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Registry No.—**10** bisulfate, 32066-79-8; **11**, 106-44-5; **12**, 5428-54-6; **13** BF_4, 1427-01-6; **13** HSO_4, 62058-61-1; **15**, 13073-29-5; **16** BF_4, 54616-48-7; **21** BF_4, 62058-63-3; *p*-toluidine, 106-49-0; 5-nitro-2-methylaniline, 99-55-8; 2-methyl-6-nitroaniline, 570-24-1; fluoroboric acid, 16872-11-0; 7-nitro-1*H*-indazole, 2942-42-9; *o*-amino-*N*,*N*-dimethylbenzamide, 6526-66-5; *o*-nitro-*N*,*N*-dimethylbenzamide, 2018-71-5; *cis*-2-nitrostilbene, 52208-62-5; *trans*-o-nitro-α-phenylcinnamic acid, 19319-35-8; *cis*-2-aminostilbene, 62058-64-4.

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Protonated Cyclopropanes. 9. Protonated Methylcyclopropane Intermediates in the Trifluoroacetolysis of 1-Butyl-*1*-^{14}C-mercuric Perchlorate

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The trifluoroacetolysis of 1-butyl-*1*-^{14}C-mercuric perchlorate was carried out at 35, 50, and 72 °C. At 35 °C, ^{14}C was scrambled only between C-1 and C-4 in the major 2-butyl product and there was no isotopic scrambling in the minor 1-butyl product. At 50 or 72 °C, all four isomeric butyl products were obtained. In the major product, 2-butyl-^{14}C trifluoroacetate, the label was scrambled over all four carbon positions. There was a small amount of ^{14}C scrambling from C-1 to C-2 in the 1-butyl product, while in the isobutyl ester, a 50:50 split of the label between C-1 and the rest of the molecule was observed. These results indicated that at 35 °C, the only scrambling processes were successive 1,2-hydride shifts involving classical 1-butyl and 2-butyl cations. At 50 or 72 °C, however, the scrambling data could be explained only by invoking some involvement (about 8–14%) of equilibrating protonated methylcyclopropanes in the overall reaction.

Work on protonated cyclopropanes has been the subject of a number of reviews,[1] and much of the evidence implicating such species as reaction intermediates has been derived from studies using isotopes as labels. In contrast to the unsubstituted protonated cyclopropane intermediates, definitive evidence from isotopic scrambling for protonated methylcyclopropane has been rather limited. Deno et al.[2] have reported that according to NMR studies, the addition of DCl to

Table I. Yields (%) of Isomeric Butyl Alcohols Derived from the Ester Products in the Trifluoroacetolysis of 1-Butyl-*1*-^{14}C-mercuric Perchlorate as Determined by Isotopic Dilution Calculations

Reaction conditions	1-BuOH		2-BuOH		*i*-BuOH		*t*-BuOH	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
35 °C, 10 days	2.5	2.4	26.8	26.5	Trace	Trace	0	0
50 °C, 4 days	3.0	3.2	63.5	59.5	2.5	2.8	0.1	0.1
72 °C, 1 h	2.8	2.7	51.0	50.7	0.4	0.4	0.9	0.9

methylcyclopropane (1) gave only $CH_3CHClCH_2CH_2D$, and it was suggested that addition of D^+ to 1 gave rise to the 2-butyl cation either directly or via a short-lived, nonisomerizing protonated methylcyclopropane. On the other hand, Deno and Billup[3] noted that the ionic addition of Cl_2 to 1 gave a mixture of 1,3-, 1,2-, and 2,3-dichlorobutanes which were interpreted as arising, at least partially, from protonated methylcyclopropane intermediates.

From the mass spectral analysis and NMR examination of the alcohols derived from the aqueous acid deamination of a number of D-labeled 1-butyl- and isobutylamines, Karabatsos, Meyerson, and co-workers[4] failed to obtain any scrambling data in support of protonated methylcyclopropanes as important intermediates. It was stated, however, that this did not exclude a minor degree of intervention by such intermediates, since small extents of rearrangements might be within the experimental errors of the method of measurement. Small amounts of 1 were detected among the products from these reactions, and it was concluded that the only evidence for the intermediacy of protonated methylcyclopropane in aqueous acid deamination of 1-butylamine or isobutylamine was the formation of 1.

