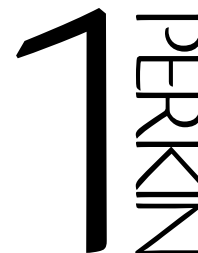


Rhenium catalysed epoxidations with hydrogen peroxide: tertiary arsines as effective cocatalysts



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Perrhenic acid in combination with tertiary arsines gives a versatile catalytic system for epoxidation of alkenes with hydrogen peroxide. The best results are obtained with diphenylmethylarsine. A wide range of alkenes could be epoxidised with aqueous hydrogen peroxide (60%) in 60–100% yields with substrate to catalyst ratios of up to 1000.

Introduction

In the last two decades metal-catalysed epoxidations with hydrogen peroxide have been extensively studied.¹ Rhenium-based systems have attracted particular attention because rhenium, in contrast to many other transition metals, exhibits low activity in competing, non-productive decomposition of hydrogen peroxide. Herrmann and co-workers² showed that methylrhenium trioxide (CH_3ReO_3 ; MTO) is an active catalyst for olefin epoxidation with anhydrous hydrogen peroxide. In initial studies³ selectivities were often low, however, owing to acid-catalysed ring opening of the epoxide product. The addition of basic ligands resulted in increased selectivities but at the expense of the reaction rate. The use of aqueous hydrogen peroxide resulted in both lower rates and lower selectivity. Subsequently, Sharpless and co-workers⁴ discovered that the addition of a large excess of a basic ligand (pyridine or 3-cyanopyridine), based on MTO, afforded both higher selectivities and reaction rates and provided the possibility of using aqueous hydrogen peroxide. More recently, pyrazole was shown to be even more effective.⁵ However, major disadvantages of MTO are its limited stability under the reaction conditions and its rather difficult and, hence, expensive synthesis.⁶

Consequently, there is still an incentive to develop inorganic rhenium catalysts that are effective with commercially available aqueous hydrogen peroxide.⁷ Inorganic rhenium compounds catalyse olefin epoxidations⁸ albeit with low selectivities. The main problem is the high acidity of perrhenic acid, HReO_4 , which leads to facile ring opening of the epoxide product. Addition of bases offers no solution to this problem as it leads to the formation of catalytically inactive perrhenate salts. We now report our results on a new system, comprising perrhenic acid in combination with tertiary arsines, which catalyses the efficient epoxidation of a variety of olefins.

Results and discussion

Cocatalyst screening

Inspired by earlier reports of Inoue and co-workers^{1h} on the effect of dialkyltin oxides on the molybdenum catalysed epoxidation of styrenes with aqueous H_2O_2 , we initially investigated the effect of various main group organometallic oxides on HReO_4 catalysed epoxidations of cyclooctene and dec-1-ene. The results are shown in Table 1. Cyclooctene yields an extremely stable epoxide and, hence, only provides information regarding the activity of an epoxidation reaction; the selectivity rarely deviates from 100%. Dec-1-ene on the other hand has a much lower reactivity in epoxidation and forms an acid-labile

Table 1 Cocatalysis in HReO_4 -catalysed epoxidation with aqueous H_2O_2 ^a

Cocatalyst	Substrate			
	Dec-1-ene		Cyclooctene	
	Initial rate/h ⁻¹	Yield (%) ^c	Initial rate/h ⁻¹	Yield (%) ^d
None	0	0.7 (70 h)	2	9
Ph_3P	0.08	4	1.2	20
Ph_3As	2.4	69	48	97
Ph_3Sb	0.7	22	1.8	34
Ph_3Bi	0	≤1	0.6	4
$\text{Bu}_2\text{Ge}(\text{OH})\text{OMe}$	2.3	26 (24 h)	7	71
Bu_2SnO	0.8	32	2.6	63

^a Conditions: 5 mmol alkene, 1 mmol *n*-decane, 0.05 mmol HReO_4 (1 mol%), 0.1 mmol cocatalyst (2 mol%), 10 mmol 60% H_2O_2 in 5 ml CH_2Cl_2 , stirring at room temperature. ^b Moles of alkene converted per mol of catalyst per hour. ^c Yield at 168 h or at indicated time. ^d After 24 h.

epoxide. Therefore, this substrate yields information on both activity and selectivity of the epoxidation. Perrhenic acid alone was almost inactive in epoxidation under these mild conditions. Addition of triphenylphosphine and triphenylbismuth gave only a minor improvement in conversion. Major improvements were achieved by using triphenylarsine, triphenylstibine, dibutylgermanium oxide or dibutyltin oxide. The best results, with regard to both activity and selectivity, were obtained with triphenylarsine. The accelerating effect of organotin oxides on molybdenum^{1h} and tungsten^{8c} has been reported before. However, when triphenylarsine was applied in ammonium heptamolybdate catalysed epoxidation^{1h} no conversion was observed. Phenylarsonic acid (which was shown to be a catalyst for epoxidation^{1a}) in combination with perrhenic acid was also inactive. Triphenylarsine alone showed a very low activity (3600 times slower).

