tional data are presented. It has been shown that oxygen exerts a similar inhibiting action on thermal polymerization as well, and that both these processes involve peroxide formation in preference to polymerization.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Racemization, Alkylsulfuric Acid Formation and Exchange in the Reaction between Sulfuric Acid-d_2 and Optically Active 2-Butanol[1]

BY ROBERT L. BURWELL, JR.[1a]

The racemization of optically active *s*-butyl alcohol by sulfuric acid was recently reported.[2] In this paper further data on this reaction are presented and a hydrogen exchange reaction is reported which accompanies the racemization when sulfuric acid-d_2 is employed. The interrelations among these and the other accompanying reactions, dehydration of the alcohol to butylene and formation of *s*-butylsulfuric acid are considered.

Experimental

Materials.—The preparation of *d*- and *l*-2-butanol has been reported as has the origin and analysis of the sulfuric acid.[2] The rotation of the alcohol in equilibrium with a saturated solution of potassium carbonate dihydrate will be denoted by β. Such an alcohol contains 3.3% water and its rotation is 92.7% of that of the corresponding anhydrous alcohol.[2]

Sulfur trioxide was distilled from 60% fuming sulfuric acid.

Deuterium oxide (99.5%) was purchased from the Ohio Chemical Company.

Commercial dioxane was refluxed with 6 *M* hydrochloric acid. After separation by potassium hydroxide and drying with potassium carbonate, final drying and purification were effected by fractionation in a 12-plate column of the Fenske glass-helix type.

Preparation of Barium *d*-*s*-Butyl Sulfate

Preparation from Sulfur Trioxide in Dioxane Solution.[3]—Into 20 cc. of dioxane cooled in ice, 0.0538 mole of sulfur trioxide was distilled from fuming sulfuric acid. To this, 0.0545 mole of *d*-*s*-butyl alcohol (β^{25}D +5.29°) was added at room temperatures. After ten minutes, the reaction mixture was poured into a suspension of excess barium carbonate in water. After filtering, the solution was placed in a distilling flask in water at 35° and aspirated for six hours during which the volume was reduced from 70 to 18 cc. To this, 14 cc. of water was added and the volume was reduced from 70 to 18 cc. To this, 14 cc. of water was added and the volume reduced again to 23.6 cc., α^{25}D +1.91°. Rotations refer to a one dm. tube save where otherwise noted. One cc. was evaporated and ignited to yield a residue of 0.2306 g. of barium sulfate, whence the yield of barium *s*-butyl sulfate was 0.02345 mole or 87% and $[\alpha]^{25}$D +4.34° (on the anhydrous salt). Upon adding water to the solution and reëvaporating, a similar specific rotation resulted, thus demonstrating the absence of *d*-*s*-butyl alcohol.

Hydrolysis of Barium *d*-*s*-Butyl Sulfate.—To 22.25 cc. of the solution obtained above was added a solution of 2.4 g. of sulfuric acid in 30 g. of water. The precipitated barium sulfate was removed by centrifuging. The clear solution was transferred to a small fractionation apparatus and so heated that the alcohol–water azeotrope distilled as the alcohol was produced. This process required about one and one-half hours. Upon its completion, steam was passed through the residue to carry over any unrecovered alcohol. The outlet of the apparatus led to a gas buret.

The alcohol, isolated over saturated potassium carbonate solution, amounted to 3.09 cc. or 0.0328 mole; β^{25}D +1.56°. 137 cc. (27°, 730 mm.) of butylene was evolved or 0.00535 mole. Of the original 0.0426 mole of *s*-butylsulfuric acid, 76.7% was recovered as alcohol, 12.6% as butylene.

Unacidified barium *s*-butyl sulfate was negligibly hydrolyzed in one hour at 100°.

