[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NORTHWESTERN UNIVERSITY]

Cleavage Reactions of Optically Active Secondary Butyl Methyl Ether

BY ROBERT L. BURWELL, JR., LLOYD M. ELKIN AND LUCIEN G. MAURY

The stereochemistry and probable mechanism of the cleavage of optically active *s*-butyl methyl ether by hydrogen bromide, and of the catalyzed cleavage by acetyl chloride, acetyl bromide and acetic anhydride are reported. The action of hydrogen bromide, either anhydrous or dissolved in glacial acetic acid, leads to cleavage of the methyl–oxygen bond, presumably by a displacement reaction of bromide ion upon the methyl group of the conjugate acid of the ether. Configuration at the *s*-butyl group is retained. With the acetyl halides and trace amounts of catalysts the *s*-butyl–oxygen bond is cleaved, probably by addition of positive acetyl ion to the ether oxygen atom followed by separation of *s*-butyl carbonium ion which then combines with a halide ion. The *s*-butyl halide so formed is of inverted configuration and racemized about 50%. The reaction of acetic anhydride is similar but the *s*-butyl acetate so formed is more racemized. The resistance of *s*-butyl methyl ether to racemization by a number of reagents is reported.

Cleavage of ethers has been effected principally by two groups of compounds, hydrogen halides and acid anhydrides.[1]

In spite of the importance of these reactions, there has been no general survey of the stereochemistry of these reactions, an omission the seriousness of which is increased by different conclusions as to the mechanism of ether cleavage reactions proposed in recent monographs. The stereochemistry of the cleavage of optically active *s*-butyl methyl ether has accordingly been investigated with hydrogen bromide as typical of hydrogen halides and with acetyl chloride, acetyl bromide and acetic anhydride as examples of acid anhydrides. For further elucidation of the behavior of ethers, the optically active ether has been exposed to the action of a number of reagents typifying other classes of compounds.

Previous literature permits no firm prediction as to which alkyl radical should remain attached to the ether oxygen in cleavage by hydrogen bromide. In reaction of the ether and hydrogen bromide, mole for mole, at 50°, the methyl–oxygen bond is broken and only a trace of *s*-butyl bromide is formed.[2] The main recovered product is unracemized *s*-butyl alcohol of the same configuration as the reactant ether. The other product, though not isolated, is presumably methyl bromide. These products agree with a rule of Michael and Wilson.[3]

In glacial acetic acid as solvent, the same system at 25° leads apparently to unracemized *s*-butyl acetate of the same configuration as the reactant ether. With a large excess of hydrogen bromide and acetic acid as solvent, *s*-butyl bromide of inverted configuration results. Its rotation *vs.* *s*-butyl alcohol is as high as any previously reported and in view of the data of Letsinger[4] its loss of optical purity, if any, cannot exceed 20%.

Recent proposals for the mechanism of reactions of this nature have agreed that the first step is the formation of an oxonium salt or of something resembling one. Some[5,6] have proposed a subsequent step involving dissociation into a carbonium ion and an alcohol molecule. Others[7,8] formulate the second step as a bimolecular nucleophilic displacement; the halide ion displaces an alcohol molecule from one of the carbon atoms attached to the ether oxygen atom.

If the first mechanism were correct, a *s*-butyl carbonium ion would separate from the oxonium salt and an inverted and partially racemized *s*-butyl bromide and methanol would result.

In the second mechanism, the entering halide ion would more readily attack a primary than a secondary carbon atom. Consequently the products would be methyl bromide and *s*-butyl alcohol of unchanged configuration. The second mechanism is consistent with the facts adduced in this investigation; the first one is excluded. In the light of current theories of organic reaction mechanisms, the reaction may be written crudely as

$$s\text{-}C_4H_9OCH_3 + HBr = \left[s\text{-}C_4H_9\overset{H}{O}CH_3\right]^+ + Br^- \quad (1)$$

$$\left[s\text{-}C_4H_9\overset{H}{O}CH_3\right]^+ + Br^- = s\text{-}C_4H_9OH + CH_3Br \quad (2)$$

The data provide no test of such questions as the degree of dissociation of the oxonium salt, whether the reacting species in (2) is bromide ion or hydrogen bromide, etc. Furthermore, while extension of the mechanism to primary–primary ethers should be valid, extension to secondary–secondary ethers is questionable. The very rapid rate of reaction of tertiary ethers makes it likely that these proceed *via* carbonium ion intermediates.

