J. Org. Chem. 1980, 45, 4278-4280

Base-Catalyzed SO_2-Induced Allylic Oxidation of Cyclohexene with Molecular Oxygen

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Received January 4, 1980

Sulfur dioxide has been found to promote a novel liquid-phase oxidation of cyclohexene with molecular oxygen in acetic acid as solvent. Oxidation at the allylic position occurs only if the reaction is base-catalyzed; with added acetoxy ions, e.g., the major product obtained is 2-cyclohexen-1-one together with minor amounts of 1,2-cyclohexanediol diacetate (mainly as the trans isomer), while a competitive autoxidation of sulfur dioxide to sulfur trioxide is observed. The results are discussed on the basis of an anion-radical mechanism involving the formation of sulfur dioxide stabilized peroxide ions.

Sulfur dioxide has never been considered before as a possible activating agent in olefin oxidations since, probably due to its relatively high electrophilicity, it has been shown in many instances to exhibit specific interferences. It is known, e.g., that the palladium chloride catalyzed oxidation of ethylene by oxygen to give acetaldehyde[1] is apparently inhibited by sulfur dioxide since ethyl butenyl sulfone and ethyl vinyl sulfone are the major products reported[2] to be formed in its presence.

On the other hand, we have recently found[3] that sulfur dioxide promotes a novel liquid-phase diacetoxylation of 1,3-butadiene in acetic anhydride with oxygen gas and catalytic amounts of concentrated protic acids. For further elucidation of this original effect of SO_2 on double bond oxidations, the general procedure employed for the conjugated diene has now been extended to a simple isolated olefin (cyclohexene) which has been thoroughly investigated with many oxidizing systems.

We report here, on this new oxidation of cyclohexene, those aspects of our results which are most relevant to its mechanistic implications and preparative potential.

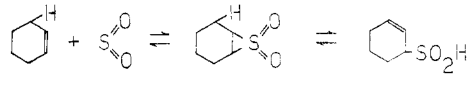
Results and Discussion

Relative to other known oxidative procedures, the SO_2-induced liquid-phase oxidation of cyclohexene has been found to be distinctively different.

When potassium acetate was employed as the base in acetic acid as solvent (100 mL, 0.8 M), the reaction of cyclohexene (160 mmol) with approximately equimolar amounts of molecular oxygen at 110 °C in the presence of sulfur dioxide (40.58 mmol) yielded after 1 h 2-cyclohexen-1-one as the major product (43.10%; unless stated otherwise, yields are quoted relative to unrecovered cyclohexene) together with minor amounts of 1,2-cyclohexanediol diacetate (3.58%; 44% cis and 56% trans). At the end of the reaction, the sulfur dioxide was almost quantitatively recovered as sulfur trioxide. Under the same experimental conditions, but with no added sulfur dioxide, a conversion to carbonyl products of less than 2%, defined as the mole percent of reacted cyclohexene, was observed. Thus in this case, the autoxidation of cyclohexene, which is known to yield detectable amounts of hydroperoxides and epoxides,[4] cannot be assumed to contribute significantly to the product formation reported above.

In order to elucidate the specific effect displayed by sulfur dioxide in this reaction, we have investigated on its interaction with cyclohexene at atmospheric pressure. The addition of sulfur dioxide to cyclohexene performed under dry nitrogen at −30 °C instantly develops a blue-green color while a white precipitate is formed. The white precipitate, removed by quick filtration at room temperature and carefully dried, is fairly stable. Its infrared spectrum (solid in KBr), registered immediately, suggests the formation of an adduct between SO_2 and cyclohexene with a sulfone-like structure since a disappearance of the bands at 3024 (=CH) and 1649 cm^{-1} (C=C) and two strong bands at 1114 (SO sym) and 1300 cm^{-1} (SO asym)[5] are observed. If the addition of sulfur dioxide to cyclohexene (8 mmol) dissolved in deuterated acetic acid (2 mL) is performed under dry nitrogen at 0 °C, on reaching room temperature a fairly homogeneous clear solution is obtained. Its ^1H NMR spectra, registered immediately and after 3 h, suggest the establishment of an equilibrium between the cyclohexene–sulfur dioxide adduct and an allylsulfinic acid since the integrated intensities of the CH_2C= (δ 1.96; δ values are quoted in parts per million downfield from internal tetramethylsilane) and =CH (δ 5.60) protons relative to that for the CCH_2C (δ 1.65) protons vary from 4.0 H and 2.0 H to 3.8 H and 1.8 H, respectively, while two new signals are observed: a broad multiplet (δ 4.05, 0.16 H) and an acid proton (δ 11.51, 0.16 H). The relative intensities of these new signals increase by 65% while the ratio of the integrated intensities of the CH_2C= to =CH protons approaches unity when the same addition of sulfur dioxide to cyclohexene is performed under the same experimental conditions but with added potassium acetate (4 mmol). These evidences have been further supported (see Experimental Section) by alkaline hydrolysis of the cyclohexene–sulfur dioxide adduct to the corresponding allylsulfinate sodium salt.

