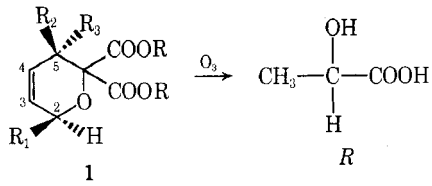
Scheme I



1

Compd	R	R_1	R_2	R_3
1	H	CH_3	H	H
2	C_2H_5	CH_3	H	H
3	CH_3	CH_3	H	H
4	C_2H_5	CH_3	CH_3	H
5	C_2H_5	CH_3	H	CH_3

5,6-dihydro-α-pyran 6,6-diacids. The five compounds we used were (2*R*)-2-methyl-5,6-dihydro-α-pyrano-6,6-dicarboxylic acid (**1**), the dimethyl ester of this acid (**3**), diethyl 2-methyl-5,6-dihydro-α-pyrano-6,6-dicarboxylate (**2**), diethyl *cis*-2,5-dimethyl-5,6-dihydro-α-pyrano-6,6-dicarboxylate (**4**), and diethyl *trans*-2,5-dimethyl-5,6-dihydro-α-pyranodicarboxylate (**5**). The conformation of this family of compounds has recently been established.[1-3] The working principle of our study is that the ozonolysis of optically active compound **1** (or **3**) gives the lactic acid[4] (Scheme I). Comparison of the NMR spectra of model optical isomers of lactic acid (*R* or *S*) and the lactic acid obtained from the ozonolysis—recorded in the presence of Eu(hfac)$_3$ in ethanol-*d*—permitted us to conclude that the lactic acid from the ozonolysis is 70% *R*. In fact, the induced shifts of CH and CH_3 protons were different for the isomers of lactic acid. These shifts are bigger for the complex of the *R* acid and Eu(hfac)$_3$. We reexamined the 220-MHz NMR spectra of compounds **1** and **3** (optically active) and their racemic derivatives **2**, **4**, and **5**. The spectrum of **3** recorded in the presence of Eu(hfac)$_3$ revealed that the induced shifts of the H-2 and CH_3-2 protons are δ 0.98 and 0.52,[5] respectively (Table I).

The direct application of Eu(hfac)$_3$ to the racemic compounds **2**–**5** showed a separation of the signals for H-2 and CH_3-2. Comparison of the values of the induced shift for the racemic and the optically active (*R*)-**3**—with the same quantity of the shift reagent—permitted us to conclude that of the pairs of optical isomers the one with a larger $\Delta\delta$ has the *R* configuration. On searching for the verification of this conclusion, we observed a similar splitting of signals for the ester **2**, which means that the complex *R* ester-*d* shift reagent showed a slightly larger $\Delta\delta$ than the epimeric complex *S* ester-*d* shift reagent. The quasiracemate formation between the optically active shift reagent and the asymmetric center of the compound is characterized by the smaller $\Delta\delta$. This is a different representation of the fact that the lanthanide complex has its own symmetry.

For the two diastereomers **4** and **5** (asymmetric centers at C-2 and C-5), the corresponding racemic mixtures are composed of *R,S* + *S,R* and *R,R* + *S,S*, respectively. A separation of signals by the same method was observed for the protons of H-2 and CH_3-2 but the corresponding signals of H-5 and CH_3-5 remained unchanged. These results can be explained by the position of the complexation site, which for the dihydropyranol esters is known to be on the oxygen close to C-2.[1]

The successful application of the optically active shift reagent technique to the reactions of epimerization, racemization, asymmetric induction, or simply to the identification of configuration depends mainly on the use of a high-resolution spectrometer and an appropriate solvent, and on the asymmetric center being relatively close to the complexation site.

Table I
Chemical Shifts of Selected Protons[a]

		H-2	CH_3-2	H-5	CH_3-5	H-3	H-4
Lactic acid	(*R*)[b]	4.50	1.34				
Lactic acid	(*S*)[b]	4.28	1.19				
1	(*R*)	4.84	1.45	3.10		5.52	5.92
2	(2*R*)	5.01	1.62	3.19		5.55	5.86
	(2*S*)	4.90	1.52			5.51	
3	(2*R*)	5.12	1.57	3.22		5.82	6.17
	(2*S*)	4.90	1.49				
4	(2*R*,5*S*)	5.22	1.81	3.25	1.25	5.66	6.03
	(2*S*,5*R*)	5.11	1.73			5.62	
5	(2*R*,5*R*)	4.89	1.64	3.30	1.28	5.73	6.02
	(2*S*,5*S*)	4.78	1.53			5.70	

[a] After addition of 0.1 mol of Eu(hfac)$_3$ in $CDCl_3$ (10.0%). [b] In ethanol-*d*.

