[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Rearrangements in the Solvolysis of 2-Butyl-1-C^{14} *p*-Toluenesulfonate[1,2]

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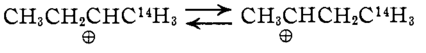
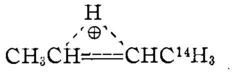
Solvolysis of 2-butyl-1-C^{14} *p*-toluenesulfonate in acetic acid in the presence of acetate ion under conditions where the reaction rate is essentially independent of the acetate ion concentration leads to a mixture of 91 ± 1% of 2-butyl-1-C^{14} acetate and 9 ± 1% of the rearranged product, 2-butyl-4-C^{14} acetate. It has been shown that the rearrangement is not due to rearrangement of the starting material or to elimination to yield butenes followed by addition of acetic acid. Much less rearrangement occurs in the hydrolysis of 2-butyl-1-C^{14} *p*-toluenesulfonate in 75% acetone–25% water (by volume). It is concluded that a non-classical cation of the type $CH_3CH\underset{\underset{H}{\oplus}}{=\!=\!=}CHCH_3$ is not an important intermediate in the unimolecular hydrolysis or acetolysis of 2-butyl *p*-toluenesulfonate.

In an earlier investigation,[3] it was shown that isotope position rearrangements do not occur in the usual essentially irreversible, carbonium ion-type metathetical or elimination reactions of *t*-butyl and *t*-amyl derivatives. Such behavior was expected on the basis of the carbonium ion theory[4] of molecular rearrangements since any isotope position rearrangements with *t*-butyl or *t*-amyl derivatives would involve interconversion of tertiary to less stable secondary (or primary) cations under unfavorable conditions. The situation with 2-butyl derivatives is quite different in that the interconversion equilibrium of, for example, 2-butyl-1-C^{14} (I) and 2-butyl-4-C^{14} (II) cations could be established by simple 1,2-hydride shifts. The role of a more or less stable "ethyleneprotonium" ion[5] intermediate like III[6] in such processes has not yet been established. It is possible that III is no more than



$$\underset{\oplus}{CH_3CH_2CHC^{14}H_3} \rightleftharpoons \underset{\oplus}{CH_3CHCH_2C^{14}H_3}$$

I II



$$CH_3CH\overset{\overset{H}{\oplus}}{=\!=\!=}CHC^{14}H_3$$

III

a transition state through which rearrangement could occur more or less readily as shown schematically in the top curve of the energy diagram (Fig. 1). Alternatively, III and the isomeric cations I and II could have similar energies and be in more or less a dynamic equilibrium[7] as indicated by the middle curve of Fig. 1. As a final clear-cut possibility, III could be substantially more stable than either of the cations I and II and could be formed directly and react without their intervention as indicated by the lowest curve of Fig. 1.

Information as to the best approximation to the actual state of affairs was sought in the present research by measurement of the extent of rearrangement in solvolyses of 2-butyl-1-C^{14} *p*-toluenesulfonate (IV) under conditions where these processes are irreversible. It was expected that extensive rearrangement to yield 2-butyl-4-C^{14} derivatives would be observed if reasonably free cationic intermediates were involved and if III possesses comparable or greater stability than I or II.

