

Tertiary arsine oxides: active and selective catalysts for epoxidation with hydrogen peroxide

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Abstract: Tertiary arsines are active and selective catalysts for the epoxidation of a variety of alkenes with hydrogen peroxide at low catalyst loading (1–5 mol%); highly fluorinated analogues of these arsines can be recovered and reused with moderate efficiency. © 1999 Elsevier Science Ltd. All rights reserved.

The catalytic epoxidation of alkenes with hydrogen peroxide has attracted much attention over the last two decades.^{1–3} Several efficient catalytic systems have been developed but most are based on expensive precious metals,² or require expensive ligands.³

The number of catalysts based on main group organometallic or organoelement compounds remains rather limited. Highly fluorinated ketones (e.g. hexafluoroacetone) are selective catalysts, but their catalytic activity remains low.⁴ Recently we developed a perfluoroketone catalyst, with enhanced catalytic activity and a simple and almost quantitative recovery.⁵ The synthesis of this catalyst, however, was laborious and could not easily be scaled up beyond a few grams per synthesis. Other known main group organoelement catalysts are based on arsenic⁶ and selenium.⁷ Both arylarsonic acids and arylseleninic acids are active and selective catalysts for epoxidation and other oxidative conversions with hydrogen peroxide. Both types of catalysts could be heterogenised on a polystyrene support.^{8,9}

Very recently the catalytic activity of tertiary arsines and the epoxidation activity of hydrogen peroxide adducts of tertiary phosphine oxides and tertiary arsine oxides has been claimed.⁹ The tertiary phosphine oxides were only active in a stoichiometric reaction, whereas the arsines could also be used in catalytic amounts. The substrate to catalyst ratio of the latter reaction was only 5, indicating that these tertiary arsines were not very efficient catalysts under the conditions used.

In spite of the low activity, these results prompted us to further investigate this system. Initially, we tested several triaryl arsines and triaryl arsine oxides in the catalytic epoxidation of cyclooctene. The preferred reaction conditions were aqueous hydrogen peroxide in combination with trifluoroethanol as a solvent. As is shown in table 1, the triaryl arsines are highly active in cyclooctene epoxidation. No clear difference was observed when the corresponding triaryl arsine oxides were used. Separate experiments showed that the oxidation of tertiary arsines to the corresponding arsine oxides was very fast and selective using aqueous hydrogen peroxide. This indicates that the tertiary arsine oxides are the only arsenic compound present, even when the trivalent arsine is the catalyst precursor.

Table 1 also shows a clear influence of the electron density of the tertiary arsine on the reaction rate. Electron donating substituents on the phenyl group increase the reaction rate and electron-withdrawing substituents decrease the reaction rate. No information on the selectivity of the reaction could be obtained by using cyclooctene, since this alkene forms a very stable epoxide and selectivities rarely deviate from 100 %.

Table 1. Cyclooctene epoxidation with 60 % H₂O₂ in trifluoroethanol catalysed by triaryl arsines and triaryl arsine oxides^a

Catalyst	Initial rate/ mol mol ⁻¹ h ⁻¹	Yield (%) ^b	Catalyst	Initial rate/ mol mol ⁻¹ h ⁻¹	Yield (%) ^b
Ph ₃ As	51	95	(3,5-(CF ₃) ₂ C ₆ H ₃) ₃ As	16	47
Ph ₃ AsO	48	93	(3,5-(CF ₃) ₂ C ₆ H ₃) ₃ AsO	14	55
(C ₆ F ₅) ₃ As	16	60	(4-MeO-3,5-Me ₂ C ₆ H ₂) ₃ AsO	74	95

^a Conditions: 5 mmol cyclooctene, 1 mmol dibutylether (internal standard), 0.25 mmol triaryl arsine (oxide) (5 mol%), 10 mmol 60% H₂O₂ in 5 ml trifluoroethanol. Reflux under N₂. Analysis by GC. ^b After 1 h.

The clear increase in reaction rate with the electron rich arsine prompted us to screen more electron rich mixed alkyl aryl arsines for catalytic activity. In this case we used cyclohexene as a substrate. The reactivity of this alkene is comparable with cyclooctene, but its epoxide is much more sensitive towards acid catalysed hydrolysis. As table 2 shows, high yields of the epoxide were obtained for all tertiary arsines. Exceptionally high activity was displayed by dibutylphenylarsine. The high activity of this arsine when compared to other tertiary arsines was also observed under other conditions; 1,2-dichloroethane with anhydrous hydrogen peroxide (initial rate 56 mol mol⁻¹h⁻¹) and 1,2-dichloroethane with 60 % H₂O₂ (initial rate 18 mol mol⁻¹h⁻¹). In contrast, the known phenylarsonic acid catalyst showed a high activity, but low selectivity for epoxide over hydrolysis products (diols) under identical conditions (see table 2).

Table 2 Cyclohexene epoxidation with 60 % H₂O₂ in trifluoroethanol catalysed by tertiary arsines^a

Catalyst	Initial rate/ mol mol ⁻¹ h ⁻¹	t/h	Yield (%)
Ph ₃ As	40	2	65
Ph ₂ AsMe	60	2	75
PhAsBu ₂	165	1	94
AsBu ₃	80	2	80
PhAsO ₃ H ₂	270	0.17	48 ^b

^a Conditions: 5 mmol cyclohexene, 1 mmol dibutylether (internal standard), 0.1 mmol tertiary arsine or phenylarsonic acid (2 mol%), 10 mmol 60% H₂O₂ in 5 ml trifluoroethanol. Reflux under N₂. Analysis by GC. ^b Maximum yield; after 1 h 6 % epoxide and 60 % cyclohexanediol were detected.

