Table I
Acetal Formation

Registry no.	Aldehyde	Alcohol	Mole ratio aldehyde/alcohol	Temp, °C	Time, hr	% yield[a] No catalyst	% yield[a] Ⓟ-$AlCl_3$[b]
100-52-7	Benzaldehyde	1-Butanol[c]	0.21	95	2.5	8	21
	Benzaldehyde	2-Butanol[d]	0.21	95	92	0	0
552-89-6	*o*-Nitrobenzaldehyde	1-Butanol	0.21	45	3	1	40
	o-Nitrobenzaldehyde	1-Butanol	0.21	95	18	0	62
104-88-1	*p*-Chlorobenzaldehyde	1-Butanol	0.21	95	18	1	32
123-11-5	*p*-Anisaldehyde	1-Butanol	0.21	95	93	0	0
90-02-8	*o*-Salicylaldehyde	1-Butanol	0.21	95	47	0	0
535-16-8	*p*-Nitrobenzaldehyde	1-Butanol	0.21	95	24	0	48

[a] Yields determined by VPC with added internal standard of *m*-chlorotoluene. [b] One-half gram of Ⓟ-$AlCl_3$ used per 20 mmol of aldehyde [c] Registry no., 71-36-3. [d] Registry no., 78-92-2.

Table II
Competitive Rate Factors for Dibutyl Acetal Formation from Para-Substituted Benzaldehydes[a]

Substituent	R_x/k_H
NO_2	1.36
$N(CH_3)_2$[b]	0.00
H	1.00
Cl	1.06

[a] 20 mmol of substituted benzaldehyde, 20 mmol of benzaldehyde, excess 1-butanol, and 0.55 g of Ⓟ-$AlCl_3$ stirred at 55°. [b] Registry no., 100-10-7.

itive rate data (see Table II) for various para-substituted benzaldehyde reactions with 1-butanol and Ⓟ-$AlCl_3$.

Consistency of Ⓟ-$AlCl_3$ preparation was demonstrated by two different batches which gave yields of the acetal from *o*-nitrobenzylaldehyde and 1-butanol within 0.1%. Some catalysis by polymer (styrene–1.8% divinylbenzene copolymer) alone was also shown in the case of the *o*-nitrobenzaldehyde–1-butanol reaction. Yields of 67% acetal compared to the Ⓟ-$AlCl_3$ catalysts were observed. The cross-linked polystyrene alone probably works as an entrapment agent for the water formed in the reaction. The total catalytic activity of Ⓟ-$AlCl_3$ is no doubt derived from both its Lewis acid nature of the bound aluminum chloride plus the ability of the cross-linked polystyrene to entrap water.

The Ⓟ-$AlCl_3$ was also an effective catalyst for the hydrolysis of acetals. For example, heating the diethyl acetal of *o*-chlorobenzaldehyde with Ⓟ-$AlCl_3$ in benzene–methanol–water (2:6:1) for 17.5 hr gave a 61% yield of *o*-chlorobenzaldehyde together with 34% of *o*-chlorobenzaldehyde dimethyl acetal and 5% of a product tentatively identified as the methyl ethyl acetal. Under similar conditions a blank containing all reagents but Ⓟ-$AlCl_3$ produced only 4% of the aldehyde and 2% of the mixed methyl ethyl acetal.

Ⓟ-$AlCl_3$ is a useful catalyst for synthetic reactions which require both a dehydrating agent and a Lewis acid. Though its versatility is rather limited, on a larger scale, it may be quite useful because the reagents can be recycled and because the catalyst's reactivity is somewhat attenuated because of the presence of the polymer. For reactions requiring an acid catalyst in compounds with a sensitive secondary functional group, Ⓟ-$AlCl_3$ may well be the reagent of choice. Extensive electron microscopic studies detailing the exact structure of Ⓟ-$AlCl_3$ will be published shortly.

