It was identified through ^1H NMR [($DCCl_3$) δ 2.36 (s, 3, $COCH_3$), 2.46 (s, 3, $ArCH_3$ at C-4'), 2.48 (s, 3, $ArCH_3$ at C-2'), 7.02-7.10 (m, 2, Ar H) 7.62 (d, 1, J = 8 Hz, Ar H at C-6')], mass spectrum [m/e 248 (M^+)], and the preparation of the orange 2,4-dinitrophenylhydrazone, mp 168–170 °C [lit.[12] mp 169–170 °C].

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Registry No. 3,4,5,6,7,8-Hexahydro-1(2*H*)-anthracenone, 5440-71-1; 2,3,5,6,7,8-hexahydro-4(1*H*)-phenanthrenone, 13250-73-2; 2,3-dihydro-4(1*H*)-phenanthrenone, 778-48-3; 3,4-dihydro-1(2*H*)-phenanthrenone, 573-22-8; 5,8,9,10-tetrahydrobenz[*a*]anthracen-11-(6*H*)-one, 1470-04-8; 2,3-dihydro-4(1*H*)-chrysenone, 66267-06-9; 9,10-dihydro-11(8*H*)-benz[a]anthracenone, 60968-15-2; 3,4-dihydro-1(2*H*)-naphthalenone, 529-34-0; 2-methyl-3,4-dihydro-1(2*H*)-naphthalenone, 1590-08-5; 2,3-dihydroinden-1(1*H*)-one, 83-33-0; 3-methyl-2,3-dihydroinden-1(1*H*)-one, 6072-57-7; 6-methyl-2,3-dihydroinden-1(1*H*)-one, 24623-20-9; 7-methyl-2,3-dihydroinden-1-(1*H*)-one, 39627-61-7; 5-methyl-2,3-dihydroinden-1(1*H*)-one, 4593-38-8; 4-methyl-2,3-dihydroinden-1(1*H*)-one, 24644-78-8; methanesulfonic acid, 75-75-2; *m*-xylene, 108-38-3; 2',4'-dimethylacetophenone, 89-74-7; 5,6,7,8-tetrahydro-2-naphthalenebutanoic acid, 782-27-4; 2-naphthalenebutanoic acid, 782-28-5; 1-naphthalenebutanoic acid, 781-74-8; 9,10-dihydro-2-phenanthrenebutanoic acid, 7494-59-9; 2-phenanthrenebutanoic acid, 77520-30-0; benzenebutanoic acid, 1821-12-1; α-methylbenzenebutanoic acid, 1949-41-3; benzenepropanoic acid, 501-52-0; β-methylbenzenebutanoic acid, 4593-90-2; 4-methylbenzenepropanoic acid, 1505-50-6; 3-methylbenzenepropanoic acid, 3751-48-2; 2-methylbenzenepropanoic acid, 22084-89-5; 2',4'-dimethylacetophenone 2,4-DNP derivative, 77520-31-1.

(12) Pollock, J. R. A., Stevens, R., Eds. "Dictionary of Organic Compounds", 4th ed.; Oxford University Press: New York, 1965; Vol. 2, p 1135.

Stereoselective, Catalytic Reduction of L-Ascorbic Acid: A Convenient Synthesis of L-Gulono-1,4-lactone

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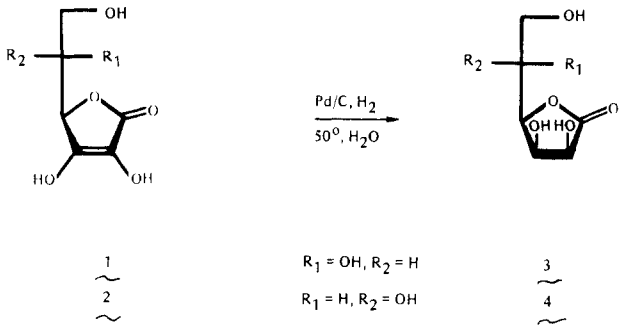
While the chemistry of the derivatization[1] and oxidative degradation[2] of L-ascorbic acid (1) is well documented, its behavior under reductive conditions has been little studied. During early work directed toward the structural elucidation of 1, catalytic reduction over PtO_2 was reported to afford a mixture of products of which only L-idonic acid was identified.[3a] Other workers reported that reduction of 1 afforded a lactone which was not identified further.[3b] More recently it has been reported that catalytic reduction of 1 gave poor results.[2b] 3-*O*-Methyl-L-ascorbic acid has been reported to hydrogenate in the presence of Pd/C to afford a saturated γ-lactone which was assigned the L-manno configuration.[4]



1 ~ 2 ~ R_1 = OH, R_2 = H; R_1 = H, R_2 = OH; 3 ~ 4 ~

During our investigations[5] into different syntheses of 1, we had occasion to determine the stability of 1 to different conditions of catalytic hydrogenation.[6] L-Ascorbic acid was found to be stable to hydrogenation over Raney Ni catalyst at moderate pressure and temperature (50 °C, 50 psi) and, as was previously reported,[3a] to afford a complex mixture of products over Pt catalyst.