With excess hydrogen bromide in acetic acid as solvent, a step subsequent to (2) must be assumed.

$$s\text{-}C_4H_9OH + HBr = s\text{-}C_4H_9Br + H_2O \quad (3)$$

Step (3) must be assumed to take place predominately as a bimolecular nucleophilic displacement with inversion of configuration and little or no racemization. With a mole ratio of one for hydrogen bromide and ether in acetic acid, the alcohol formed in step (2) is subsequently esterified. The data permit no decision as to whether step (3) involves alcohol as written or whether the alcohol is esterified first.

These considerations cannot necessarily be extended to aqueous solutions of hydrogen halides.

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[1] The papers of (a) H. Meerwein and H. Maier-Hüser, *J. prakt. Chem.*, **134**, 51 (1932), and (b) J. F. Norris and G. W. Rigby, THIS JOURNAL, **54**, 2088 (1932), are leading references to previous literature.

[2] Clearly, the ether reacts with hydrogen bromide more rapidly than does *s*-butyl alcohol under these conditions. The common view that ethers are much less reactive than alcohols should not be applied to reactions in which the carbon–oxygen bond of the alcohol is broken.

[3] A. Michael and F. D. Wilson, *Ber.*, **39**, 2569 (1906).

[4] R. L. Letsinger, THIS JOURNAL, **70**, 406 (1948).

[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 300.

[6] A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, 2nd ed., p. 400.

[7] F. R. Mayo, W. B. Hardy and C. G. Schultz, THIS JOURNAL, **63**, 426 (1941).

[8] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 218.

Indeed, Hammett[5] favored a carbonium ion mechanism because of the demonstration[1b,9] that secondary ethers are cleaved more rapidly than primary ethers by aqueous solutions of strong acids. However, this argument neglects the relative basicity of the ethers as reflected in the degree to which reaction (1) proceeds and the greater rate of reaction of secondary ethers may result from this. In any case, in glacial acetic acid, a solvent usually considered to favor ionic reactions, a carbonium ion mechanism as currently understood would appear unlikely. For, with excess hydrogen bromide, *s*-butyl bromide of high optical purity (greater than 80%) results; with a mole ratio to the ether of one, *s*-butyl acetate not *s*-butyl bromide is the predominant product. Of course, in aqueous solutions, one may be dealing with reactions intermediate between carbonium ion reactions and displacement reactions. Coördinated measurement of rates, stereochemistry and product distribution with appropriate ethers should be of considerable interest in this regard.

Upon refluxing 55% aqueous hydrogen iodide with *s*-butyl methyl ether a drastically racemized *s*-butyl iodide of inverted configuration results. In view of the probable racemization by iodide ion of the *s*-butyl iodide subsequent to its formation and of the consequent difficulty of separating the various stereochemical factors, this reaction has not been investigated further.

Cleavage with Acetyl Chloride.—Acetyl chloride reacts with ethers only at high temperatures but Meerwein and Maier-Hüser[1a] reported that, in the presence of gross amounts of anhydrous halides of the class of Lewis acids, reaction proceeds at slightly above room temperatures. Zinc chloride and stannic chloride were particularly suitable. In view of its convenience, stannic chloride has been used in this research. Norris and Rigby[1b] reported that *s*-butyl ethyl ether with zinc chloride as a catalyst gave only *s*-butyl chloride and ethyl acetate in a reaction which proceeded for 12 days at 25°.

In agreement with Norris and Rigby we have found that *s*-butyl methyl ether yields *s*-butyl chloride and methyl acetate though there is apparently some elimination reaction leading to butylene. The *s*-butyl chloride is of inverted configuration and racemized to the extent of about 50%.