Preparation from Chlorosulfonic Acid.—To 6.5 cc. of ethylene dichloride, 0.0169 mole of *d*-2-butanol (β^{25}D +5.29°) was added. To this mixture, kept at −10°, 0.0167 mole of chlorosulfonic acid was added. Hydrogen chloride was evolved slowly and in an hour a lower layer separated. The reaction mixture was processed like that resulting from the mixture of sulfur trioxide, alcohol and dioxane to yield 5.0 cc. of an aqueous solution of barium *s*-butyl sulfate, α^{25}D +0.15°. A one-cc. sample was hydrolyzed at 100° with the addition of 6 *M* hydrochloric acid and barium chloride to yield 0.3158 g. of barium sulfate. The direct addition of sulfuric acid to one cc. of sample gave 0.2536 g. of barium sulfate, whence there was 4.1×10^{-4} mole of barium chloride per cc., and 6.75×10^{-4} mole of barium *s*-butyl sulfate per cc. Whence, the yield was 40%, $[\alpha]^{25}$D +0.50. In an experiment in which dioxane was substituted for ethylene dichloride as the solvent, reaction was found to begin only at 100° and to lead to a yield of but 7% in an hour and a half, α^{25}D 0.00°.

Preparation from Sulfuric Acid.—A mixture of *l*-2-butanol (β^{25}D −2.09°) and sulfuric acid was prepared in the same way as in earlier racemization studies[2] (moles: alcohol, 0.0525; acid, 0.0538; water, 0.0128). After 1.45 hours at 26.9° the reaction mixture was poured into a suspension of barium carbonate in water. The resulting mixture was filtered and the filtrate was evacuated. During both processes the exhaust line led through a liquid air trap. The initial volume was 60 cc. The final volume was 24.3 cc.

The condensate in the trap was distilled to isolate the alcohol which was recovered over a saturated solution of potassium carbonate, 0.0292 mole; β^{25}D −1.77°.

Five cc. of the barium *s*-butyl sulfate solution was evaporated and ignited to yield 0.3607 g. of barium sulfate. The rotation of the solution was determined in a 2 dm. tube, α^{25}D −0.105°. Whence the yield of barium *s*-butyl sulfate was 32%, $[\alpha]^{25}$D −0.38°, and the recovery of the alcohol was 56%.

Exchange Reactions

Procedure.—To prepare heavy sulfuric acid, an all-glass apparatus was constructed consisting of a bulb containing sulfur trioxide connected to one outlet of a manifold by a valve patterned after that of Willard.[4]

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(1) Presented at the Buffalo meeting, September, 1942.

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(2) Burwell, THIS JOURNAL, **64**, 1025 (1942).

(3) Suter, Evans and Kiefer, *ibid.*, **60**, 538–540 (1938). The writer is indebted to Dr. C. M. Suter for suggesting this reaction.

(4) Willard, THIS JOURNAL, **57**, 2328 (1935). Willard's valve was opened by melting and blowing out a Pyrex capillary enclosed within a quartz tube. It was closed by heating the quartz and thus fusing the Pyrex capillary tip. In the present research it was found difficult to get a vacuum-tight seal at the tip of the Pyrex capillary. When, by a Pyrex–soft glass seal, a soft glass capillary was substituted, excellent results were obtained.

From the center of the manifold hung the outer portion of an 18/35 standard taper joint for connection to the reaction flask and at the other end of the manifold was connected a graduated tube for the heavy water. Above this graduated tube was a small tube which by cutting and subsequent sealing allowed the addition of heavy water. The manifold was connected through a stopcock to liquid air traps and pumps and to the air.

The 25-cc. reaction flask was joined to an 18-mm. tube which contracted to 10 mm. in the form of the inner portion of an 18/35 standard taper joint. The 10-mm. portion terminated in a ground joint for which a cap was provided so that the reaction flask could be removed and weighed without allowing water vapor to enter.

With the reaction flask in place, the system under vacuum and liquid air about the sulfur trioxide bulb, the valve was opened and by appropriate application of liquid air, sulfur trioxide was sublimed into the reaction flask which after admission of dry air was removed, capped and weighed. The proper quantity of deuterium oxide was placed in the graduated tube and sublimed under vacuum to the walls of the tube above the reaction bulb. Upon judicious manipulation in a freezing mixture, the heavy water was allowed to melt and react. 2-Butanol was added from a microburet to the flask containing heavy sulfuric acid cooled in liquid air. Slow warming allowed the mixing of alcohol and acid.

