

ketone:LiAl-		an an anna an anna ann an Anna				
	(O-t-Bu)3H	Cis	Trans	Cis	Trans	
	0.03	98.2	1.70,0			
	0.5	62.3	37.50,0		97 <sup>d</sup> , g	
	1.0		97 <sup>6, e</sup>		97 <sup>d</sup> , s	
	2.0		$97^{b,f}$		$97^{d,s}$	

<sup>a</sup> Equivalent reduction ratio (ERR). <sup>b</sup> 24-hr reaction time, followed by hydrolysis. <sup>c</sup> 95% conversion, based on NMR. <sup>d</sup> 6-hr reaction time, followed by hydrolysis. e 77% conversion, based on NMR. / 66% conversion, based on NMR. # 25% conversion based on NMR.

reductions with LiAlH<sub>4</sub> generally proceed uniquely from  $AlH_4^{-1}$  and not the mixed alkoxy hydrides,  $AlH_2(OR)_2^{-1}$ .

To exclude an intramolecular hydride transfer pathway, all but one of the hydrides on the reducing agent must be replaced. Reduction with LiAl(O-t-Bu)<sub>3</sub>H fulfills this requirement. Examination of Table II reveals that as the equivalent amount of LiAl(O-t-Bu)<sub>3</sub>H is decreased the trans-diol increases. Presumably the trans-diol results from the approach of a second LiAl(O-t-Bu)<sub>3</sub>H from the same side as the bulky alkoxyaluminum function. Since the data from the LiAlH<sub>4</sub> reductions parallels that of the  $LiAl(O-t-Bu)_{3}H$ , we see no need, at least at present, to invoke an intramolecular hydride transfer to explain the trans-diol in the LiAlH<sub>4</sub> case.

In both the LiAlH<sub>4</sub> and LiAl $(O-t-Br)_3H$  cases, it is possible that the carbonyl function first reduced may act as a neighboring group.<sup>9</sup> This group may then preferentially solvate the next reducing anion species, thus steering it in so that the trans product is formed. This explanation is consistent with the results obtained with minimal hydride and at low temperatures.

We are currently investigating 3-hydroxy-2,2-dimethylindanone under the same reaction conditions. Its aluminate is a possible intermediate in the reduction of 2,2-dimethylindandione. Experimental details and the completed work on this study will be reported at a later date.

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## 1-Phospha-2.8.9-trioxaadamantane Ozonide. A Convenient Source of Singlet Molecular Oxygen<sup>1</sup>

Summary: Thermal decomposition of 1-phospha-2,8,9trioxaadamantane ozonide produces singlet molecular oxygen in quantitative yield  $(k_1 = 1.01 \times 10^{-3} \text{ sec}^{-1} \text{ at } 18^\circ \text{ in}$ CH<sub>2</sub>Cl<sub>2</sub>).

Sir: The reactions of singlet molecular oxygen  $({}^{1}O_{2})$  with various organic substrates have been extensively investigated in recent years.<sup>2</sup> The possible role of <sup>1</sup>O<sub>2</sub> in biological oxidation processes has also been of interest.<sup>3</sup> Singlet oxygen can be generated by photosensitization and by chemical methods such as the spontaneous decomposition of phosphite ozonides. Murray<sup>4</sup> and coworkers have shown that triphenyl phosphite ozonide decomposes at  $-30^{\circ}$  to yield  ${}^{1}O_{2}$  which may be trapped by an acceptor in solution. However, separation of the oxidation products from the triphenyl phosphate is often difficult. In addition, triphenyl phosphite ozonide is not sufficiently stable to permit storing this reagent conveniently.

It has been suggested that polycyclic phosphite ozonides should exhibit unusual stability as a result of restricted pseudorotation.<sup>5,6</sup> We wish to report that the adduct 2 obtained from the addition of ozone to 1-phospha-2,8,9trioxaadamantane  $(1)^7$  is a relatively stable ozonide which decomposes quantitatively to  ${}^{1}O_{2}$  and phosphate 3.



Singlet oxygen exhibits three modes of reaction with alkenes: 1,4 cycloaddition with conjugated dienes to yield cyclic peroxides, the "ene" reaction to form allylic hydroperoxides, and 1,2 cycloaddition to give 1,2-dioxetanes which subsequently cleave to carbonyl-containing products. Examples of these reactions using the ozonide 2 as the source of <sup>1</sup>O<sub>2</sub> are summarized in Table I. A trapping experiment using a 5:1 excess of acceptor 8 gave a 95% yield of the product 9 based on ozonide 2. One criterion for the intermediacy of singlet oxygen in a reaction is the product distribution obtained from 1,2-dimethylcyclohexene (10).8 Decomposition of 2 in the presence of 10 in  $CH_2Cl_2$  yields a ratio of the two hydroperoxides 11 and 12 which is consistent with the formation of free  ${}^{1}O_{2}$  in the reaction.

