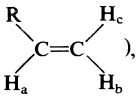
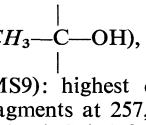
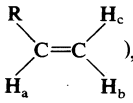
4.15 (1H, quartet, J_{trans} = 17.5 Hz, J_{cis} = 10.5 Hz, H_a in system ), 4.88 (1H, quartet J_{trans} = 17.5 Hz, J_{gem} = 1.5 Hz, H_c), 5.05 (1H, quartet, J_{cis} = 10.5 Hz, J_{gem} = 1.5 Hz, H_b), 5.26 and 5.55 (2H, pair of wide multiplets, exocyclic methylene), 8.57 (singlet, OH, moved to 8.65 when temperature raised from 30 to 50°), 8.79 (), and 9.17–9.36 (CH_3). Mass spectrum (MS9): highest observed fragment at *m/e* 272, major fragments at 257, 204, 189, 161, 137, and 135.

Anal. Calcd. for $C_{20}H_{34}O$: C, 82.69; H, 11.80; O, 5.51. Found: C, 82.20; H, 12.19; O, 5.62.

The mass spectrum did not reveal a molecular ion peak. However, high resolution mass measurement on the *m/e* 272 peak gave the value 272.251. Mol. Wt. Calcd. for $C_{20}H_{32}$: 272.250. This peak therefore corresponds to $M^+ - H_2O$.

The alcohol (227 mg) was reacted with freshly prepared and recrystallized 3,5-dinitrobenzoyl chloride (227 mg) in dry pyridine (3 ml) for 2 days. The pyridine was removed by distillation *in vacuo* and the product recrystallized twice from CH_2Cl_2—MeOH. Needles, m.p. 119–120 °C; $[\alpha]_D^{22}$ (*c*, 1.0, $CHCl_3$) + 36.6°. The n.m.r.: 0.80 (1H, triplet, J = 2.0 Hz, aromatic C_4), 0.88 and 0.90 (2H, singlets, aromatic C_2 and C_6), 3.89 (1H, quartet, J_{trans} = 18 Hz, J_{cis} = 10 Hz, H_a in system ), 4.74 and 4.76 (2H, overlapping multiplets, H_c and H_b), 5.15 and 5.49 (2H, multiplets, exocyclic methylene), 8.27 (3H, singlet,), and 9.12–9.32 (CH_3).

Anal. Calcd. for $C_{27}H_{36}N_2O_6$: C, 66.92; H, 7.49; N, 5.78. Found: C, 66.99; H, 7.60; N, 5.67.

Compounds **1**, **4**, and **5** were first isolated in the course of doctoral thesis work in the Chemistry Department, University of British Columbia.

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Notes 25 (1), 2 (1969).

Protonated cyclopropanes. IV.[1] Trifluoroacetolysis of 1-^{14}C-1-propyl tosylate

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The trifluoroacetolysis of 1-^{14}C-1-propyl tosylate was carried out either with or without the presence of an equivalent of sodium trifluoroacetate. Both 1-propyl and 2-propyl trifluoroacetates were obtained, the latter being the major product if the sodium salt was not present. Isotope position rearrangements from C-1 to C-2 and C-3 were observed in the 1-propyl trifluoroacetate to the extent of about 2 and 17%, respectively, for the reactions effected with and without sodium trifluoroacetate. The rearranged ^{14}C-label was about equally distributed at C-2 and C-3. It is proposed that these rearrangements may be explained on the assumption that part of the overall reaction proceeds through equilibrating protonated cyclopropane intermediates.

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As a part of a general scrutiny of reactions with the 1-propyl system that might involve protonated cyclopropane intermediates (1–5), a study was made on the solvolysis of 1-^{14}C-1-propyl tosylate (**1**-OTs-1-^{14}C) in trifluoroacetic acid. The use of trifluoroacetic acid is of interest since it is an even more "limiting" solvent than the commonly used formic acid because of its higher ionizing power and/or more poorly nucleophilic character (6).

[1]For paper III, see ref. 4.

