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A NEW ACID CATALYZED OXIDATION OF SOME ACETYLENIC COMPOUNDS WITH SELENIUM DIOXIDE

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It was found that oxidation of some acetylenic compounds with selenium dioxide was easily proceeded in the presence of catalytic amount of sulfuric acid. The oxidation took place mainly at the triple bond, and α-keto acid or α-diketone was isolated as a main product.

It has been generally accepted that oxidation of unsaturated hydrocarbons with selenium dioxide essentially takes place at α-position to the double bond or triple bond leading to an α-hydroxy derivatives.[1,2] Recently we have reported that direct oxidation at a double bond of olefin occurs when the oxidation is carried out in the presence of a small amount of concentrated sulfuric acid.[3,4] This result prompted us to examine the similar treatment of acetylenic compounds, and we found that oxidation of acetylenic hydrocarbons with selenium dioxide was affected drastically by the use of a catalytic amount of sulfuric acid.

Phenylacetylene (I) was oxidized with selenium dioxide in aqueous acetic acid solution* in the presence of a small amount of sulfuric acid at 100°C to give benzoylformic acid (II) selectively in 66 % yield, whereas it was oxidized in acetic acid without sulfuric acid to yield phenyl glyoxal (III, 26 %) and benzoic acid (IV, 34 %). In ethanol solution phenylacetylene was not oxidized with selenium dioxide under reflux condition, however, addition of a catalytic amount of sulfuric acid caused the oxidation to produce ethyl benzoylformate (V, 33 %),

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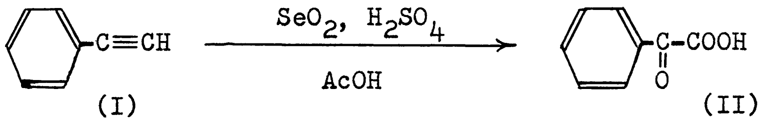
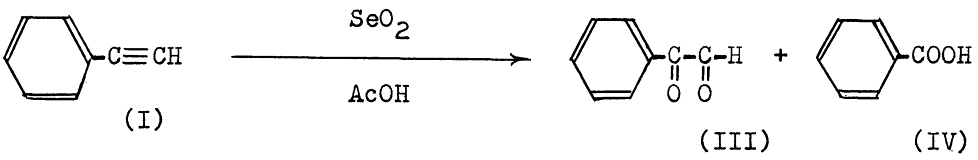
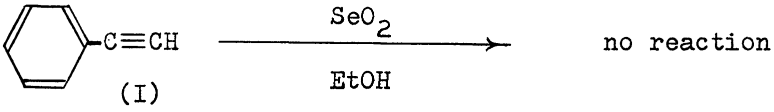
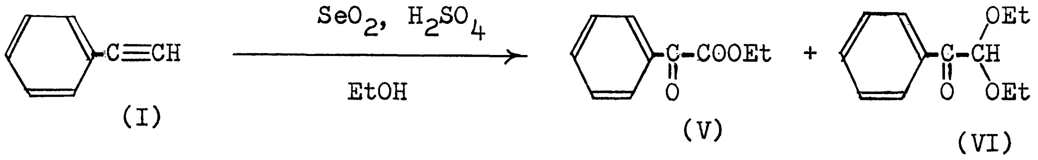
* Five % of water was containing. Somewhat better yield was obtained when such an aqueous acetic acid was used.

and dietylacetal of phenyl glyoxal (VI, 8 %), as well as small amounts of ethyl benzoate and acetophenone. Astin et al.[5] have reported that oxidation of acetylene with selenium dioxide gives oxalyl aldehyde. Analogously, it is considered that phenyl glyoxal may be the intermediate in the formation of benzoylformic acid. However, acetophenone and phenyl glyoxal were confirmed experimentally not to be precursors of benzoylformic acid in the present oxidation.

