Silver-mediated Epoxidations

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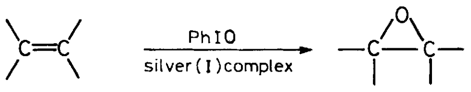
It has been shown that Ag_2O and $AgNO_3$, the latter in the presence of tertiary amines, *e.g.* pyridine, can achieve the oxidation of alkenes to epoxides with iodosylbenzene as the oxygen donor. The reactions have been studied with different alkenes and it has been found that the oxygen-transfer reaction takes place in a non-stereoselective manner, *trans*-epoxides being the major oxidized product when *cis*-alkenes are the substrates. The influence of different types of tertiary amines on the epoxidation with $AgNO_3$ as the 'catalyst' has been investigated and it has been found that the presence of electron-withdrawing groups in the pyridine ring leads to a better epoxidation system. Labelling studies with [^{18}O]iodosylbenzene or [^{18}O]water indicate that the epoxide oxygen is derived from iodosylbenzene or water, suggesting an oxosilver intermediate. The epoxidation of alkenes can also be achieved by Ag_2O_2, and the yield of epoxides and stereoselectivity are comparable to those with Ag_2O and iodosylbenzene, indicating an identical reaction path. The reactive high-valent oxosilver intermediate and the mechanism for the oxygen-transfer reaction are discussed in the light of the related transition metal–iodosylbenzene and the silver surface–molecular oxygen epoxidations.

The field of transition metal-catalysed epoxidation of alkenes is in intensive development.[1] A variety of different systems are found to catalyse the reaction:[1] transition-metal ions, transition-metal peroxo and oxo complexes, organotransition-metal complexes, and transition-metal surfaces.[1,2]

Surface-catalysed epoxidation is mainly restricted to silver with molecular oxygen as oxygen donor and ethylene being the only substrate;[2] other alkenes as substrates lead to low yields of the corresponding epoxide.[2] It should however be noted that styrene has been reported to be oxidized to styrene oxide on a silver surface[3a] and that norbornene is epoxidized by atomic oxygen on Ag(110) under ultrahigh vacuum.[3b] The mechanism of activation of molecular oxygen on the silver surface and the transfer of an oxygen atom to ethylene leading to ethylene oxide has been subject to intensive investigations.[1i,2] Based on both experimental[1i,2] and theoretical[4] studies it has been suggested that the reactive species is an oxosilver surface species which transfers the oxygen atom to ethylene in a non-stereospecific manner.[5]

If we move to silver compounds it has been shown that $AgNO_3$ in CH_3CN in combination with iodosylbenzene as oxygen donor does not catalyse the epoxidation of alkenes,[6] whereas copper as well as other transition-metal salts are active under the same conditions.[6,7] It should also be noted that an electrochemically generated silver–pyridine complex has recently been shown to be able to transfer an oxygen atom to a homogeneously dissolved alkene.[8] One might wonder if the silver surface is the only silver system which can achieve catalysis of alkene epoxidation, or if there is a bridge from the silver surface to the molecular silver compounds. We here report that silver complexes in combination with iodosylbenzene can achieve alkene epoxidation [equation (1)].



(1)

Results

It has been found that both Ag_2O and $AgNO_3$ in combination with iodosylbenzene can mediate the epoxidation of alkenes. Treatment of, *e.g.*, styrene (1.5 mmol) with iodosylbenzene (3.0 mmol) as oxygen donor and Ag_2O (1.5 mmol) in $CHCl_3$ (10 cm^3) at room temperature leads to the formation of styrene oxide and benzaldehyde in 7 and 5% yield, respectively. Changing the solvent to $CH_3C(O)CH_3$, $CH_3CH_2OCH_2CH_3$, or CH_3CN affords no reaction, and similar result is also obtained if Ag_2O or iodosylbenzene is excluded. Increasing the reaction temperature to 60 °C causes an increase in the yield of styrene oxide. The by-products formed are mainly phenyl acetate, benzaldehyde, phenylacetaldehyde, and acetophenone. Table 1 gives the results for epoxidation of a series of alkenes using the Ag_2O–iodosylbenzene system at 60 °C (see Experimental section for details). The presence of tertiary amine bases, *e.g.* pyridine, which are known to increase the reactivity and stereoselectivity in some transition metal-catalysed epoxidations[1h,i,9] leads in the case of the Ag_2O–iodosylbenzene system to a significant decrease in the epoxide yield.