In a typical experiment, a 0.12 M solution of the ozonide 2 in  $CH_2Cl_2$  was prepared by the slow addition of a solution of 0.24 g (1.5 mmol) of 1 in 3 ml of CH<sub>2</sub>Cl<sub>2</sub> to 10 ml of  $CH_2Cl_2$  at  $-78^\circ$  continuously saturated with ozone. After the addition is complete, dry nitrogen is bubbled through the solution to remove the excess ozone. A solution of the singlet oxygen acceptor in 1 ml of CH<sub>2</sub>Cl<sub>2</sub> is added to an al-

Table I Oxidations with 1-Phospha-2.8.9-trioxaadamantane Ozonide (2)

		( )			
Singlet oxygen acceptor	Products	Acceptor concn, M	Ozonide concn <sub>4</sub> M	% yield (isold) <sup>a</sup> , b	-
CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	$CH_2$ $CH_3$ $CH_3$ $CH_4$ $CH_3$ $O_2H$	0.11 0.11	0.11 0.22	52 77	
		0.11	0.22	82	
8	9	0.11 0.11 0.55	0.11 0.33 0.11	56 89 95°	
CH <sub>3</sub>	CH <sub>2</sub> O <sub>2</sub> H CH <sub>3</sub> H <sup>2</sup>	0.11	0.11	95	
10 CH3	CH. O.H. CH.			5	

<sup>a</sup> Products were identified by comparison with authentic samples. <sup>b</sup> The isolated yields are based on starting alkene. <sup>c</sup> Yield based on ozonide 2. <sup>d</sup> 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<sub>2</sub>Cl<sub>2</sub>

<i>т,</i> °с	k <sub>1</sub> , sec <sup>-1</sup>	<sup>t</sup> <sub>1/2</sub> , <sup>min</sup>
18.2	$1.07  imes 10^{-3}$	10.8
10.9	$4.63 imes10^{-4}$	24.9
3.3	$2.55 imes10^{-4}$	90,6
1.1	$9.94 imes10^{-5}$	116
-4.4	$6.97 imes10^{-5}$	166

Table III **Transition-State Parameters for** Decomposition of 2 in CH<sub>2</sub>Cl<sub>2</sub>

$E_{a}$ Log A	$19.1 \pm 1.2 \text{ kcal mol}^{-1}$ 11.45
$\Delta G^{\ddagger}(9^{\circ})$	20.3 kcal mol <sup>-1</sup>
$\Delta H^{\ddagger}(9^{\circ})$	18.6 kcal mol <sup>-1</sup>
$\Delta S^{\ddagger}(9^{\circ})$	-6.3 eu

iquot of the ozonide solution at  $-78^{\circ}$ . The resultant solution is then allowed to warm to ambient temperature over a period of 30 min. The CH<sub>2</sub>Cl<sub>2</sub> is removed under vacuum and the residue treated with CCl<sub>4</sub> to give a CCl<sub>4</sub> solution of the product. The phosphate 3 is almost totally insoluble in CCl4.

The rate of decomposition of 2 in CH<sub>2</sub>Cl<sub>2</sub> has been measured at a series of temperatures by following the oxygen evolution.<sup>9</sup> 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-2,8,9trioxaadamantane ozonide (2) is 106 times more stable at  $-5^{\circ}$  than triphenyl phosphite ozonide and 1.4 times more stable than the ozonide from the bicyclic phosphite, 1ethyl-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**

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- kcal/mol.<sup>4</sup> Using the rate constants reported by Brennan<sup>5</sup> and Stephenson<sup>6</sup> for the decomposition of 1-ethyl-4-phospha-35,5-krioxabicycl-o[2.2.2]octane ozonide, we calculate a value of 4.4 kcal/mol for the Therefore additional experiments on the thermal stability of this ozonide seem to be required.
- (11) Alfred P. Sloan Research Fellow, 1974-1976.

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## An Asymmetric Synthesis of 2-Substituted $\gamma$ -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 (4S, 5S)-2methyl-4-methoxymethyl-5-phenyl-2-oxazoline (1) as a precursor to (R)- and (S)-dialkylacetic acids in 60-80% enantiomeric purity<sup>1</sup> 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,<sup>2</sup> 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  $(-78^{\circ})$  in dimethoxyethane (DME) followed by addition of ethylene oxide (5 equiv,  $-78^\circ$ , then 18 hr at  $0^\circ$ ) produced the lithio salt 2 which was directly treated with chlorotrimethylsilane furnishing the oxazoline trimethyl silvl ether 3 [80%; 150° (0.01 Torr); ir (film) 1670 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) § 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<sub>3</sub>)]. 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  $-98^{\circ}$  (liquid N<sub>2</sub>–MeOH) and treated with 1.05 equiv of the alkyl halide;<sup>3</sup> the temperature was maintained for 1-2 hr and then allowed to warm slowly to ambient. After quenching (saturated NH<sub>4</sub>Cl) and ethereal extraction, the crude alkylated oxazolines 4 ( $\sim$ 100%) were hydrolyzed without further purification (4.5 N HCl, 15 min, reflux) to the 2-substituted