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A NEW REACTION IN THE SELENIUM DIOXIDE OXIDATION OF OLEFINS

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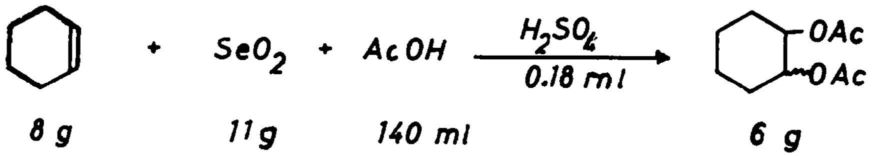
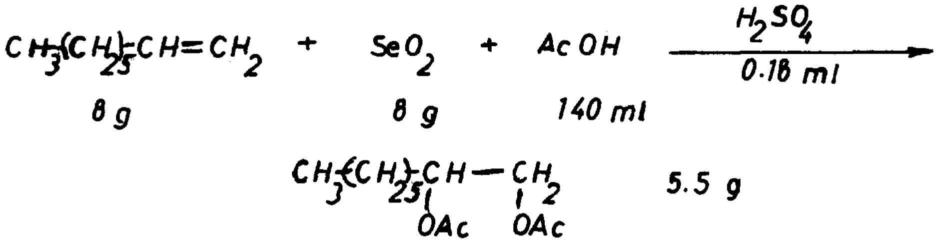
Selenium dioxide oxidation of olefins in acetic acid is known to produce allylic products, but we have found that a drastic change in the reaction path occurs when the oxidation is catalyzed by H_2SO_4. Thus oxidation of cyclohexene with equimolar amount of SeO_2 in acetic acid containing a catalytic amount of H_2SO_4 in a stirred glass autoclave at 110°C produced 1,2-cyclohexanediol diacetate (32%) as a mixture of cis (55%) and trans (45%) isomers. Cyclohexyl acetate and cyclohexenone were obtained as the minor products. These results present a unique contrast to the previously known oxidation of cyclohexene with SeO_2 in a mixture of acetic acid and acetic anhydride that produces only 1-acetoxy-3-cyclohexene (32%) (1). Qualitative and quantitative analyses of the products in all cases were carried out by IR, NMR and GLC, P.E.G.20M column was found suitable for separating the isomers.



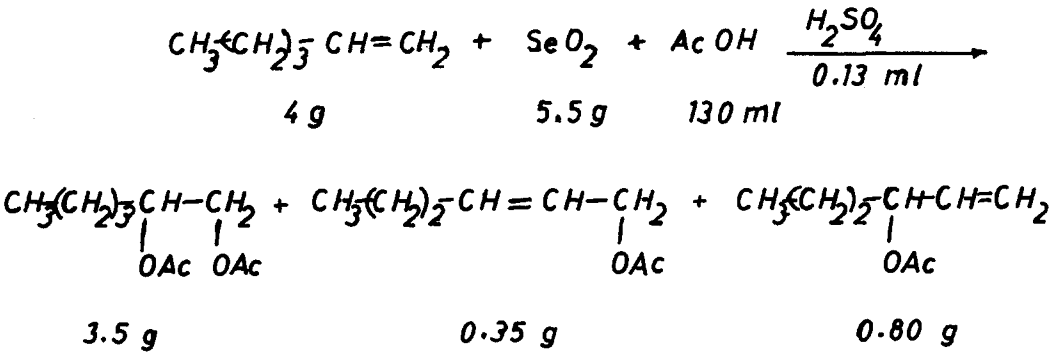
On the basis of the new results obtained from the oxidation of cyclohexene, studies were extended to some terminal olefins such as 1-octene and 1-hexene to investigate the scope of the reaction. Oxidation of 1-octene with equimolar amount of SeO_2 in acetic acid containing a catalytic amount of H_2SO_4 at 115°C for 10 hours gave 1,2-octanediol diacetate (35%) and a trace amount of 1-acetoxy-3-octene. On the other hand a recent report (2)



$$\underset{8\ g}{CH_3(CH_2)_5CH=CH_2} + \underset{8\ g}{SeO_2} + \underset{140\ ml}{AcOH} \xrightarrow[0.18\ ml]{H_2SO_4} \underset{5.5\ g}{CH_3(CH_2)_5\underset{OAc}{\underset{|}{C}}H-\underset{OAc}{\underset{|}{C}}H_2}$$

reveals that bis(2-acetoxyoctyl) selenide, acetic acid adduct of bis(2-acetoxyoctyl) selenide and a small amount of 1-acetoxy-3-octene were isolated when 1-octene was oxidized with SeO_2 in acetic acid by bubbling air into the reaction mixture.

Similarly 1,2-hexanediol diacetate (35%), 3-acetoxy-1-hexene (12%) and 1-acetoxy-3-hexene (5%) were produced when 1-hexene was oxidized with equimolar amount of SeO_2 in acetic acid containing a catalytic amount of H_2SO_4 at 105°C for 10 hours, whereas Guillemonat (3) reported that 1-acetoxy-3-hexene and a small amount of 3-acetoxy-1-hexene were produced when it was treated with SeO_2 in a mixture of acetic acid and acetic anhydride.



$$\underset{4\ g}{CH_3(CH_2)_3CH=CH_2} + \underset{5.5\ g}{SeO_2} + \underset{130\ ml}{AcOH} \xrightarrow[0.13\ ml]{H_2SO_4}$$

$$\underset{3.5\ g}{CH_3(CH_2)_3\underset{OAc}{\underset{|}{C}}H-\underset{OAc}{\underset{|}{C}}H_2} + \underset{0.35\ g}{CH_3(CH_2)_2CH=CH-\underset{OAc}{\underset{|}{C}}H_2} + \underset{0.80\ g}{CH_3(CH_2)_2\underset{OAc}{\underset{|}{C}}H-CH=CH_2}$$

In recent years considerable work has been done to clarify the reaction mechanism for SeO_2 oxidations (4,5,6,7,). Now it is generally accepted that electrophilic attack of SeO_2 or conjugate acid of SeO_2 occurs on the double bond of the olefin forming a carbonium ion which rearranges and in turn leads tothe products. Our results show that the rate of the reaction increased, no organoselenium compound was produced and altogether new products emerged when a proton was added as the catalyst. These results can be attributed to an assumption that addition of the proton might have changed the active species there by leading to the addition products rather than to the expected organoselenium compound which is known to produce allylic products on thermal decomposition.

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