Experimental Section

The prefix *dl* has been omitted from the names of most racemic compounds described. The NMR spectra in $CDCl_3$, CD_3OD, or C_2D_5OD were registered on a Varian HR 220 MHz spectrometer. The shift reagent Eu(hfac)$_3$ was purchased from Norell Chemical Co., Ltd. The compounds **1**–**5** were prepared in a bomb tube and purified by preparative VPC.[1,4] The ozonolysis was carried out in the Mathieson ozonizer in 10% methanol solution. The physical constants of the compounds follow: **1**, mp 112–114° (yield 60%); **2**, bp 79° (0.1 mm) (55%); **3**, mp 92–93° (50%); **4**, bp 82° (0.17 mm) (47%); and **5**, bp 84° (0.12 mm) (34%). The separation of the optical isomers of **1** [αD (H_2O) +14°] has been carried out through the brucine salt recrystallization. The (*R*)-lactic acid [αD (H_2O) +3.8°] was bought from Sigma Chemicals Co.

Acknowledgments. The authors are indebted to the National Research Council of Canada and to the Conseil de Recherches of the Université de Moncton for the financial support. We appreciate the collaboration of N. E. Cundasawmy, R. Luce, and J. Couturier as well as Nicolet Inc.

Registry No.—**1**, 53951-35-2; **2** (2*R*), 53951-36-3; **2** (2*S*), 53951-37-4; **3** (2*R*), 53951-38-5; **3** (2*S*), 53951-39-6; **4** (2*R*,5*S*), 53991-02-9; **4** (2*S*,5*R*), 53991-03-0; **5** (2*R*,5*R*), 53991-04-1; **5** (2*S*,5*S*), 53991-05-2; lactic acid (*R*), 10326-41-7; lactic acid (*S*), 79-33-4; europium 3-trifluoroacetyl-*d*-camphorate, 34830-11-0.

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Deamination of 2-Amino-1-cyclopropylethanol

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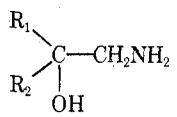
The 1,2 shift of cyclopropyl to an electrophilic center relative to hydride, alkyl, and phenyl shifts has been investigated in a number of reactions. In the reaction with nitrous acid of 2-cyclopropylethylamine[2] and in the solvolysis of

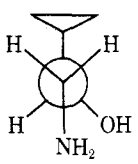
alkyl brosylates and tosylates,[3] the ratio of cyclopropyl to hydride and methyl shifts was greater than 1, but solvolysis reactions of cyclopropyl have often been complicated by ring-opening reactions[4,5] and diazotization reactions of aliphatic amines have given contradictory results in other cases. Although hydride shift predominates over alkyl or cycloalkyl group shifts in most reactions reported, it is difficult, for example, to interpret the variations in the hydride:alkyl shift ratio from 1.3–1.6 found in the reaction with nitrous acid of isobutylamine[6] to the predominant methyl shift found in the reaction of *threo*-3-phenyl-2-butylamine[7] and to the strong predominance of hydride over ethyl and cyclohexyl shift products (93:4.5:2.5) in the reaction of (*S*)-1-amino-2-cyclohexylbutane investigated by Kirmse.[8] We have sought to compare cyclopropyl vs. hydride shifts in a reaction with fewer complications.

The reaction of amino alcohols with nitrous acid has served in somewhat the same way as the pinacol rearrangement as a test of the relative ability of substituent groups to donate an electron pair to an electrophilic site.[9,10] Relative shifts are known to be affected by the conformational equilibria of the amino alcohols.[10,11] To equalize these, we have compared the cyclopropyl and isopropyl shift products with hydride shift products formed in the reaction with nitrous acid of amines **1** and **2**.

2-Amino-1-cyclopropylethanol (**1**) and 1-amino-3-methyl-2-butanol (**2**) were synthesized from cyclopropanecarboxaldehyde and 2-methylpropanal by condensation with nitromethane and reduction of the nitro alcohols.



1, R_1 = H; R_2 = cyclopropyl
2, R_1 = H; R_2 = isopropyl
4, R_1 = phenyl; R_2 = isopropyl



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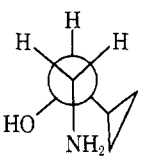

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The reaction of nitrous acid with **1** yielded cyclopropylacetaldehyde, cyclopropanecarboxaldehyde (in an overall 40% yield of carbonyl compounds, cyclopropylacetaldehyde was the major portion) and cyclopropyloxirane (**3**, 10%). The formation of cyclopropanecarboxaldehyde probably resulted from oxidative cleavage of the starting material or of cyclopropylethylene glycol. Under similar conditions, propylene glycol gave rise to carbonyl compounds, one of which was tentatively identified as acetaldehyde. The cyclopropyl shift was the only one observed; it is estimated that less than 2% of cyclopropyl methyl ketone could have been formed.