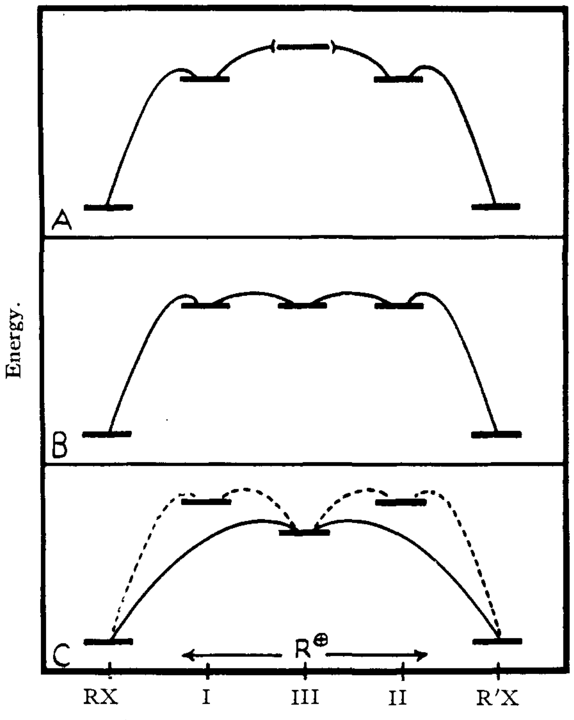


Fig. 1.—Schematic energy diagram for extreme and intermediate formulations of reactions involving possible cations from 2-butyl derivatives labeled with C^{14}. RX and R'X represent 2-butyl-1-C^{14} and 2-butyl-4-C^{14} derivatives, respectively. Curve A depicts a situation where cation III is less stable than I or II. Curve B has III of comparable stability and readily interconvertible with I and II. Curve C has III much more stable than I or II with solid lines representing the usual course of reaction, *i.e.*, III being formed directly from RX or R'X without intervention of I or II being required.

Synthetic and Degradative Methods

The 2-butyl-1-C^{14} *p*-toluenesulfonate was pre-

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[1] Supported in part by the joint program of the Office of Naval Research and the United States Atomic Energy Commission.

[2] Presented in part at the Symposium on Reaction Mechanisms at the 75th Anniversary Meeting of the American Chemical Society, September 7, 1951.

[3] J. D. Roberts, R. E. McMahon and J. S. Hine, THIS JOURNAL, **71**, 1896 (1949); **72**, 4237 (1950).

[4] *Cf.*, L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 317–325; G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 451–534.

[5] *Cf.*, D. J. Cram, THIS JOURNAL, **74**, 2137 (1952).

[6] For refs. to some other situations where intermediates similar to III have been proposed see S. Winstein and D. S. Trifan, *ibid.*, **71**, 2953 (1949).

[7] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 211–213.

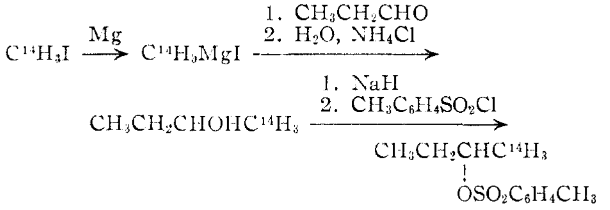
TABLE I

RATE CONSTANTS FOR SOLVOLYSIS OF 2-BUTYL p-TOLUENESULFONATE (ROTs)

Solvent	Temp., °C.	Initial [ROTs], M	Initial [KOAc], M	Initial [KOTs],[a] M	k_1, hr.$^{-1}$	k_2, (mole/l.)$^{-1}$ hr.$^{-1}$	Olefin,[b] %	F_1[c]
HOAc[d]	60.0	0.62	0.61	..	0.06	0.14	...	0.63
HOAc[d]	65.0	.46	.46	..	.11	.22	...	.71
HOAc[d]	65.0	.51	.46	0.45	.16	.19	38	.81
HOAc[d]	65.0	.099	.100	.89	.22	(.19)[e]	33	.95
H_2O-acetone[f]	65.0	.148	...	..	.32	...	(23)[g]	1.00

[a] Potassium p-toluenesulfonate. [b] Percentage of theoretical amount of olefin formed at practical completion of solvolysis; determined by the hydrogenation procedure of J. D. Roberts, THIS JOURNAL, **71**, 1980 (1949). [c] Fraction of reaction proceeding by first-order processes at practical completion; calculated from k_1 and k_2 by the equation given in ref. 10. [d] Acetic acid containing 1% acetic anhydride. [e] Assumed to be the same as in the preceding run. The kinetics in this run were quite accurately first-order to over 90% reaction after a small correction for the infinity titer was made. [f] 25% water–75% acetone (by volume). [g] Calculated from the C^{14}-activity of the carrier-diluted product from the hydrolysis of IV.

