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Studies in Organic Peroxides. VIII. *t*-Butyl Hydroperoxide and Di-*t*-butyl Peroxide¹

BY NICHOLAS A. MILAS AND DOUGLAS M. SURGENOR

Recently there was reported² a general method for the production of alkyl peroxides and hydroperoxides. However, no extensive study has been made of this method, nor have any attempts been made to isolate other peroxides than alkyl hydroperoxides. The present investigation reports a careful study of this reaction, the isolation of two of the peroxides formed and a study of some of their properties.

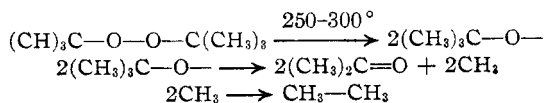
The process simply involves the reaction, in the cold, of an alkyl hydrogen sulfate with a concentrated solution of hydrogen peroxide. For example, when molar quantities of *t*-butyl alcohol or isobutylene are allowed to react, in the cold, with sulfuric acid (70%) and an equivalent quantity of 30% hydrogen peroxide is slowly added, a mixture is obtained which contains 50–70% *t*-butyl hydroperoxide. A careful fractionation of this mixture under reduced pressure yields, in addition to *t*-butyl hydroperoxide, an appreciable amount (30–50%) of di-*t*-butyl peroxide boiling at 12–13° (20 mm.), or 109–109.2° (760 mm.). From the same mixture one can also separate this peroxide in relatively pure form by extracting the hydroperoxide, either with a strong alkali solution or several times with water. By adjusting the concentration of sulfuric acid one can obtain this peroxide in 85% yield. Furthermore, it can be prepared in 92% yield by allowing *t*-butyl hydroperoxide to react with *t*-butyl hydrogen sulfate.

Of the simple di-alkyl peroxides thus far reported, dimethyl,³ methylethyl,⁴ diethyl^{4,5} and di-*n*-propyl,⁶ di-*t*-butyl peroxide is by far the most stable member of the group. The pure product can be distilled at atmospheric pressure without decomposition. Unlike other organic peroxides it fails to respond to usual peroxide tests. Titanium trichloride, which is sometimes used to estimate active oxygen of relatively inert organic peroxides, has little or no effect on di-*t*-butyl peroxide even on refluxing in an inert atmosphere. Even concentrated hydriodic acid fails to reduce it. Furthermore, it is unaffected by catalytic hydrogenation at room temperature using platinum oxide catalyst, although, with Raney nickel catalyst at 126° and under a hydrogen pressure

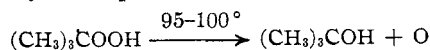
of 1250 lb., it is readily reduced to about two moles of *t*-butyl alcohol. Unlike diethyl peroxide,⁵ which is not attacked by metallic sodium, di-*t*-butyl peroxide is easily reduced at room temperature with finely divided sodium in xylene to give exclusively sodium *t*-butylate. Zinc dust in glacial acetic acid also effects the reduction to *t*-butyl alcohol.

Di-*t*-butyl peroxide is exceedingly stable in the presence of strong bases. Concentrated hydrochloric acid, which decomposes di-*t*-butyl ether,⁷ has no effect on this peroxide. Concentrated sulfuric acid dissolves di-*t*-butyl peroxide and polymeric hydrocarbons separate slowly from the solution.

Di-*t*-butyl peroxide has been found to be a very active high temperature polymerization catalyst.⁸ Since it is one of the most stable and inert organic peroxides known, this catalytic activity may be related to its mode of thermal decomposition. A study was therefore made of its pyrolysis at temperatures between 200 and 300°. It has been found that the only products formed under these conditions were acetone and ethane. On the basis of these results the most probable interpretation of the thermal decomposition of di-*t*-butyl peroxide is that which assumes the formation of intermediate free radicals. In fact the formation of ethane cannot be explained easily by any other view.



Like di-*t*-butyl peroxide, *t*-butyl hydroperoxide, first reported by Milas and Harris,⁹ is one of the most stable hydroperoxides, and a study of its pyrolysis may yield some useful information with regard to its catalytic activity in polymerization reactions. At room temperature or even at 50–75° there is no appreciable decomposition of this peroxide. When, however, it is slowly heated at 95–100°, the only gaseous product formed is oxygen. After about twenty-four hours of heating, the only product recovered was *t*-butyl alcohol. On this basis the decomposition of *t*-butyl hydroperoxide at about 100° may be represented by the equation



It may be seen therefore that at temperatures lower than 100°, *t*-butyl hydroperoxide behaves

(1) For the last paper in this series, see *THIS JOURNAL*, **62**, 1878 (1940).

