, 9.7% carbon dioxide, 10.5% nitrogen, and 0.6% oxygen. (Air was not swept from the apparatus at the start of the run).

Cyclohexanones by NaOH fusions. Using the hydrogenated material, a fusion of 20.8 g. with 9.8 g. of NaOH resulted in gas liberation at 270°. After heating 6 hours to a maximum temperature of 310°, the products were studied. The gas was essentially hydrogen. Carbon dioxide was collected, and 2.5 cc. of water distilled off. From 1 ml. of organic distillate, a ketone was isolated which gave the 2,4-dinitrophenylhydrazone of cyclohexanone, m.p. 156°. The residue in the flask was soluble, and was extracted by ether to give a crystalline material with the same neutralization equivalent (168) as the original acid.

In another test, to 400° fusion temperature, 20 ml. of water was collected, with 3200 ml. of gas, 4.32 g. of CO_2, and 10 ml. of organic distillate. The latter boiled from 37° to 180°. Plateaus near 155° and 165° were observed. The first proved to be cyclohexanone, the second a mixture with another ketone. In still another test, 40 g. was heated with 40 g. of NaOH in 40 ml. of H_2O. After evaporation, it was heated red hot for three hours. A few ml. of organic liquid was extracted from the residue by ether. The fraction boiling at 160–163° was identified as 2-methylcyclohexanone by comparison of its 2,4-dinitrophenylhydrazone, m.p. 132.5–133° with an authentic sample. The mixture melting point was 131.5–132.5°.

SUMMARY

A crystalline product, produced by the interaction of butadiene and aqueous furfural, and isolated in quantity from the wastes from furfural purification in the commercial extractive distillation of butadiene has been shown to be the lactone of *cis*-α-hydroxy-β-(4-cyclohexene-2-ol)propionic acid.

Bartlesville, Oklahoma

REFERENCES

(1) Hillyer, Swadesh, Leslie, and Dunlop, *Ind. Eng. Chem.*, **40**, 2216 (1948).
(2) Buell and Boatright, *Ind. Eng. Chem.*, **39**, 695 (1947).
(3) Kendall, Private communication.
(4) Newman and VanderWerf, *J. Am. Chem. Soc.*, **67**, 233 (1945).