pared starting with methyl-C^{14} iodide[8] by the following series of reactions. The solvolysis reactions were carried out in acetic acid and aqueous acetone



$$C^{14}H_3I \xrightarrow{Mg} C^{14}H_3MgI \xrightarrow[2.\ H_2O,\ NH_4Cl]{1.\ CH_3CH_2CHO}$$

$$CH_3CH_2CHOHC^{14}H_3 \xrightarrow[2.\ CH_3C_6H_4SO_2Cl]{1.\ NaH} \underset{\displaystyle OSO_2C_6H_4CH_3}{CH_3CH_2\overset{}{C}HC^{14}H_3}$$

IV

and yielded 2-butyl acetate or 2-butanol. In the former event, the ester was converted to 2-butanol by alkaline hydrolysis for degradation. The most satisfactory degradation procedure involved oxidation of labeled 2-butanol with excess sodium hypobromite to yield carbon tetrabromide, the C^{14}-activity of which gives the activity at C-1 of the 2-butanol. Purification of carbon tetrabromide was found to be somewhat simpler than that of the iodoform obtained in the analogous oxidation with sodium hypoiodite solution.

Experimental Results and Discussion

It was considered particularly desirable to study the unimolecular solvolysis products of IV in acetic acid since much work has been done on reaction rates and rearrangements of benzenesulfonate esters in this solvent.[6,9] Some difficulty was encountered in selecting appropriate reaction conditions since it was considered imperative to use at least one equivalent of acetate ion to each equivalent of IV to avoid formation of the free sulfonic acid. However, complications were then introduced by bimolecular substitution (S_N2) and elimination (E2) reactions between acetate ion and IV. Presumably, bimolecular substitution would proceed without rearrangement and suitable corrections could be made if the appropriate rate constants were known. However, since both the unimolecular and bimolecular reactions may lead to substitution and elimination, complete analysis of the kinetics would be difficult and it was deemed preferable to find conditions where the bimolecular reaction is essentially negligible. The kinetics of the reaction of unlabeled IV with potassium acetate were studied[10] under several different conditions (see Table I) and, as would be expected, the most satisfactory circumstances for practical elimination of the bimolecular reaction involved low concentrations of IV and acetate ion with considerable neutral salt present.

The extent of rearrangement in the acetolysis of IV was measured at ionic strengths of 0.9 and 1.0 M using acetate ion concentrations of 0.46 and 0.10 M. The experimental results along with those obtained in the hydrolysis of IV in aqueous acetone and some controls are given in Table II. At 0.10 M acetate,

TABLE II

EXTENT OF REARRANGEMENT IN THE SOLVOLYSIS OF 2-BUTYL-1-C^{14} p-TOLUENESULFONATE AT 65°

Solvent	Initial [ROTs], M	Initial [KOAc], M	Initial [KOTs], M	Radioactivity[a] 2-butanol	Radioactivity[a] CBr_4	Rearrange.,[b] %
HOAc[c]	0.51	0.46	0.45	1005 ± 15[d] 980 ± 20[e]	915 ± 5	7.9[f]
HOAc[c]	.10	.10	.89	656 ± 4	603 ± 4	8.8
HOAc[c]	.18	.10	.89	1557 ± 21[g]	1540 ± 8	1.1[h]
HOAc[c]	.72[i] .62[j]	.10	.89	−1 ± 4[k]	......	(<1)[l]
H_2O-acetone[m]	.15	..	..	636 ± 12	617 ± 8	3.0[n]