TABLE 1

Yields of 1-propyl trifluoroacetate (**1**-TFA) and 2-propyl trifluoroacetate (**2**-TFA) from trifluoroacetolyses of 1-propyl tosylate (**1**-OTs) with or without added sodium trifluoroacetate (NaTFA)*

Reaction time (days)	3		4		5		6	
	With NaTFA	No NaTFA	With NaTFA	No NaTFA	With NaTFA	No NaTFA	With NaTFA	No NaTFA
Unreacted **1**-OTs (g)	2.55	3.37	1.94	1.71	1.26	0.51	0.81	0.00
1-TFA (g)	1.77	0.54	1.62	0.47	1.79	0.37	1.65	0.24
2-TFA (g)	1.28	3.00	1.12	3.50	1.27	2.94	1.20	1.78

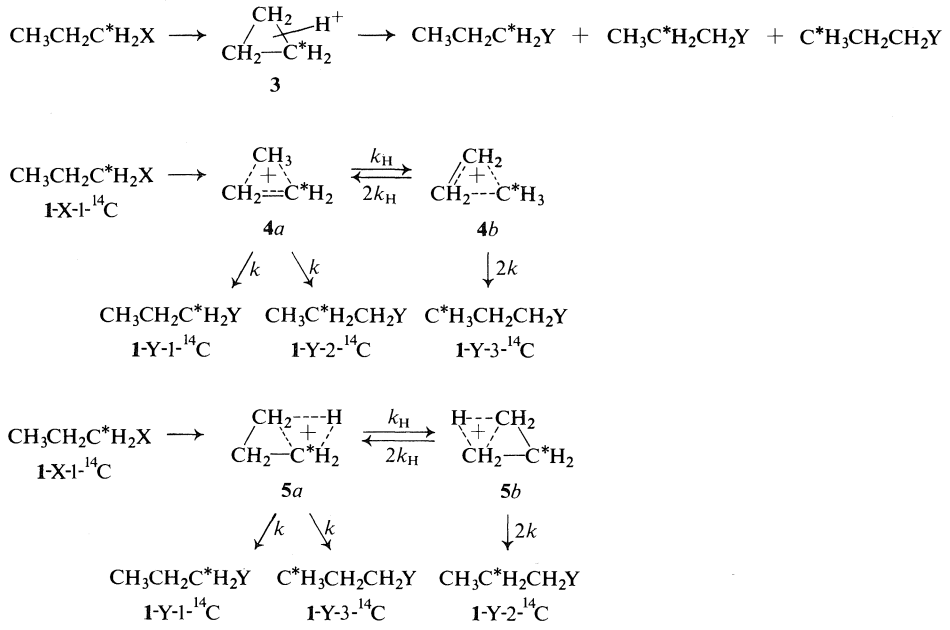
*Each experiment was carried out at reflux temperature using 8.00 g of 1-OTs, with or without an equivalent of NaTFA, in 35 ml of F_3CCOOH; the product mixture was analyzed by n.m.r. (see Experimental).

The trifluoroacetolysis of **1**-OTs-1-^{14}C, either with or without the presence of an equivalent of sodium trifluoroacetate, was carried out by refluxing the reaction mixture for 5 days. Both 1-propyl trifluoroacetate (**1**-TFA-^{14}C) and 2-propyl trifluoroacetate (**2**-TFA-^{14}C) were obtained. The reaction time of 5 days was chosen because results from preliminary trials with inactive materials, given in Table 1, suggested that this length of refluxing gave reasonably good yields of **1**-TFA relative to the yields of **2**-TFA and unreacted **1**-OTs. It should also be noted from Table 1 that when the solvolysis was effected without any sodium trifluoroacetate, the dominant product was **2**-TFA. However, when sodium trifluoroacetate was present in the reaction mixture, more **1**-TFA was formed. The mixture of **1**-TFA-^{14}C and **2**-TFA-^{14}C obtained from each solvolysis run was hydrolyzed to give the alcohols, **1**-OH-^{14}C and **2**-OH-^{14}C, which were subsequently separated by preparative vapor phase chromatography (v.p.c.) (1). The active 1-propanol (**1**-OH-^{14}C) so obtained was degraded by conversion to propionic acid, to acetic acid, to methylamine, as described previously (1) to give the ^{14}C- distribution in the 1-propyl group; the results are summarized in Table 2.

From Table 2, it is seen that there was much less isotopic scrambling in the **1**-TFA-^{14}C when the trifluoroacetolysis of **1**-OTs-1-^{14}C was carried out with added sodium trifluoroacetate. Moreover, the rearranged isotopic label was about equally distributed between C-2 and C-3. When the reaction was effected in the presence of trifluoroacetate ions from the added salt, apparently there was a larger S_N2 component which gave rise to unrearranged **1**-TFA. This conclusion would be compatible with the product distribution given in Table 1, which showed that the presence of sodium trifluoroacetate led to the formation of more **1**-TFA. When the trifluoroacetolysis was effected without added salt, the S_N1 component, which could give rise to **2**-TFA and to isotopically rearranged **1**-TFA, would be the dominant process.

