Abnormal Ozonolysis of Allyl Acetates: a Structural Factor

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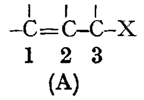
Summary The allyl acetates possessing an acetoxy-substituent at the double bond underwent abnormal ozonolysis [*e.g.* (**11**) → (**13**)], in contrast to those having no such substituent.

OZONOLYSIS of the allylic system (A) has been known to afford in considerable amounts abnormal products formed by oxidative cleavage of the C-2–C-3 bond with fission of the double bond.[1] The extent of the abnormal reaction was shown to depend on the electron-donating ability of the group, X in (A),[1] and in the case of the allyl acetates



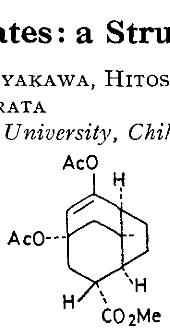
$$\underset{1}{-\overset{|}{C}}=\underset{2}{\overset{|}{C}}-\underset{3}{\overset{|}{C}}-X \quad (X = OH, OPh, NEt_2\,etc.)$$

(A)

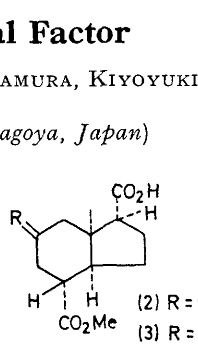
(A; X = OAc) no abnormal ozonolysis products were isolated.[1,2]

In our synthesis[3] of dendrobine, the key intermediate (**2**) was prepared by abnormal ozonolysis of the allyl acetate (**1**) under a variety of conditions, including those[2] reported to effect normal ozonolysis.

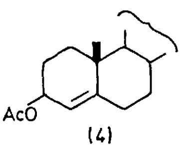
For clarifying the structural factor(s) causing the abnormal ozonolysis of the allyl acetate (**1**), ozonolysis of other allyl acetates and the related systems was carried out using conditions [EtOAc–AcOH (9 : 1 v/v), 0°; then treatment with H_2O, *ca.* 20°] under which the allyl acetate (**1**) afforded the keto-acid (**2**) (60%)† as the the major product together with the dicarboxylic acid (**3**)‡ (8%).† On ozonolysis of 4-cholesten-3-ol acetate (**4**),[4] only the normal



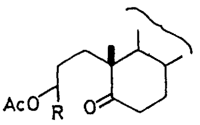
(1)



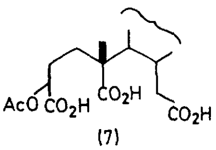
(2) R = O
(3) R = $<^{CO_2H}_{OAc}$



(4)



(5) R = CO_2H
(6) R = CHO



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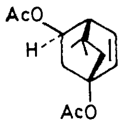
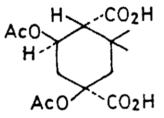


(8)



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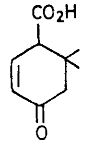

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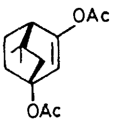

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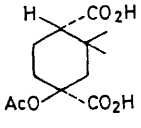

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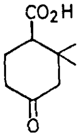
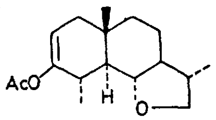
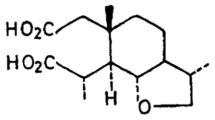


(13)



(14)



(15)

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† On ozonolysis in the absence of AcOH, (**2**) and (**3**) were isolated in 42 and 18% yields, respectively.

‡ The spectral data for all compounds reported were in accord with the structures assigned. Satisfactory microanalyses or high resolution m.s. data were obtained.

ozonolysis products, (**5**)§ (35%), (**6**) (10%), and the derivative (**7**)§ (16%) were isolated. The result for the allyl acetate (**8**) in which the tertiary acetoxy-group occupied the bridgehead position was slightly different, but again the major product was the normal ozonolysis product (**9**) (47%), m.p. 230—232°, and the minor one was (**10**)§ (6%). In contrast, the allyl acetate (**11**), structurally similar to (**8**) but carrying an acetoxy-substituent at the double bond, afforded mainly the keto-acid (**13**) (52%), m.p. 58—61°, a product of abnormal ozonolysis, together with a small amount of (**12**)§ (5%). The simple enol acetate (**14**) gave the normal ozonolysis product (**15**) (61%), m.p. 173—176°.

These results indicate that, in addition to the well established electronic effect[1,2] of the group, X of (A) on abnormal ozonolysis, the substituent at the double bond of (A) is an important factor in deciding the course of the ozonolysis reaction.

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§ Isolated and characterized as the corresponding methyl ester [trimethyl ester in the case of (**7**)], which was purified by preparative g.l.c.

[1] P. S. Bailey, *Chem. Rev.*, 1958, **58**, 925.

[2] W. G. Young, A. C. McKinnis, I. D. Webb, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 293.

[3] K. Yamada, M. Suzuki, Y. Hayakawa, K. Aoki, H. Nakamura, H. Nagase, and Y. Hirata, *J. Amer. Chem. Soc.*, 1972, **94**, 8278.

[4] A mixture of two diastereoisomers at C-3; *cf.* Pl. A. Plattner, H. Heusser, and A. B. Kulkarni, *Helv. Chim. Acta*, 1949, **32**, 265.