[a] C^{14}-activities determined with a windowless methane-filled counter ("Nucleometer") with standard deviations; corrected for background, self-absorption and dilution by non-labeled carbon atoms and expressed in dis./min./mg. of barium carbonate. The samples were of "infinite" thickness, had cross-sectional areas of 2.90 cm.^{2} and were prepared as described by J. D. Roberts, W. Bennett, E. W. Holroyd and C. H. Fugitt, *Anal. Chem.*, 20, 904 (1948). The methods of calculation of the activities are described in ref. 3. [b] % Rearrangement = [Activity of 2-butanol − activity of CBr_4)/activity of 2-butanol] × 100. [c] Acetic acid containing 1% acetic anhydride. [d] Activity of 2-butanol. [e] Activity of 2-butyl N-phenylcarbamate prepared from the 2-butanol. [f] Calculated using the average activity of the 2-butanol and the N-phenylcarbamate. [g] Activity of the 2-butanol obtained by hydrolysis in water-acetone of the unreacted p-toluenesulfonate after two half-lives. [h] % Rearrangement of the p-toluenesulfonate over two half-lives of the solvolysis reaction. [i] Concentration of butene mixture with activity of 308 ± 6 counts/min./mg. of barium carbonate present in reaction medium. [j] Concentration of non-labeled 2-butyl acetate in reaction medium. [k] Activity of 2-butanol obtained from the hydrolysis of the recovered 2-butyl acetate. [l] % of labeled butene which was converted to 2-butyl acetate by reaction with acetic acid. [m] 25%–75% acetone. [n] This figure may be slightly high due to the presence of a small amount of acetone in the 2-butanol.

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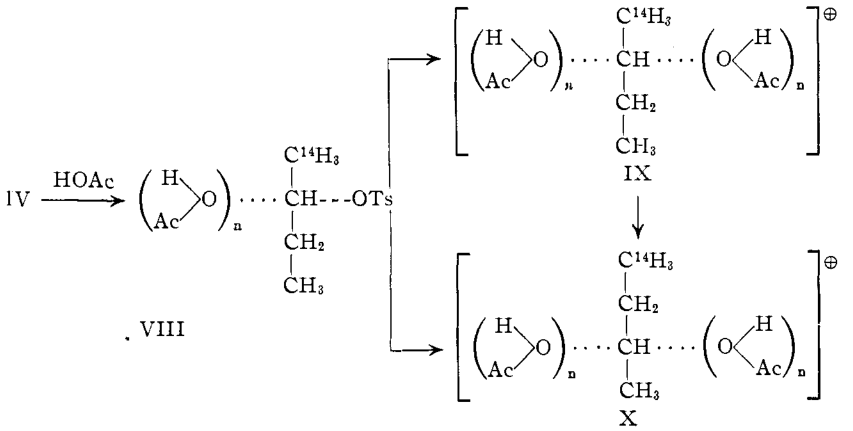
(8) The methyl-C^{14} iodide was obtained from Tracerlab, Inc., on allocation from the United States Atomic Energy Commission.

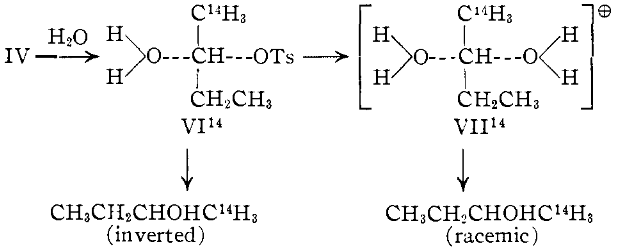
(9) (a) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951); (b) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); (c) S. Winstein and co-workers, *ibid.*, **70**, 812, 816, 821, 839 (1948), and earlier papers.

(10) The procedures were similar to those used previously, J. D. Roberts, W. G. Young and S. Winstein, *ibid.*, **64**, 2157 (1942); J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

where the reaction proceeded about 95% by first-order kinetics, the amount of rearrangement was 9% which corresponds to 9% of formation of II or 18% of III. As would be expected from the rarity of carbon skeleton rearrangements in bimolecular displacement reactions of saturated halides, the amount of rearrangement drops somewhat at 0.46 *M* acetate ion under conditions where 81% of the reaction is first-order. Quantitative comparison of the results at different acetate concentrations is difficult since it is not certain how much of the 19% second-order reaction at 0.46 *M* acetate ion yielded butenes. The acetolysis rearrangement is unlikely to be due to isomerization of the final product, 2-butyl acetate, since norbornyl-2,3-C$_2^{14}$ acetate, which is expected to be considerably more labile, does not rearrange significantly with comparable salt concentrations in refluxing acetic acid.[11] The rearrangement cannot be due to the type of "internal return" isomerization process postulated by Trifan and Winstein[12] for the racemization of *exo*-norbornyl p-bromobenzenesulfonate, which might convert IV into the isomeric 2-butyl-4-C^{14} p-toluenesulfonate (V), since the unreacted labeled 2-butyl p-toluenesulfonate isolated from the reaction mixture containing 0.10 *M* acetate ion after two half-lives on hydrolysis in aqueous acetone actually gave slightly less-rearranged 2-butanol than was found in the corresponding hydrolysis of IV. Furthermore, the rearrangement on acetolysis does not result by formation of 2-butene and subsequent addition of acetic acid since no measurable amount of labeled 2-butyl acetate was formed under the solvolysis conditions from a C^{14}-containing butene mixture at a concentration several-fold greater than was present in the solvolysis of IV. Considerably less rearrangement was observed in the hydrolysis of IV in 25% water–75% acetone than in the acetolysis reactions.