(2) Milas, U. S. Patent 2,223,807, Dec. 3 (1940).

(3) Baeyer and Villiger, *Ber.*, **34**, 738 (1901); Rieche and Brumshagen, *ibid.*, **61**, 951 (1928).

(4) Rieche and Hitz, *ibid.*, **62**, 218 (1929).

(5) Baeyer and Villiger, *ibid.*, **33**, 3387 (1900); Strecker and Spitaler, *ibid.*, **59**, 1754 (1926).

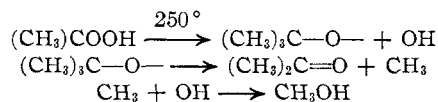
(6) Harris, *Proc. Roy. Soc. (London)*, **A173**, 126 (1939); Wiley, U. S. Patent 2,357,298, Sept. 5, 1944.

(7) Erickson and Ashton, *THIS JOURNAL*, **63**, 1769 (1941).

(8) Unpublished results from this Laboratory.

(9) Milas and Harris, *THIS JOURNAL*, **60**, 2434 (1938).

like a peracid¹⁰ in its mode of decomposition. At higher temperatures, however, the decomposition follows a somewhat different course. When, for example, *t*-butyl hydroperoxide was allowed to decompose explosively at 250°, the condensable products consisted of appreciable quantities of acetone, methanol, *t*-butyl alcohol, formaldehyde, water and a small amount of a tarry residue. The combustible non-condensable gas was chiefly methane. The thermal decomposition of *t*-butyl hydroperoxide at 250° may also be interpreted on the basis of the formation of intermediate free radicals.



These reactions taken together find ample support in the decomposition of two other known tertiary hydroperoxides. Triphenyl methyl hydroperoxide¹¹ decomposes spontaneously to benzophenone and phenol, while dimethylphenyl hydroperoxide¹² yields acetone and phenol. Experimentally we have found that, in the absence of catalysts, methanol is not oxidized by molecular oxygen at 250°. Since formaldehyde is formed in the decomposition of *t*-butyl hydroperoxide, it must be derived from the oxidation of methanol by some active oxidizing group such as the hydroxyl radical or the *t*-butyl hydroperoxide itself. Methane may form as the result of decomposition of the methyl radicals themselves or by some other as yet undetermined reaction. That some of the decomposition proceeds as it does at lower temperatures is shown by the presence in the reaction mixture of *t*-butyl alcohol.

Pure *t*-butyl hydroperoxide, as obtained by careful fractionation, is a clear colorless liquid soluble in water to the extent of about 12%, the aqueous solutions being perfectly stable for long periods of time. It has weak acidic properties, its pH in water (2% solution) being 4.55 as measured with a glass electrode. With alkali and alkaline earth bases, it forms salts of fair stability. Furthermore, it can be easily esterified and alkylated forming relatively stable *t*-butyl alkyl peroxides and *t*-butyl peresters¹³ which have shown unusual catalytic properties in polymerization reactions.⁸

Experimental

***t*-Butyl Hydroperoxide and Di-*t*-butyl Peroxide.**—*t*-Butyl hydrogen sulfate was prepared by adding, at 5°, 74 g. (1 mole) of *t*-butyl alcohol, m. p. 25.2°, to 140 g. (1 mole) of 70% sulfuric acid. To this mixture was then added at 0–5° with stirring 126 g. (1 mole) of 27% hydrogen peroxide in the course of thirty minutes. The ice-bath was then removed and the mixture allowed to stand overnight at room temperature. The mixture had separated into two layers, and the organic layer was removed, neu-

tralized with a suspension of magnesium carbonate in 10 cc. of water, then washed with 20 cc. of water and dried over anhydrous magnesium sulfate. Yield of the crude product was 70.5 g. [active (0), 11.71, 11.77] which was found to be composed of approximately 66% *t*-butyl hydroperoxide and 34% di-*t*-butyl peroxide.

In another experiment the hydrogen peroxide was added to the *t*-butyl hydrogen sulfate at 30–35°. A lower yield (60 g.) was obtained containing 53% *t*-butyl hydroperoxide and 47% di-*t*-butyl peroxide.

