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A NEW HYDROXY-LACTONIZATION OF OLEFINIC ACIDS

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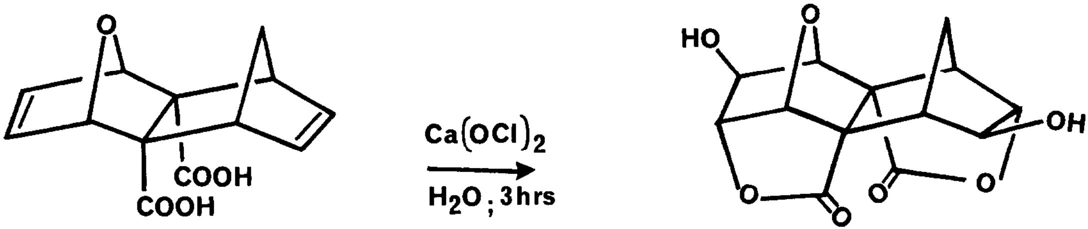
SUMMARY: Bicyclic olefin acids afford *trans*-hydroxy-lactones with aqueous calcium hypochlorite. Monocyclic and acyclic olefin acids yield mainly the corresponding (opened) dihydroxy acids.

In the course of some synthetic work using bicyclic lactones we required a quick preparation of *trans*-hydroxy-lactones,especially 2 from the double adduct,1[1]. m-Chloroperbenzoic acid yielded only complex products and excess p-nitroperbenzoic acid afforded only the monohydroxylactone on the furan side in 20 hours. Furthermore, the action of Lewis acid ($BF_3.Et_2O$) on the *bis*-epoxide of the diester of 1 failed to provide any *bis*-lactone, 2. However, when the diacid, 1, was dissolved in commercial bleach (aqueous $Ca(OCl)_2$ + $Ca(OH)_2$) for three hours at room temperature and acidified, the double hydroxy-lactone, 2, was obtained in nearly 90% yield. Accordingly we submitted several Diels-Alder adducts to these oxidizing conditions with generally clean results as illustrated in Table I.

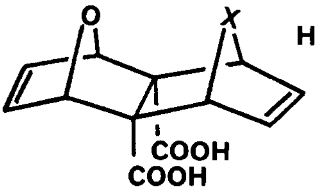
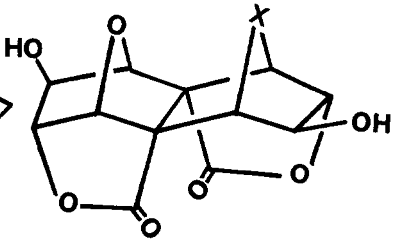
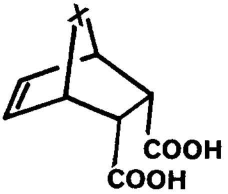
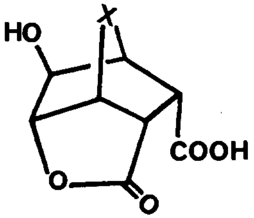
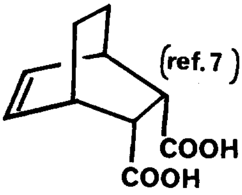
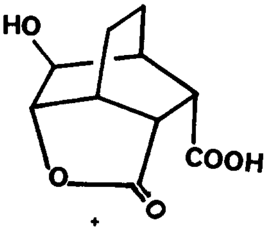
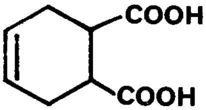
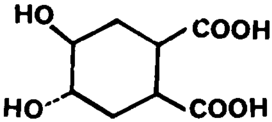


1

2

We presume the mechanism of this unusual oxidation involves initial formation of the acyl hypochlorite, 3, followed by internal oxidation of the

Table I. Hydroxy-lactonization of Olefinic Acids:

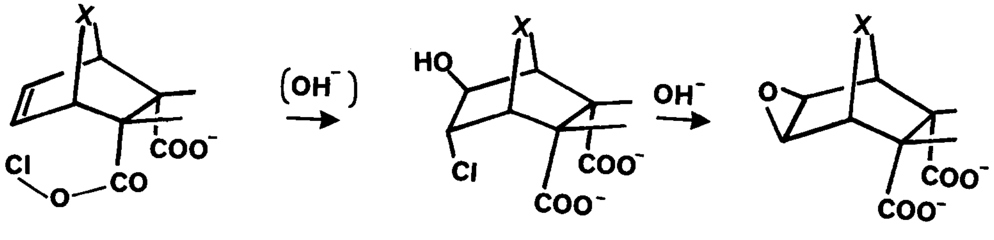
Substrate	Products(b)	yield	m.p.	IR(KBr) (cm^{-1})	Mass(m/e)
					