The products and stereochemistry suggest a carbonium ion fission of the ether. The data are consistent with the mechanism

$$2CH_3COCl + SnCl_4 = 2CH_3CO^+ + SnCl_6^= \quad (4)$$

$$CH_3CO^+ + s\text{-}C_4H_9OCH_3 = \left[s\text{-}C_4H_9\underset{CH_3}{O}COCH_3\right]^+ \quad (5)$$

$$\left[s\text{-}C_4H_9\underset{CH_3}{O}COCH_3\right]^+ = s\text{-}C_4H_9^+ + CH_3COOCH_3 \quad (6)$$

$$s\text{-}C_4H_9^+ + [Cl^-] = s\text{-}C_4H_9Cl \quad (7)$$

Meerwein and Maier-Hüser[1a] likewise proposed an oxonium salt as an intermediate. The preparation of acetyl fluoroborate and the reactions and conductivity of compounds of this nature[10] in liquid sulfur dioxide provide convincing evidence of the stable, independent existence of the acyl ion. A similar situation exists in solutions of aluminum chloride in carbonyl chloride,[11] and, in fact, Germann was the first to propose the existence of ions of this nature. In view of his results with carbonyl chloride it appears not unreasonable to extend the results of Seel to acetyl chloride–ether solutions.

In view of the relatively large rotation of the product *s*-butyl chloride, reactions (6) and (7) must be closely related in time and neither can be reversible.[12] The very much more rapid reaction of tertiary ethers[1b] would suggest that reaction (6) is the rate-determining step.

Sulfuric acid can substitute for stannic chloride as the catalyst, perhaps, as

$$CH_3COCl + H_2SO_4 = CH_3CO^+ + HSO_4^- + HCl \quad (8)$$

This involves in essence the formation of acetylsulfuric acid which is known to be a strong acetylating reagent. It is, however, only slightly ionized in liquid sulfur dioxide.[10]

Previous literature prepares one neither for the very small quantities of catalyst required nor for the rapidity of the reaction. With 0.0005 mole fraction of stannic chloride, the reaction is relatively rapid even at 0°, while if the reaction is started at 25° and its temperature is not controlled, the reaction mixture rapidly comes to reflux.

Cleavage with Acetyl Bromide.—With acetyl bromide, products and stereochemistry resemble those with acetyl chloride. However, the reaction proceeds more readily than with acetyl chloride. In fact, with commercial acetyl bromide no catalyst need be added. The addition of traces of stannic chloride augments the rate but does not affect the products or stereochemistry. There is some evidence that purified acetyl bromide is much less reactive than the commercial but this point has not been thoroughly investigated. The increased activity of acetyl bromide is in line with the behavior of acetyl iodide which also reacts without added catalyst.[13]

Cleavage with Acetic Anhydride.—Acetic anhydride is less reactive than acetyl chloride but, again, with small quantities of stannic chloride the reaction proceeds more rapidly than one would expect from previous literature. In fact, Meerwein and Maier-Hüser[1a] report that a mole ratio of halide to anhydride of one is necessary. The small quantity of stannic chloride is most desirable as it prevents the formation of substantial quantities of *s*-butyl chloride.

In reaction with acetic anhydride, the acetates of both ether fragments are obtained. The *s*-butyl acetate is about 80% racemized and of inverted configuration. This contrasts particularly with the reaction with hydrogen bromide in glacial acetic acid in which case the *s*-butyl acetate is a substantially unracemized product of retained configuration.

The results with acetic anhydride are also con-

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(9) A. Skrabal and R. Skrabal, *Z. physik. Chem.*, **181**, 449 (1938).

(10) F. Seel, *Z. anorg. allgem. Chem.*, **250**, 331 (1943); F. Seel and H. Bauer, *Z. Naturforsch.*, **2b**, 397 (1947).

(11) A. F. O. Germann, THIS JOURNAL, **47**, 2461 (1925); *J. Phys. Chem.*, **29**, 1148 (1925).

(12) The present experiments provide no compelling proof that the racemization of the chloride is not subsequent to its formation but the results with sulfuric acid as a catalyst and with acetyl bromide with and without a catalyst are consistent with this assumption.

(13) E. L. Gustus and P. G. Stevens, THIS JOURNAL, **55**, 378 (1933).

sistent with the mechanism expressed in equations (4) through (7): This involves the ionization of acetic anhydride to acetyl and complexed acetate ions. Ionization of acetic anhydride to acetyl and acetate ions has been demonstrated.[14]

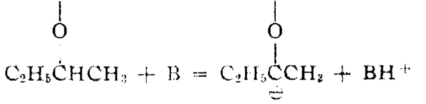
Other reactions of acetyl chloride and acetic anhydride which are catalyzed by Lewis acids or strong proton acids may well proceed *via* similar ionic species; for example, the boron trifluoride catalyzed addition of acetic anhydride to propionaldehyde[15] and the stannic chloride catalyzed addition of acetyl chloride to alkylacetylenes.[16]

Comparison of Hydrogen Halide *vs.* Acid Anhydride Cleavage.—The two mechanisms resemble one another in involving an oxonium intermediate. The difference in the nature of the cleavage may result from the presence of good nucleophilic substituting species, halide ions, in the case of hydrogen halides and their low concentration in the second case. Thus with hydrogen halides the rate of reaction (2) exceeds that of a reaction similar to (6).