The stopcocks and the 18/35 standard taper joint were lubricated with Apiezon Grease L which was sufficiently inert to last one run.

After a suitable reaction period, the contents of the flask were poured into water and the alcohol was recovered as previously described.[3] To eliminate deuterium from the hydroxyl group the recovered alcohol was dissolved in seven times its volume of water and the alcohol recovered by the technique described under the hydrolysis of barium *s*-butyl sulfate. This was twice repeated. The rotation of the alcohol was measured. It was then burned over hot copper oxide, the resulting water was weight-diluted with standard water, and the density of this water measured by the float method.[5]

Racemization and Exchange, Integral Recovery.—A mixture of the following composition was prepared: *l*-2-butanol (β^{25}_{D} $-2.09°$), 0.0383 mole; heavy sulfuric acid, 0.0392; heavy water, 0.0098. After a reaction period of two hours at 25° the alcohol was recovered, β^{25}_{D} $-1.30°$. The alcohol after drying with "Drierite" was burned to yield 1.993 g. of water. To this, 0.651 g. of standard water was added. The resulting water was 739 parts per million heavy at 25.8°, whence the fraction of one skeletal hydrogen substituted by deuterium was 0.094.[5] Allowing for this exchange and for the immediate exchange of the hydroxyl hydrogen, 69% of the hydrogen in the exchange "pool" was the heavy isotope. Whence, one skeletal hydrogen had been 9.4/0.69 or 13.7% exchanged.

In a similar experiment with a mixture of the composition: *d*-2-butanol (β^{25}_{D} $+5.29°$), 0.0398 mole; heavy sulfuric acid, 0.0409; and heavy water, 0.0097, and a reaction period of eleven and one-half hours at 25° there was recovered an alcohol, β^{25}_{D} $+0.47°$. After drying, this sample was burned. 0.823 g. of the resulting water was diluted with 2.161 g. of standard water and 2.931 g. of this mixture was diluted with 39.42 g. of standard water. The resulting water was 114 parts per million heavy. This corresponds to the substitution of one skeletal hydrogen to an extent of 55.7%. The percentage of deuterium in the pool was 56. Thus the exchange of one skeletal hydrogen was 100%.

Racemization and Exchange, Separation Recovery.—A mixture of the following composition was prepared: *d*-2-butanol (β^{25}_{D} $+5.29°$), 0.0667 mole; heavy sulfuric acid, 0.0690; and heavy water, 0.0168. After a reaction period of four hours at 25° the mixture was poured into water. One-third was processed as described immediately above. Recovered alcohol over saturated potassium carbonate solution corresponded to a yield of 73%, β^{25}_{D} $+1.58°$. This sample containing 3.3% water was burned without further drying. To 1.178 g. of the resulting water was added 14.95 g. of standard water. The mixture was 228 parts per million heavy.

The remaining two-thirds of the reaction product was separated into barium *s*-butyl sulfate and alcohol present as such by methods already described: recovered alcohol, 38.5%, β^{25}_{D} $+2.33°$. Of the water resulting from burning the dry alcohol, 1.330 g. was diluted with 14.95 g. of standard water. This was 212 parts per million heavy.

The solution containing the barium *s*-butyl sulfate was concentrated as before. The solid monohydrate was obtained by allowing the concentrated solution to remain in a vacuum desiccator until constant weight was reached. The yield was 42%. For 0.268 g. of anhydrous salt per cc., α^{25}_{D} $+0.28°$ (2 dm.), $[\alpha]^{25}_{\mathrm{D}}$ $+0.52°$. The solid salt was mixed with a slight excess of barium carbonate and heated to 100–110°. The salt decomposed smoothly. The evolved gases were burned over hot copper oxide. To 1.374 g. of the resulting water was added 15.72 g. of standard water: density, 375 parts per million heavy.

From the densities of the samples from the acid ester and from the alcohol present as such, the percentage of deuterium in the pool was 62.6. The percentage of exchange of one skeletal hydrogen was: integral sample, 47.6%; alcohol as such, 38.6%; ester, 69.1%.