1. $X=CH_2$ (ref.1)		89%	212°	1780	280;197
2. $X=O$ (ref.4)		80%	330°	1775	282
					
3.[c] $X=CH_2$ (ref.5)		85%	152°	1710;1765	198
4.[c] $X=O$(a)		60%	211°	1715;1780	200;156
5.[c]  (ref.7)		65%	152°	1725;1760	212
	+ dihydroxy acid	13%	157°	1705	230
6.[c] 		86%	151°	1715	204;186

Notes: (a) The furan-maleic acid adduct is not isolated and indeed is only incompletely formed[6].

(b) The products were characterized by fully resolved NMR spectra at 90 or 270 MHz as well as by IR and Mass spectra(above).

(c) The acids were also characterized through their esters obtained by reaction with diazomethane.

olefin to chlorohydrin, 4, which in the basic milieu is converted to exo-epoxide, 5. This epoxide,as in the peracid oxidation, then affords the *trans*-hydroxy-lactone on acidification. Indeed extraction of the reaction mixture from 1 before acidification yields no products.



3 4 5

In the bicyclo-octane system (case 5, Table I) the initial lactone is partially opened in the aqueous acid work-up, while with the simple cyclohexene the dihydroxy-diacid is the sole product (case 6, Table I). In another monocyclic acid, 4-cyclohepten-1-carboxylic acid^8, however, no oxidation occurred. It appears that the carboxyl group must be oriented axially to the ring in order to participate internally in the olefin oxidation, as it is in all cases in Table I but not in the cycloheptene acid. Two acyclic acids which were at hand were briefly examined: itaconic acid and monoethyl α-methyl glutaconate. Both were oxidized in 30 minutes but neither yielded lactones. Diazomethane esterification showed two non-olefinic **ester** , presumably diol and chlorohydrin, but these were not further investigated.

The oxidation mechanism proposed above violates Baldwin's Rules^9 in that the cyclic σ-bond transfer at chlorine (3) is 6-endo-tet. However, if the olefin carbon-chlorine bond is formed before breaking the chlorine-oxygen bond of the acyl hypochlorite, i.e., invoking a hypervalent chlorine intermediate, then the rules are presumably not applicable.

Experimental Procedure: Preparation of 2 from 1.

To a suspension of diacid 1 (250 mg, 1mmole) in 15 ml of distilled water was added with stirring an aqueous solution of commercial calcium hypochlorite^{10}(500 mg, 3.49 mmole) in about 15 minutes. After 3.5 hours 2 ml of conc. hydrochloric acid was carefully added and stirring was continued for 10 more minutes. Excess oxidant was then destroyed with sodium sulphite (negative test/starch-iodine) and the reaction mixture was thoroughly extracted with ethyl acetate (4 x 50 ml); drying and removal of solvent gave a foamy solid which was crystallized from ethyl acetate and hexane to furnish 222 mg (88.7%) crystalline solid.

References:

1. The bis adduct 1 was prepared by reaction between dimethyl bicyclo(2.2.1.)-7-oxa-2,5-dien-2,3-dicarboxylate[2] and cyclopentadiene at room temperature in near quantitative yield followed by basic hydrolysis of the diester. It is remarkable to note that the above mentioned Diels-Alder reaction gave the single isomer with not even a trace of other possible isomers as evidenced by its NMR analysis. This is presumably due to the oxygen in the bridge. A similar observation by Bartlett[3] appeared during preparation of this manuscript.
2. K.Alder and H.F. Rickert, Ber., 70, 1354 (1937).
3. P.D. Bartlett, G.L. Combs, Jr., Ai-Xuan Thi le, W.H. Watson, J. Galloy and M. Kimura, J. Am. Chem. Soc., 104, 3131 (1982).
4. (a) O. Diels and K. Alder, Ann., 490,243 (1931).
   (b) J. Kallos and P. Deslongchamps, Can. J. Chem., 44, 1239 (1964).
5. K. Alder and G. Stein, Ann., 504, 224 (1933).
6. J.A. Berson and R. Swidler, J. Am. Chem. Soc., 75, 1721 (1953).
7. Prepared by hydrolysis of bicyclo (2.2.2.)-5-en-2,3-dicarboxylic anhydride,which was purchased from Aldrich Chemical Co.
8. G. Stork and K. Landesman, J. Am. Chem. Soc., 78, 5129 (1956).
9. J.E. Baldwin, Chem. Comm., 1976,734.
10. Fisher Certified Calcium Hypochlorite was used.

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