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THE LEAD (IV) ACETATE OXIDATION OF CYCLOPROPANE DERIVATIVES: A NOVEL FRAGMENTATION REACTION

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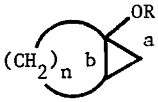
The potential use of 1-trimethylsilyloxybicyclo[n.1.0]alkanes, 1,[1] as useful synthetic intermediates has recently been demonstrated. Not only do 1 serve as precursors to the corresponding cyclopropanols, 2,[2] but treatment of 1 with acid,[3] base,[4] or halogen[5] results in the production of products related to specific "a" bond cleavage. Further, treatment of 1 with iron (III) chloride leads to specific "b" bond rupture.[6,7]



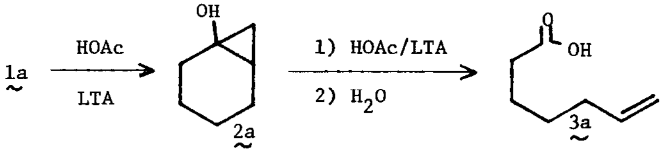
1: R=TMS
2: R=H

We would like to report that the reaction of 1 with lead (IV) acetate (LTA) in acetic acid affords 3 via a novel fragmentation reaction involving both the "a" and "b" bonds of 1 (Equation 1).[8,9]

$$\mathbf{1} \xrightarrow[2)\ H_2O]{1)\ LTA/HOAc} \underset{\mathbf{3}}{HO_2C\text{-}(CH_2)_n\text{-}CH{=}CH_2} \qquad \text{(Eq. 1)}$$

An indication of the scope of the process may be obtained from the data included in Table I. In terms of yield and the control of the positioning of the remote double bond, the reaction holds great promise as general synthetic technique. Since the regiospecific generation of 1 has been well established,[1] control of the site of fragmentation is also possible with respect to other functionality in 1. This aspect of the work is shown by the transformation of 1b into 3b.

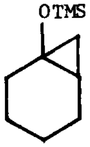
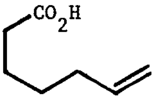
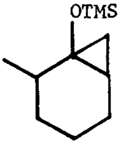
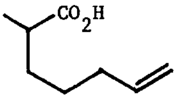
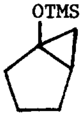
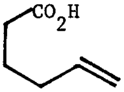
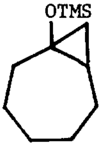
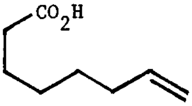
Although 1a appears to be quite stable in acetic acid, introduction of a small quantity of lead (II) acetate promotes the rapid conversion of 1a into 2a (NMR study). This data indicates that the fragmentation process is actually an oxidation reaction involving 2.[10] Cyclopropanol 2a affords 3a in 83% yield upon LTA treatment followed by aqueous workup (Equation 2). If this reasoning is correct, a trimethylsilyloxycyclopropane with a greater ring nucleophilicity



83% (Eq. 2)

Table I

The LTA Oxidation of 1

1[a,b]	3[b]	% Yield of Isolated 3	Physical Properties of 3
 1a	 3a	83	bp 99.5-100°C (0.85) mm; n $^{19}_{D}$ 1.4440 lit[c] bp 125°C (15) mm; n $^{14.9}_{D}$ 1.4404
 1b	 3b	64	100°C (0.85) m; n $^{17.5}_{D}$ 1.4477
 1c	 3c	62	(GLPC isolation); n $^{23}_{D}$ 1.4350 lit[d] bp 203-204°C (760) mm; n $^{19}_{D}$ 1.4375
 1d	 3d	92	113-115°C (5) mm; n $^{23}_{D}$ 1.4450 lit[e] bp 123-125°C (15) mm

a) Prepared by the method cited in reference 1. b) All compounds have ir, NMR, and ms properties consistent with the proposed structures. All new compounds show C and H analyses within ± 0.3% of theoretical. c) P. Gaubert, R. P. Linstead, and H. N. Rydon, J. Chem. Soc., 1971 (1937). d) O. Wallach, Ann., 343, 48 (1905). e) Fairweather, Pr. R. Soc. Edinb., 46, 74 (1876) (Beils., II, 2, 413).

than that of 1[12] might be expected to react with LTA prior to conversion into the corresponding cyclopropanol, and, hence, fragmentation would not occur. Compounds 4 and 5 allowed testing of this hypothesis, and proved it to be correct (Scheme I). LTA treatment of 4 gave predominant production of 6[13] while fragmentation occurred with 5 to afford 7 (Table II).[14]