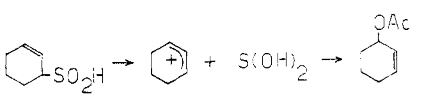
Considering these findings we may reasonably assume that sulfur dioxide, through its reversible interaction with cyclohexene, promotes the establishement of the equilibria shown in eq 1, while the addition of bases sensibly shifts



(1)

the same equilibria to the right.

However, under our specific experimental conditions the reaction does not seem to proceed merely through a solvolytic pathway of the allylic cation to products (see eq 2) since 2-cyclohexen-1-one (and no cyclohexenyl acetate)



(2)

is the major product obtained. Thus, in analogy with the most recent findings obtained while investigating the

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(1) K. Fujimoto, H. Takeda, and T. Kunugi, *Ind. Eng. Chem. Prod. Res. Dev.*, **13**, 237 (1974).

(2) H. S. Klein, *Chem. Commun.*, 377 (1968).

(3) E. Tempesti and L. Giuffrè, *J. Heterocycl. Chem.*, **16**, 533 (1979).

(4) W. F. Brill, *J. Am. Chem. Soc.*, **85**, 141 (1963).

(5) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

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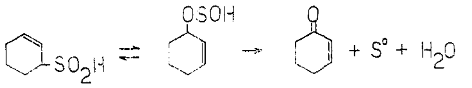
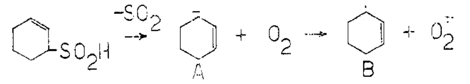
mechanism of allylic oxidation of olefins with selenium dioxide,[6] we have to consider the possibility of a preliminary [2,3] sigmatropic rearrangement of the allylsulfinic acid to a sulfur(II) ester (see eq 3) which may collapse to



(3)

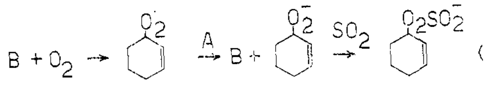
the corresponding carbonyl product. This rearrangement is well-known for allylic sulfinates[7] and especially allylic sulfoxides;[8] although the equilibrium generally lies on the side of the sulfur(IV) derivative due to the strength of the S=O bond,[9] the difference in free energy between the two forms is of the order of a few kilocalories per mole[10] and one might therefore expect the presence of the sulfur(II) ester at equilibrium.

While 2-cyclohexen-1-one is indeed found among our reaction products, no evidences of elemental or bivalent sulfur have been obtained; rather, at the end of the reaction, the sulfur dioxide is almost quantitatively recovered as sulfur trioxide. In addition, control experiments run without molecular oxygen indicate that neither the base-catalyzed SO_2-induced allylic oxidation of cyclohexene nor the concurrent autoxidation of SO_2 to SO_3 occurs. Then we have to assume that the inferred [2,3] rearrangement reported above probably involves initial formation of a carbanion; oxidation of this carbanion, as reported for the base-catalyzed oxidation of organic sulfides with molecular oxygen,[11] may imply the formation of radicals from the anion by electron transfer to oxygen[12] as shown in eq 4.



