

SELENIUM DIOXIDE OXIDATION OF OLEFINS

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Selenium dioxide occupies a unique position as an olefin oxidant since the oxidation product is an allylic alcohol or a derivative of that alcohol such as an ether or an ester; ketone formation is also occasionally observed. We now report the results of a study on the oxidation of 1,3-diphenylpropene (I) which provide an insight to the mechanism of this reaction.

Oxidation of I with selenium dioxide in 99% acetic acid at 115° was rapid and produced in high yield 1,3-diphenyl-2-propen-1-ol acetate (II); this was the only detectable organic product under these reaction conditions. To assess the influence of electronic and steric factors five 1,3-diarylpropenes were synthesized. An equimolar mixture of I and a 1,3-diarylpropene was reacted with a limited quantity of selenium dioxide and, after reaction, the remaining percentages of olefins were estimated by gas chromatographic analysis. The results of these experiments are tabulated in Table I.

The data for entries 2 and 4 are in accord with electrophilic attack of the double bond by selenium dioxide (or its conjugate acid,  $\text{HSeO}_2^+$ ). Direct attack of the olefinic linkage by an electrophile is further supported by entry 5 which demonstrates that shielding of the double bond results in a pronounced retardation of the rate of oxidation. Substituent effects observed by varying the electronic environment of the methylene group were

small (entries 1 and 3) but are consistent with the development of an electron deficient center at that site.

TABLE I

Competition of 1,3-diarylpropenes and I for Selenium Dioxide

$\text{ArCH}_2\text{CH}=\text{CHAr}'$		$\frac{[\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5]^a}{[\text{ArCH}_2\text{CH}=\text{CHAr}']}$	% Oxidation <sup>b</sup>
Ar	Ar'		
1. p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>4</sub>	0.83	59-68
2. C <sub>6</sub> H <sub>5</sub>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	0.56	42-47
3. p-ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	1.18	64-73
4. C <sub>6</sub> H <sub>5</sub>	p-ClC <sub>6</sub> H <sub>4</sub>	1.76	65-73
5. C <sub>6</sub> H <sub>5</sub>	Mesityl	>13.5 <sup>c</sup>	82

a. Experiments utilized molar ratios of one mole of each olefin and one-half mole of selenium dioxide. The ratios reported are the ratios of olefins consumed during reaction. b. Measured by the weight of selenium precipitated. Reactions were run in duplicate. c. This represents a minimum value.

To elucidate further the role of the allylic methylene group in the oxidation process 3-deuterio-1,3-diphenylpropene (I-D) was prepared. Oxidation of I-D containing 0.87D produced allylic acetate (II-D) which contained 0.66D; this corresponds to a value of  $k_H/k_D$  of 3.1 at 115°. The magnitude of this isotope effect suggests that a carbon-hydrogen bond is being broken in the rate determining step of the reaction.

To determine the distribution of deuterium in II-D the allylic acetate was reduced with lithium aluminum hydride to 1,3-diphenylpropan-1-ol (III-D) which was oxidized to 1,3-diphenylpropan-1-one (IV-D) (See Chart I).

Since IV-D contained only half of the deuterium present in II-D this result requires that the two benzylic positions become equivalent at some stage of the reaction.

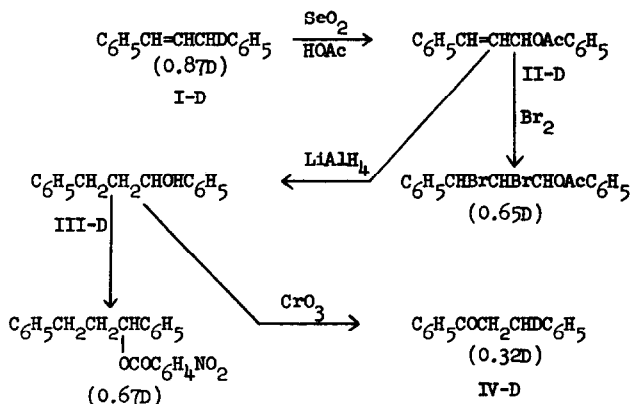


CHART I. OXIDATION OF 3-DEUTERIO-1,3-DIPHENYLPROPENE.

The possibility of isomerization of the olefin before oxidation was eliminated by refluxing I-D in acetic acid-phosphoric acid for an extended period of time; the NMR spectrum of the reisolated olefin was superimposable on that of I-D. The absence of rearrangement during the isolation procedure and degradation reactions was ascertained by the preparation of 3-deuterio-1,3-diphenyl-2-propen-1-ol (V-D'), acetylation of V-D' to the allylic acetate (II-D'), and conversion of II-D' to 1,3-diphenylpropan-1-one (IV-D') without loss of deuterium (see Chart II). When II-D' was refluxed in acetic acid for a period of time slightly longer than that required for oxidation of I it was found that equilibration of the benzylic positions was far from complete. This series of experiments require that

during the reaction a symmetrical intermediate such as the 1,3-diphenylpropenyl cation must have formed.