The present results agree well with the conclusions of Winstein, Grunwald and Jones[9a] as to the mechanism of solvolysis of isopropyl halides and arylsulfonates in good-ionizing solvents possessing different degrees of nucleophilic character. In a medium like 25% water–75% acetone, solvolysis of IV (here considered as a single stereoisomer) would be expected to proceed through a transition state in which a water molecule (or molecules) would be substantially covalently bonded to the backside of the carbon undergoing displacement. The first intermediate (VI) may then collapse giving inverted, unrearranged product or partially proceed to a symmetrically solvated intermediate (VII) which would give racemic, unrearranged product. Apparently the degrees of covalent bonding in VI and VII are at all times sufficient to preclude substantial rearrangement. The importance of VII is indicated by the partial racemization accompanying the solvolysis of *s*-alkyl derivatives in aqueous solvents.[9a,13]



In acetic acid, the degree of covalent bonding involving solvent in the transition state and the first intermediate (VIII) is expected to be considerably less than in aqueous media and VIII, besides yielding inverted, unrearranged acetate has more of an opportunity to be converted to symmetrically solvated IX[15] or X by a 1,2-hydride shift.[4] IX like VII would give racemic, unrearranged acetate while X would yield racemic, rearranged product.[16]

X is probably formed from VIII or IX by way of III; however, because of the low tendency for rearrangement, it is doubtful that III is an important intermediate of comparable or greater stability to IX or X (I or II) and the situation seems described by the top curve of Fig. 1.[17] It is interesting to contrast the solvolysis of IV with the corresponding reactions of secondary derivatives where the non-classical cations appear to be particularly stable. Thus, with *endo*-norbornyl derivatives, even though a non-classical cation analogous to III cannot be

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(11) Unpublished experiments by Dr. C. C. Lee; *cf.* J. D. Roberts and C. C. Lee, THIS JOURNAL, **73**, 5009 (1951).

(12) D. S. Trifan and S. Winstein, Abstracts of the 119th Meeting of the American Chemical Society, April, 1951, p. 53M. An example of this type of process yielding products with rearrangement of carbon skeleton is afforded by J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

(13) E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 1196 (1937).

(14) For economy of representation, the water molecules which solvate VI and VII have been omitted.

(15) IX and X are essentially equivalent to I and II, respectively, solvated by acetic acid.

(16) The reasoning leads to prediction of more racemization in the solvolysis of optically-active 2-butyl derivatives in acetic acid than in aqueous acetone. Our projected investigation of this point was abandoned when we learned that Professor S. Winstein and his co-workers were already engaged in a critical scrutiny of the stereochemistry of the solvolysis of 2-butyl derivatives.