Experimental Section

All alcohols and aldehydes were reagent grade and the latter were redistilled prior to use. Ⓟ-$AlCl_3$ was prepared as before.[3]

General Procedure. Reactant concentrations, temperatures, times, product, and yield data are given in Table I. The aldehyde, alcohol, anhydrous benzene (5 ml/20 mmol of aldehyde), and 0.5 g of Ⓟ-$AlCl_3$ per 20 mmol of aldehyde were stirred in a closed reaction tube for the appropriate temperature. After the desired reaction time, aliquots were removed and analyzed by gas–liquid chromatography on a Hewlett-Packard Model 5750 flame ionization gas chromatograph. The columns used were 6 ft × 0.125 in. 3% silicon gum rubber on Chromosorb W and 10% Carbowax 20M on Chromosorb P. Yields were determined by the addition of the internal standard of *m*-chlorotoluene. Preparative reactions were performed as above. Isolation of products was accomplished by filtration of Ⓟ-$AlCl_3$ and distillation of the filtrate. Products were identified by VPC, NMR, ir, and comparison with authentic samples.

Acknowledgment. We thank the National Science Foundation (Grant No. GP-33566) and the Research Corporation for support. In addition, support from the National Institutes of Health—General Medical Sciences for a special postdoctoral fellowship for one of us (E.C.B.) is gratefully acknowledged.

Registry No.—*p*-Nitrobenzaldehyde dibutyl acetal, 19706-87-7; *p*-(dimethylamino)benzaldehyde dibutyl acetal, 53951-32-9; benzaldehyde dibutyl acetal, 5395-08-4; *p*-chlorobenzaldehyde dibutyl acetal, 53951-33-0; *o*-nitrobenzaldehyde dibutyl acetal, 53951-34-1; $AlCl_3$, 7446-70-0.

References and Notes

(1) On leave from Rollins College, 1972–1973.
(2) Fellow of the Alfred P. Sloan Foundation, 1971–1973.
(3) D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Am. Chem. Soc.*, **94**, 9284 (1972).
(4) E. C. Blossey, L. M. Turner, and D. C. Neckers, *Tetrahedron Lett.*, 1823 (1973).

Application of an Optically Active Nuclear Magnetic Resonance Shift Reagent to Configurational Problems

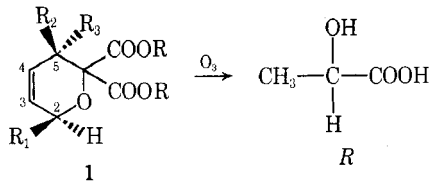
Krzysztof Jankowski* and Andrzej Rabczenko

Université de Moncton, Moncton, N.B., Canada, and Max Planck Institut für Experimentelle Medizin, Göttingen, Germany

Received September 20, 1974

The use of an optically active NMR shift reagent, such as $Eu(hfac)_3$, offered an interesting approach to the problem of the determination and correlation of configuration, or the evaluation of the optical yield of reactions. The principal effect of such optically active shift reagents is the separation of NMR signals for the corresponding enantiomers by the selective complexation of one enantiomer. In this study we report the application of $Eu(hfac)_3$ (europium 3-trifluoroacetyl-*d*-camphorate) to the determination of the configuration at C-2 of a series of derivatives of 2-methyl-

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.

References and Notes

(1) K. Jankowski and J. Couturier, *J. Org. Chem.*, **37**, 3997 (1972).
(2) O. Achmatowicz, J. Jurczak, A. Konowal, and A. Zamojski, *Org. Magn. Reson.*, **2**, 55 (1970).
(3) (a) R. J. Ferrier and G. H. Sankey, *J. Chem. Soc.*, 581 (1969); 1417 (1967); (b) K. Jankowski and R. Luce, *Tetrahedron Lett.*, 2069 (1974).
(4) O. Achmatowicz and A. Zamojski, *Rocz. Chem.*, **35**, 1251 (1961).
(5) K. Jankowski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **21**, 741 (1973).
(6) The spectrum of **3** showed also the residual signals corresponding to the partially racemized compound.
(7) G. N. LaMar, *J. Chem. Phys.*, **42**, 1985 (1965).

Deamination of 2-Amino-1-cyclopropylethanol

Stanley C. Bunce,* Stephen D. Clemans, and Bruce A. Bennett[1]

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Received October 7, 1974

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