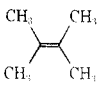
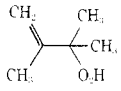
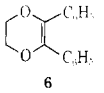
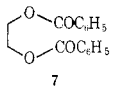
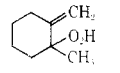
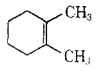
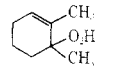
Table I
Oxidations with 1-Phospha-2,8,9-trioxaadamantane Ozonide (2)

Singlet oxygen acceptor	Products	Acceptor concn, M	Ozonide concn, M	% yield (isold) [a, b]
 4	 5	0.11 0.11	0.11 0.22	52 77
 6	 7	0.11	0.22	82
 8	 9	0.11 0.11 0.55	0.11 0.33 0.11	56 89 95[c]
	 11[d]			95
 10	 12[d]	0.11	0.11	5

[a] Products were identified by comparison with authentic samples. [b] The isolated yields are based on starting alkene. [c] Yield based on ozonide 2. [d] Products from this reaction were analyzed by gas chromatography as the alcohols obtained by triphenylphosphine reduction of 11 and 12.

Table II
First-Order Rate Constants for the Decomposition of 2 in CH_2Cl_2

T, °C	k_1, sec^{-1}	$t_{1/2}$, min
18.2	1.07×10^{-3}	10.8
10.9	4.63×10^{-4}	24.9
3.3	2.55×10^{-4}	90.6
1.1	9.94×10^{-5}	116
−4.4	6.97×10^{-5}	166

Table III
Transition-State Parameters for Decomposition of 2 in CH_2Cl_2

E_a	19.1 ± 1.2 kcal mol^{-1}
Log A	11.45
$\Delta G^{\ddagger}(9°)$	20.3 kcal mol^{-1}
$\Delta H^{\ddagger}(9°)$	18.6 kcal mol^{-1}
$\Delta S^{\ddagger}(9°)$	−6.3 eu

iquot of the ozonide solution at −78°. The resultant solution is then allowed to warm to ambient temperature over a period of 30 min. The CH_2Cl_2 is removed under vacuum and the residue treated with CCl_4 to give a CCl_4 solution of the product. The phosphate **3** is almost totally insoluble in CCl_4.

The rate of decomposition of **2** in CH_2Cl_2 has been measured at a series of temperatures by following the oxygen evolution.[9] The first-order rate constants are given in Table II. These data were used to calculate the activation energy and the transition-state parameters for decomposition (Table III). We, therefore, find that 1-phospha-2,8,9-trioxaadamantane ozonide (**2**) is 106 times more stable at −5° than triphenyl phosphite ozonide and 1.4 times more stable than the ozonide from the bicyclic phosphite, 1-ethyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane.[5,6,10]

Of further interest is the fact that **2** is soluble in water and can be used as a source of singlet oxygen in H_2O. These experiments will be described shortly.

References and Notes

(1) The authors gratefully acknowledge the support of the U.S. Army Research Office—Durham, the Petroleum Research Fund, administered by the American Chemical Society, and Eli Lilly and Co. This work was presented in part at the 6th Central Region Meeting of the American Chemical Society, Detroit, Mich., April 1974.
(2) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968); W. R. Adam in "Oxidation," Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N.Y., 1971, p 65; T. Wilson and J. T. Hastings, *Photophysiology*, **5**, 49 (1970); R. W. Denny and A. Nickon, *Org. React.*, **20**, 133 (1973).
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(5) M. E. Brennan, *Chem. Commun.*, 956 (1970).
(6) L. M. Stephenson and D. E. McClure, *J. Amer. Chem. Soc.*, **95**, 3074 (1973).
(7) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965). As bicyclic phosphate esters are known to be toxic [*Chem. Eng. News*, **52** (1), 56 (1974)] one should also handle the phosphite **1** with caution.
(8) E. C. Blossey, D. C. Neckers, A. L. Thayer, and A. P. Schaap, *J. Amer. Chem. Soc.*, **95**, 5820 (1973).
(9) The rates of decomposition of *2* were measured in carefully dried CH_2Cl_2 (washed with concentrated H_2SO_4 and distilled from P_2O_5) using *freshly* sublimed phosphite **1**.
(10) The E_a for the decomposition of triphenyl phosphite ozonide is 14.1 kcal/mol.[4] Using the rate constants reported by Brennan[5] and Stephenson[6] for the decomposition of 1-ethyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane ozonide, we calculate a value of 4.4 kcal/mol for the E_a. Therefore additional experiments on the thermal stability of this ozonide seem to be required.
(11) Alfred P. Sloan Research Fellow, 1974–1976.

