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# A CORRECTION TO "A NOVEL PERIODATE CLEAVAGE"

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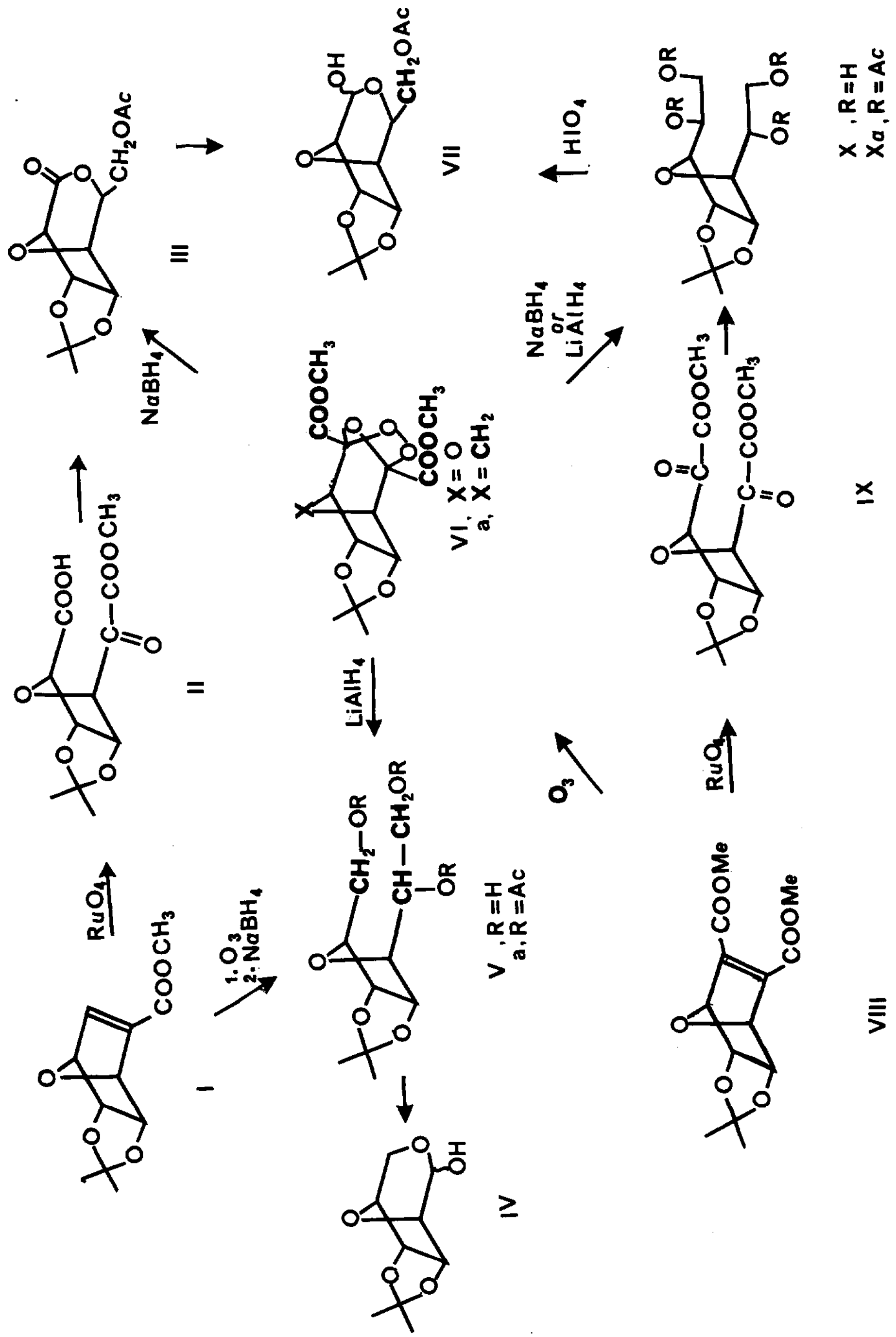
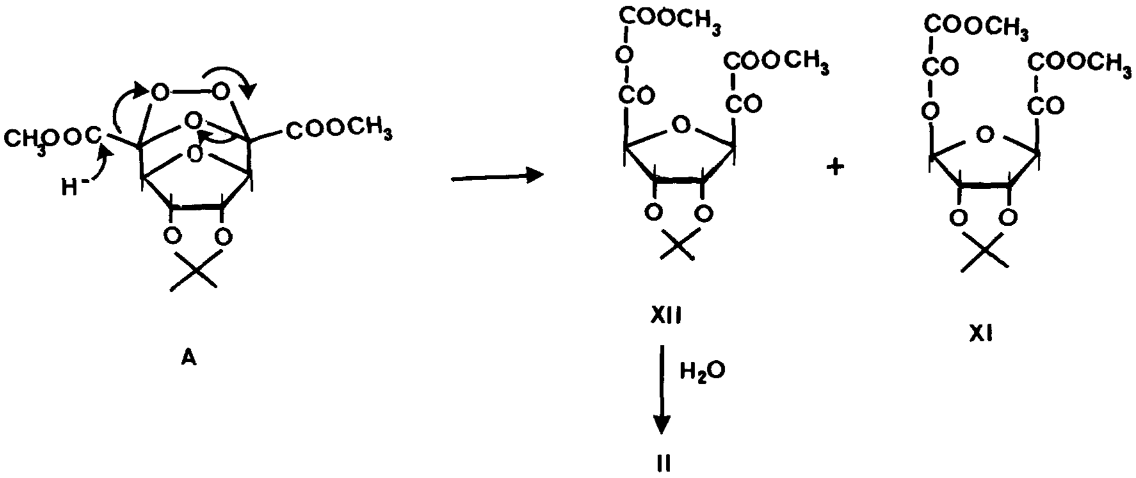
We recently reported[1] that tetraol X, obtained by reduction of ozonide VI with lithium aluminum hydride in boiling tetrahydrofuran, gave anhydroallose IV upon periodate cleavage.

