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ORGANIC REACTIONS OF SULFUR DIOXIDE. 5.
REACTIONS WITH CYCLIC DIENES: A DUAL PATHWAY FOR AROMATIZATION OF THE 1,3- AND 1,4-CYCLOHEXADIENES

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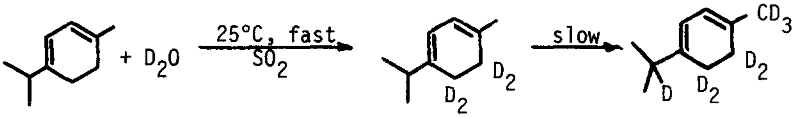
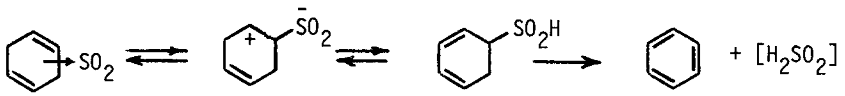
We proposed[1] that the facile regiospecific isomerization of trisubstituted olefins in liquid sulfur dioxide involves a reversible ene reaction of the olefin-sulfur dioxide adduct followed by the 1,3-rearrangement of the resulting allylic sulfinic acid intermediates, the retroene reaction, and elimination of sulfur dioxide. We have also shown that the presence of water suppressed the above isomerization, and unexpectedly provided (with D_2O) a facile and direct method for regiospecific hydrogen/deuterium exchange of allylic hydrogens.[2]

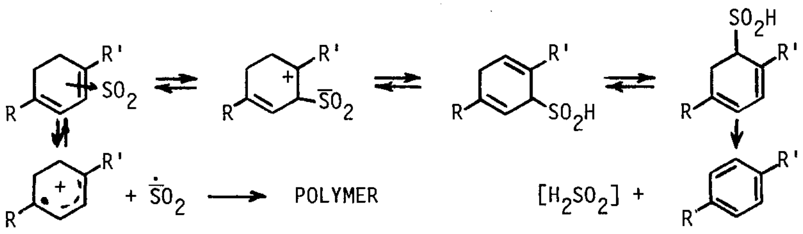
We have now observed that 1,4-cyclohexadiene undergoes a slow reaction in liquid sulfur dioxide at room temperature to give benzene quantitatively, elemental sulfur and water,[3] whereas 1,3-cyclohexadiene gives a high molecular weight polysulfone and only about 5% of benzene.[4] The presence of alkyl groups at the termini of the 1,3-diene (p-menthadiene), suppresses formation of the polysulfone and instead in sixty hours gives in addition to 35% of unreacted diene about 3% of p-cymene and a polymeric hydrocarbon.[5] On the other hand, the presence of an alkyl group on the double bond of 1,4-cyclohexadiene (1-ethyl-1,4-cyclohexadiene, 1-methyl-4-isopropyl-1,4-cyclohexadiene) did significantly increase the rate of aromatization.[6] When the reaction with p-menthadiene was carried out with added water (or deuterium oxide), both the polymerization and aromatization were effectively suppressed. However, as in the case of trisubstituted olefins,[2] a rapid hydrogen/deuterium exchange occurs at all allylic carbon atoms.[7]



The aromatization of 1,4-cyclohexadiene in sulfur dioxide can be rationalized by invoking the mechanism for the isomerization of olefins with sulfur dioxide.[1,2] Presumably, the reaction involves a reversible attack of sulfur dioxide at the double bond of the 1,4-diene to give the corresponding dipolar ion with the positive charge on the secondary carbon atom, an ene reaction with formation of the cyclohexa-2,4-dienyl sulfinic acid, and the 1,2 elimination to benzene and sulfoxylic acid[8] which undergoes further disproportionation to sulfur, sulfur dioxide and water.