It is possible under certain conditions for alkyl epoxides to isomerize to aldehydes in the presence of acid;[12] so it was necessary to determine whether the cyclopropylacetaldehyde might have resulted from the ring opening of protonated **3**, a reaction path which would involve no 1,2-cyclopropyl shift. To investigate this possibility, **3** was prepared in 31% yield by the action of dimethylsulfonium methylide on cyclopropanecarboxaldehyde and in very low yield by the epoxidation of vinylcyclopropane. When **3** was subjected to the identical reaction conditions used in the reaction of **1** with nitrous acid no cyclopropaneacetaldehyde was formed.

The reaction of nitrous acid with **2** yielded 3-methyl-2-butanone (30%) and 3-methyl-1,2-epoxybutane (10%). The presence of 3-methyl-2-butanone and the absence of any detectable quantity of 3-methylbutanal in the product indicates that the isopropyl group is unable to compete successfully with hydride for migration.

In this case also the possibility that the 3-methyl-2-butanone was formed via the intermediate 3-methyl-1,2-epoxybutane was tested. 3-Methyl-1,2-epoxybutane was prepared by the epoxidation of 3-methyl-1-butene. When this epoxide was subjected to the identical reaction conditions used in the reaction with nitrous acid of 1-amino-3-methyl-2-butanol, no carbonyl compound was formed.

It is expected[10] that the conformation of the hydroxy diazonium ion formed from **1** should be a major factor in determining relative shifts; related amino alcohols have been shown[13] to have hydroxyl and amino functions in gauche conformation. The ratio of conformation **5** (preferred), with the bulky group trans to the amino group, to conformation **6**, with β hydrogen trans to the amino group, should differ little between cyclopropyl and isopropyl. There is precedence for the marked predominance of 1,2 shift of a group in which anchimeric assistance is facile in the work of House,[14] who found 99% phenyl shift in the reaction with nitrous acid of **4**. The formation of 3-methyl-2-butanone is consistent with the predominant shift of hydride in the nitrous acid reaction of aminobutanes.[8] The formation of cyclopropylacetaldehyde is consistent with conformational preferences and with earlier observations[2–5] of anchimeric assistance by cyclopropyl. The stabilization of an intermediate leading to cyclopropyl shift may be attributed to a π complex as suggested by Dewar and Harris.[4] This interpretation is related to our earlier explanation of the results of deamination of 2-cyclopropylethylamine.[2] Whatever the explanation, the marked difference in behavior of **1** and **2** is further evidence of the ready participation of cyclopropyl in reactions involving a neighboring electrophilic center.

Experimental Section[15]

1-Cyclopropyl-2-nitroethanol. To a stirred solution of 70 g (1.0 mol) of cyclopropanecarboxaldehyde and 61 g (1.0 mol) of nitromethane in 150 ml of methanol, cooled in ice, 40 g (1.0 mol) of sodium hydroxide in 150 ml of water was added dropwise. A white solid precipitated during the 1-hr addition; after stirring for an additional 30 min, 62 g (1.0 mol) of glacial acetic acid was added dropwise. The organic layer was combined with ether extracts (2 × 500 ml) of the aqueous layer and dried with anhydrous sodium sulfate. Solvent was then removed under vacuum and gentle warming, and 119 g (90%) of 2-nitro-1-cyclopropylethanol, bp 74–74.5° (2.0 mm), was obtained. Anal.[16] Calcd for $C_5H_9NO_3$: C, 45.80; H, 6.92; N, 10.68. Found C, 45.58; H, 7.44; N, 10.98.

2-Amino-1-cyclopropylethanol (1). 1-Cyclopropyl-2-nitroethanol, 100 g (0.76 mol), in 250 ml of dry ether was added dropwise during 3 hr to a stirred refluxing slurry of 64 g (1.7 mol) of lithium aluminum hydride in 2 l. of dry ether. Reflux was maintained for 2 hr, and the mixture was decomposed by dropwise addition of 600 ml of 2-propanol followed by 170 ml of water saturated with sodium chloride. After stirring for 5 hr, the mixture was filtered and the white precipitate of aluminum and lithium hydroxide was continuously extracted with 1:3 2-propanol–ether. The extracts and the original filtrate gave 40 g (51%) of **1**, bp 89–94° (12 mm). Anal.[16] Calcd for $C_5H_{11}NO$: C, 59.37; H, 10.96; N, 13.84. Found: C, 59.40, 59.30; H, 10.53, 10.67; N, 14.10.