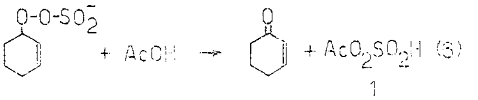
(4)

The resultant radicals can react with oxygen by a free-radical chain reaction to form sulfur dioxide stabilized peroxide ions as shown in eq 5. The following decom-



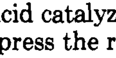
(5)

position of these sulfur dioxide stabilized peroxide ions to the corresponding carbonyl compound may occur with concomitant formation through solvolysis of an unstable mixed anhydride of peracetic acid (see eq 6) with sulfurous acid which, as already reported,[3] may lose sulfur dioxide or oxidize it to sulfur trioxide.



Control experiments on the base-catalyzed SO_2-induced allylic oxidation of cyclohexene with molecular oxygen were run with added free-radical scavengers such as hydroquinone to support the proposed reaction mechanism. The allylic product formation (monitored by GC) and the concurrent autoxidation of SO_2 to SO_3 were found to be both retarded.

The formation of the unstable mixed anhydride of peracetic acid with sulfurous acid reported above may also elucidate the formation of vicinal diacetates. Indeed, larger amounts of 1,2-cyclohexanediol diacetate (8.14%; 26% cis and 74% trans) were obtained when the SO_2-induced (40.15 mmol) reaction of cyclohexene (160 mmol) with nearly equimolar amounts of molecular oxygen was performed for 1 h at 110 °C in acetic acid as solvent (100 mL) with no added alkali acetate. Under these experimental conditions, cyclohexyl acetate is the major product obtained (46.24%) while a reduced autoxidation of SO_2 to SO_3 (18.38 mmol) is observed. The formation of cyclohexyl acetate obviously implies direct addition of acetic acid to the double bond; accordingly the drastic change in the reaction pattern which occurs when the reaction is not base catalyzed has to be mainly attributed to the acidity of the reaction medium. This acidity, in agreement with the reported behavior of other mixed anhydrides (e.g., mixed sulfuric carboxylic anhydrides) as far as ease of formation[13] and thermal stability[14] are concerned, is consistent with the formation of a mixed anhydride between acetic acid and sulfurous acid which may also be responsible for the in situ generation of the corresponding highly unstable mixed anhydride of peracetic acid with sulfurous acid. The reduced autoxidation of SO_2 to SO_3 observed with no added alkali acetate supports the intermediacy of a peracetylsulfurous[15] acid **1** rather than an acetylpersulfurous acid **2** since only the former structure is compatible with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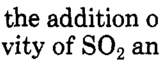
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an increased autoxidation of SO_2 accelerated by acetoxy ions. Thus the formation of vicinal diacetates may be assumed to occur rather independently through an epoxidation of cyclohexene by the highly unstable peranhydride **1** followed by acetolysis of the epoxide (mainly by trans ring opening) to 1,2-cyclohexanediol diacetate.

Since the rate of epoxidation of olefins with peracids in general is not acid catalyzed,[16] the addition of acids in our case should depress the reactivity of SO_2 and thus affect the formation of the mixed peranhydride **1**. This expectation has been supported by the observation that the SO_2-induced (40.88 mmol) reaction of cyclohexene (160 mmol) with nearly equimolar amounts of molecular oxygen performed at 110 °C in acetic acid as solvent (100 mL) for 1 h with added catalytic amounts of protic acids (anhydrous hydrogen bromide, 5 mmol) yields again cyclohexyl acetate as the major product (47.31%), while the yield of diacetoxy derivatives slightly decreases (6.18%; 24% cis and 76% trans). These findings are in marked contrast with the known acid-catalyzed selenium dioxide oxidation

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[6] K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972).

[7] Q. E. Thompson, *J. Org. Chem.*, **30**, 2703 (1965).

[8] P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4869 (1968); D. A. Evans, G. C. Andrews, and C. L. Sims, *ibid.*, **93**, 4956 (1971); P. A. Grieco, *J. Chem. Soc., Chem. Commun.*, 702 (1972).

[9] H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

[10] R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **92**, 2100 (1970).

[11] T. J. Wallace, H. Pobiner, F. A. Baron, and A. Schriesheim, *J. Org. Chem.*, **30**, 3147 (1965). An eventual participation of SO_3 in the oxidation step is unlikely since olefin sulfonation would prevail; in this case no sulfonation is observed since the overall oxidation of cyclohexene with O_2 to 2-cyclohexen-1-one implies formation of H_2O.