However, the hydrogenation of 1 over 10% Pd/C at 50 °C and 50 psi hydrogen pressure resulted in the uptake of the stoichiometric amount of hydrogen to afford, quantitatively, a single new product as evidenced by GLC[7] and ^{13}C NMR of the isolated product. Recrystallization of a sample of this material from methanol–ethyl acetate gave material [mp 182–183.5 (lit.[8] mp 180–181 °C)] identical in spectral and physical characteristics with authentic L-gulono-1,4-lactone (3).

Similarly, D-erythorbic acid (2) under the same conditions affords a single major product in greater than 90% purity (by GLC analysis of the silylated reaction mixture)[7] from which D-mannono-1,4-lactone (4) is isolated in 71% yield [mp 151–151.5 °C (lit.[9] mp 151 °C)] after crystallization from methanol–ethyl acetate. In both cases, the hydrogenation appears to proceed stereoselectively via the delivery of hydrogen from the least hindered side of the enono-lactone moiety opposite the side chain.

These results suggest that the previously reported reduction of 3-*O*-methyl-L-ascorbic acid in fact affords 3-*O*-methyl-L-gulono-1,4-lactone not 3-*O*-methyl-L-mannono-1,4-lactone as reported.[4] The formation of 3-*O*-methyl-L-mannono-1,4-lactone would require delivery of hydrogen both from the more hindered face of the olefin *and* the highly unlikely epimerization at C-4.

Interestingly, both 1 and 2 are unstable to the conditions required for the hydrogenation *in the absence of hydrogen*. Heating 1 or 2 under a nitrogen atmosphere, in water, with Pd/C catalyst results in the disappearance of starting material and the formation of lactone 3 or 4, respectively. In the case of 2, lactone 4 has been isolated in 29% yield after removal of catalyst, neutralization with sodium hydroxide, precipitation of the sodium salt with methanol, and deionization with ion-exchange resin (Dowex-50, H^+ form). The course of the reaction appears to involve the disproportionation of the reductone over the Pd catalyst to neutral oxidized intermediates and hydrogen followed

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by the subsequent reduction of available enono-lactone. A similar transfer hydrogenation has recently been observed with D-glucose and D-mannose over Pt, Pd, and Rh castalysts.[10]

L-Gulono-1,4-lactone has been prepared by the catalytic reduction of D-glucurono-6,3-lactone,[8] and D-mannono-1,4-lactone is available via either bromine or catalytic air oxidation of D-mannose.[9] As both L-ascorbic acid and erythorbic acid are items of commerce, their stereoselective reduction represents a convenient and economic alternative for the preparation of L-gulono- and D-mannono-1,4-lactone lactones.[11-13]

Experimental Section

L-Gulono-1,4-lactone (3). A solution of 23.1 g (0.13 mol) of L-ascorbic acid in 170 mL of H_2O was hydrogenated over 2.2 g of 10% Pd/C (Lot 21,005, Engelhard) in a Parr hydrogenator at 50 °C and 50 psi hydrogen pressure for 24 h. The catalyst was removed by filtration and the water removed in vacuo to afford 23.2 g (0.13 mol, 99%) of a white crystalline solid which was shown to be homogeneous by GLC and ^{13}C NMR analysis. On recrystallization of a sample from methanol–ethyl acetate, material which was identical with authentic L-gulono-1,4-lactone was obtained: mp 182–183.5 °C; mmp 182–184 °C; mp of authentic material 183.5–185.2 °C (lit.[8] mp 180–181 °C); $[\alpha]^{23}_D$ +55.3° (H_2O); $[\alpha]^{23}_D$ of authentic material +55.2° (H_2O);[8] IR (KBr) 1770 cm^{-1}; NMR (Me_2SO-d_6) δ 5.80 (d, 1, OH), 5.30 (d, 1, OH), 4.95 (d, 1, OH), 4.65 (t, 1, OH), 4.45–4.07 (m, 3), 4.00–3.35 (m, 3); ^{13}C NMR (Me_2SO-d_6) δ 177.8 (s), 81.3 (d), 70.8 (d), 70.1 (d), 69.6 (d), 61.6 (t).

