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Selenium Dioxide Oxidation of Styrene and Norbornene

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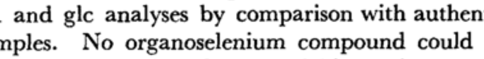
Oxidation of olefins by selenium dioxide generally produces allylic derivatives resulting from the oxidation at α-methyl or α-methylenic carbon atom.[1-6] So it was interesting to study the behavior of the olefins like styrene and norbornene where such carbon atom is not present. Norbornene was selected also for studying the ionic nature of the reaction. Styrene reportedly did not react with selenium dioxide in a sealed tube.[7] Here we report the oxidation of these olefins using glacial acetic acid and some other solvents.

Results and Discussion

Oxidation of styrene with selenium dioxide in glacial acetic acid at 150—160°C in an autoclave produced styrene glycol diacetate in a good yield. The other products were phenylglyoxal and styrene glycol monoacetate.



The identification of the products was carried out by IR and glc analyses by comparison with authentic samples. No organoselenium compound could be characterized. An almost stoichiometric amount of metallic selenium was deposited under suitably controlled experimental conditions. Base-catalyzed hydrolysis of the products gave styrene glycol.

When dioxane was used as the solvent phenyl-

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[1] N. Rabjohn, "Organic Reactions," Vol. 5, John Wiley & Sons, Inc., New York and London (1949), p. 331.

[2] A. Guillemonat, *Ann. Chim.*, **11**, 143 (1939).

[3] J. P. Schaefer and B. Horvath, and H. R. Klein, *J. Org. Chem.*, **33**, 2647 (1968).

[4] J. P. Schaefer and B. Horvath, *Tetrahedron Letters*, **1964**, 2023.

[5] K. Wiberg and S. D. Neilsen, *J. Org. Chem.*, **29**, 3353 (1964).

[6] J. L. Huguet, Presented at International Oxidation Symposium, San Francisco, California, August 28, 1967.

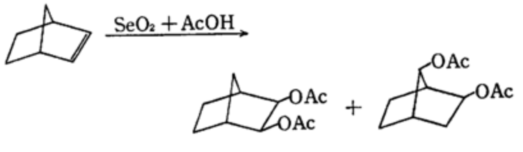
[7] H. L. Riley and N. A. Friend, *J. Chem. Soc.*, **1932**, 2342.

glyoxal was obtained in an 11% yield with a trace of benzaldehyde. To examine the possibility of styrene glycol formation, water was added to the dioxane, but styrene glycol could be obtained in trace only. Some other solvents like methyl alcohol, *t*-butyl alcohol and DMSO were also tried. The results are summarized in Table 2. Polymerization of styrene was observed in all cases except when the acetic acid was used as the solvent.

Oxidation of norbornene with selenium dioxide in glacial acetic acid under the similar conditions as employed for the oxidation of styrene produced 2,3-*exo-cis*-norbornane diacetate and 2,7-*exo-syn*-norbornane diacetate in the ratio of 2 to 1. Appreciable amounts of monoacetates could not be detected as the qualitative glc analysis remained almost the same after treatment of the reaction products with acetic anhydride. The base-catalyzed hydrolysis of the reaction products gave a mixture of 2,7-*exo-syn*-norbornane diol and 2,3-*exo-cis*-norbornanediol which showed a positive test for vicinal alcohols by periodic acid.

Our results are in good agreement with the mechanism postulated by Schaefer[3,4] which suggests the electrophilic attack of selenium dioxide itself or conjugate acid of selenium dioxide on the double bond of the olefin. Again, in the oxidation of norbornene the formation of rearranged product 2,7-*exo-syn*-norbornane diacetate apart from the 2,3-*exo-cis*-norbornane diacetate, indicates that oxidation is passing through a carbonium ion.

Strained olefins such as bicycloheptene or bicyclooctene usually add electrophiles with rearrangement,[8b] or with trans stereochemistry,[8a] but many reagents as mercuric acetate,[9] nitrosyl chloride[10] and hydrogen halides,[8b] *etc.* have been observed to add in cis fashion. In our experiments, both cis addition and rearrangement occurred with preference to cis addition.



The formation of cis product can be attributed to the torsional and windshield wiper effects.[9] From the experimental data it can be further noted that the yields are very low in the solvents other than

TABLE 1. OXIDATION OF STYRENE AND NORBORNENE WITH SELENIUM DIOXIDE IN GLACIAL ACETIC ACID

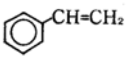
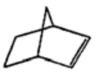
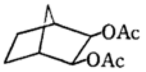
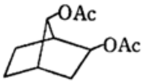
Olefin	Reaction Temp. °C	Reaction Time hr	Product	Yield %
	150	10	$C_6H_5CHOAcCH_2OAc$	52.0
			$C_6H_5CHOAcCH_2OH$	7.0
			C_6H_5COCHO	3.0
	150	10		25.0
				15.0