[12] L. J. Chinn, "Selection of Oxidants in Synthesis: Oxidation at the Carbon Atom", Marcel Dekker, New York, 1971, p 128.

[13] E. Montoneri, M. Fornaroli, L. Giuffrè, E. Tempesti, and G. Sioli, *J. Chem. Soc., Perkin Trans. 2*, 1784 (1976).

[14] E. Tempesti, L. Giuffrè, G. Sioli, M. Fornaroli, and G. Airoldi, *J. Chem. Soc., Perkin Trans. 1*, 771 (1974).

[15] It has been recently reported that mixed peranhydrides with peroxide O–O bonds between acetyl and sulfonyl groups may be formed when the photochemical reaction of aliphatic hydrocarbons with liquid sulfur dioxide in the presence of oxygen is carried out in acetic acid or acetic anhydride; see D. I. Davies and M. J. Parrott in "Free Radicals in Organic Synthesis", K. Hafner et al., Eds., Springer-Verlag, Berlin, 1978, p 118. These anhydrides are thermally unstable and decompose with oxygen evolution.

[16] S. O. Lawesson and G. Schroll in "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Interscience Publishers, New York and London, 1969, p 673.

of cyclohexene[17] which is reported to yield mainly vicinal diacetates.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 457 instrument while nuclear magnetic resonance spectra were obtained on a Varian HA 100 spectrometer. Qualitative and quantitative gas chromatographic analyses were performed on Porapak Q, PEG 20M and SE-30 columns fitted on a Carlo Erba Model GT 200 gas chromatograph.

Reagents and Solvents. Cyclohexene (Fluka, high purity) was fractionally distilled over Drierite several times: bp 83 °C (760 mm); $n^{20}{}_D$ 1.4451 [lit.[18] bp 82.8 °C (759 mm); $n^{20.05}{}_D$ 1.446 37]. Oxygen and nitrogen (chromatographic purity) were supplied by Sapio. Sulfur dioxide (SiO) was purified[19] by passage of gaseous SO_2 through concentrated sulfuric acid and P_2O_5; after it was condensed over P_2O_5 at −78 °C, it was degassed by evacuation for 1 h, refluxed over P_2O_5 for 1 h, and distilled. Acetic acid (Carlo Erba) was always fractionally distilled immediately before use; the acid used had a freezing point of 16.6 °C which agrees with the value reported[20] for acetic acid of minimum conductivity. Potassium acetate (Carlo Erba) was reagent grade and was not further purified.

Cyclohexene–SO_2 Adduct. Alkaline Hydrolysis. At −30 °C dry nitrogen was used to sweep sulfur dioxide (2.50 g, 39.02 mmol) into 3.32 g of cyclohexene (40.41 mmol); a blue-green color instantly developed while a white precipitate was formed. The gas stream was reverted to nitrogen while the solution was allowed to warm to room temperature; 20 mL of diethyl ether was added to the solution and the white precipitate, removed by quick filtration, was carefully dried. Unreacted cyclohexene (2.40 g, 29.21 mmol) was recovered by fractionating the filtrate while the white precipitate was immediately neutralized with sodium hydroxide in ethanol. The isolated sodium salt, which is stable at room temperature, was recrystallized (1.09 g, 6.48 mmol) from water–ethanol. The infrared spectrum (solid in KBr) contained a weak band at 1640 cm^{-1} (C=C),[21] a strong band at 1016 cm^{-1}, and a band of medium intensity at 962 cm^{-1} which may be assigned to the SO asymmetric and symmetric vibrations, respectively.[22] The ^1H NMR spectrum (in D_2O; sodium 3-(trimethylsilyl)-propanesulfonate as internal standard) showed signals at δ 1.63 (CCH_2C, m, 4 H), 2.01 ($CH_2C{=}$, m, 2 H), 3.60 ($CHSO_2Na$, m, 1 H; relative to the value reported for the free acid, the observed shift to higher fields is consistent with previous data reported for some alkylsulfinic acids, e.g., 1-hydroxyethanesulfinic acid[23]), and 6.10 (=CH, m, 2 H).