0.4430 g. of the solid barium *s*-butyl sulfate was ignited to yield 0.2232 g. of barium sulfate. The molecular weight of the salt is thus 462.8; calculated for the monohydrate containing the observed quantity of deuterium, 463.1.

Discussion

Configurational Relation of *d*-Barium *s*-Butyl Sulfate and *d*-*s*-Butyl Alcohol.—The reaction between chlorosulfonic acid and 2-butanol involves merely the elimination of hydrogen chloride. There is little reason to believe that the oxygen–carbon bond is affected. Since, in this reaction, a *d*-alcohol gives a *d*-barium salt, the like rotating alcohol and salt have the same configuration. The considerable racemization which accompanies the reaction is attributable to the high acidity of the reaction mixture.

With sulfur trioxide in dioxane less, if any, racemization takes place probably because the basic dioxane reduces the acidity through oxonium ion formation. A *d*-alcohol yields a *d*-barium salt. Similarly the barium *s*-butyl sulfate formed from sulfuric acid and 2-butanol has the same sign as the alcohol. There is, thus, good reason to believe in all cases here studied that the alcohol and alkylsulfuric acid derived from it are configurationally related.

Hydrolysis of *s*-Butylsulfuric Acid.—In the hydrolysis of the *s*-butylsulfuric acid formed by the dioxane–sulfur trioxide method, an alcohol with but 30% of the original rotation was obtained in 77% yield. No data are available which allow a definite decision as to whether the racemization occurs during the formation or during the hydrolysis of the *s*-butylsulfuric acid or during both. However, one expects racemization of this order of magnitude in solvolytic reactions such as this hydrolysis. Since there is no reason to believe that the carbon–oxygen bond is involved in the formation of the alkylsulfuric

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(5) Dole and Slobod, THIS JOURNAL, **62**, 471 (1940). The author is indebted to Professor Dole for the use of his apparatus and to Mr. Glenn Jenks and Mr. William Roake for their assistance.

acid by the sulfur trioxide–dioxane process, it will be assumed that no racemization occurs in this reaction. On this basis, for a fully resolved barium *s*-butyl sulfate, $[\alpha]^{25}\text{D} + 8.34°$ (for *d*-*s*-butyl alcohol $\beta^{25}\text{D} + 10.17°$, $\alpha^{25}\text{D} + 10.97°$).

Accompanying the hydrolysis was the evolution of about 13% of butylene. This was reported also by Meth.[6] Butylene appears always to accompany the hydrolysis in dilute aqueous solution, a fact significant in the over-all picture.

A neutral solution of the barium salt is not hydrolyzed at 100°. Thus, either the *s*-butyl sulfate ion is not a reacting species or the activated complex in the hydrolysis involves an hydronium ion.

Since the reaction proceeds without change in configuration, *s*-butylsulfuric acid cannot be formed from 2-butanol and sulfuric acid by a Walden inversion reaction between the bisulfate ion and the alcohol. The reason may be partly that the alcohol is present almost exclusively as its conjugate acid, in which case the charge distribution will not favor an inversion substitution. In general, in sufficiently acid solutions, one may expect an inversion substitution of a basic group such as hydroxyl or amino to be unlikely.

Robey[7] has shown that sulfuric acid and 2-butanol react to form an equilibrium mixture of *s*-butylsulfuric acid and the conjugate acid of the alcohol. The same equilibrium mixture results from the interaction of butylene and sulfuric acid of appropriate dilution and would presumably result from the reaction between water and the alkylsulfuric acid.

Racemization and Exchange.—In the reaction of a mixture of *l*-2-butanol ($\beta^{25}\text{D} -2.09°$), sulfuric acid and water of mole proportions, 1.000:1.026:0.244, for 1.75 hours at 26.9°, a barium *s*-butyl sulfate $[\alpha]^{25}\text{D} -0.38°$ was obtained in 32% yield. Following the assumption that the formation of the barium salt by the action of sulfur trioxide in dioxane proceeds without racemization, the fractional maintenance of configuration, α/α_0 was 0.22. In the alcohol present as such in the reaction mixture β/β_0 was 0.85. The alkylsulfuric acid is, thus, clearly involved in the racemization of 2-butanol by sulfuric acid. It should be noted that if, contrary to the assumption here made, the formation of the alkylsulfuric acid by sulfur trioxide in dioxane solution was to involve racemization the value of α/α_0 would be reduced.