In a third experiment *t*-butyl hydrogen sulfate, kept at 0°, was added to 30% hydrogen peroxide at 0–5°. A yield of 69 g. was obtained containing 75.5% *t*-butyl hydroperoxide and 24.5% di-*t*-butyl peroxide.

When a crude product containing approximately 60% *t*-butyl hydroperoxide and 40% di-*t*-butyl peroxide was fractionated in a four-foot one-inch column packed with glass helices, the di-*t*-butyl peroxide distilled first at 12–13° (20 mm.), then as the distillate became richer in *t*-butyl hydroperoxide, the pressure was lowered and the pure hydroperoxide [calcd. for C₄H₁₀O₂: O, 17.77. Found: 17.69, 17.75] distilled at 4.5–5° (2 mm.). The two peroxides can thus be separated by fractional distillation without any difficulty. Although di-*t*-butyl peroxide can be distilled at atmospheric pressure (b. p. 109–109.2°), *t*-butyl hydroperoxide explodes violently under similar conditions.

The two peroxides have also been separated with very little loss by extracting from the mixture at low temperatures (10–15°) *t*-butyl hydroperoxide with strong potassium hydroxide (50%) or sodium hydroxide (30%) and regenerating the latter by acidification in the cold with dilute sulfuric acid.

Some of the physical constants of the two peroxides are given in Table I, and carbon and hydrogen analyses¹⁴ for the di-*t*-butyl peroxide are as follows

Anal. Calcd. for C₈H₁₈O₂: C, 65.70; H, 12.40. Found: C, 65.5, 65.3; H, 12.4, 12.4.

TABLE I

PHYSICAL CONSTANTS OF *t*-BUTYL HYDROPEROXIDE AND DI-*t*-BUTYL PEROXIDE

Peroxide	B. p., °C.	M. p., °C.	d_{4}^{20}	n_D^{20}	MR _D	
<i>t</i> -Butyl hydroperoxide ^a	4.5–5	2	3.8–4.8	0.896	1.4013	24.42
Di- <i>t</i> -butyl peroxide	109–109.2 12–13	2 20	–18	.793	1.3872	43.36

^a Some of the physical constants reported by Milas and Harris (ref. 9) for this peroxide are at slight variance with those given in Table I, and the discrepancy was cleared by further work in this Laboratory by L. H. Perry who prepared a large sample of the peroxide using their method and fractionated it through a four-foot one-inch packed column. He also obtained two peroxides: (a) Di-*t*-butyl peroxide: b. p. 12–13° (20 mm.); m. p. –18°; *d*₄²⁰, 0.793; *n*_D²⁰ 1.3838. This peroxide is identical in every respect with that obtained by the present method. (b) *t*-Butyl hydroperoxide: b. p. 33–34° (17 mm.); m. p. 4.0–4.5°; *d*₄²⁰, 0.896; *n*_D²⁰ 1.3983. *Anal.* Calcd. for C₄H₁₀O₂: O, 17.77. Found: O, 17.57, 17.68, 17.55.

Di-*t*-butyl Peroxide from *t*-Butyl Alcohol and Hydrogen Peroxide.—Concentrated sulfuric acid (383 g.) and 27% hydrogen peroxide (126 g.) were added simultaneously and dropwise with high speed stirring to *t*-butyl hydrogen sulfate, prepared from 222 g. of *t*-butyl alcohol and 140 g. of 70% sulfuric acid, at –2° in the course of ninety minutes. Stirring was continued for two hours longer, then the organic layer washed three times with 25-cc. portions of water, dried and filtered; yield 124 g. (85%) of di-*t*-butyl peroxide; *d*₄²⁰, 0.795; *n*_D²⁰ 1.3863.

Di-*t*-butyl Peroxide from *t*-Butyl Hydroperoxide.—To a mixture of *t*-butyl hydrogen sulfate, prepared from 140 g.

(10) Milas and McAlevy, *THIS JOURNAL*, **56**, 1221 (1934).

(11) Wieland and Maier, *Ber.*, **64**, 1205 (1931).

(12) Hock and Lang, *ibid.*, **77**, 257 (1944).

(13) Milas and Surgenor, unpublished results.

(14) The samples were allowed to explode in the combustion tube since no checks could be obtained otherwise.