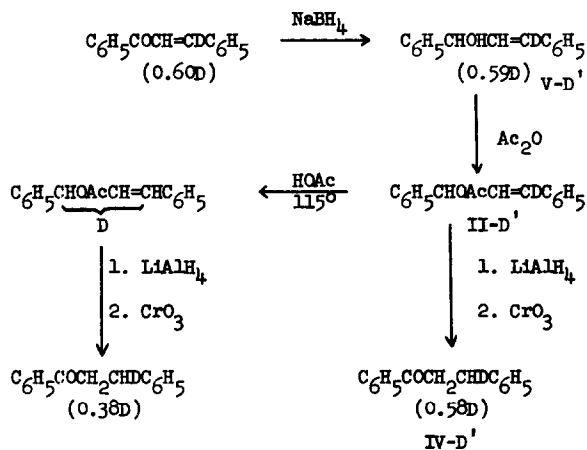
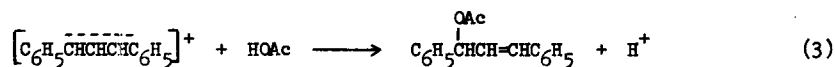
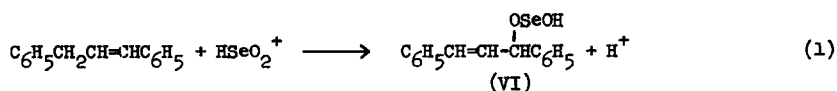
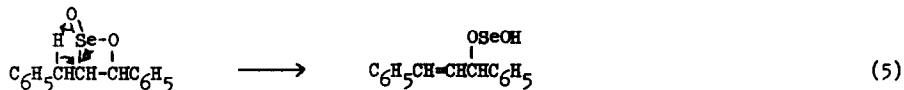
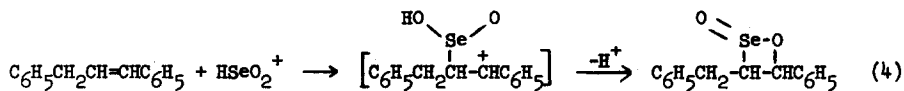


CHART II. ISOMERIZATION OF DEUTERIATED 1,3-DIPHENYLPROPEN-1-OL ACETATE

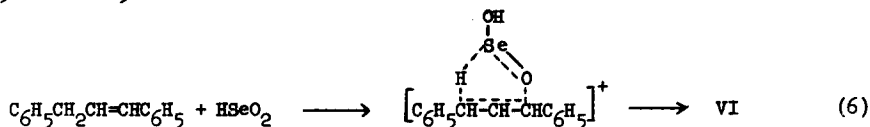
Qualitative observations indicated that the reaction was not inhibited by free-radical inhibitors. The relative rate of reaction appears to be acid catalyzed since oxidation was more rapid in dichloroacetic acid than in acetic acid which was in turn, a more effective solvent than an alcohol for promoting oxidation. A mechanism which accommodates the above data is the following:



Several detailed pathways for the formation of the selenium(II) ester, VI, can be written. Two possibilities are the following:



or



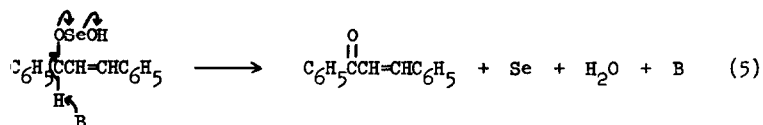
Reaction 4 is similar to the initial reaction which is thought to occur on ozonolysis of an olefin; in view of the periodic relationship between ozone and selenium dioxide this step is probably not unreasonable. Equation 5 represents a molecular reorganization in which a new double bond is generated as the selenium(II) ester is formed. A more reasonable alternative may involve direct formation of VI in a single step through a transition state such as that formulated in equation 6 but no clear distinction can be made between these possibilities with the present data.

Electrophilic attack by selenium dioxide (or  $\text{HSeO}_2^+$ ) on the olefin is consistent with the substituent effects observed and with the previously found behavior of this reagent toward ketones (1). In view of the large isotope effect observed (vide supra) the formation of VI is probably rate determining. Solvolysis of this ester (equations 2 and 3) would produce the product observed and result in equilibration of the benzylic positions.

The postulate of a selenium(II) ester of the type indicated is attractive since a spectrum of decomposition paths are available to it which can account for many of the observations in the literature (2). In solvents of low ionizing power a merger of reactions 3 and 4 would be expected so that the product determining step may approach as  $\text{S}_\text{N}2$  (or  $\text{S}_\text{N}2'$ ) extreme.

For optically active olefins such a pathway for decomposition would accommodate the formation of optically active products which is occasionally observed (3, 4).

In solvents of high ionizing power or, in systems where internal factors would favor the formation of an allylic carbonium ion, a limiting solvolysis should be favored as a pathway for decomposition. This situation probably obtains in the 1,3-diphenylpropene system and in the majority of the cases cited in the literature (3). A beta elimination reaction from the selenium(II) ester also accounts conveniently for ketone formation which is occasionally observed although this could also arise by a secondary oxidation of the alcohol.



Although many details of the oxidation mechanism are subject to question, it appears that the general features of the reaction are adequately described by the considerations outlined above. We are currently subjecting various aspects of the above mechanisms to experimental test and hope to report on these in the future.

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#### References

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