Silver nitrate shows also under our reaction conditions no catalytic effect for alkene epoxidation in solvents as $CH_3C(O)CH_3$, $CHCl_3$, or CH_3CN. However, addition of pyridine to $AgNO_3$ dissolved in $CHCl_3$ leads to a complex, which with iodosylbenzene can mediate epoxidation. The same series of alkenes shown in Table 1 has also been investigated for epoxidation with $AgNO_3$ in the presence of pyridine ($AgNO_3$/pyridine = 1:5) and iodosylbenzene as oxygen donor under similar reaction conditions as above. However, the yield of epoxides is significantly lower compared with Ag_2O–iodosylbenzene, and higher amounts of by-products are formed.

The phenyl acetate formed by epoxidation of styrene is interesting, and we have tried to trace its origin. Treatment of both styrene oxide, (**1**), and acetophenone, (**2**), with iodosylbenzene in the presence of Ag_2O leads to the formation of phenyl acetate, (**3**) [equation (2)], in about 6% yield, which indicates that both (**1**) and (**2**) are oxidized to (**3**) or that (**1**) rearranges to (**2**) which then by an oxidative rearrangement forms (**3**). Reaction of compounds (**1**) and (**2**) with iodosylbenzene or Ag_2O does not produce (**3**), indicating that a complex formed from iodosylbenzene and Ag_2O is responsible for the oxidative-rearrangement reaction.

To achieve the epoxidation with $AgNO_3$–iodosylbenzene the

Table 1. Epoxidation of alkenes with the Ag_2O–iodosylbenzene system[a]

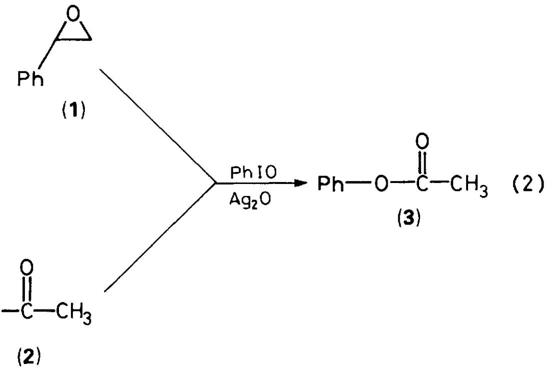
Alkene	Yield of epoxide[b]/%	Other products (% yield)[b]
$PhCH=CH_2$	15	PhCHO (2), $PhCH_2CHO$ (2), $PhC(O)CH_3$ (2), $PhOC(O)CH_3$ (10)
Cyclohexene	2	Cyclohexenone (< 2), cyclohexen-1-ol (< 2)
cis-PhCH=CHPh	2 (*cis*) 10 (*trans*)	PhCHO (< 2), *trans*-PhCH=CHPh (5)
trans-PhCH=CHPh	15 (*trans*)	PhCHO (< 2)
cis-$PhCH=CHCH_3$	< 2 (*cis*) 16 (*trans*)	PhCHO (< 2), *trans*-$PhCH=CHCH_3$ (< 2)
trans-$PhCH=CHCH_3$	25 (*trans*)	PhCHO (< 2)

[a] See Experimental section for details. [b] Based on starting alkene.

Table 2. Epoxidation of alkenes with Ag_2O_2[a]

Alkene	Yield of epoxide[b]/%	Other products (% yield)[b]
$PhCH=CH_2$	19	PhCHO (3)
cis-PhCH=CHPh	< 2 (*cis*) 8 (*trans*)	PhCHO (< 2)
trans-$PhCH=CHCH_3$	18 (*trans*)	PhCHO (2)
cis-$PhCH=CHCH_3$	2 (*cis*) 18 (*trans*)	PhCHO (2)

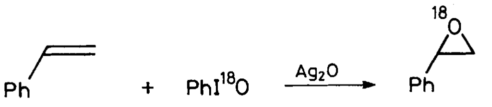
[a] See Experimental section for details. [b] Based on starting alkene.



presence of *e.g.* pyridine is necessary. We have studied the effect of a series of tertiary nitrogen bases on the yield of the products in the oxidation of styrene with iodosylbenzene as oxygen donor. The influence of the following amine bases has been investigated: pyridine, pentachloropyridine, 4-nitropyridine, 4-dimethylaminopyridine, imidazole, and phenanthroline.