Considerably greater amounts of 1 were observed among the hydrocarbon products by Friedman et al.[5] from the deamination of 1-butyl- and isobutylamines under aprotic conditions. The D contents of 1 from the diazotization of several D-labeled isobutyl- and 2-butylamines in protic and aprotic solvents also led to the conclusion that a minor amount of the methylcyclopropane (1) did arise via partially equilibrated protonated methylcyclopropanes.[5c] In superacids, extensive scramblings via protonated methylcyclopropanes have been proposed. Thus the scrambling of all the protons in the 2-butyl cation observed by NMR in SbF_5–SO_2ClF solution,[1e,6] and the HF–SbF_5 catalyzed isomerization of butane-*1*-^{13}C to butane-*2*-^{13}C,[7] have been interpreted as proceeding via protonated methylcyclopropane intermediates.

Lee and Zea Ponce[8] have reported the observation of extensive and complex rearrangements when 1-butyl-*1*-^{14}C chloride was treated with $AlCl_3$, but no definitive evidence for protonated methylcyclopropanes could be deduced. Support for equilibrating protonated methylcyclopropane intermediates was obtained in the trifluoroacetolysis of 1-butyl-*1*-^{14}C tosylate (2-OTs-*1*-^{14}C).[9] The 2-butyl product from this reaction was found to contain some of the ^{14}C label in all four carbon positions. Since 1,2-hydride shifts in the 2-butyl cation would only scramble the label over C-1 and C-4, and after eliminating a mechanism solely involving 1,2 shifts in classical ions, it was proposed[9] that a minor pathway involving equilibrating protonated methylcyclopropane intermediates could account for the overall ^{14}C distribution in the 2-butyl product. In the same investigation,[9] it was also found that the trifluoroacetolysis of 1-propyl-*1*-^{14}C-mercuric perchlorate gave a 1-propyl product with more of the label scrambled to C-3 than C-2. This result agreed with the prediction of Collins[1a] for product formation from equilibrating edge-protonated cyclopropane intermediates. Even if corner-protonated cyclopropane were more stable than the edge-protonated species,[1e,10] the observed result could arise from kinetically controlled processes. In the trifluoroacetolysis of $RHgClO_4$, since the loss of Hg^0 from RHg^+ gave no counterion for ion pair formation, and since the low nucleophilic character of CF_3COOH would render the solvent poorly solvating, it was suggested[9] that the carbocation formed in such a reaction more likely would give rise to a kinetically controlled rather than a thermodynamically controlled product. In the present work, the trifluoroacetolysis of 2-OTs-*1*-^{14}C was extended to include a study on the trifluoroacetolysis of 1-butyl-*1*-^{14}C-mercuric perchlorate (2-$HgClO_4$-*1*-^{14}C) in an attempt to obtain further scrambling data in support of protonated methylcyclopropane intermediates.

Results

1-Butyl-*1*-^{14}C-mercuric acetate (2-HgOAc-*1*-^{14}C) was prepared by the method of Ouellette,[11] which involved the conversion of 2-Cl-*1*-^{14}C[8] to the Grignard reagent, followed by reaction with $HgCl_2$ to give 2-HgCl-*1*-^{14}C and then treatment with AgOAc to give 2-HgOAc-*1*-^{14}C. As was done in the preparation of 1-propyl-*1*-^{14}C-mercuric acetate,[12] the 2-HgOAc-*1*-^{14}C was hydrolyzed in aqueous dioxane containing NaOH to give 1-butyl-*1*-^{14}C alcohol (2-OH-*1*-^{14}C), the degradation of which showed that all of the ^{14}C label was located at C-1.

