monomeric species $[LMn(OH_2)_3]^{2+}$. Rapid oxidation of this monomer to a LMn^{III} species can then be achieved by the O_2 present in solution. When the same reaction was carried out in a solution containing chloride ions (0.5 M) at pH 3, under otherwise identical conditions, 100% O_2 was released. The spectrum of the resulting solution is very similar to that of $LMn^{III}Cl_3$.[13] Thus the above disproportionation reaction does not occur. This result may have interesting implications on the functional role of Cl^- in PS II.

Presently we are studying the mechanism of formation and decomposition and the reactivity of **1** in detail.

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Supplementary Material Available: Tables of complete crystallographic data, atom coordinates, calculated positions of H atoms, and anisotropic thermal parameters for $[L_2Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2)](ClO_4)_2$ (6 pages); listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Diazotization of 1-Aminocyclopropanecarboxylic Acid. Solution Chemistry of Oxaspiropentanone

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The retention of stereochemistry in the nitrosative deamination of α-amino acids is explained by the intermediate formation of α-lactones.[2] Neighboring-group participation occurs with inversion of stereochemistry, followed by nucleophilic α-alkyl C–O bond cleavage. The strain of α-lactones makes them intrinsically reactive; they are generally unstable, undergoing polymerization at temperatures above −100 °C in a process explainable via zwitterionic no-bond resonance forms.[3] Theoretical studies suggest, though, that such zwitterions are chimeric.[4]

The reactivity of α-lactones is influenced by steric and by electronic factors. The behavior of tertiary α-amino acids under diazotization conditions is consistent with an increased zwitterionic character of the α-lactone; some racemization and carbonium ion rearrangements are observed.[5] On the other hand, di-*tert*-butylacetolactone persists at −60 °C,[6] bis(trifluoromethyl)acetolactone is stable in solution or the gas phase,[7] and a hindered perfluoroacetolactone is isolable.[8] It may be considered that oxaspiropentanone (**1**) would be stabilized by decreased contribution of the no-bond resonance form **2** due to the high energy of a cyclopropyl carbocation (eq 1). Alternatively, the combined strain of two three-membered rings might confer decreased stability. A number of α-lactones, including **1**, have been accessible for study by matrix isolation at 77 K,[9] but no solution chemistry of **1** is known. This communication reports the first evidence for the existence of **1** in solution and its participation in synthetic transformations.

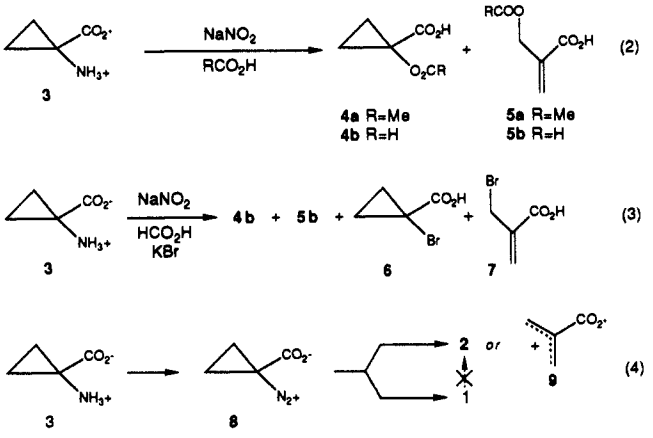
(1)

1 **2**

Table I

[ACC], mM	[KBr], mM	4b:6	5b:7	(4b + 6): (5b + 7)
180	0 (0 equiv)	100:0	100:0	86:14
135	135 (1 equiv)	93:7	>99:1	86:14
145	435 (3 equiv)	92:8	>99:1	86:14
125	635 (5 equiv)	89:11	83:17	86:14
140	995 (7 equiv)	71:29	71:29	87:13
260	sat (10 equiv)	58:42	67:33	87:13

Standard conditions for diazotization[10] (1 equiv of sodium nitrite, glacial acetic acid) were applied to 1-aminocyclopropanecarboxylic acid (ACC, eq 2). The major product, isolated in 60% yield, is 1-acetoxycyclopropanecarboxylic acid (**4a**).[11] (Hydroxymethyl)acrylic acid derivative **5a** is obtained as 3% of the total product. Increasing the solvent polarity (anhydrous formic acid) leads to a greater proportion of ring-opening product **5b** (13%). The hypothesis that the α-lactone is the precursor to both **5** (via **2**) and **4** was tested by a competition study between formate and bromide as nucleophiles (eq 3). As shown herein, it is possible to obtain substitution products with other nucleophiles in solvents of low nucleophilicity. The data in Table I show both ring-opening and substitution products incorporating both nucleophiles. As expected, the proportion of bromides increases with increasing bromide ion concentration, but the proportion of ring-opening products remains constant. Therefore, α-lactone **1** cannot be the common intermediate, and diazonium ion **8** is suggested. Partitioning between the two pathways must be an irreversible, unimolecular, and solvent-dependent process. There must be an intermediate between **8** and substitution products which does not ring-open. Likewise, **2** may not be involved in substitution. These requirements are met by eq 4. It is not possible on the basis of these data to determine whether loss of nitrogen leads to **2** or directly to the allyl cation **9**.