Reaction of 1 with Nitrous Acid. A solution of 10.5 g (0.15 mol) of sodium nitrite in 50 ml of water was added dropwise to a stirred solution of 15 g (0.15 mol) of **1**, 12 ml of 12 *M* hydrochloric acid, and 150 ml of water. The temperature was kept below 5° during the addition and for 1 hr afterwards. The reaction mixture was then warmed to 50° until evidence of nitrogen evolution had ceased and extracted with 10 ml of ether, and the extract was dried over anhydrous sodium sulfate. Vapor chromatography on columns A and B[17] showed only two peaks. The smallest one of these was shown to have retention times on both columns identical with those of a sample of **3** which was synthesized for reference.[18] The larger peak exhibited retention times that were different from that of cyclopropyl methyl ketone and identical with those of both cyclopropanecarboxaldehyde and cyclopropylacetaldehyde on both columns. Silica gel TLC of the 2,4-dinitrophenylhydrazone derivative of the crude reaction mixture (3:1 benzene–petroleum ether) indicated the presence of both aldehydes. Identification was made

by preparing and chromatographing samples of the dinitrophenylhydrazones. Fractional crystallization of the crude mixture of 2,4-dinitrophenylhydrazones from ethanol gave a sample (mp 131–132°) which did not depress the melting point of a known sample of cyclopropylacetaldehyde 2,4-dinitrophenylhydrazone.

Cyclopropyloxirane (3). Cyclopropanecarboxaldehyde, 7.0 g (0.10 mol), was stirred under nitrogen with 28.6 g (0.14 mol) of trimethylsulfonium iodide in 60 ml of dimethyl sulfoxide. A solution of 14.0 g of potassium *tert*-butoxide in 150 ml of dimethyl sulfoxide was added dropwise with stirring during 30 min while cooling. After stirring for an additional 15 min, 300 ml of water was added slowly while cooling with ice. The solution was extracted with ether (3 × 500 ml) and the extract was washed with water and dried over molecular sieves. Distillation on a Teflon spinning band column gave, after removal of ether and *tert*-butyl alcohol, 2.6 g of **3**: bp 85–90° (lit.[12b] bp 100°); NMR (neat) δ 0.1–0.4 (m, 4 H, cyclopropyl CH_2), 0.5–0.8 (m, 1 H, cyclopropyl CH), 2.4–2.7 (m, 2 H, oxirane CH_2), 2.1–2.3 (m, 1 H, oxirane CH).[18] Anal.[19] Calcd for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.12; H, 9.75.

Cyclopropyloxirane (**3**) was first prepared from vinylcyclopropane but the amount was not sufficient for complete identification. A solution of 35 g (0.20 mol) of *m*-chloroperoxybenzoic acid in 60 ml of dry ether was added dropwise during 1 hr to a stirred solution of 10.5 g (0.15 mol) of vinylcyclopropane[20] maintained at 20°. After stirring for 2 hr, the mixture was extracted with 10% sodium hydroxide solution, washed with water, and dried. After removal of the ether, VPC using column B[17] indicated one volatile product in addition to ether and a small amount of vinylcyclopropane.

Reaction of Nitrous Acid with 3. A solution of 1.66 g (0.024 mol) of sodium nitrite in 8.0 ml of water was added dropwise to a stirred solution of 2.0 g (0.024 mol) of **3**, 1.9 ml of 12 *M* hydrochloric acid, and 23.5 ml of water. The conditions of the reaction of **1** with nitrous acid were duplicated. The mixture was extracted with two 4-ml portions of ether and the extracts were dried over molecular sieves. Gas chromatography of the ether solution on column B[17] showed only one major component besides ether. This component had a retention time identical with that of **3** and different from those of cyclopropylacetaldehyde, cyclopropanecarboxaldehyde, and cyclopropyl methyl ketone. Treatment of the product with 2,4-dinitrophenylhydrazine yielded no precipitate.