The solvolytic demercuration reaction is generally carried out by treatment of RHgOAc in the appropriate solvent in the presence of $HClO_4$.[13] The present solvolysis studies were effected by treating 2-HgOAc-*1*-^{14}C in CF_3COOH in the presence of $HClO_4$ at 35 °C for 10 days, at 50 °C for 4 days, and at 72 °C (the reflux temperature) for 1 h. The various reaction times were chosen so as to give about the maximum yield of the major product, 2-butyl trifluoroacetate (3-$OAcF_3$). These reaction times were determined in preliminary experiments by NMR examination of the reaction mixture using nonlabeled 2-HgOAc. At 35 and 50 °C, reaction times longer than 10 and 4 days, respectively, gave only very slight increases in yields of 3-$OAcF_3$, while at 72 °C, reaction times longer than 1 h caused a sharp decrease in yield, presumably because of decomposition. In the experiments with active 2-HgOAc-*1*-^{14}C, the isomeric butyl ester products were hydrolyzed directly to give a mixture of the isomeric butyl alcohols (1-butyl-^{14}C, 2-butyl-^{14}C, isobutyl-^{14}C, and *tert*-butyl-^{14}C alcohols, 2-OH-^{14}C, 3-OH-^{14}C, 4-OH-^{14}C, and 5-OH-^{14}C, respectively). The yields of these alcohols were determined by isotopic dilution,[8,9] and the results are given in Table I.

After the separation of the isomeric butyl alcohols by preparative VPC in the isotopic dilution experiments, additional carriers were added to 2-OH-^{14}C, 3-OH-^{14}C, and 4-OH-^{14}C and these three alcohols were then degraded in order to give the ^{14}C distributions. Degradations of 2-OH-^{14}C and 3-OH-^{14}C were carried out as previously described,[8,9] involving the conversion of 2-OH-^{14}C to butyric acid, propylamine, propionic acid, and acetic acid, and the conversion of 3-OH-^{14}C to CBr_4 and propionic acid, and the latter in turn was converted to acetic acid and methylamine. 4-OH-^{14}C, which was not degraded in the previous studies,[8,9] was oxidized to isobutyric acid and then converted to isopropylamine. The relevant ac-

Table II. ^{14}C Distributions in the 1-Butyl-^{14}C Alcohol (2-OH-^{14}C) Derived from the Trifluoroacetolysis of 1-Butyl-*1*-^{14}C-mercuric Perchlorate

Reaction conditions		Specific activity, dpm/mmol[a]			^{14}C distribution, %		
		1-BuOH[b]	CH_3CH_2COOH[c]	CH_3COOH[c]	C-1	C-2	C-3,4
35 °C, 10 days	Run 1	32 700	0	0	100	0	0
	Run 2	39 400	0	0	100	0	0
50 °C, 4 days	Run 1	61 800	2530	0	95.9	4.1	0
	Run 2	56 500	2330	0	95.9	4.0	0
72 °C, 1 h	Run 1	39 800	917	0	97.7	2.3	0
	Run 2	42 400	1020	0	97.6	2.4	0

[a] ^{14}C activities in this and other tables were measured by a liquid scintillation counter. Statistical counting errors were ±1% or less. [b] Assayed as the α-naphthylurethane. [c] Assayed as the *S*-benzylisothiouronium salt.

Table III. ^{14}C Distribution in the 2-Butyl-^{14}C Alcohol (3-OH-^{14}C) Derived from the Trifluoroacetolysis of 1-Butyl-*1*-^{14}C-mercuric Perchlorate

Reaction conditions		Specific activity, dpm/mmol					^{14}C distribution, %			
		2-BuOH[a]	CBr_4	CH_3CH_2COOH[b]	CH_3COOH[b]	CH_3NH_2[c]	C-1	C-2	C-3	C-4
35 °C, 10 days	Run 1	382 000	241 000	141 000	141 000	141 000	63.1	0	0	36.9
	Run 2	449 000	274 000	175 000	175 000	175 000	61.0	0	0	39.0
50 °C, 4 days	Run 1	843 000	504 000	339 000	336 000	278 000	59.8	0.3	6.9	33.0
	Run 2	906 000	544 000	362 000	359 000	295 000	60.1	0.3	6.9	32.6
72 °C, 1 h	Run 1	664 000	335 000	329 000	318 000	303 000	50.5	1.7	2.3	45.6
	Run 2	690 000	348 000	342 000	331 000	316 000	50.4	1.6	2.3	45.8

[a] Assayed as the α-naphthylurethane. [b] Assayed as the *S*-benzylisothiouronium salt. [c] Assayed as the *p*-toluenesulfonamide.