The finding of about equal amounts of rearranged ^{14}C-label at C-2 and C-3 in the **1**-TFA-^{14}C product from the present work is similar to the results observed in the nitrous acid deamination of 1-^{14}C-1-propylamine (1, 5), although the extents of rearrangement were different for the different reactions. As was concluded in the earlier work (1–5), the rearrangement of the label in the 1-propyl system from C-1 to both C-2 and C-3 could be best accommodated by the intervention of equilibrating protonated cyclopropane intermediates. Thus the 1-propyl cation generated in the trifluoroacetolysis of **1**-OTs-1-^{14}C could rearrange to the 2-propyl cation and to equilibrating protonated cyclopropanes, the latter giving rise to **1**-TFA with equal amounts of ^{14}C-label at each of the 3 carbon positions.

The equal distribution of the rearranged label at C-2 and C-3 does not permit a differentiation between face-protonated cyclopropane (**3**), equilibrating corner-protonated cyclopropanes (methyl-bridged ions) (***4a*** $\rightleftarrows$ ***4b***), and equilibrating edge-protonated cyclopropanes (***5a*** $\rightleftarrows$ ***5b***) (7) (Scheme 1). There is, however, general agreement that face-protonated **3** is not the stable structure (8–10) and that probably, the edge-protonated intermediates may be preferred over the corner-protonated species (1, 8–11). Collins has pointed out (7 and private communications) that starting from **1**-X-1-^{14}C, after all intermediates have reached equilibrium, equal amounts of **1**-Y-2-^{14}C and **1**-Y-3-^{14}C would be obtained from either ***4a*** $\rightleftarrows$ ***4b*** or ***5a*** $\rightleftarrows$ ***5b***. On the



SCHEME 1

other hand, if products were formed before equilibrium has been established, from processes involving corner-protonation (**4***a* ⇄ **4***b*), **1**-Y-3-^{14}C can never be greater than **1**-Y-2-^{14}C, while from processes involving edge-protonation (**5***a* ⇄ **5***b*), **1**-Y-3-^{14}C can be greater than **1**-Y-2-^{14}C. One of the original objectives of the present work was to find out if the trifluoroacetolysis of **1**-OTs-1-^{14}C would give a **1**-TFA-^{14}C product with more ^{14}C-label at C-3 than C-2, thus providing experimental evidence for edge-protonation. Since the results indicated about equal amounts of ^{14}C-label at C-2 and C-3, in the trifluoroacetolysis of **1**-OTs-1-^{14}C, the equilibrating protonated cyclopropane intermediates must have reached equilibrium before formation of the product, **1**-TFA-^{14}C.

ADDENDUM

When the present note was being prepared for publication, a communication by Reich *et al.* (13) on the trifluoroacetolysis of certain primary alkyl tosylates has appeared. Among the compounds studied was **1**-OTs labelled with deuterium in various positions. The products obtained (at 100 or 125°) ranged from 10.3–16.3% **1**-TFA and 83.7–89.7% **2**-TFA. These product distributions can be regarded as in substantial agreement with those observed in the present work; for example, it can be seen from Table 1 that when the trifluoroacetolysis mixture was refluxed (about 73°) for 6 days without the presence of sodium trifluoroacetate, the product ratio was 12% **1**-TFA and 88% **2**-TFA. Reich *et al.* also reported that the nuclear magnetic resonance (n.m.r.) examination of the **1**-TFA derived from D-labelled **1**-OTs, such as **1**-OTs-1,1-d_2, showed essentially no isotopic scrambling (less than 2%), and this is distinctly at variance with the present results. The determination of isotope position rearrangements by ^{14}C-tracers would be more sensitive than the n.m.r. technique. The isotope position rearrangement of about 1% from C-1 to each of C-2 and C-3, observed in the trifluoroacetolysis of **1**-OTs-1-^{14}C with added sodium trifluoroacetate, would have been missed by the n.m.r. method. On the other hand, the total of about 17% rearrangement from C-1 to C-2 and C-3, found in the trifluoroacetolysis of **1**-OTs-1-^{14}C without the presence of sodium trifluoroacetate, should be readily detectable by n.m.r. and D-labelling. The absence of isotope position rearrangements reported by

TABLE 2

Activity distributions in the x-^{14}C-1-propyl trifluoroacetate (**1**-TFA-^{14}C) from trifluoroacetolysis of 1-^{14}C-1-propyl tosylate (**1**-OTs-1-^{14}C) with or without added sodium trifluoroacetate (NaTFA)

Compound assayed	Specific activity (c.p.m./mmole)*				% ^{14}C at C-2,3				% ^{14}C at C-3			
	With NaTFA		No NaTFA		With NaTFA		No NaTFA		With NaTFA		No NaTFA	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
C_2H_5COOH†	106 500	106 800	30 700	118 000	—	—	—	—	—	—	—	—
CH_3COOH†	2 040	2 220	5 400	18 900	1.9	2.1	17.6	16.0	—	—	—	—
CH_3NH_2‡	950	1 000	2 590	9 710	—	—	—	—	0.9	0.9	8.4	8.2

*Measured by a liquid scintillation counter.
†Assayed as the *p*-bromophenacyl ester.
‡Assayed as *N*-methyl-*p*-toluenesulfonamide.