Similar mixtures had been previously studied[2] in which the recovery was of an integral rather than of a separation type. An alcohol thus obtained would consist of all that present as the conjugate acid plus 76.7% of that present as the alkylsulfuric acid which substance would be further racemized to the extent of 70% in the hydrolysis stage. Had the recovery in the experiment described in the previous paragraph been of the integral type, β/β_0 would be, thus, 0.61. The rate constants and the temperature coefficient given in ref. 2 predict a value of 0.63.

Table I presents the results of experiments in which *d*-*s*-butyl alcohol was treated with heavy sulfuric acid with integral recovery.

TABLE I

CONCURRENT RACEMIZATION AND EXCHANGE AT 25°

Time, hr.	$(\beta_0 - \beta)/\beta_0$	Fractional exchange of one skeletal H
2	0.378	0.137
4	.701	0.476
11.5	.912	1.00

This table compares the rates of racemization and exchange. The rates are directly comparable only in the first stage since the upper limit of the degree of racemization is 1.00 while that of the exchange must be at least 3 and perhaps 11. The formation of appreciable amounts of polymer in experiments more protracted than the last prevented the determination of the number of exchangeable skeletal hydrogens. However, the rate of racemization is initially about three times greater than the rate of exchange.

The corresponding values for the degree of racemization obtained previously[2] with ordinary sulfuric acid were: two hours, 0.377; four hours, 0.642. Owing to slight variations in the molar ratios of the reactants inevitable in the microprocedure employed in this research, one may conclude only that the rates of racemization in light and heavy sulfuric acid can differ by not more than about 15%.

An experiment in which two recoveries were made, one of the separation and one of the integral type, and in which the reaction period was four hours at 25° gives further details as to the nature of the exchange reaction. The degrees of racemization and exchange were, respectively: integral recovery, 0.701, 0.476; alcohol present as such, 0.560, 0.386; and *s*-butylsulfuric acid, 0.880, 0.691. As a check, the values for the degrees of racemization and exchange may be calculated for the integral recovery from the results of the separation recovery in a way similar to that described in the third paragraph above. These values are 0.699 and 0.496. It is evident that the exchange reaction parallels the racemization reaction and that the deuterium concentrates in the *s*-butylsulfuric acid.

The Mechanism of the Racemization and Exchange Reactions.—The reactions which occur in mixtures of ordinary sulfuric acid and optically active *s*-butyl alcohol have been treated according to the carbonium ion hypothesis.[2] The exchange reaction allows an additional test as to its applicability. A formulation of the mechanism for these reactions may be given thus

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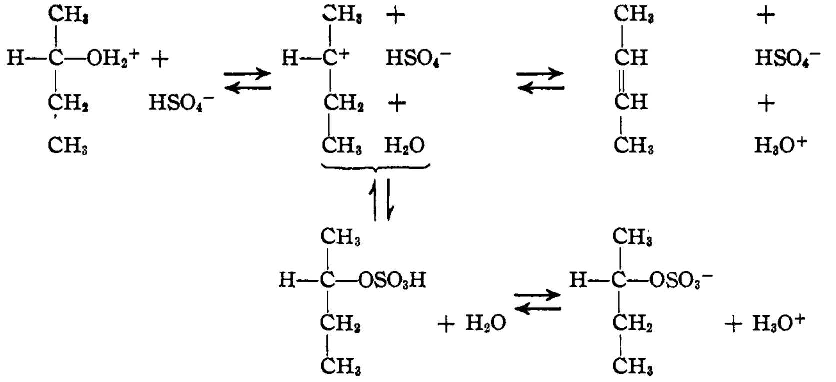
(6) Meth, *Ber.*, **40**, 695 (1907).

(7) Robey, *Ind. Eng. Chem.*, **33**, 1076 (1941).



Since barium *s*-butyl sulfate does not hydrolyze in neutral solution, the un-ionized acid, not the alkylsulfate ion, must be made the reacting species. This is not unreasonable, since otherwise in the formation of the carbonium ion a doubly negatively charged ion would have to separate from a positive ion. With the un-ionized acid, the separation is of singly charged ions.