Table IV. ^{14}C Distribution in the Isobutyl-^{14}C Alcohol (4-OH-^{14}C) Derived from the Trifluoroacetolysis of 1-Butyl-*1*-^{14}C-mercuric Perchlorate

Reaction conditions		Specific activity, dpm/mmol		^{14}C distribution, %	
		i-BuOH[a]	$(CH_3)_2CHNH_2$[b]	C-1	Rest of molecule
50 °C, 4 days	Run 1	44 900	21 200	52.6	47.4
	Run 2	45 700	22 900	49.8	50.1
72 °C, 1 h	Run 1	6 770	3 460	48.9	51.1
	Run 2	7 510	3 810	49.3	50.7

[a] Assayed as the α-naphthylurethane. [b] Assayed as the *p*-toluenesulfonamide.

tivity data and the ^{14}C distributions are summarized in Tables II–IV.

Discussion

Hydrolysis of the products from the trifluoroacetolysis of 2-$HgClO_4$-*1*-^{14}C at 35 °C for 10 days gave 2-butyl-^{14}C alcohol (3-OH-^{14}C) as the major product, with a minor amount of 1-butyl-^{14}C alcohol (2-OH-^{14}C) and essentially no isobutyl and *tert*-butyl alcohols (Table I). The 2-OH-^{14}C was the isotopically unrearranged 2-OH-*1*-^{14}C (Table II), while in the 3-OH-^{14}C, the label was scrambled only between C-1 and C-4 (Table III). These results indicate no involvement of protonated methylcyclopropane in the reaction at 35 °C. The unrearranged 2-OH-*1*-^{14}C could be derived from a direct displacement and/or the trapping of the 1-butyl-*1*-^{14}C cation from the demercuration of 2-Hg^+-*1*-^{14}C. Successive 1,2-hydride shifts involving only classical butyl cations also would account for the scrambling of ^{14}C over C-1 and C-4 in the 2-butyl product (Scheme I). The fact that more 2-butyl-*1*-^{14}C than 2-butyl-*4*-^{14}C product was formed would suggest that under the reaction conditions employed, trapping of the 2-butyl cation to give product was more rapid than the 1,2-hydride shifts that interconverted the degenerate 2-butyl cations.

Scheme I

$$CH_3CH_2CH_2{}^{14}CH_2^+ \longrightarrow CH_3CH_2\overset{+}{C}H{}^{14}CH_3 \rightleftharpoons CH_3\overset{+}{C}HCH_2{}^{14}CH_3$$

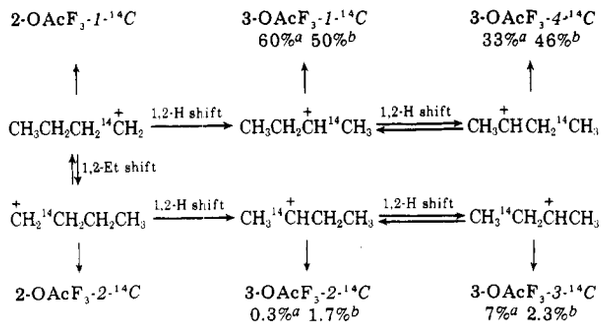
$$\downarrow \qquad\qquad \downarrow$$

3-$OAcF_3$-*1*-^{14}C (62%) 3-$OAcF_3$-*4*-^{14}C (38%)

From the reaction at 50 °C for 4 days or at 72 °C for 1 h, all four isomeric butyl products were detected (Table I) and scramblings of the label were more extensive. In the major 2-butyl product, ^{14}C was found in all four carbon positions (Table III), while in the 1-butyl product, there was some scrambling to C-2 (Table II). As discussed in previous studies,[8,9] if one were to invoke only classical ions to explain these results, the processes depicted in Scheme II may be proposed. Since the 2-butyl-*1*-^{14}C cation and the 2-butyl-*2*-^{14}C cation differ only in the position of the label, one would expect these ions to give the same subsequent reactions. Thus according to Scheme II, the ratio of 3-$OAcF_3$-*4*-^{14}C/3-$OAcF_3$-*1*-^{14}C should be equal to the ratio of 3-$OAcF_3$-*3*-^{14}C/3-$OAcF_3$-*2*-^{14}C. Clearly this is not the case since 33/60 and 7/0.3, or 46/50 and 2.2/1.7, are not equal. Scheme II, involving only classical ions, therefore, is not adequate in accounting for the scrambling results.