TABLE 2. EFFECT OF SOLVENTS ON THE STYRENE OXIDATION

No.	Solvent	Reaction temp °C	Reaction time, hr	Product	Yield %
1	Dioxane	140—150	10	C_6H_5CHO	Trace
				C_6H_5COCHO	11.0
2	Dioxane water 15%	145—150	10	C_6H_5CHO	0.4
				C_6H_5COCHO	6.0
				$C_6H_5COCH_2OH$	2.0
				$C_6H_5CHOHCH_2OH$	1.0
3	Dioxane water 15% H_2SO_4 0.3%	145—150	10	C_6H_5CHO	0.8
				C_6H_5COCHO	6.0
				$C_6H_5COCH_2OH$	4.0
4	Dioxane CH_3OH 20%	120—130	11	No reaction	
5	Dioxane CH_3OH 20%	170—180	11	C_6H_5CHO	4.0
				C_6H_5COCHO	2.0
				Unknown	2.0
6	*t*-BuOH	120	10	C_6H_5CHO	Trace
				C_6H_5COCHO	8.0
				Unknown	6.0
7	*t*-BuOH	160—170	10	C_6H_5CHO	Trace
				C_6H_5COCHO	5.0
				Decomposition products	

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[8] a) H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964). b) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956).

[9] A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968); T. Tidwell and T. G. Traylor, *ibid.*, **33**, 2614 (1968).

[10] J. Meinwald, Y. C. Meinwald and T. N. Baker, *J. Am. Chem. Soc.*, **86**, 4074 (1964).

acetic acid. This catalytic effect of acetic acid has been well explained by Olson.[11]

Experimental

Oxidation of Styrene in Acetic Acid. In a 30 m*l* of glacial acetic acid 5 g of anhydrous selenium dioxide was dissolved and 5 g of freshly distilled styrene was added. The solution was put in a 50-m*l* autoclave and volume made up to 40 m*l* with acetic acid. Heating was continued at 150—160°C for 10 hr. The temperature was raised to 180°C for the last two hours. The metallic selenium was filtered off. Acetic acid was removed by distillation under reduced pressure. The fraction boiling at 118—125°C/2mmHg was identified to be a mixture of phenylglyoxal[12] (3%) bp 95—97°C/25mmHg, styrene glycol monoacetate[13] (7%) and styrene glycol diacetate[14] (52%) bp 159.5°C/18mmHg by comparison of their glc and IR with authentic samples. Base-catalyzed hydrolysis gave white needles after recrystallization from *n*-hexane. Its IR and mixture melting point were in complete agreement with that of authentic styrene glycol.[15]

Oxidation of Styrene in Different Solvents. The same procedure as mentioned above was repeated using dioxane, dioxane-water, dioxane-water-sulfuric acid, dioxane-methyl alcohol and *t*-butyl alcohol respectively. The experimental conditions are given in Table 2. Qualitative and quantitative analyses of the products were carried out by IR and glc.

Oxidation of Notbornene in Acetic Acid. Five grams of selenium dioxide was dissolved in 30 m*l* of acetic acid and 5 g of norbornene was added. The reactants were heated for 10 hr at 140—150°C in the 50-m*l* autoclave. After filtering off the metallic selenium and removing the acetic acid by distillation under vacuum, the distillate boiling at 70—99°C/2mmHg was collected. Product identification was carried mainly by glc techniques. S. E. 30 column was found suitable for separating the isomers of norbornane diacetate. 2,3-*exo-cis*-Norbornane diacetate (25%) and 2,7-*exo-syn*-norbornane diacetate (15%)[16] were found as main products by comparison with authentic samples. Authentic 2,3-*exo-cis*-norbornane diacetate was prepared by esterification of 2,3-*exo-cis*-norbornanediol.[17] Four grams of 2,3-diol was treated with 40 m*l* of acetic anhydride in 100 m*l* of pyridine for 4 hr under reflux.

Base-Catalyzed Hydrolysis of the Products. To 1 g of reaction products were added 50 m*l* of methyl alcohol, 5 g of sodium hydroxide and 5 m*l* of water. The mixture was refluxed for 4 hr. After filtration and adjusting the pH to 6, methyl alcohol was distilled off and the remaining liquid was extracted with hot *t*-butyl alcohol, dark sticky crystals were obtained which were dissolved in a small amount of ethyl alcohol and the solution was put in the sublimation tube. Ethyl alcohol was evaporated at 100°C and then sublimation was carried out at 120—130°C/20mmHg. White crystals melting near 165°C were obtained. The IR was analogous to a mixture of 2,3-*exo-cis*-norbornane diol and 2,7-*exo-syn*-norbornanediol and their presence was confirmed by glc analysis. The crystals also gave a positive periodic acid test for vicinal alcohols due to the presence of 2,3-exo-*cis*-norbornanediol.

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[11] D. H. Olson, *Tetrahedron Letters*, **1966**, 2053.

[12] H. A. Riley and A. R. Grey, "Organic Syntheses," Vol. 15, p. 67 (1935).

[13] T. Cohen, M. Dughi, V. A. Notaro and G. Pinkus. *J. Org. Chem.*, **27**, 814 (1962).

[14] W. L. Evans and E. H. Morgan, *J. Am. Chem. Soc.*, **35**, 54 (1913).

[15] M. A. Nicholas and S. Sussman, *ibid.*, **59**, 2345 (1937).

[16] N. Sonoda and S. Tsutsumi, This Bulletin, **38**, 958, (1965).

[17] H. Kwart and W. G. Vosbugh, *J. Am. Chem Soc.*, **76**, 5400 (1954).