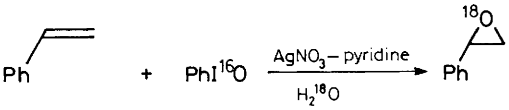
The yield of styrene oxide and other oxidized products is dependent on the presence of nitrogen bases; increasing the $AgNO_3$/pyridine ratio up to 1:50 does not increase the yield of oxidized products compared with an $AgNO_3$/pyridine ratio of 1:5 where the main products are styrene oxide (2%) and phenyl acetate (8%). The presence of an electron-donating group in the 4 position in pyridine leads to a very poor epoxidation system as less than 2% of styrene oxide is obtained. However the presence of a pyridine with electron-withdrawing groups, *e.g.* 4-nitropyridine, leads to a more selective and better epoxidation system as 15% of styrene oxide is formed with only minor amounts of other oxidized products. Changing the tertiary amine to imidazole or phenanthroline does not improve the epoxidation properties of the system compared with $AgNO_3$–pyridine. Pyridine *N*-oxide or substituted pyridine *N*-oxides could in these reactions be an oxygen donor or transfer the oxygen atom direct to the alkene itself, but addition of excess of pyridine *N*-oxide to the reaction mixture does not improve the yield of epoxide when styrene is the substrate.

The course of the oxygen-atom transfer during the epoxidation reaction has been examined by the incorporation of ^{18}O into the epoxide by ^{18}O-labelled iodosylbenzene or ^{18}O-labelled water. The incorporation of ^{18}O has been tested for both Ag_2O and $AgNO_3$–pyridine. In a typical experiment with ^{18}O-labelled iodosylbenzene (30% enriched), 0.22 mmol of styrene was dissolved in $CHCl_3$ (2 cm^3) and 0.22 mmol of Ag_2O and 0.45 mmol ^{18}O-labelled iodosylbenzene added. The reaction mixture was subjected to gas chromatographic–mass spectrometric (g.c.–m.s.) analysis for styrene [^{18}O]oxide. The isotopic composition of the labelled styrene oxide (25—30%) is identical to the composition in iodosylbenzene indicating that the oxygen is derived from ^{18}O-labelled iodosylbenzene [equation (3)].



(3)

In the case of the $AgNO_3$–pyridine system, the incorporation of the atomic oxygen into the epoxide was tested using ^{18}O-labelled water. In a typical experiment, 0.22 mmol $AgNO_3$, 1.00 mmol pyridine, and 0.22 mmol styrene were dissolved in $CHCl_3$ (2 cm^3) containing 4.00 mmol $H_2{}^{18}O$. After reaction with 0.45 mmol iodosylbenzene the reaction mixture was analysed as above and the results indicated that the incorporated oxygen (40%) was derived from water, *i.e.* as in equation (4).

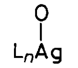


(4)

The labelling results support a mechanism involving an oxosilver intermediate (see below). In the epoxidation achieved by the Ag_2O–iodosylbenzene system the reaction takes place probably by an oxygen transfer from iodosylbenzene to Ag_2O, and in the reaction mediated by $AgNO_3$–pyridine probably *via* an oxosilver intermediate too, where the latter undergoes a rapid exchange of oxygen with $H_2{}^{18}O$. In the case of Ag_2O the reactive intermediate could be Ag_2O_2. This led us to investigate whether Ag_2O_2 could be an epoxidation reagent. In a typical experiment 1 mmol of the alkene was dissolved in $CHCl_3$ (10 cm^3) and 1 mmol of Ag_2O_2 was added. The reaction mixture was stirred for 24 h at 60 °C. The results reported in Table 2 show that the yield and stereochemistry of the epoxides obtained by oxidation with Ag_2O_2 are comparable to those with the Ag_2O–iodosylbenzene system. It is interesting that in the oxidation of styrene only benzaldehyde is observed as by-product. We have also found that reaction of compound (**2**) with Ag_2O_2 under similar conditions to those used in Table 2 did not lead to (**3**).

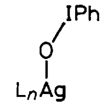
Discussion

It appears that Ag_2O and $AgNO_3$ in combination with iodosylbenzene can generate a reactive oxidant which can achieve epoxidation, and that the Ag_2O–iodosylbenzene system and Ag_2O_2 show some similarities in the oxygen-transfer step. However, it appears also from the results in Tables 1 and 2 that the Ag_2O–iodosylbenzene system probably generates other oxidation species than the one responsible for the epoxidation reaction as other oxidized products are formed compared with the results for Ag_2O_2 as oxidant. The structure of the reactive intermediate in these types of epoxidation reactions is still unknown, but the following three structures, (**4**)—(**6**) could be candidates.



$$\overset{\displaystyle O}{\overset{|}{L_nAg}}$$

(**4**)



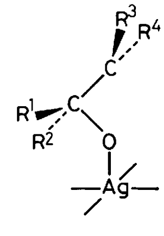
(**5**)

$L_nAg—O—AgL_n$

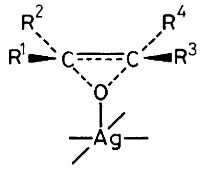
(**6**)