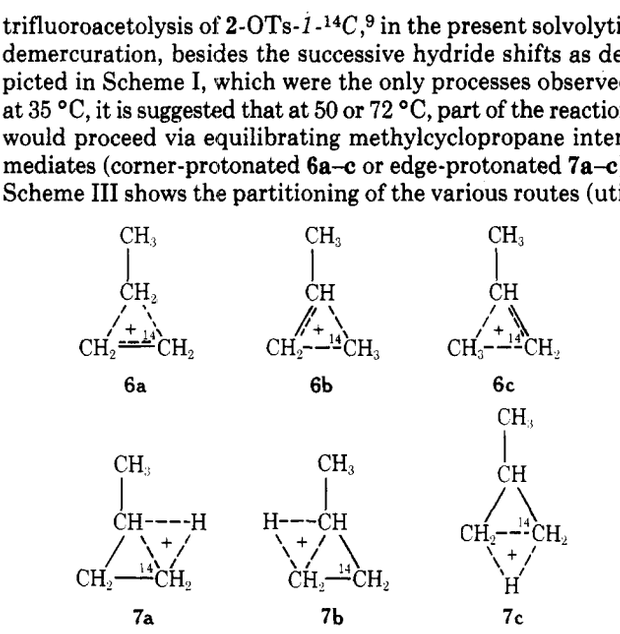
In order to scramble the ^{14}C label to the C-2 and C-3 positions of the 2-butyl product, as an alternative to the 1,2-ethyl shift, equilibrating protonated methylcyclopropanes could be involved. Analogous to the mechanism proposed for the

Scheme II

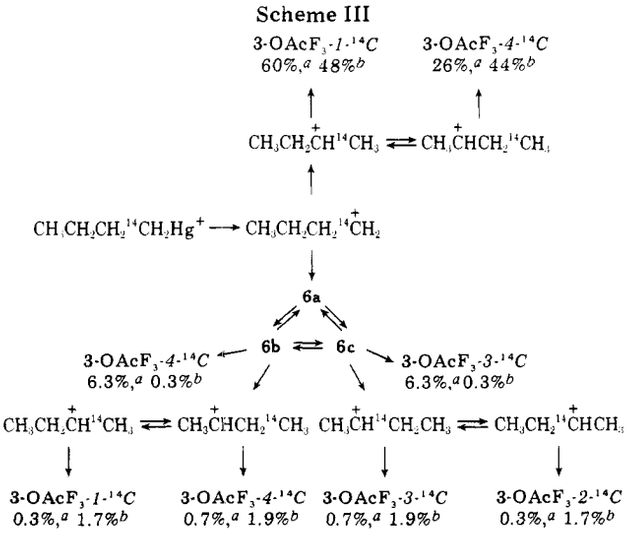


[a] Mean values from Table III for reaction at 50 °C for 4 days. [b] Mean values from Table III for reaction at 72 °C for 1 h.

trifluoroacetolysis of 2-OTs-*1*-^{14}C,[9] in the present solvolytic demercuration, besides the successive hydride shifts as depicted in Scheme I, which were the only processes observed at 35 °C, it is suggested that at 50 or 72 °C, part of the reaction would proceed via equilibrating methylcyclopropane intermediates (corner-protonated **6a–c** or edge-protonated **7a–c**). Scheme III shows the partitioning of the various routes (utilizing corner-protonated **6a–c**) leading to the ^{14}C scrambling in the 2-butyl product, 3-OAcF$_3$-^{14}C. In this scheme it is proposed that **6b** and **6c** could give the 2-butyl ester without further scrambling, or give rise to the more stable 2-butyl cation which subsequently would undergo degenerate hydride shifts. Moreover, in the various routes leading to 3-OAcF$_3$-^{14}C, the equality of the product ratios derived from equilibrating degenerate 2-butyl cations was maintained (26/60 = 0.3/0.7 at 50 °C and 44/48 = 1.7/1.9 at 72 °C). The net ^{14}C contents would be 60 + 0.3, 0.3, 6.3 + 0.7, and 26 + 6.3 + 0.7, or 60, 0.3, 7.0, and 33%, respectively, at C-1, C-2, C-3, and C-4 for the reaction at 50 °C; and 48 + 1.7, 1.7, 0.3 + 1.9, and 44 + 0.3 + 1.9, or 50, 1.7, 2.2, and 46%, respectively, at C-1, C-2, C-3, and C-4 for the reaction at 72 °C. These calculated ^{14}C distributions are in good agreement with the mean observed values recorded in Table III.