(1 mole) of 70% sulfuric acid and 74 g. (1 mole) of *t*-butyl alcohol, was added slowly with stirring at 1°, 45 g. (0.49 mole) of 98.2% of *t*-butyl hydroperoxide in the course of twenty-five minutes. The mixture was stirred overnight at room temperature, then the organic layer separated, washed three times with 15-cc. portions of 40% potassium hydroxide, then with water, dried and filtered; yield 66 g. (92%); d_{20}^{20} 0.792; n_D^{20} 1.3894.

Hydrogenation of Di-*t*-butyl Peroxide.—Di-*t*-butyl peroxide (73 g., 0.5 mole) was hydrogenated in a glass-lined bomb at 126° and 1250 lb. of hydrogen pressure using Raney nickel as catalyst. At the end of eight hours the crude recovered product (58 g.) gave a negative test for water with anhydrous copper sulfate and had a d_{20}^{20} 0.788 and a n_D^{25} 1.3851. Fractionation through a Podbielniak column gave 50.6 g. (88.4%) of *t*-butyl alcohol, b. p. 81.0–82.5°; d_{20}^{20} 0.787; n_D^{25} 1.3891. Attempts to hydrogenate this peroxide in glacial acetic acid using platinum oxide catalyst were unsuccessful.

Reaction of Di-*t*-butyl Peroxide with Sodium.—Di-*t*-butyl peroxide (15 g.) was added dropwise with stirring to 6 g. of sodium sand in 200 g. of xylene. The reaction was complete in two hours when the excess sodium was destroyed with 10 g. of water and the mixture acidified with 150 g. of 6 N sulfuric acid. The aqueous layer was separated and the xylene extracted with three 50-cc. portions of water and the combined aqueous layers neutralized with sodium carbonate. Approximately one-half of the solution was then distilled, the distillate saturated with sodium chloride and extracted three times with 25-cc. portions of ether. On drying and fractionating, 8.9 g. (58.3%) of *t*-butyl alcohol was obtained, b. p. 79.5–82.5°; d_{20}^{20} 0.789; n_D^{20} 1.3869.

Thermal Decomposition of Di-*t*-butyl Peroxide.—In carrying out the thermal decomposition, the peroxide vapors were passed through a 20-mm. Pyrex tube loosely packed with glass wool and heated in a vertical furnace the temperature of which was carefully controlled electrically and measured by means of a thermocouple inserted half way down between the tube and the inner core of the furnace. The condensable pyrolysis products were caught in three traps connected in series and immersed in acetone–solid carbon dioxide mixtures while the uncondensed vapors were collected over water. In a typical run, the system was first flushed with nitrogen, then 50 g. of pure di-*t*-butyl peroxide was passed through the tube maintained at 254–256°, in the course of four hours. The total condensate amounted to 38.5 g. which on careful fractionation through a Podbielniak column gave 34.8 g. of acetone boiling at 55.4–56.4° [d_{20}^{20} 0.793; 2,4-dinitrophenylhydrazone, m. p. 124.7–125.7° (cor.)] and a small fraction (0.5 g.) boiling at 56.5–63° which was found to consist chiefly of acetone.

The uncondensed gas contained no unsaturated hydrocarbons, and when analyzed it proved to be entirely ethane.

Anal. Calcd. for C_2H_6 : O_2/C_2H_6 , 3.5; CO_2/C_2H_6 , 2.0. Found: O_2 /gas, 3.7, 3.6; CO_2 /gas, 2.0, 2.1.

Attempts to detect formaldehyde or methanol which form an azeotrope with acetone b. p. 55.7° were unsuccessful. Acetone and ethane appear to be the sole products of the pyrolysis of di-*t*-butyl peroxide at 250°. Experiments conducted at 300° gave wholly comparable results with those obtained at 250°. At 200° the pyrolysis was incomplete, 45% of the original peroxide having been recovered unchanged. When nitrogen was used as a diluent of the peroxide vapor, the course of the reaction remained unchanged.

Thermal Decomposition of *t*-Butyl Hydroperoxide.

(1) **At 95–100°.**—*t*-Butyl hydroperoxide (15 g.) was heated for about twenty-four hours in a 30-cc. flask attached to a 2½-foot Podbielniak column and immersed in an oil-bath maintained at 95–100°. A steady evolution of gas took place and when a sample of it was analyzed by absorption in alkaline pyrogallol it was found to contain 91% oxygen. No formaldehyde was found in the exit gases since a methone solution gave no precipitate. When

the evolution of the gas was complete, the residual liquid was distilled and 10.6 g. (86.2%) of *t*-butyl alcohol was recovered, b. p. 81–82.5°; d_{20}^{20} 0.785; n_D^{20} 1.3842.