Species (**4**), an oxosilver complex, in the case of $AgNO_3$–pyridine is probably an $OAg^{III}(py)_n$ (*n* might be two)[10] type of complex, and with Ag_2O probably an $OAg^{III}OAg^{I}$ type of complex.[11] The silver–iodosylbenzene species, (**5**), is also a potential oxidant, and species (**6**) is a μ-oxo dimer silver complex.[11] As Ag_2O_2 and the Ag_2O–iodosylbenzene system show nearly the same oxygen-transfer ability for alkenes in the formation of epoxides, an Ag_2O_2 species might be the reactive intermediate in the former case. The crystal structure of Ag_2O_2 shows that two different oxygen–silver distances are present, 2.04 and 2.35 Å,[12] indicating that one of the oxygens is more weakly bound than the other. The weakly bound oxygen might be the one which is used in the oxygen-transfer process. The reactive oxosilver complex, (**4**), is similar to the oxometal species proposed to be the oxidants in other molecular transition metal-catalysed epoxidations [1a,h,i] and also the silver surface-catalysed epoxidation of ethylene.[2b,4] The isotopic ^{18}O-labelling studies of incorporation of atomic oxygen into the epoxide support mainly an oxosilver complex, (**4**) [as well as (**5**)], as the reactive intermediate. The incorporation of oxygen from $H_2{}^{18}O$ into the epoxide is consistent with an independent oxosilver intermediate which undergoes isotopic exchange with ^{18}O-enriched water.[13] Species (**6**) is comparable to the μ-oxo dimers of metal porphyrin and Schiff-base complexes which are generally inactive as alkene oxidants,[14] but can dissociate to active oxygen donors.[14a] We will regard (**4**) as the reactive intermediate in the following, although (**5**) or (**6**) cannot be excluded.

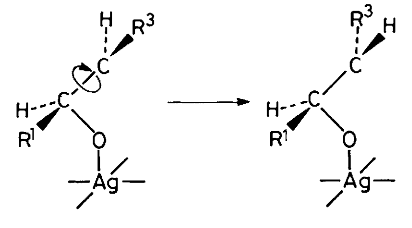
Based on the electronic structure of the oxo–silver bond on a silver surface it has been suggested that the interaction of the oxygen in the oxosilver complex with an alkene takes place with only one of the carbons, (**7**), rather than as in the symmetrical π complex (**8**). The electronic reason for this preference is that both the bonding and the antibonding orbitals of the oxygen–silver bond are occupied, or that the oxygen shows significant radical character. Intermediate (**7**) is a complex where rotation around the C–C bond is possible [equation (5)], whereas in (**8**) such rotation is not possible. Our results for the epoxidation of *cis*-alkenes support an intermediate with free rotation around the C–C bond, as the major products from the reaction are the *trans*-epoxides. These observations can indicate that the intermediate in these silver-mediated epoxidations lives long enough to allow the rotation around the C–C bond giving the more stable intermediate (**9**), from which the *trans*-epoxide is formed.



(**7**)



(**8**)



(**7**) (**9**)

(5)

The oxygen-transfer properties of $AgNO_3$ are dependent on the presence of tertiary amines. The more favourable properties of $AgNO_3$–4-nitropyridine compared with $AgNO_3$–4-dimethylaminopyridine might be due to the presence of an electron-withdrawing group in the 4 position of pyridine making the silver atom more electron poor compared with an electron-donating group present in the 4 position, which could lead to a faster reaction of the silver complex with the oxygen in iodosylbenzene. On the other hand, could pyridines with electron-withdrawing groups also lead to a weakening of the oxo–silver bond making the oxygen more labile. Similar arguments have been applied to explain the increased reactivity of oxygen on a silver surface in the presence of chlorine as moderator.[4c] It should also be noted that the presence of electron-withdrawing groups around the oxo–transition metal function in other molecular systems increases the reactivity of the complex.[1h,15]

One might ask here: 'is there a relation to the silver surface-catalysed epoxidation of ethylene?' The present investigation shows some analogy to some of the results obtained for the silver surface-catalysed epoxidation of ethylene as the oxygen-atom-transfer step in both types of reaction takes place in a *non*-stereospecific manner. With regard to the active oxidant the present results indicate that it could be an oxosilver species, which has also been suggested for the silver surface-catalysed epoxidation with molecular oxygen as the oxygen donor. It seems thus as there is a bridge between the silver surface and silver complexes as mediator for alkene epoxidation, although the surface-catalysed reaction takes place at much higher temperatures.