Careful reinvestigation of the reaction revealed that the lithium aluminum hydride reduction of the ozonide produced triol V in addition to tetraol X. Although their respective acetates Va and Xa could not be separated by t.l.c., they were clearly distinguishable by g.l.c. Whatmore, triol V and tetraol X could be separated by t.l.c., albeit with great difficulty. Their identities were confirmed by comparison with samples prepared by sequence I → V and by oxidizing VIII with ruthenium tetroxide[2] to diketoester IX[3], and converting IX by sodium borohydride reduction in iso-propanol, followed by acetylation, to tetraacetate Xa[3]. Pure X gave upon periodate cleavage the expected diol aldehyde VII, m.p. 138-140°, as its hemiacetal, and no trace of anhydroallose IV.

Analogous results were obtained when ozonide VI was treated with sodium borohydride in refluxing iso-propanol. After acetylation, lactone acetate III[3], m.p. 156-157°, was obtained. Its structure was proven in the following manner. Ester I was oxidized with ruthenium tetroxide[2] to ketoester II[3], m.p. 112-114°. Reduction of II with sodium borohydride, followed by acetylation, gave III, m.p. 156-157°. Further reduction with diisobutyl aluminum hydride (2 equiv.) in toluene under nitrogen at -78° for 10 min.[4] gave VII[3].


COOCH$_3$
I
RuO$_4$
COOH
C—COOCH$_3$
II
NaBH$_4$
CH$_2$OAc
III
1. O$_3$
2. NaBH$_4$
CH$_2$—OR
CH—CH$_2$OR
OR
V, R = H
a, R = Ac
OH
IV
LiAlH$_4$
X
COOCH$_3$
COOCH$_3$
VI, X = O
a, X = CH$_2$
OH
CH$_2$OAc
VII
O$_3$
NaBH$_4$
or
LiAlH$_4$
HIO$_4$
COOMe
COOMe
VIII
RuO$_4$
C—COOCH$_3$
C—COOCH$_3$
IX
OR
OR
OR
OR
X, R = H
Xa, R = Ac



Similar results were obtained when ozonide VIa[5] was submitted to the action of lithium aluminum hydride in boiling tetrahydrofuran.

In order to explain the loss of a skeletal carbon atom upon heating ozonide VI in the presence of hydride, the thermal reaction of ozonide VI was studied. Warming the ozonide VI in ethyl acetate, benzene or acetone gave in over 90% yield ketoester XI, m.p. 114-116°. In iso-propanol and tetrahydrofuran, the yields of ketoester XI were lower, and ketoester acid II was isolated after mild hydrolysis in 14 and 25% yield respectively. The formation of XI, and XII from ozonide VI takes place by a Baeyer-Villiger-like rearrangement[6]. Loss of methyl carbonate from the intermediate mixed anhydride XII leads to II, the observed product. This explains, although not quantitatively, the loss of a skeletal carbon atom during reduction. It is therefore at present not possible to exclude a reductive decarboxylation (see arrows, A) of the ozonide VI.

## References and Footnotes

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