Scheme I

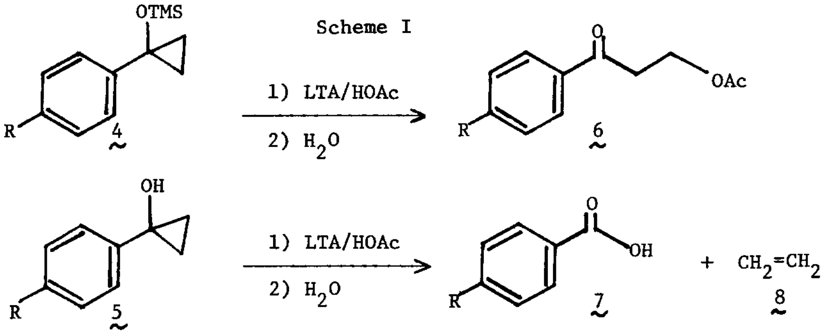


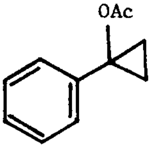
Table II

The LTA Oxidation of 4 and 5

4[a,b]	6[b] (% yield of isolated 6; mp, lit mp)	5[b,c]	7[b] (% yield of isolated 7; mp, lit mp)
R	R	R	R
4a:H	6a:H (70; 54-55°C, lit[d] 53-54°C)	5a:H	7a:H (77; 120-122°C, lit[e] 121.5°C)
4b:F	6b:F (80; 86.5-87.5°C)	5b:F	7b:F (80; 182-185°C, lit[f] 182°C)
4c:Cl	6c:Cl (95; 140°C, dec)	5c:Cl	7c:Cl (93; 238-240°C, lit[g], 243°C)

a) Prepared by the method cited in reference 1. b) All compounds have ir, NMR, and ms properties consistent with the proposed structures. All new compounds show C and H analyses within ± 0.3% of theoretical. c) Prepared by the method cited in reference 2. d) Auwers and Muller, J. Prak. Chem., 137, 102, 124 (1933) (Beils., III, 8, 396). e) Kellas, Z. Phys. Chem., 24, 222 (1911) (Beils., I, 9, 96). f) Jaeger, Mineral., 32, 389 (1909) (Beils., I, 9, 333). g) Fels, Z. Krystall. Mineral., 32, 389 (1909) (Beils., I, 9, 340).

Further, 9 and 10 are inert to LTA under the reaction conditions employed, due, presumably to the deactivating influence of the acetoxy group.[12]



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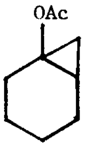

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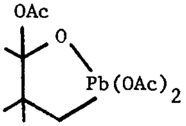
A likely reaction intermediate in the fragmentation process is 11, and studies designed to clarify this point are currently underway.



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Footnotes and References:

1) Prepared from the reaction of Simmons-Smith reagent and the appropriate trimethylsilyl enol ether, see: M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, New York, N.Y., 1975, volume 5, p. 588.
2) S. Murai, T. Aya, and N. Sonoda, J. Org. Chem., 38, 4354 (1973).
3) I. Ryu, S. Murai, S. Otani, and N. Sonoda, Tetrahedron Lett., 1995 (1977), and references cited therein.

4) a) G. M. Rubottom and M. I. Lopez, *J. Org. Chem.*, *38*, 2097 (1973). b) J. M. Conia and C. Girard, *Tetrahedron Lett.*, 2767 (1973).

5) S. Murai, Y. Seki, and N. Sonoda, *J. Chem. Soc. Chem. Commun.*, 1032 (1974).

6) Y. Ito, S. Fujii, and T. Saegusa, *J. Org. Chem.*, *41*, 2073 (1976).

7) See, also: P. Amice, L. Blanco, and J. M. Conia, *Synthesis*, 196 (1976).

8) In a typical oxidation, a solution of 5 mmol of LTA in 30 mL of glacial acetic acid was treated with 5 mmol of neat **1**. After 8 hr of stirring under N_2 at room temperature the mixture was diluted with 30 mL of water and extracted with 2 x 200 mL of pentane. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and solvent removed *in vacuo* to afford crude **3**. Purification of **3** was then effected by preparative GLPC or distillation to give pure **3**.

9) Presented, in part, at the 32nd Northwest Regional Meeting of the ACS, Portland, Oregon, June 15-17, 1977, Abstract 176.

10) For other examples of the cyclopropanol oxidation see: C. H. DePuy and R. J. Van Lanen, *J. Org. Chem.*, *39*, 3360 (1974); and references cited therein.

11) Prepared according to the method cited in reference 2.

12) A. De Boer and C. H. DePuy, *J. Am. Chem. Soc.*, *92*, 4008 (1970).

13) NMR analyses of crude reaction mixtures indicated the presence of small amounts of **7**.

14) In the reaction of **5a** with LTA, **8** was trapped and isolated as 1,2-dibromoethane.