It is shown that silver compounds such as Ag_2O and $AgNO_3$, the latter in the presence of pyridine can, in combination with iodosylbenzene achieve epoxidation. The 'catalytic' properties of the silver compounds are not as good as, *e.g.*, many manganese and iron compounds, but the present results show that silver should be included among the transition metals as of interest for epoxidation. The oxidation products obtained by the silver-mediated reactions indicate that the reaction path for the oxygen transfer or the oxidation properties of the oxosilver intermediate are slightly different from those usually observed in many transition metal-catalysed epoxidations.

Experimental

Proton and ^{13}C n.m.r. spectra were recorded on a Varian Gemini 200 spectrometer, mass spectra on a Micromass 7070F or Trio-2 spectrometer (g.c.–m.s.) operating at 70 eV (1.12×10^{-17} J) using a direct inlet. Gas chromatography was performed on a HP 5890 instrument.

Materials.—The compounds Ag_2O, $AgNO_3$, the substituted pyridines, imidazole, and phenanthroline are commercially available and were used as received. Iodosylbenzene was prepared from iodosylbenzene diacetate.[15,16] The compound Ag_2O_2 was prepared according to the literature.[17] Chloroform (Merck, p.a.) was refluxed for 2 h in the presence of $KMnO_4$ and then distilled three times before use. Labelled water ($H_2{}^{18}O$) of 97% isotopic purity was obtained from ICN Stable Isotopes and used as such; ^{18}O-labelled iodosylbenzene was prepared according to the literature.[18]

General Procedure for the Alkene Oxidation.—Ag_2O-*Mediated epoxidations.* The alkene (1.5 mmol) was dissolved in $CHCl_3$ (10 cm^3). Then Ag_2O (1.5 mmol) and iodosylbenzene (3.0 mmol) were added and the reaction mixture was stirred for 24 h at 60 °C in the absence of light. After filtration through Celite to remove Ag_2O and excess of iodosylbenzene, the reaction mixture was analysed by ^1H and ^{13}C n.m.r. spectroscopy or g.c.–m.s. Proton and ^{13}C n.m.r. data for the epoxides are available in the literature.[19]

$AgNO_3$-*Pyridine-mediated epoxidations.* Pyridine (7.5 mmol) (or another of the tertiary amine bases studied) was dissolved in $CHCl_3$ (10 cm^3). Silver nitrate (1.5 mmol) was added and the mixture stirred until it had dissolved. Then the alkene (1.5 mmol) and iodosylbenzene (3.0 mmol) were added and the reaction mixture was stirred for 24 h at 60 °C in the absence of light. After filtration through Celite to remove excess of iodosylbenzene the reaction mixture was analysed as above.

Reaction of Styrene Oxide or Acetophenone with Iodosylbenzene in the Presence of Ag_2O.—Styrene oxide or acetophenone (1.5 mmol) was dissolved in $CHCl_3$ (10 cm^3). Then Ag_2O (1.5 mmol) and iodosylbenzene (3.0 mmol) were added and the reaction mixture was stirred for 24 h at 60 °C in the absence of light. After filtration through Celite to remove Ag_2O and excess of iodosylbenzene the reaction mixture was separated on a silica plate and phenyl acetate isolated and characterized by i.r., n.m.r. spectroscopy, and m.s.

Epoxidation by Ag_2O_2.—The alkene (1 mmol) was dissolved in $CHCl_3$ (10 cm^3). Then Ag_2O_2 (2 mmol) was added and the reaction mixture was stirred for 24 h at 60 °C in the absence of light. After filtration through Celite to remove insoluble silver species the reaction mixture was analysed by ^1H and ^{13}C n.m.r. spectroscopy or g.c.–m.s. Proton and ^{13}C n.m.r. data for the epoxides are available in the literature.[19]

Reactions with ^{18}O-*labelled Iodosylbenzene and Water.*—Styrene (0.22 mmol) was dissolved in $CHCl_3$ (2 cm^3); Ag_2O (0.22 mmol) and ^{18}O-labelled iodosylbenzene (0.45 mmol) were added. After the reaction mixture had been stirred for 24 h in the absence of light, the styrene oxide was analysed by g.c.–m.s. (on an OV-17 column) for its isotopic composition.

Pyridine (1.00 mmol), $AgNO_3$ (0.22 mmol), and styrene (0.22 mmol) were dissolved in $CHCl_3$ (2 cm^3) and $H_2{}^{18}O$ (4.00 mmol) added. [^{16}O]Iodosylbenzene (0.45 mmol) was added and the reaction mixture stirred for 24 h in the absence of light. The styrene oxide was analysed by g.c.–m.s. (on a OV-17 column) for its isotopic composition.

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