D-Mannono-1,4-lactone (4). The above procedure was repeated, using 10 g (0.057 mol) of D-erythorbic acid (2) in 100 mL of H_2O at 50 °C, 7.0 g of 5% Pd/C, and 50 psi hydrogen pressure for 6h. Isolation as above afforded an oil which crystallized on standing and was shown to be >90% pure by GLC[7] analysis of a persilylated derivative and by ^{13}C NMR analysis of a neutralized sample. Crystallization from methanol–ethyl acetate afforded 4.8 g (50%) of the pure γ-lactone 4: mp 151–151.5 °C (lit.[9] mp 151 °C); $[\alpha]_D^{23}$ 50.3° (H_2O) [lit.[9] $[\alpha]^{23}_D$ 51.3° (H_2O)]; ^{13}C NMR (Me_2SO-d_6) δ 176.3 (s), 78.2 (d), 71.0 (d), 69.4 (d), 68.0 (d), 63.1 (t).

An additional 2.4 g of crystalline lactone was obtained from the mother liquor after concentration for a total yield of 71%.

Registry No. 1, 50-81-7; 2, 89-65-6; 3, 1128-23-0; 4, 26301-79-1.

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(11) These materials are now readily available and reasonably inexpensive chiral starting materials for use in synthesis. For a review on the chemistry of gulono-1,4-lactone, see: Crawford, T. C. *Adv. Carbohydr. Chem. Biochem.* **1981**, *38*, 287.

(12) See ref 2b for an example in which ascorbic acid was used as the source of subsequent chirality.

(13) For an example in which erythorbic acid was used as the source of subsequent chirality, see: Cohen, N.; Banner, B. L.; Lopresti, R. J. *Tetrahedron Lett.* **1980**, 4163.

Oxacarbene Intermediates Generated by the Photolysis of 12-Acyloxy[4.4.2]propellan-11-ones

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Recently, the chemistry of propellanes has attracted much attention, especially in view of structure–reactivity relationships,[1] and we have been deeply interested in these relationships on [*m.n.*2]propellane derivatives.[2] In this connection, we have recently reported on the novel dimerization of oxacarbene intermediates generated by the photolysis of the cyclobutanone rings incorporated into 12-acyloxy[4.4.2]propellan-11-ones (**1a,b**), in an aprotic solvent[2i] (Scheme I).

In these reactions, the most significant feature is the regiospecific ring expansions via primary α-cleavages[3] to give the oxacarbene intermediates (**2a,b**) exclusively, judging from the structure of the obtainable oxacarbene dimers (**3a,b**). An essential question is whether or not the formation of the other oxacarbene intermediates (**4a,b**) is inhibited, probably by the electron-withdrawing α-acyloxyl substituent, in analogy with the cases of some cyclobutanones carrying the α-electron-withdrawing substituent, such as dichloro- and trifluoromethyl groups.[4] In order to solve the above problem, the present work has been done. The photoreaction of **1a,b** was examined in methanol, which is a good trapping agent for oxacarbene intermediates. Irradiation of **1a,b** in methanol (0.01 M) in a degassed Pyrex tube at 20 °C with a high-pressure Hg lamp gave the ring-expanded acetals (**5a,b**, Scheme II) along with a new type of ring-expanded 11,13-dimethoxy-12-oxatricyclo[4.4.3.$0^{1,6}$]tridecane (**6**). Significantly, the formation of acetic acid or propionic acid was also observed, which was nearly equivalent to the quantity of **6**. But, we have been unable to obtain any evidence for the formation of the ring-expanded acetals (**7a,b**) via **4a,b**.

In order to obtain instructive information about the relation between **6** and **7a,b**, similar irradiation of *endo*-8-acetoxybicyclo[4.2.0]octan-7-one (**8**) was undertaken[5] (Scheme III). Fortunately, three kinds of ring-expanded acetals (**9**, **10**, and **11**) were formed in good yields together with the cycloeliminated product **12** and acetic acid. With the lapse of reaction time, the quantity of **9** (a mixture of two epimers) increases gradually with decreasing **10** (a mixture of two epimers).[6] In addition, both irradiation and dark reactions of the isolated acetal **10** proceeded appreciably on irradiation, but slowly in the dark reaction. From the above facts, it is reasonable to assume that the generation of **4a,b** via a photochemical ring expansion of **1a,b** takes place smoothly to result in labile **7a,b** in methanol, followed by rapid replacement of an acyloxyl group of **7a,b** by a methoxyl group to give **6** as an isolable product. In an aprotic solvent, the dimerization of **4a,b** might be suppressed, because they have greatly hindered carbene sites owing to the steric requirement of the con-

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(3) The addition of 1,3-pentadiene has no influence on the present photoreaction. However, this result does not always mean that α-cleavage proceeds via the singlet state.

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(5) Quantum yields for the disappearance of these ketones in methanol at 20 °C are observed as follows: **1a**, 0.08; **1b**, 0.06; **8**, 0.23.

(6) For example, irradiation of **8** gave the following products at the indicated times: 1 h, **9** (30%), **10** (33%), **11** (19%), and **12** (11%); for 2 h, **9** (38%) and **10** (23%); for 3 h, **9** (45%) and **10** (17%); for 4 h, **9** (49%) and **10** (14%).

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