Reaction of Nitrous Acid with 1-Amino-3-methyl-2-butanol. 1-Amino-3-methyl-2-butanol, bp 88–90° (40 mm) [lit.[21] bp 174° (734 mm)], was prepared in 42% overall yield from 2-methylpropanal by the same route used for 2-amino-1-cyclopropylethanol. Dropwise addition of 32 g (0.45 mol) of sodium nitrite in 100 ml of water to a stirred solution of 45 g (0.45 mol) of 1-amino-3-methyl-2-butanol in 500 ml of water containing 35 ml of 12 *M* hydrochloric acid, maintained below 5°, was followed by stirring (30 min), warming, and refluxing (10 min). The reaction mixture was extracted with two 75-ml portions of ether, and the dried ether solution was concentrated. Vapor chromatography on columns A and B[17] showed the presence of only 3-methyl-1,2-epoxybutane and 3-methyl-2-butanone, in a ratio of 1:3 (in approximate 40% yield), identified by comparison of retention times with those of authentic samples. 3-Methylbutanal, with a different retention time, was not present. The 2,4-dinitrophenylhydrazone, mp 123–124°, was prepared and did not depress the melting point of an authentic sample of 3-methyl-2-butanone 2,4-dinitrophenylhydrazone.

Reaction of 3-Methyl-1,2-epoxybutane with Nitrous Acid. The epoxide was prepared in 63% yield from 3-methyl-1-butene by reaction with *m*-chloroperoxybenzoic acid.[22] A solution containing 2.0 g (0.023 mol) of 3-methyl-1,2-epoxybutane, 1.75 ml of 12 *M* HCl, and 25 ml of water was stirred and the temperature maintained below 5° while a solution of 1.60 g (0.023 mol) of sodium nitrite in 5 ml of water was added dropwise. After 30 min, the stirred solution was warmed to 20° and then refluxed for 10 min. It was then extracted with two 4-ml portions of ether, and the ether extract was dried over molecular sieves. Gas chromatography on column B[17] indicated the presence only of ether and 3-methyl-1,2-epoxybutane. Treatment with 2,4-dinitrophenylhydrazine gave no solid.

Registry No.—**1**, 54120-02-4; **2**, 17687-58-0; **3**, 21994-19-4; 1-cyclopropyl-2-nitroethanol, 54120-03-5; cyclopropanecarboxaldehyde, 1489-69-6; nitromethane, 75-52-5; nitrous acid, 7782-77-6; cyclopropanecarboxaldehyde 2,4-dinitrophenylhydrazone, 36873-36-6; cyclopropylacetaldehyde 2,4-dinitrophenylhydrazone, 54120-04-6; potassium *tert*-butoxide, 865-47-4; 2-methylpropanal, 78-84-2; 3-methyl-1,2-epoxybutane, 1438-14-8; 3-methyl-2-butanone, 563-80-4; 3-methyl-2-butanone 2,4-dinitrophenylhydrazone, 3077-97-2.

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(16) Analysis by Dr. F. B. Strauss Microanalytical Laboratory, Oxford, England OX2 7SA.
(17) A, 20% di-2-ethylhexyl sebacate on Chromosorb W; B, 20% Carbowax 4000 on Chromosorb P; C, 10% diethylene glycol adipate on Chromosorb W.
(18) A report of the preparation of **3** (ref 12b) appeared subsequently; our physical constants (boiling point, NMR spectrum) are somewhat at variance, but the spectral data are obtained under different conditions.
(19) Analysis by Instranal Laboratory, Inc., Rensselaer, N.Y.
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A New Reaction of Trithioorthoacetates. Reaction with Acylating Reagents

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Reactions of trithioorthocarboxylates are relatively unknown.[1] In our earlier work[2] it was found that when aryl trithioorthoacetates $(ArS)_3CCH_3$ were dissolved in trifluoroacetic acid-*d*, rapid and complete isotopic exchange occurred at room temperature and on evaporation of the solvent deuterated compounds $(ArS)_3C-CD_3$ were obtained quantitatively. As an extension of this work trifluoroacetylation of $(ArS)_3C-CH_3$ was tried and we now wish to report the results.

As anticipated, the reaction did proceed quite easily at room temperature, but the products, obtained in high yields, were $(ArS)_2C{=}CHCOCF_3$ instead of $(ArS)_3C-CH_2COCF_3$ (Ar, yield, %: *p*-$CH_3OC_6H_4$, 58; *p*-$CH_3C_6H_4$,

$$(ArS)_3C{-}CH_3 \xrightarrow[rT]{(CF_3CO)_2O} (ArS)_2C{=}CHCOCF_3$$

98; C_6H_5, 100; *p*-ClC_6H_4, 75). Physical properties together with analytical data for the acylation products are listed in Table I.

Similarly, reactions of $(ArS)_3C-CH_3$ with $(CCl_3CO)_2O$ (refluxing for 1 day in $CHCl_3$) gave $(ArS)_2C{=}CHCOCCl_3$ (Ar, yield, %: Ph, 76; *p*-$CH_3C_6H_4$, 28). The acid chloride CCl_3COCl can also be used, the yields being improved in