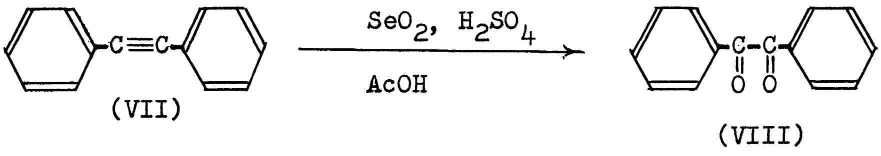






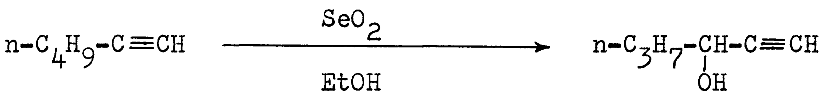


Postowsky[6] has shown that diphenylacetylene is oxidized with selenium dioxide to benzil only at elevated temperature such as 280°C in 35 % yield. We found diphenylacetylene (VII) was readily oxidized at 110°C in aqueous acetic acid containing sulfuric acid catalyst to give benzil (VIII) selectively in 84 % yield.



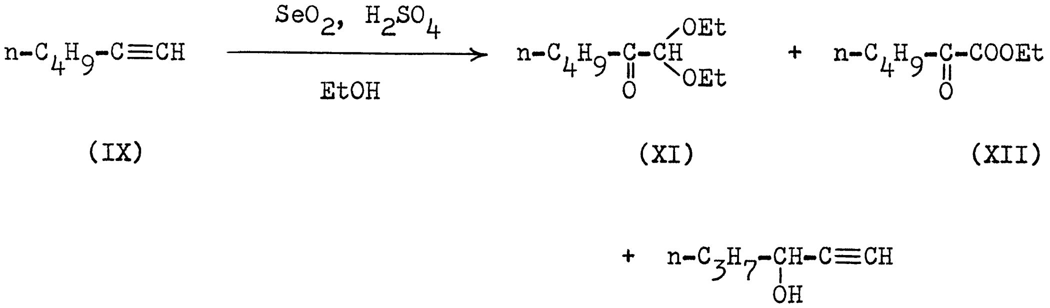
It is clear from these results that presence of the acid in the reaction system is favorable for the oxidation of acetylenic compounds with selenium dioxide and changes the selectivity of the oxidation in some cases.

The remarkable change of the reaction products was observed in the oxidation of acetylenic compound having hydrogen atoms in α-position. The oxidation of 1-hexyne (IX) with selenium dioxide in ethanol at 78°C gave 1-hexyne-3-ol (X) in 27 % yield according to the general scheme,[2] whereas in the presence of a small amount of sulfuric acid, 1-hexyne (IX) converted into diethylacetal of n-butylglyoxal (XI, 16.3 %), ethyl 2-oxo-hexanoate (XII, 8.7 %), and 1-hexyne-3-ol (X, 6.3 %).



$$\text{n-C}_4\text{H}_9\text{-C}\equiv\text{CH} \xrightarrow[\text{EtOH}]{\text{SeO}_2} \text{n-C}_3\text{H}_7\text{-}\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{-C}\equiv\text{CH}$$

(IX) (X)



$$\text{n-C}_4\text{H}_9\text{-C}\equiv\text{CH} \xrightarrow[\text{EtOH}]{\text{SeO}_2,\ \text{H}_2\text{SO}_4} \text{n-C}_4\text{H}_9\text{-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-CH}\begin{smallmatrix}\diagup\text{OEt}\\ \diagdown\text{OEt}\end{smallmatrix} + \text{n-C}_4\text{H}_9\text{-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-COOEt} + \text{n-C}_3\text{H}_7\text{-}\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{-C}\equiv\text{CH}$$

(IX) (XI) (XII)

(X)

These facts suggest that acid catalyst may be preferred for the oxidation at a triple bond of acetylenic compound rather than at the α-position.

Although little information is available on the reaction mechanism at the present time it may be considered from the recent studies on the selenium dioxide oxidation of olefins[4,7] that the addition of sulfuric acid may convert selenium dioxide to protonated species such as $\text{HO-}\overset{+}{\text{Se}}\text{=O}$ which might cause a new type of oxidation as a strong electrophilic oxidant.

Further works to elucidate the reaction mechanism and to apply to various acetylenic compounds are in progress.

References

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