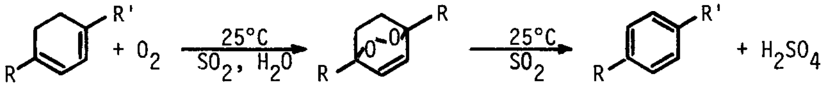


The slow aromatization of 1,3-cyclohexadienes probably involves a prior isomerization to the 1,4-cyclohexadiene which then undergoes further reaction as already outlined. A reversible electron transfer to sulfur dioxide from one of the carbon termini in the initially formed complex between the diene and sulfur dioxide could provide a high energy diradical intermediate possibly in equilibrium with the corresponding tight radical ion pair. Intramolecular cyclization to give the unknown bicyclic sulfone[9] does not take place probably for steric reasons, and instead an intermolecular reaction affords the observed polysulfone polymer. The significantly slower polymerization in the case of 1,4-dialkyl-1,3-cyclohexadienes is very likely a consequence of the presence of the substituents at the terminal carbons of the diene which should suppress both the attack of sulfur dioxide on these carbon atoms and the subsequent polymerization of the intermediates that have been formed. The observed aromatization then could be a result of a competitive transformation of the initially formed diene-sulfur dioxide complex to give a dipolar ion with the positive charge on the adjacent <u>tertiary</u> carbon. The ene reaction followed by the 1,3-rearrangement of the generated allylic sulfinic acid intermediate would provide the corresponding cyclohexa-2,4-dienyl sulfinic acid which could afford p-cymene and sulfoxylic acid either directly or by a prior reversible generation of the 1,4-cyclohexadiene as a transient intermediate. When water was



present, both the polymerization and isomerization of the double bond (and hence aromatization) were prevented. However, the fact that the hydrogen-deuterium exchange at the allylic carbons was not suppressed shows that the attack of sulfur dioxide at the middle carbon atoms of the diene system was still very effective.

Somewhat unexpectedly, when the reaction with p-menthadiene was carried out in the presence of oxygen, the p-cymene was formed almost exclusively.[10] This reaction involves ascaridole as an unstable intermediate which under the reaction conditions reacts with sulfur dioxide further to give p-cymene and sulfuric acid.[11]



While this facile reaction of p-menthadiene with oxygen in the presence of sulfur dioxide possibly involves either a diene-sulfur dioxide diradical intermediate or the corresponding tight radical ion pair, the precise mechanism is yet to be established.[12]

Evidently, aromatization of cyclohexadienes by sulfur dioxide rests on the ability of sulfur dioxide to remove electrons from the organic substrate. In the case of 1,4-cyclohexadienes the electrons end up on the sulfur dioxide which is being reduced to elemental sulfur and water. In the case of 1,3-cyclohexadienes a complete electron transfer from the substrate to sulfur dioxide is prevented by the competing polymerization reactions. These side reactions are effectively circumvented in the presence of molecular oxygen which now becomes the ultimate electron acceptor. Consequently, in this transformation sulfur dioxide assumes the role of an electron carrier from the substrate to molecular oxygen and in the overall process becomes oxidized to sulfuric acid.

References and Notes

1) M. M. Rogić and D. Masilamani, J. Am. Chem. Soc., 99, 5219 (1977); for earlier papers in this series see M. M. Rogić and J. Vitrone, J. Am. Chem. Soc., 94, 8642 (1972); M. M. Rogić, K. P. Klein, J. M. Balquist, and B. C. Oxenrider, J. Org. Chem., 41, 482 (1976).

2) D. Masilamani and M. M. Rogić, J. Am. Chem. Soc., in print.

3) Reaction is typically carried out in a sealed tube at room temperature over several weeks and is conveniently followed by NMR.

4) Extremely fast reaction. Addition of the diene to liquid sulfur dioxide at -10°C leads to an instantaneous precipitation of the white polymer.

5) The nature of the polymeric hydrocarbon was not determined.

6) While the reaction with the 1,4-cyclohexadiene required several weeks, the aromatization of the 1-ethyl-1,4-cyclohexadiene was complete in two days.

7) The hydrogen-deuterium exchange was monitored by NMR.

8) T. Moeller, Inorganic Chemistry, John Wiley & Sons, New York, NY, 1952, p.527.

9) S. D. Turk and R. L. Cobb in "1,4-Cycloaddition Reaction", J. Hamer, Ed., Academic Press, New York, NY, 1967, p. 31.

10) A Fisher pressure bottle containing 4 ml of p-menthadiene and 4 ml of water in 60 ml of sulfur dioxide was pressurized with oxygen at room temperature at 50-60 psi. After complete reaction, analyses showed that p-cymene and sulfuric acid were virtually the only products formed.

11) When the reaction was carried out at -20°C, ascaridole together with p-cymene were isolated after the evaporation of solvents. Authentic peroxide reacts with sulfur dioxide at room temperature in the presence and absence of water to give p-cymene and sulfuric acid.

12) For more elaborate discussion of the possible mechanisms for similar facile spin inversion on oxygen see D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus, and I. D. Menzies, J. Chem. Soc., Perkin Trans., I, 1975, 2055; D. H. R. Barton and R. K. Haynes, ibid, 1975, 22064 , R. K. Haynes, Aust. J. Chem., 31 125, 131 (1978); J. Eriksen, C. S. Foote, and T. L. Parker, J. Am. Chem. Soc., 99, 6455 (1977).

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