(17) Similar conclusions have been reached by Bartlett and Lefferts in a study of the interconversion of cyclohexyldimethylcarbinyl and α-isopropylcyclohexyl derivatives; P. D. Bartlett, paper presented at the Organic Symposium at Denver, June, 1951.

formed directly in the rate-determining step, very extensive rearrangement is noted even in aqueous acetone.[11]

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Experimental

2-Butanol-1-C^{14} and 2-Butyl-1-C^{14} *p*-Toluenesulfonate.—To a stirred Dry Ice-cooled solution of methyl-C^{14}-magnesium iodide in 300 ml. of ether prepared from 26 g. (0.18 mole) of methyl-C^{14} iodide[8] and 5.0 g. (0.21 gram-atom) of magnesium turnings was added slowly 10.2 g. (0.18 mole) of freshly-distilled propionaldehyde. The mixture was brought to 0° and 30 ml. of saturated solution of ammonium chloride added dropwise. The ethereal layer was siphoned off and the salt cake washed with three 100-ml. portions of fresh ether. The combined extracts were dried over calcium sulfate, filtered and the ether removed through a glass-helix packed column. The residue was fractionated through an efficient center-tube column[18] and yielded, besides 0.5 g. of forerun, b.p. 98.5–100.3°, 6.89 g. (53%) of 2-butanol-1-C^{14}, b.p. 100.3–100.5° (uncor.). The product had an activity of 16,090 ± 90 dis./min./mg. of barium carbonate.

In 500-ml. three-necked flask equipped with stirrer, reflux condenser and dropping funnel was placed 2.0 g. (0.086 mole) of sodium hydride and 50 ml. of dry ether. A nitrogen atmosphere was maintained and 4.9 g. (0.066 mole) of 2-butanol-1-C^{14} dissolved in 20 ml. of ether was added. The mixture was refluxed for six hours, allowed to stand overnight and then treated dropwise with an ethereal solution of 11.4 g. (0.060 mole) of *p*-toluenesulfonyl chloride. After the addition was complete, the mixture was refluxed for 30 min. and 40 ml. of water added cautiously. The ethereal layer was separated, washed with 10% sodium carbonate solution and dried over a mixture of magnesium sulfate and potassium carbonate. The ether was removed under reduced pressure and the residue transferred to the boiler of a molecular still containing 1 g. of anhydrous potassium carbonate. The 2-butyl-1-C^{14} *p*-toluenesulfonate distilled at 3 microns with a bath temperature of 59–61°; the yield was 9.9 g. (72%). The product was shown to be free of *p*-toluenesulfonyl chloride by lack of reaction with alcoholic silver nitrate. The C^{14}-activity was 15,290 ± 88 dis./min./mg. of barium carbonate.

The rate runs with this material were carried out as described earlier.[10]

Acetolysis of 2-Butyl-1-C^{14} *p*-Toluenesulfonate.—The details of a single typical experiment will be given. 2-Butyl-1-C^{14} *p*-toluenesulfonate (2.23 g., 0.010 mole) was dissolved in 100 ml. of an acetic acid stock solution (used also for the rate runs) containing 0.100 *M* potassium acetate, 0.89 *M* potassium *p*-toluenesulfonate and 1% of acetic anhydride and the mixture heated at 65° for 24 hours. The acetic acid was then neutralized with strong potassium hydroxide solution and about 0.2 mole of excess potassium hydroxide added. Water was run in until the salts dissolved and the mixture was heated at 100° for six hours. Unlabeled, redistilled 2-butanol (5.0 g.) was added as a carrier and the mixture extracted continuously with ether for six hours. The ether extract was dried over magnesium sulfate, the ether removed through a glass helix-packed column and the residue fractionated through a center-tube column.[18] The yield of 2-butanol of b.p. 100.0–101.0° (uncor.) was 1.74 g.

Hydrolysis of 2-Butyl-1-C^{14} *p*-Toluenesulfonate.—A solution of 1.715 g. (0.0075 mole) of 2-butyl-1-C^{14} *p*-toluenesulfonate in 50 ml. of 25% water–75% acetone was heated in a sealed tube at 65° for 26 hours. The mixture was cooled, 10.00 g. of unlabeled redistilled 2-butanol added as a carrier and the *p*-toluenesulfonic acid neutralized with sodium hydroxide solution. The solution was saturated with sodium chloride and extracted continuously with ether for 60 hours. The extract was dried over magnesium sulfate, the ether removed through a stainless-steel helix-packed column and the residue fractionated through a center-tube column.[18] The yield of 2-butanol of b.p. 100.5–101.0° (uncor.) was 4.9 g. The C^{14}-activity of this material was 636 dis./min./mg. of barium carbonate while that of the sulfonate ester was 15,290. The amount of 2-butanol formed in the hydrolysis was thus 0.434 g. (77%). The balance of the reaction product was presumed to be butene.