The hydrolysis of barium *s*-butyl sulfate apparently resembles that of the barium salt of the ethylsulfuric acid. Drushel and Linhart[8] have shown that this salt hydrolyzes extremely slowly in water alone but that in dil. hydrochloric acid the reaction proceeds at a convenient rate. The rate in the more dilute solutions is nearly proportional to the first powers of the concentrations of the salt and of the hydrogen ion.

Since but partial racemization results from the intertransformations of alcohol and alkylsulfuric acid, the life of the carbonium ion must be assumed slight. It would probably be more satisfactory to express the mechanism in terms of an activated complex. The concentration of deuterium in the alkylsulfuric acid and the relative rates of racemization and deuterization require the rate of interconversion of alcohol and alkene at equilibrium to be smaller than the rates of the other two interconversions.

Any mechanism in which butylene is an intermediate, is excluded by the but partial racemization. While *s*-butylsulfuric acid is not so excluded, it is difficult to avoid similar intermediates in the dehydration and hydrolysis reactions unless one allows the unimolecular decomposition of the alkylsulfuric acid to butylene.

Summary

1. The action of sulfuric acid-d_2 on optically active *s*-butyl alcohol results in the introduction of deuterium on the carbon skeleton concurrently with the racemization of the alcohol.

2. The *s*-butylsulfuric acid present in the reaction mixture is both more racemized and further exchanged than the alcohol present as such.

3. The velocity of the racemization reaction is about the same in heavy sulfuric acid as in ordinary acid. Its rate is several times greater than that of the exchange reaction.

4. The formation of *s*-butylsulfuric acid from *s*-butyl alcohol by reaction with (a) sulfuric acid, (b) chlorosulfonic acid, and (c) sulfur trioxide in solution in dioxane proceeds without change in configuration.

EVANSTON, ILLINOIS RECEIVED AUGUST 10, 1944

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[8] Drushel and Linhart, *Am. J. Sci.*, **32**, 51 (1911).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

Chlorothiocyanates of Phosphorus and Silicon. Phosphorus Chloro(iso)cyanate

BY HERBERT H. ANDERSON

Previous papers in this series dealing with the pseudohalide derivatives of elements of the fourth and fifth groups have described the thiocyanates and the (iso)cyanates of phosphorus and silicon,[1,2] the chloroisocyanates of silicon,[3] and related compounds. The present investigation deals with the chloro(iso)cyanates of phosphorus and the chlorothiocyanates of silicon and phosphorus, prepared by the action of silver (iso)cyanate or silver thiocyanate with the appropriate chlorides in benzene solution, or in carbon disulfide solution. The present compounds are believed to include the first inorganic mixed halides containing thiocyanate as a constituent.

Silicon Trichlorothiocyanate.—The optimum yield of $SiCl_3SCN$ was obtained using a ratio of 0.54 mole of $SiCl_4$ to 0.60 mole of AgSCN; the silver salt was added in six separate portions, with intermittent half-hour periods of reflux on a steam-bath. Products were $SiCl_3SCN$ and $Si(SCN)_4$, in the molar ratio 0.33 to 0.08. Numerous efforts were made to isolate other products, including the use of low-pressure distillation and fractional freezing. 200 ml. of pure benzene was used as solvent in each run. There was no evidence of $SiCl_2(SCN)_2$, or $SiCl(SCN)_3$ at any time.

A small weighed sample of the pure distillate, b. p. 129–130°, after decomposition in absolute alcohol and dilution with water, gave a ratio for SCN^-/Cl^- equal to 1.00/3.00 ± 0.02, in accordance with theory. Dr. J. J. Lingane of this Laboratory made his electrometric titration

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[1] Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940); **65**, 2271 (1943). In the latter paper it should have been stated that monomeric sulfur monothiocyanate had previously been prepared by Lecher and Goebel, *Ber.*, **55B**, 1483 (1922).

[2] Anderson, *ibid.*, **64**, 1757 (1942).

[3] Anderson, *ibid.*, **66**, 934 (1944).