Cleavage with Chloroacetyl Iodide.—Stevens[17] has reported that (+)*s*-hexyl methyl ether is cleaved by chloroacetyl iodide on long standing at room temperature in the absence of a catalyst. Roughly one-third of the product is *s*-hexyl iodide, about 50% racemized and of inverted configuration, and two-thirds of *s*-hexyl chloroacetate of like sign and presumably like configuration. Stevens assumed the formation of a complex identical with the one postulated in reaction (5) but he proposed that it was cleaved by reaction with iodide ion in a nucleophilic displacement reaction. Iodide ion was assumed to attack the methyl twice as fast as the *s*-hexyl. It would hardly be assumed now that iodide ion would attack a secondary carbon one-half as fast as a methyl in such a reaction. More likely, a reaction analogous to (2) competes with reaction (6). Reaction (2) is favored over the cases studied in this paper by the probably greater concentration of halide ions and by the greater nucleophilic displacing activity of the iodide ion.

Resistance of *s*-Butyl Methyl Ether to Racemization.—The action of a number of reagents on optically active *s*-butyl methyl ether was examined for possible racemization. The ether was either recovered unchanged and unracemized or the ether was attacked but any recovered ether was unracemized. Results are given in Table I. Recoveries were substantially quantitative unless otherwise indicated.

Resistance to the action of basic reagents is particularly noteworthy. The reaction



$$C_2H_5\overset{\overset{CH_3}{|}}{\overset{O}{\overset{|}{C}}}HCH_3 + B = C_2H_5\underset{\ominus}{\overset{\overset{CH_3}{|}}{\overset{O}{\overset{|}{C}}}}CH_3 + BH^+$$

occurs to a detectable extent in no case. The reaction

$$CH_3O^- + (+)C_4H_9OCH_3 = (-)CH_3OC_4H_9 + CH_3O^-$$

is likewise of negligible rate in accord with the nonoccurrence of the analogous reaction between phenylmethylcarbinol and hydroxide ion.[18] With sulfuric acid, the ether is presumably cleaved but the *s*-butyl fragment is polymerized.

Conjunct polymerization of the ether by sulfuric acid or boron trifluoride–methanol leads to an optically inactive product as was the case for similar conjunct polymerization of optically active *s*-butyl alcohol.[19]

TABLE I

ACTION OF REAGENTS ON 0.042 MOLE OF (+)SECONDARY BUTYL METHYL ETHER

Reagent	Moles[a]	Bath temp., °C.[b]	Time, hr.
$(CH_3)_2SO_4$	0.0070	95	23
	.054	95	1.5[c]
H_2SO_4 (96%)	5.0 cc.	23	1.0[d]
$C_2H_5SO_3H$	0.061	23	4[e]
$C_7H_7SO_3CH_3$	.061	80	18[f]
P_2O_5	.014	80	12[g]
$NaOCH_3$	[h]	200	5
CaO	.071	80	2
K	.002	80	24
Na	.087	90	120
NaH	.083	90	120
$LiNH_2$	.087	80	20
$LiAlH_4$	.053	80	20

[a] For concd. H_2SO_4, cc. [b] A flask with attached reflux condenser was employed save for $NaOCH_3$ for which a sealed tube was used. [c] Recovery but 60%. For a reaction time of 12 hr., no ether was recovered. Addition of CaO did not change this result. [d] Recovery but 28%. [e] At 80°, 4 hr., recovery was 30% and the loss in rotation was 35%. The recovered ether was obviously impure. [f] In a sealed tube at 180° for 10 hr., no ether was recovered. [g] Recovery 50%. [h] 5 cc. of a saturated solution of $NaOCH_3$ in CH_3OH.

Experimental

The symbol $\alpha^{25}D$ designates the homogeneous rotation in a 1-dm. tube.