Degradation Procedure for 2-Butanol.—A typical experiment is described. Labeled 2-butanol (0.62 ml., 0.5 g.) in 5 ml. of water was added to a stirred solution maintained below 10° of sodium hypobromite prepared by dissolving 4.3 g. of bromine in 6 ml. of clear saturated sodium hydroxide solution diluted with 20 ml. of boiled water. The mixture was kept at 10° or below for 6 hours and then steam distilled. The carbon tetrabromide in the steam distillate was collected by filtration and purified by sublimation at 55° (2 mm.). The yield was 0.13 g.

Investigation of the Rearrangement of 2-Butyl-1-C^{14} *p*-Toluenesulfonate during the Acetolysis Reaction.—2-Butyl-1-C^{14} *p*-toluenesulfonate (3.015 g.) was dissolved in 75 ml. of acetic acid solution containing 0.100 *M* potassium acetate, 0.89 *M* potassium *p*-toluenesulfonate and 1% acetic anhydride and the mixture was heated to 65° for 3.0 hours (two half-lives). The stirred mixture was cooled in an ice-bath and carefully neutralized with potassium hydroxide solution. The salts were dissolved by addition of cold water and 1.02 g. of carrier unlabeled 2-butyl *p*-toluenesulfonate added. The mixture was extracted continuously for 17 hours with ether. At the start of the extraction, the extraction flask was ice-cooled. The extract was dried over magnesium sulfate and the bulk of the ether distilled. The residue was placed under reduced pressure to remove any 2-butanol which was present and finally degassed at one micron for an hour with a mercury vapor pump.

The crude residual 2-butyl *p*-toluenesulfonate was hydrolyzed with 10 ml. of 25% water–75% acetone at 65° for 18 hours. The mixture was neutralized with potassium carbonate and extracted with ether. The extract was dried over magnesium sulfate and the ether removed. The residue on fractionation yielded 0.95 g. of 2-butanol, b.p. 98–99°, after 0.1 g. of forerun, b.p. 87–98°. The activity data are given in Table II.

Investigation of the Reaction of C^{14}-Labeled Butenes with Acetic Acid.—2-Butanol-1-C^{14} (5.0 g., C^{14}-activity of 308 dis./min./mg. of barium carbonate) was dehydrated by heating with 15 ml. of water and 20 ml. of concd. sulfuric acid.[19] The resulting butenes were passed through 10% sodium hydroxide solution, 50% sulfuric acid, a Drierite tube and finally condensed in a Dry Ice-cooled trap. The yield was 2 g. (50%). The butenes were then transferred by distillation into a Dry Ice-cooled heavy-walled glass tube equipped with a pressure stopcock and containing 3.65 g. of unlabeled 2-butyl acetate and 50 ml. of the acetic acid stock solution used in the preceding experiment. The mixture was cooled with liquid nitrogen and degassed by evacuation with an oil pump. The pump was disconnected, the mixture warmed to room temperature then cooled with liquid nitrogen and degassed again. The cycle was repeated and the mixture then heated at 65° for 24 hours. The solution was cooled, just neutralized with potassium hydroxide solution and continuously extracted with ether. The ethereal solution was dried over calcium chloride and the ether distilled through a glass-helix packed column. The residue was fractionated through a center tube column and yielded 1.0 g. of 2-butyl acetate, b.p. 113.5°, $n^{25}D$ 1.3860. The C^{14}-activity of this material was equal to background within experimental error and showed that no detectable addition of acetic acid to butenes occurs under these conditions.

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[18] The fractionating section of this column was similar to that described by E. A. Naragon and C. E. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **18**, 448 (1946).

[19] C. E. Wilson and H. J. Lucas, THIS JOURNAL, **58**, 2396 (1936), report that with 1-butanol these conditions give 68% *trans*- and 32% *cis*-2-butene.