3 **6** **7** **8** **9**

Stereochemical studies also support oxaspiropentanone **1** as the intermediate in the substitution reaction. Both (1*R**,2*S**)- and (1*R**,2*R**)-2-ethyl-1-aminocyclopropanecarboxylic acid are available from a previous study.[12] When treated under the above

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(11) After acetylation of the crude reaction mixture. Omitting this step reduces the yield to 42%, presumably because the extremely water soluble 1-hydroxycyclopropanecarboxylic acid is also produced by competitive nucleophilic trapping with water. Including sodium acetate (10 equiv) in the diazotization reaction similarly increases the yield to 50%.

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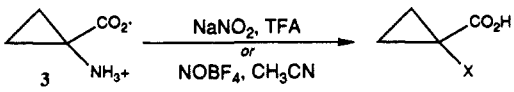
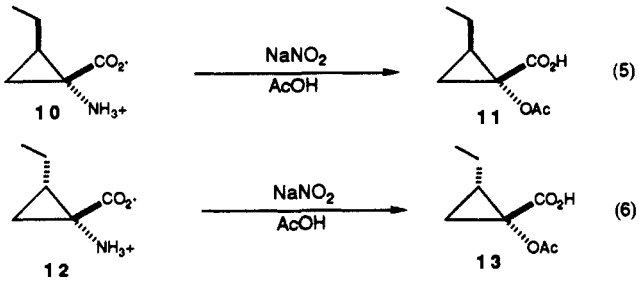
Table II



compd	nucleophile	yield, %
6	LiBr	73
14	KCl	75
15	EtOH	65
16	CH_3COSH	60
17	KCN	64
18	$CH_2{=}CHCH_2Si(CH_3)_3$	30

diazotization conditions, each produces a different diastereomeric acetoxy acid (75 and 78%, eqs 5 and 6). That these processes proceed with overall *retention* of stereochemistry was established by comparison with an authentic sample of **13** prepared by literature methods.[13]



The reactions of **1** in trifluoroacetic acid with other nucleophiles were examined. This solvent change eliminates competing nucleophilic trapping. Substitution can also be effected in acetonitrile with nitrosonium tetrafluoroborate[14] as the diazotizing agent. As summarized in Table II, halide, sulfur, and even carbon nucleophiles (allyltrimethylsilane, cyanide) provide substitution products in respectable yields. For comparison with bis(trifluoromethyl)acetolactone, the only α-lactone that reacts with ethanol via acyl-C–O cleavage (presumably due to decreased polarization of the alkyl-C–O bond), diazotization of **3** was conducted in the presence of ethanol. The exclusive formation of the α-alkoxy acid was observed.

Both kinetic and stereochemical studies imply the generation of oxaspiropentanone **1** in the deamination of ACC.[15] The reactivity of **1** with ethanol suggests greater α-alkyl-C–O bond polarization compared with bis(trifluoromethyl)acetolactone. Evidence from this reaction that **8** is the common intermediate and that ring-opening products cannot be derived from the α-lactone suggests that the rearrangements and racemization observed on diazotization of tertiary amino acids may be occurring not through opening of their α-lactones but via the diazonium ions.

These transformations provide ready access to substituted cyclopropanecarboxylic acid derivatives that are otherwise difficult to obtain, particularly because the enolate chemistry of cyclopropanecarboxylic acid is extremely limited.[16] Oxaspiropentanone is thus an umpolung synthon for **2**.[17]

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Supplementary Material Available: Experimental procedures for the syntheses of **4a,b**, **6**, **11**, and **13–18** and Table S1 containing spectral data (11 pages). Ordering information is given on any current masthead page.

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Simple One-Pot Syntheses of Spiroketals and Oxaspirolactones by Addition of γ- and δ-Cerioalkoxides to Lactones and Cyclic Anhydrides

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We present here a method of preventing the ring opening, leading to double addition, that often occurs when organometallics react with lactones, and the utility of this method is illustrated by novel one-pot syntheses of spiroketals, including two pheromones. Reactions of organolithium compounds or Grignard reagents with lactones are unpredictable, giving products derived from the addition of 1 or 2 equiv of the nucleophile to the carbonyl group.[1,2] Unsubstituted, saturated lactones tend to undergo double organometallic attack to give diols,[1-3] whereas polysubstituted lactones are somewhat more prone to monoaddition of organolithium compounds and Grignard reagents.[4,5] Lithium acetylides are widely employed since they give satisfactory yields of monoaddition products which are important intermediates in the synthesis of natural spiroketals.[8]

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