Reich *et al.* apparently applies to trifluoroacetolysis without added salt, and this discrepancy, therefore, remains to be resolved.[2]

Experimental

The Solvolysis Reaction

A solution of 8.00 g (0.037 mole) of 1-^{14}C-1-propyl tosylate (**1**-OTs-1-^{14}C) (2) in 35 ml of trifluoroacetic acid, with or without 5.10 g (0.037 mole) of sodium trifluoroacetate, was heated under reflux in an oil-bath for 5 days, the top of the reflux condenser being protected by a drying tube. The resulting solution was poured into a separatory funnel containing about 200 ml of ice and water. The organic layer (about 4.0 g) was separated, washed with a small amount of water, and then distilled, the fraction boiling between 65 and 90° being collected. (The b.p. of 1-propyl and 2-propyl trifluoroacetates (**1**-TFA and **2**-TFA) (12) are 82.5 and 73.5°, respectively.)

The above crude product was hydrolyzed by heating under reflux for 3 h with 50 ml of 10% NaOH solution. To the hydrolyzate, about 1.0 g of ordinary 1-propanol (**1**-OH) was added as carrier, and the material was then continuously extracted with ether for 24 h. After drying over anhydrous $MgSO_4$, the ether was fractionated off. From the residue, the **1**-OH-^{14}C was separated from the **2**-OH-^{14}C by preparative v.p.c. as previously described (1). More **1**-OH carrier was added, if necessary, to give a total of about 3.0 g of x-^{14}C-1-propanol before it was used for the subsequent degradation.

Product Analysis Studies

The trifluoroacetolysis, using 8.00 g of ordinary **1**-OTs, with or without an equivalent of sodium trifluoroacetate, in 35 ml of trifluoroacetic acid, was carried out as described above, the reaction time being 3, 4, 5, or 6 days. The organic material recovered from the reaction mixture was not distilled, and after weighing, it was analyzed directly by n.m.r. using an HA-100 spectrometer. Comparison with the n.m.r. spectra of authentic samples showed the presence of **1**-TFA, **2**-TFA and unreacted **1**-OTs. Based on the integration of the absorptions centered at τ 4.85, 5.74, and 6.07, respectively, for the one C-2 proton of **2**-TFA, the two C-1 protons of **1**-TFA, and the two C-1 protons of unreacted **1**-OTs, the relative molar composition of the product mixture was estimated. Knowing the mole fractions and molecular weights of the three components and the total weight of the mixture, the weights of each component can be calculated. The results are summarized in Table 1.

As a test of the stability of **1**-TFA and **2**-TFA in the trifluoroacetolysis medium, an authentic sample of each of these compounds was refluxed in trifluoroacetic acid for 5 days. The n.m.r. analysis of the recovered material showed no isomerization of **1**-TFA to **2**-TFA or vice versa.

Degradations

Each sample of **1**-OH-^{14}C derived from the solvolysis runs was degraded by conversion to propionic acid, to acetic acid, and then to methylamine as described previously by Lee and Kruger (1). The degradation products were converted to the appropriate solid derivatives which were rigorously purified before being used for the determination of their radioactivity (1).

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[2]In a private communication from Dr. Diaz, it was pointed out that the n.m.r. assays were carried out on the reaction mixture itself, which would contain unreacted **1**-OTs-d_2 and **2**-TFA-d_2 besides the **1**-TFA-d_2. Thus the amount of C-1 H-absorption for the **1**-TFA-d_2 product would be difficult to measure with great accuracy. The conclusion drawn was that the extent of isotopic scrambling from C-1 to C-2 and C-3 was low, perhaps no more than 10% and this conclusion may be regarded as indicating no substantial disagreement between the results obtained with D- or ^{14}C-labeling. It was also pointed out that in the present work, the concentration of **1**-OTs-1-^{14}C in the reaction solution was relatively high and there could be the possibility that the HOTs liberated during the solvolysis might cause more extensive isotopic scrambling.