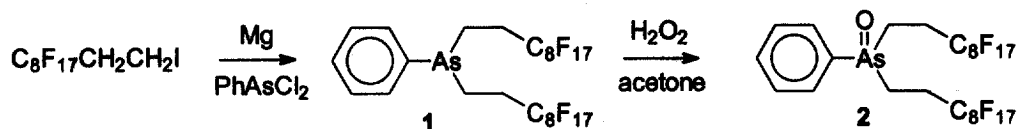
The high activity of dibutylphenylarsine prompted us to examine the scope of this catalyst. Table 3 shows the results for a number of alkenes. All alkenes are converted into their corresponding epoxides in high yields. Several alkenes that form very sensitive epoxides require the addition of a small amount of phosphate buffer. The normal trend for electrophilic epoxidation is followed; higher substituted (more nucleophilic) alkenes are epoxidised at a higher rate. The high selectivity for the monoepoxide of limonene is indicative of this trend; the disubstituted double bond is epoxidised at a rate 15 times slower than the trisubstituted double bond. The use of preformed dibutylphenyl arsine oxide as a catalyst resulted in a lower initial rate, but almost the same yield of epoxide.

Table 3: Epoxidation with 60 % H₂O₂ in trifluoroethanol catalysed by dibutylphenyl arsine^a

Alkene	S/C ^b	Initial rate/ mol mol ⁻¹ h ⁻¹	t/h	Yield (%)
Cyclohexene	50	165	1	94
Cycloheptene	50	205	1	98
Cyclooctene	50	260	1	100
Cyclooctene ^c	50	180	1	96
Methylenecyclohexane ^d	50	97	1.5	88
2-Methylhept-1-ene ^d	50	75	2	78
2-Methylhept-2-ene ^d	50	180	1	88
1-Methylcyclohexene ^d	100	410	1	97 (73) ^e
Limonene ^d	100	520	1.5	79 ^f
Dec-1-ene ^d	20	5.3	2	54

^a Conditions: 5 mmol alkene, 1 mmol dibutylether (internal standard), the indicated amount of PhAsBu₂, 10 mmol 60% H₂O₂ in 5 ml trifluoroethanol. Reflux under N₂. Analysis by GC. ^b Substrate to catalyst ratio. ^c Preformed dibutylphenyl arsine oxide was used. ^d 5 mol% of Na₂HPO₄ was added as a buffer. ^e Isolated yield. ^f 5 % of the diepoxide was also detected.

Homogeneous epoxidation catalysed by a non-reusable arsenic containing catalyst has obvious disadvantages. The most important one is the bad environmental and toxicological reputation of arsenic compounds. A clear requirement for the use of an arsenic-containing catalyst is therefore the very efficient separation of the catalyst from the product in combination with the possibility of reusing the catalyst. We examined one possible approach with the synthesis of a highly fluorinated analogue of dibutylphenylarsine to allow a fluororous biphasic extraction^{10,11} of the catalyst from the reaction mixture. The synthesis is straightforward and is shown in the scheme below. The alternative synthesis, the radical addition of phenylarsine to 1H,1H,2H-perfluoro-1-decene, that was used for the synthesis of phosphine ligands,¹⁰ was unsuccessful.



The arsine 1 was soluble in a large number of organic solvents. A partition experiment of 100 mg 1 between hexane and perfluorohexane (5 ml each) showed that 1 could be extracted from the hexane layer by perfluorohexane (partition coefficient 3.8). The same experiment with the arsine oxide 2 was unsuccessful due to the low solubility (< 1 mg/ml) of 2 in both solvents. The most convenient procedure for recovering 2 is therefore not extraction with a perfluorinated solvent, but crystallisation from hexane or acetone. Table 4 shows the results for the epoxidation of cyclooctene catalysed by 1 and 2. As was observed in the PhAsBu₂ catalysed epoxidation, the arsine oxide 2 was slightly less active than 1. In both cases a major amount of the catalyst could be recovered by crystallisation. The recoveries were not quantitative, but on the small scale of the catalytic reactions a significant loss of product cannot be avoided. More important was the observation that the recovered catalyst was still active in epoxidation, but with a lower activity. This implies that some decomposition of the catalyst is occurring, possibly related to the short insulating spacer between the arsine and the perfluoroalkyl group.

Table 4 Epoxidation of cyclooctene in trifluoroethanol catalysed by 1 and 2^a

Catalyst	Initial rate/ mol mol ⁻¹ h ⁻¹	Yield (%) ^b	Recovery (%) ^c
1	120	95	60 ^d
2	80	91	81 ^e
2'	49	78	86 ^e

^a Conditions: 5 mmol cyclooctene, 1 mmol dibutylether (internal standard), 0.1 mmol 1 or 2 (2 mol%), 10 mmol 60% H₂O₂ in 5 ml trifluoroethanol. Reflux under N₂. Analysis by GC. ^b After 2 h. ^c Amount of isolated 2 based on initial amount 1 or 2. ^d Crystallisation from hexane after aqueous work-up of the reaction mixture. ^e Crystallisation from acetone after non-aqueous workup (10 mg MnO₂ (for decomposition of the unreacted H₂O₂), filtration and evaporation of solvent) of the reaction mixture. ^f 2 mol% of recovered 2 was used as catalyst.

In an other example of fluorous biphasic oxidation,¹² it was shown that the perfluoroalkyl group required at least a three carbon spacer to isolate it from the donor atom of the ligand for optimum performance and stability of the catalyst.

Although our current results do not meet the requirements for a reusable and stable arsenic-based catalyst, the possibility of recovering an active, reusable catalyst has been demonstrated. We are currently exploring the synthesis of other highly fluorinated tertiary arsines to obtain a more stable, more easily reusable catalyst.

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