***s*-Butyl Methyl Ether.**—The ether was prepared by several modifications of the Williamson synthesis from partially resolved *s*-butyl alcohol and methyl iodide. The most convenient involved the preparation of the sodium alkoxide by the action of the alcohol on sodium hydride, mole for mole, in an atmosphere of pure hydrogen. Low rotations were observed in several cases in which air was present.

Since the ratio of the rotations of alcohol and ether had not been previously critically examined, two preparations were made in which an excess of alcohol was used so that recovered alcohol could be examined to ensure absence of its racemization. One employed the sodium hydride synthesis. In the other, methyl *p*-toluenesulfonate and *s*-butyl alcohol were refluxed over sodium carbonate for 13 hours. Both methods agree that the ratio of the homogenous rotations of ether to alcohol is 1.59, a result in agreement with the two previous preparations. If one takes for optically pure *s*-butyl alcohol, $\alpha^{25}D$ +10.97°, then for optically pure ether of the same configuration, $\alpha^{25}D$ +17.4°. Reactions were run on 5.0 cc. (0.042 mole) of ether unless otherwise stated. With active material, yield was generally sacrificed for purity.

Cleavage by Hydrogen Bromide.—Hydrogen bromide was dissolved in inactive ether at 0° to a mole ratio of one and heated in a sealed tube for one hour at 50°. Following evaporation of methyl bromide, the material was soluble in

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(14) H. A. E. Mackenzie and E. R. S. Winter, *Trans. Faraday Soc.*, **44**, 159 (1948); G. Jander, E. Rüsberg and H. Schmidt, *Z. anorg. Chem.*, **255**, 238 (1948).

(15) E. H. Man, J. J. Sanderson and C. R. Hauser, THIS JOURNAL, **72**, 847 (1950).

(16) J. W. Kroeger, F. J. Sowa and J. A. Nieuwland, *J. Org. Chem.*, **1**, 163 (1936).

(17) Stevens, THIS JOURNAL, **62**, 1801 (1940).

(18) R. A. Ogg, Jr., *Trans. Faraday Soc.*, **31**, 1385 (1935).

(19) R. L. Burwell, Jr., THIS JOURNAL, **64**, 1025 (1942).

water save for a tiny residue. The yield of *s*-butyl alcohol after distillation and drying was 62%. The quantity of *s*-butyl bromide formed could not have exceeded 2–3%. In an experiment with optically active material, the reaction mixture was diluted with an aqueous solution of thiourea, refluxed to eliminate *s*-butyl bromide and the alcohol–water azeotrope distilled out. After equilibration with a saturated solution of potassium carbonate dihydrate, $n^{25}\text{D}$ 1.3944, yield 56%. After correction to optically pure ether and anhydrous alcohol,[19] $\alpha^{25}\text{D}$ 10.5° and of sign like to reactant ether.

With a similar mole ratio of ether to hydrogen bromide but in 0.35 mole of glacial acetic acid as solvent, the reaction mixture was diluted with water after a reaction period of 24 hours at 25°. The upper layer was dried and distilled, *s*-butyl acetate, b.p. 107–108°, $n^{25}\text{D}$ 1.3903, of like configuration to the ether, and of rotation, 88% of possible.[20] The material was apparently somewhat impure since for a sample of carefully fractionated *s*-butyl acetate, $n^{25}\text{D}$ 1.3863. The acetate forms azeotropes both with the alcohol and the bromide.

In an experiment with quantities of ether and acetic acid as above but with a mole ratio of hydrogen bromide to ether of 3.5 and a reaction period of four days at 25°, an 81% yield of *s*-butyl bromide was obtained after extraction with water and with concentrated sulfuric acid. This was distilled in a micro, unpacked column, b.p. 91°, $n^{25}\text{D}$ 1.4341. After correction to optically pure reactant, $\alpha^{25}\text{D}$ 32.2° and of sign opposite that of the ether. Thus, the bromide is of inverted configuration. The degree of racemization, if any, cannot exceed 20%.[21]