Anal. Calcd for $C_6H_9O_2SNa$: C, 42.84; H, 5.39; S, 19.06. Found: C, 43.34; H, 5.69; S, 18.71.

SO_2-Induced Oxidation of Cyclohexene. General Procedure. Oxidations were carried out in a mechanically stirred stainless-steel autoclave (475 mL). In a typical run, 100 mL of an 0.8 M solution of potassium acetate in acetic acid and 13.14 g of cyclohexene (160 mmol) were charged in the autoclave which was subsequently closed and cooled to −30 °C while deaerating under vacuum. After the required liquified amount of sulfur dioxide (2.60 g, 40.58 mmol) was injected the autoclave was brought to room temperature and pressurized with oxygen (10 atm) and nitrogen (100 atm) while stirring. On reaching (1 h) the reaction temperature (110 °C) a periodic repressurizing with nitrogen was necessary to maintain the pressure for the designated period of time (1 h); during that time, in some runs samples were periodically withdrawn through a sampling valve in order to monitor the reaction. After that time, the autoclave was rapidly cooled to room temperature; gas samples were analyzed by carefully venting known portions of the noncondensible gases into an evacuated stoppered flask. Only traces of CO_2 were found.

After the noncondensible gases were vented, the recovered reaction mixture was quenched with water and immediately extracted with chloroform; in the aqueous phase, free sulfate ions were determined (37.90 mmol).

The organic layer was repeatedly washed with aqueous sodium hydroxide to completely remove acetic acid. The aqueous layers were acidified and extracted with diethyl ether to determine if other carboxylic acids were present; the extracts were dried (Na_2SO_4), concentrated, and treated with BF_3–MeOH reagent,[24] without finding new carboxylic acids by this procedure.

After the neutralized organic solution was dried over anhydrous sodium sulfate, the solvent and unreacted cyclohexene (4.92 g, 59.89 mmol) were removed under vacuum, leaving a residue which was fractionated by vacuum distillation. The fraction boiling at 60–70 °C (12 mm) gave 6.19 g (67%) of 2-cyclohexen-1-one (4.14 g, 43.15 mmol); it was spectrally and chromatographically identical with an authentic sample prepared by lithium aluminum hydride reduction of 3-ethoxy-2-cyclohexen-1-one and subsequent acid hydrolysis.[25] A second fraction boiling at 115–125 °C (12 mm) yielded 0.72 g of 1,2-cyclohexanediol diacetate (3.59 mmol) as a mixture of cis (44%) and trans (56%) isomers. The identification of the diacetoxy derivatives was performed by comparison with independently prepared samples obtained by selenium dioxide[17] and thallic acetate[26] oxidation of cyclohexene.

Registry No. Sulfur dioxide, 7446-09-5; cyclohexene, 110-83-8; cyclohex-2-enesulfinic acid Na, 74465-45-5; 2-cyclohexen-1-one, 930-68-7; *cis*-1,2-cyclohexanediol diacetate, 2396-76-1; *trans*-1,2-cyclohexanediol diacetate, 1759-71-3; oxygen, 7782-44-7.

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(18) H. I. Waterman and H. A. VanWesten, *Recl. Trav. Chim. Pays-Bas*, 48, 637 (1929).

(19) D. F. Burow in "The Chemistry of Nonaqueous Solvents", Vol 3, J. J. Lagowski, Ed., Academic Press, New York and London, 1970, p 141.

(20) A. I. Popov in "The Chemistry of Nonaqueous Solvents", Vol 3, J. J. Lagowski, Ed., Academic Press, New York and London, 1970, p 244.

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Oxidation of Diphenylacetylene by I^{7+} and I^{5+} Compounds

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Received March 6, 1980

The oxidation of diphenylacetylene with H_5IO_6 in acetic acid affords benzil. In methanol the principal products are the monoketal and the diketal of benzil, depending upon water content. Similar products are formed in methanol when I_2O_5 is the oxidizing agent. The latter and the alkyne in ethylene glycol afford benzil and the corresponding diketal. Both systems appear to require the presence of iodine for effective action.

The extensive use of paraperiodic acid for the cleavage of vicinal glycols has overshadowed this reagent's potential for other preparative procedures, most of which have been reviewed by Fatiadi.[1] We have been examining its utility

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