(2) **At 250°.**—When *t*-butyl hydroperoxide was passed through a tube maintained at 250°, decomposition proceeded explosively and the condensable products consisted of: acetone (38.7%), identified by its 2,4-dinitrophenylhydrazone, m. p. 124–125° (cor.); methanol (7%), identified by its methyl hydrogen 3-nitrophenylthelate, m. p. 149.5–151° (cor.); *t*-butyl alcohol (11%), identified by its boiling point and camphoraceous odor; formaldehyde, identified by its dimethone, m. p. 189–190° (cor.), its 2,4-dinitrophenylhydrazone, m. p. 163.7–164.7° (cor.), and its *p*-nitrophenylhydrazone, m. p. 177–180° (cor.); water (10%); and a small amount of a tarry residue. The combustible non-condensable gas was chiefly methane as shown by analysis.

Anal. Calcd. for CH_4 : O_2/CH_4 , 2.0; CO_2/CH_4 , 1.0. Found: O_2 /gas, 1.94, 1.92, 2.02; CO_2 /gas, 1.11, 1.15, 1.08.

Salts of *t*-Butyl Hydroperoxide

Strontium *t*-Butyl Peroxide.—Strontium oxide (52 g.), freshly prepared by heating strontium hydroxide octahydrate in a blast furnace, was allowed to react with 250 g. of 60% *t*-butyl hydroperoxide. The strontium oxide dissolved with considerable evolution of heat, and, when the mixture was cooled to room temperature, the strontium *t*-butyl peroxide separated in small white crystals. The yield was 118 g. (88.7%).

Anal. Calcd. for $Sr(OOC_4H_9-t)_2$: O, 12.04. Found: O, 11.97, 12.16, 12.08.

Attempts to prepare pure strontium *t*-butyl peroxide from *t*-butyl hydroperoxide and strontium hydroxide were not successful.

Barium *t*-Butyl Peroxide.—Barium oxide (50 g.) was allowed to react with 150 g. of 60% *t*-butyl hydroperoxide, yielding a thick slurry of the barium salt which was removed by filtration, washed several times with olefin-free petroleum ether, and dried in air. The yield was 93 g. (90.4%).

Anal. Calcd. for $Ba(OOC_4H_9-t)_2$: O, 10.14. Found: O, 9.92, 9.83, 9.73.

Sodium and Potassium *t*-Butyl Peroxides.—Although *t*-butyl hydroperoxide dissolves in strong sodium and potassium hydroxides and can be recovered essentially unchanged by acidification, the pure persalts have not been prepared by this method. However, when hot solutions of sodium or potassium *t*-butylate in *t*-butyl alcohol are treated with excess *t*-butyl hydroperoxide and the solutions allowed to cool to room temperature, crystalline solids separate out which, when removed and washed with olefin-free petroleum ether, are stable for long periods of time (eighteen months). These solids have slightly less than half the theoretical active oxygen as calculated for the pure persalts. We believe that they contain *t*-butyl alcohol of crystallization. Attempts to purify them further always resulted in persalts having the same active oxygen content.

Anal. Calcd. for $NaOOC_4H_9-t$: O, 8.6. Found: O, 7.12, 7.6. Calcd. for $KOOC_4H_9-t$: O, 7.9. Found: O, 6.0, 6.2.

Acknowledgment.—The authors wish to thank the Union Bay State Chemical Company for financial support in carrying out this investigation.

Summary

1. *t*-Butyl hydroperoxide and di-*t*-butyl peroxide have been obtained in good yields from *t*-butyl hydrogen sulfate and hydrogen peroxide.
2. Barium and strontium *t*-butyl peroxides have been prepared. Sodium and potassium *t*-

butyl peroxides have also been prepared having *t*-butyl alcohol of crystallization.

3. The pyrolysis of *t*-butyl hydroperoxide has been studied at 95–100° and at 250°. At 95–100° *t*-butyl alcohol and oxygen are the only products formed, while at 250° the products formed are acetone, methyl alcohol, *t*-butyl alcohol, formaldehyde and water.