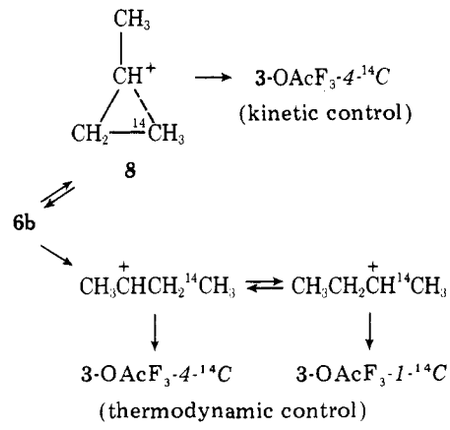
Scheme III



[a] Reaction at 50 °C for 4 days. [b] Reaction at 72 °C for 1 h.

According to Scheme III, at 50 °C, there was more 2-butyl ester formation from **6b** or **6c** without further scrambling (6.3%) than the formation of 2-butyl cation which subsequently could undergo degenerate hydride shifts (0.7 + 0.3%), while at 72 °C, the reverse was true (0.3% and 1.9 + 1.7%). These findings could be rationalized by the assumption that the more stable 2-butyl cation was formed under thermodynamic control, and at 50 °C protonated methylcyclopropanes gave rise to more kinetically controlled product. A possible formulation of such processes could be as illustrated for **6b** in Scheme IV, utilizing a partially bridged ion **8**. Calculations for

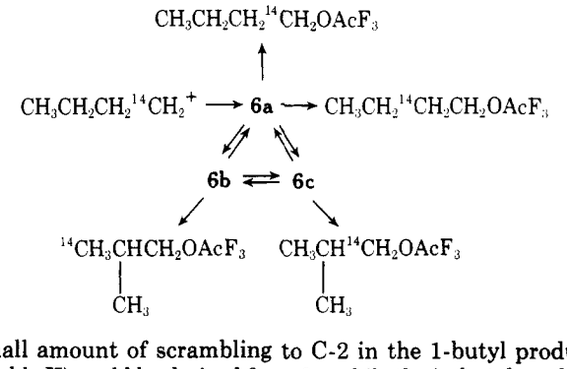
Scheme IV



the unsubstituted protonated cyclopropane intermediates indicated that a partially bridged ion analogous to **8** is of comparable stability to corner-protonated cyclopropane.[10] Thus at 50 °C, more kinetically controlled product was formed from **6b** via **8**, while at 72 °C, more thermodynamically controlled product derived from the degenerate 2-butyl cations was obtained. It is also of interest to note that, as expected, there were more extensive degenerate hydride shifts in the 2-butyl cation at 72 °C (44/48 and 1.7/1.9) than at 50 °C (26/60 and 0.3/0.7).

Equilibrating protonated methylcyclopropanes could also account for the isotopic scramblings observed in the minor products given in Tables II and IV. As shown in Scheme V, the small amount of scrambling to C-2 in the 1-butyl product (Table II) could be derived from **6a**, while the isobutyl product derived from **6b** and **6c** would result in a 50% scrambling of the label between C-1 and the rest of the molecule, and this was as observed (Table IV). The minor amounts of *tert*-butyl product, as recorded in Table I, presumably was derived from

Scheme V



the facile rearrangement of the isobutyl to the *tert*-butyl cation. Interestingly, reaction at 50 °C, which favored kinetic control of product formation from protonated methylcyclopropanes, gave only 0.1% *t*-BuOH compared to 2.5–2.8% *i*-BuOH, while in the reaction at 72 °C, which was more favorable to thermodynamic control, 0.9% *t*-BuOH compared to 0.4% *i*-BuOH was obtained (Table I). From these considerations and from the discussion on the ^{14}C scrambling processes leading to the 2-butyl product, the conclusion may be made that the present data gave support to some involvement of equilibrating protonated methylcyclopropanes in the trifluoroacetolysis of 2-$HgClO_4$-*1*-^{14}C. While the only scrambling processes occurring at 35 °C were successive 1,2-hydride shifts in classical 1-butyl and 2-butyl cations (Scheme I), besides these classical processes, reaction at 50 and 72 °C, respectively, apparently resulted in about 14 and 8% of the overall reaction (Scheme III) proceeding via equilibrating protonated methylcyclopropanes.