Department of Chemistry **A. Paul Schaap***[11]
Wayne State University **Kenneth Kees**
Detroit, Michigan 48202. **Arthur L. Thayer**

January 21, 1975

An Asymmetric Synthesis of 2-Substituted γ-Butyrolactones and 2-Substituted 1,4-Butanediols

Summary: The preparation of the titled compounds has been accomplished in 64–73% optical purity using low temperature alkylation of chiral oxazolines.

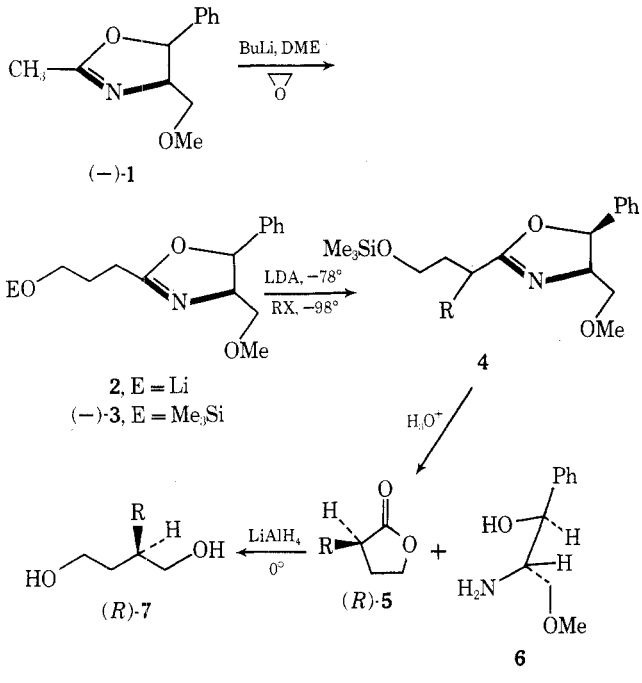
Sir: The recently demonstrated utility of (4*S*,5*S*)-2-methyl-4-methoxymethyl-5-phenyl-2-oxazoline (**1**) as a precursor to (*R*)- and (*S*)-dialkylacetic acids in 60–80% enantiomeric purity[1] has the potential to reach a variety of chiral molecules. We wish to further demonstrate that efficient avenues to lactones and 1,4-diols of high optical purity are also possible via this technique. As in previous examples,[2] the chiral amino alcohol **6** is recovered without loss of optical purity and may be recycled to oxazoline **1**.

Treatment of **1** with *n*-butyllithium (−78°) in dimethoxyethane (DME) followed by addition of ethylene oxide (5 equiv, −78°, then 18 hr at 0°) produced the lithio salt **2** which was directly treated with chlorotrimethylsilane furnishing the oxazoline trimethyl silyl ether **3** [80%; 150° (0.01 Torr); ir (film) 1670 cm^{-1}; NMR (CCl_4) δ 7.27 (s, 5), 5.2 (d, 1), 4.0 (m, 1), 3.8–3.2 (m, 4), 3.38 (s, 3), 2.4 (br t, 2), 1.85 (m, 2), 0.09 (s, 9); $[\alpha]^{23}_{589}$ −41.6° (*c* 9.8, $CHCl_3$)]. The latter now represents the starting material for all of the chiral substituted lactones and butanediols (vide infra). Addition of 1.05 equiv of lithium diisopropylamide (LDA) to **3** (−78°, THF, 30 min) formed the deep yellow anion whose solution was cooled to −98° (liquid N_2–MeOH) and treated with 1.05 equiv of the alkyl halide;[3] the temperature was maintained for 1–2 hr and then allowed to warm slowly to ambient. After quenching (saturated NH_4Cl) and ethereal extraction, the crude alkylated oxazolines **4** (~100%) were hydrolyzed without further purification (4.5 *N* HCl, 15 min, reflux) to the 2-substituted

Table I
Asymmetric Synthesis of (*R*)-γ-Butyrolactones 5 and (*R*)-1,4-Butanediols 7

Compd	R	Yield, %[a]	$[\alpha]^{23}_{589}$ (cEtOH)	Optical purity, %	CD, $[\theta]_{218\ nm}$ (CH_3CN)
(*R*)-5	Me	58	+13.80 (10.0)	64.2[b]	−1430[g]
(*R*)-5	Et	68	−7.65 (9.8)		−1750
(*R*)-5	*n*-Pr	75	−8.05 (5.7)	73.3[c]	−1870
(*R*)-5	Allyl	60	−16.50 (4.8)	72.0[c]	−1730
(*R*)-5	*n*-Bu	71	−7.30 (9.7)		−1600
(*R*)-7	*n*-Pr	90[d]	+3.47 (neat)	73.3[e]	
(*R*)-7	Allyl	92[d]	+3.60 (neat)	72.0[f]	