4. The pyrolysis of di-*t*-butyl peroxide has been studied at 200, 250 and 300°. Acetone and ethane are the only products formed.

5. A free radical mechanism has been proposed to explain the pyrolysis of both *t*-butyl hydroperoxide and di-*t*-butyl peroxide.

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[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY, PEORIA, ILLINOIS¹]

Physical Chemical Properties of the 2,3-Butanediols

By JOHN W. KNOWLTON,² N. CYRIL SCHIELTZ AND DUNCAN MACMILLAN

During the course of this Laboratory's work on the production of the 2,3-butanediols, it has been necessary to investigate a number of physical properties of these compounds. These investigations were made concurrently with the experiments on production, and consequently some of the earlier measurements were made on materials which were mixtures of stereo isomers. The most abundant material as it came from the pilot plant had a composition of about 97.5% *levo*- and 2.5% *meso*-2,3-butanediol. Another culture used for the fermentation produced a mixture composed of the *meso* isomer with small amounts of the *dextro* rotatory form. At an early stage of the work it was found that pure *meso*-2,3-butanediol could be obtained by fractional crystallization from isopropyl ether. Since the naturally occurring mixtures contained only one optically active form in addition to the *meso* isomer, separation by fractional distillation was possible. All three isomers were eventually obtained in pure condition by this method.

In this paper, values for the *meso* and *dextro* isomers are for the pure compounds. Many of the values for the *levo* form are also for the pure substance, and, in any case, the *levo*-2,3-butanediol was at least 97.5% pure, the contaminant being the *meso* isomer.

The data in Table I were obtained on pure stereo isomers.

The conductivities of the 2,3-butanediols in 0.5 *N* boric acid solution have been reported recently by Lees, Fulmer and Underkoffler.³

At this Laboratory a similar set of experiments in which 2 *N* boric acid was used gave results in substantial agreement with those of Lees, Fulmer and Underkoffler. It was found that in the case of *levo*-2,3-butanediol the conductivity increased markedly with increase in concentration, but that the conductivity of the *meso* form decreased

TABLE I
MISCELLANEOUS PHYSICAL CONSTANTS OF 2,3-BUTANEDIOLS

	<i>dextro</i>	<i>levo</i>	<i>meso</i>
Density at 25°, g./ml.	0.9872	0.9869	0.9939
Index of refraction, n_D	1.4306 (25°)	1.4308 (25°)	1.4324 (35°)
Surface tension, 25°, dynes/cm.	30.67	30.61	
Viscosity, Hoeppler, centipoises		41.1 (25°) 21.8 (35°)	65.6 (35°)
Rotatory dispersion: λ , Å.			
4358	+25.24°/decim.	-25.23°	
5481	+15.28	-15.32	
5791	+13.05	-12.95	
5896	+13.19	-13.19	
6234	+11.41	-11.38	
6908	+10.03	-10.03	

slightly with increased concentration. These results are presented in Table II.

TABLE II
SPECIFIC CONDUCTANCES OF SOLUTIONS OF *levo*- AND *meso*-2,3-BUTANEDIOLS IN 2 *N* BORIC ACID AT 20.0°

<i>levo</i> (Optical rotation = -12.9°/decim., λ 5896)		<i>meso</i> (Optical rotation = 0.00°/decim., λ 5896)	
Molar concn.	$\gamma \times 10^6$	Molar concn.	$\gamma \times 10^6$
0.000 (2 <i>N</i> H ₃ BO ₃)	7.13		
.506	10.79	0.452	6.50
.253	8.96	.226	6.76
.127	8.10	.113	6.91
.063	7.60		

Several aspects of solutions of 2,3-butanediols in water have been investigated. The freezing point diagrams of solutions of *levo*- and of *meso*-2,3-butanediols are shown in Fig. 1. The optical rotation (λ 5896) for the *meso* form was 0.00° per decimeter; that of the *levo* form was -13.0°. It will be noticed that a compound is formed consisting by weight of about 45% *meso*-2,3-butanediol and 55% water. The *levo* isomer does not form a compound with water.

Refractive indices of solutions of *levo*-butanediol (97.8% pure) in water have been determined and are shown in Table III.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

(2) Present address: Bureau of Mines, U. S. Department of Interior, Bartlesville, Oklahoma.

(3) Lees, Fulmer and Underkoffler, *Iowa State Coll. J. Sci.*, **18**, 359 (1944).