Experimental Section

1-Butyl-*1*-^{14}C-mercuric Acetate (2-HgOAc-*1*-^{14}C). Following the method of Ouellette,[11] 1-butyl-*1*-^{14}C chloride (2-Cl-*1*-^{14}C)[8] was converted successively to 2-MgCl-*1*-^{14}C, 2-HgCl-*1*-^{14}C, and 2-HgOAc-*1*-^{14}C, mp 52–53 °C (lit.[11,14] mp 53.8–54.4, 52.5–53.2 °C). Hydrolysis of 2-HgOAc-*1*-^{14}C in 10% dioxane–90% H_2O containing 10% NaOH[12] gave a 40% yield of 2-OH-*1*-^{14}C, which upon oxidation to butyric acid followed by a Schmidt reaction gave 1-propylamine[8] which contained essentially no ^{14}C activity.

Trifluoroacetolysis Reactions. A solution of 5.0 g (16 mmol) of 2-HgOAc-*1*-^{14}C and 3.6 g (25 mmol) of 70% $HClO_4$ in 50 mL of CF_3COOH was placed in a 250-mL flask equipped with a reflux condenser. The material was heated at 35 °C for 10 days, 50 °C for 4 days, or 72 °C for 1 h. After cooling, the reaction mixture was neutralized with 25% NaOH solution. After the addition of a further 60 mL of 25% NaOH solution, the mixture was heated under reflux overnight to hydrolyze the ester products. Ordinary 1-butyl, 2-butyl, isobutyl, and *tert*-butyl alcohols (2-OH, 3-OH, 4-OH, and 5-OH, respectively) were added as carriers. The mixture of diluted isomeric butyl-^{14}C alcohols were recovered by continuous extraction with ether and then separated and purified by preparative VPC.[8] From the known amount of carriers added and their specific activities before and after dilution, the yields of the four isomeric butyl alcohols (Table I) were calculated as previously described.[8]

The recovered 2-OH-^{14}C, 3-OH-^{14}C, and 4-OH-^{14}C were further diluted with appropriate amounts of inactive carriers before being subjected to degradation.

Degradation of the Butyl Alcohols. The degradation of 2-OH-^{14}C and 3-OH-^{14}C were carried out as described in previous work.[8,9] 4-OH-^{14}C was oxidized to isobutyric acid by $KMnO_4$ in Na_2CO_3 solution.[15] The isobutyric acid was converted to isopropylamine by the Schmidt reaction analogous to the conversion of butyric acid to 1-propylamine.[8]

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Registry No.—2-HgOAc-*1*-^{14}C, 61990-71-4; 2-$HgClO_4$-*1*-^{14}C, 61990-72-5; 2-OH-*1*-^{14}C, 61990-73-6; 2-OH-*2*-^{14}C, 19836-38-5; 2-$OAcF_3$-*1*-^{14}C, 61990-74-7; 2-$OAcF_3$-*2*-^{14}C, 61990-75-8; 3-OH-*1*-^{14}C, 61990-76-9; 3-OH-*2*-^{14}C, 61990-77-0; 3-OH-*3*-^{14}C, 61990-78-1; 3-OH-*4*-^{14}C, 61990-79-2; 3-$OAcF_3$-*1*-^{14}C, 61990-80-5; 3-$OAcF_3$-*2*-^{14}C, 61990-81-6; 3-$OAcF_3$-*3*-^{14}C, 61990-82-7; 3-$OAcF_3$-*4*-^{14}C, 61990-83-8; 4-OH-*1*-^{14}C, 41871-35-6; 4-OH-*2*-^{14}C, 61990-84-9; 4-OH-*3*-^{14}C, 19836-37-4; 4-$OAcF_3$-*1*-^{14}C, 61990-85-0; 4-$OAcF_3$-*2*-^{14}C, 61990-86-1; 4-$OAcF_3$-*3*-^{14}C, 61990-87-2; 5-OH, 61990-88-3; 5-$OAcF_3$-^{14}C, 61990-89-4; 6, 61990-90-7.

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