[a] Yields of 5 based upon 3 unless otherwise noted. [b] T. Kaneko, K. Wakabayashi, and H. Katsura [*Bull. Chem. Soc. Jpn.*, 35, 1149 (1962)] report $[\alpha]^{15}D$ −21.5 (c 5.5, EtOH). [c] Based upon the optical purity of the corresponding 1,4-butanediols 7 which must be a minimum value since some racemization of 5 during the reduction is possible. [d] Based upon 5. [e] Literature value[5] +4.73° (neat). [f] Literature value[5] +5.0° (neat). [g] Molecular ellipticities were determined on a Varian-Cary Model 61 CD instrument. Units are degrees centimeter squared/decimole.



γ-butyrolactones **5**, all of which possessed the *R* configuration (Table I).[4] Since the absolute configuration and maximum rotation was known only for 2-methyl-γ-butyrolactone (**5**, R = Me), and a variety of chiral shift reagents failed to provide enantiomeric compositions for the lactones, it was necessary to correlate **5** by other methods. This was readily done by reducing ($LiAlH_4$, 0°, Et_2O) the 2-(*n*-propyl)- and 2-allylbutyrolactones to their corresponding 1,4-butanediols **7** which had been previously described by Freudenberg and Lwowski.[5] The facile conversion of **5** to **7** now makes chiral 1,4-butanediols readily accessible in optical purity comparable to those of the lactones. Furthermore, since the lactones **5** were all of the *R* configuration, as indicated by their comparable CD characteristics, the diols (+)-**7** can now be assigned the *R* configuration.[6]

The production of *R* lactones via this method is consistent with the mechanism proposed in our earlier report.[1] Reversal of the order of introduction of substituents on (−)-**1** would presumably lead to the *S* lactones. Work is continuing toward further utility of this asymmetric synthesis and the potential incorporation of chiral 1,4-butanediols as precursors to chiral polyethers and polyesters.

Acknowledgment. Financial support from the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

References and Notes

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(2) A. I. Meyers, G. Knaus, and K. Kamata, *J. Am. Chem. Soc.*, **96**, 268 (1974).
(3) Saturated alkyl groups were all introduced as their iodides, allylic and benzyl groups were added as the chlorides, while methyl was added as methyl sulfate (cf. ref 1).
(4) Metalation of the lithio salt **2** (E = Li) to the dilithio salt also gave alkylation upon addition of 1.0 equiv of alkyl halide. Hydrolysis to the lactone **5** proceeded smoothly; however, the optical purity was only 10–12%.
(5) K. Freudenberg and W. Lwowski [*Justus Liebigs Ann. Chem.*, **594**, 76 (1955)] prepared **7** (R = *n*-propyl, allyl) by reduction of the corresponding succinic acids which were obtained by resolution. No absolute configurations were reported by these authors.
(6) R. Rossi, P. Diversi, and G. Ingrosso [*Gazz. Chim. Ital.*, **48**, 1391 (1968)] have correlated (*R*)-(+)-2-methylsuccinic ester with (*R*)-(+)-2-methyl-1,4-butanediol.
(7) Eastman Kodak Fellow, 1974–1975.

Department of Chemistry
Colorado State University
Ft. Collins, Colorado 80521

A. I. Meyers*
Edward D. Mihelich[7]

Received December 4, 1974

A Rapid Procedure for the Hydrolysis of Amides to Acids

Summary: The hydrolysis of amides to acids by aqueous sodium peroxide (in less than 2 hr at 50–80°) in high yield and with little decarboxylation of the acid is reported.

Sir: The conversion of amides to carboxylic acids is considered a routine procedure but in practice it is not always straightforward.[1] Often vigorous conditions[2] and strong catalysts such as concentrated sulfuric or phosphoric acid[3] and strong alkali hydroxides are needed to effect the hydrolysis. In general, the yields of these reactions are fair to good but occasionally the severe reaction conditions cause decomposition of the desired acid. For example, we have found that the usual hydrolytic conversions of heterocyclic carboxamides to the corresponding acids are particularly difficult because the acids are prone to decarboxylation. To circumvent this problem a new method was developed. Specifically, we have found sodium peroxide (caution—see final paragraph for warning for using peroxides) to be a superior reagent for the mild hydrolysis of heterocyclic amides and other amides in general. The reaction is rapid and can be carried out at relatively low temperatures. We would like to recommend it as a simple, nonstringent general procedure.