Cleavage by Acetyl Chloride.—If 0.00005 mole of stannic chloride is added to a mixture of 0.05 mole of *s*-butyl methyl ether and 0.063 mole of acetyl chloride, the mixture becomes warm and refluxes. To avoid possible side reactions from higher temperatures, stannic chloride was added to such mixtures at −80° in subsequent experiments. In such an experiment with active ether and a reaction period of one-half hour at 25°, the reaction mixture was neutralized with dilute potassium hydroxide and distilled. The organic layer was washed with concentrated hydrochloric acid, sulfuric acid, water, and then dried; yield of *s*-butyl chloride, 62%, $n^{25}\text{D}$ 1.3944.[22] After correction to optically pure reactant ether, $\alpha^{25}\text{D}$ 13.9° and of sign opposite the ether. In a similar experiment, in which the organic layer was distilled before extraction, any material higher boiling than *s*-butyl chloride could have amounted to no more than a 5% yield of *s*-butyl acetate. The corrected rotation was 16.1°.

In similar experiments with inactive ether, a 76% yield of *s*-butyl chloride resulted from a reaction period of one day at 0°, a 2% yield from one hour. In the absence of stannic chloride only a trace of material insoluble in concentrated hydrochloric acid results from a reaction period of three days at 25°. Purification of commercial acetyl chloride (Baker and Adamson) did not affect the results. Neither hydrogen chloride, 0.002 mole, nor acetic acid, 0.0012 mole, gave evidence of catalytic activity. However, the addition of 0.0006 mole of concentrated sulfuric acid resulted in a 46% yield of chloride in three hours at 25°. In a similar experiment with optically active ether and a reaction period of three days at 25°, a 57% yield of chloride was obtained, $n^{25}\text{D}$ 1.3947. After correction to optically pure ether, $\alpha^{25}\text{D}$ 12.2°, of sign opposite the ether. In this experiment, a Dry Ice trap was connected to the outlet of the apparatus. A little of the *s*-butyl chloride appeared here as well as a substance evolved at about 0° (butylene ?). Letsinger, Maury and Burwell have shown that for optically pure *s*-butyl chloride, $\alpha^{25}\text{D}$ lies between 29.3 and 33.2°.[23] Similarly rotating *s*-butyl alcohol and *s*-butyl chloride are presumed to be configurationally related.

Cleavage by Acetyl Bromide.—In similar experiments with acetyl bromide, a 72% yield of *s*-butyl bromide was obtained after three days at 25°; a 61% yield after three hours at 0°. The purity of the product was checked by infrared spectroscopy.

Commercial acetyl bromide (Eastman Kodak Company) with no added catalyst gave 63, 66 and 68% yields in three days at 25° but in three hours a yield of only a few per cent. resulted. With freshly distilled acetyl bromide erratic results were obtained. In one case a yield of only 5% resulted from a reaction period of two days at 25°.

With stannic chloride as catalyst, optically active ether, and a reaction period of three days at 25°, a 66% yield of *s*-butyl bromide, $n^{25}\text{D}$ 1.4348 resulted. Corrected to optically pure ether, $\alpha^{25}\text{D}$ 17.6°, of sign opposite the ether. In a similar experiment with no added catalyst, and a bromide distilled 18 days previously, a 35% yield resulted, $\alpha^{25}\text{D}$ 17.7°.

Reaction with Acetic Anhydride.—With 0.0007 mole of stannic chloride the reaction mixture was distilled after three days at 25°. The fraction boiling in the vicinity of 108° was washed with sodium carbonate solution to remove acetic anhydride, dried and distilled. A 15% yield of *s*-butyl acetate resulted, $n^{25}\text{D}$ 1.3891. After correction to optically pure ether, $\alpha^{25}\text{D}$ 4.22°, of sign opposite the ether (configuration −19%). In a similar experiment, but with greater attention to yield, 40% of *s*-butyl acetate was obtained.

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[20] Assuming optically pure *s*-butyl acetate, $\alpha^{25}\text{D}$ 21.64°; R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 830 (1914).

[21] Configurationally related *s*-butyl bromide has a rotation of the same sign as that of the alcohol and $\alpha^{25}\text{D}$ lies between 32.1 and 40.8°.[4] Computed from data of J. Timmermans and Y. Delcourt, *J. chim. phys.*, **31**, 85 (1934), $n^{25}\text{D}$ 1.4348.

[22] J. Timmermans and F. Martin, *J. chim. phys.*, **25**, 424 (1928), give $n^{25}\text{D}$ 1.3946.

[23] R. L. Letsinger, L. G. Maury and R. L. Burwell, Jr., THIS JOURNAL, **73**, 2373 (1951).