The influence of the triphenylarsine to rhenium ratio is shown in Table 2. The maximum rate is observed with an equimolar mixture of triphenylarsine and HReO_4 . The use of less triphenylarsine gives a lower rate and a low selectivity. When an excess of triphenylarsine is applied then a slightly lower rate is observed, but the selectivity is much higher. The yield of the reaction is almost the same for a 1:1 and a 2:1 mixture of triphenylarsine and HReO_4 . No difference in rate or yield could be observed when the ligand was introduced in the form of triphenylarsine oxide. Additional experiments showed that triphenylarsine is oxidised to the arsine oxide very quickly

under the reaction conditions. Triphenylarsine oxide is a weak base that forms H-bond adducts with acids.⁹ The stabilizing effect of the excess arsine can therefore be attributed to the buffering effect of the arsine oxide. The organic layer, which contains all the arsine oxide and the epoxide, was indeed neutral while the aqueous phase was acidic. Another effect of the arsine oxide is the phase transfer activity towards HReO_4 . HReO_4 itself is virtually inactive even in the case of cyclooctene. In homogeneous systems HReO_4 is an excellent catalyst for cyclooctene epoxidation, but when a separate water phase is present no activity is left, indicating the inability of HReO_4 to diffuse into the organic layer. Tertiary arsine oxides have been shown to extract HReO_4 from the aqueous phase into the organic phase, enabling a simple purification of rhenium which is used in metallurgy.¹⁰

Effect of arsine structure

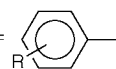
Several triarylsines were synthesised to explore electronic and steric effects in the cocatalysis by these types of compounds. Table 3 shows the results of the epoxidation of dec-1-ene by triarylsines. The presence of electron donating groups lowers the rate, but the selectivity is higher and a higher yield of epoxide is obtained than with triphenylarsine. If an electron withdrawing substituent is present, then the initial rate is

Table 2 The influence of the ratio arsenic to rhenium in dec-1-ene epoxidation^a

Ph_3As (mol%)	Initial rate/h ⁻¹	Conv. (%) ^b	Sel (%) ^{c,d}
0.5	2.5	48	90
1	3.3	56	91
2	2.5	52	99
3	2.3	47	100

^a Conditions: 10 mmol dec-1-ene, 1.6 mmol undecane, 0.1 mmol HReO_4 (1 mol%), indicated amount of Ph_3As , 20 mmol 60% H_2O_2 in 5 ml CHCl_3 . Stirring at room temperature. ^b Reaction was stopped at 47 h. ^c Selectivity towards epoxide product.

Table 3 Cocatalysis in dec-1-ene epoxidation by triarylsines^a

Ar = 	Ar_3As	
	Initial rate/h ⁻¹	Yield (%) (t/h)
H	3	58 (72)
4-Me	2.7	69 (96)
4-MeO	2	70 (96)
3-MeO	2.9	56 (72)
2-MeO	0.03 ^b	10 (168)
4-F	4	43 (21)
F_5	0	≤1
3,5-(CF_3) ₂	0 ^b	10 (48)

^a Conditions: 5 mmol dec-1-ene, 0.75 mmol undecane, 0.05 mmol HReO_4 (1 mol%), 0.06 mmol cocatalyst (1.2 mol%), 10 mmol 60% H_2O_2 in 2.5 ml CH_2Cl_2 . Stirring at room temperature. ^b Induction period of ~24 h.

Table 4 Epoxidation catalysed by HReO_4 and mixed arylalkylarsines^a

Cocatalyst	Dec-1-ene		Cyclohexene ^b		Cyclooctene	
	Initial rate/h ⁻¹	Yield (%) ^c	Initial rate/h ⁻¹	Yield (%) ^d	Initial rate/h ⁻¹	Yield (%) ^e
None	0	0	≤0.2	0	2	9
Ph_3As	1.71	62	12	9	32	100
Ph_2AsMe	1.79	83	28	35	128	100
PhAsBu_2	1.02	65	15	19	68	99
AsBu_3	0.55	46	3	36	32	95

^a Conditions: 5 mmol alkene, 1 mmol *n*-decane or undecane, 0.05 mmol HReO_4 (1 mol%), 0.075 mmol cocatalyst (1.5 mol%), 10 mmol 60% H_2O_2 in 5 ml CH_2Cl_2 . Stirring at room temperature. ^b 2 mol% cocatalyst. ^c Maximum yield in 168 h. ^d Maximum yield in 24 h. ^e Yield after 24 h.

increased, but the selectivity is much lower. In this case the triarylsine oxide is only very weakly basic and is incapable of protecting the epoxide against acid catalysed decomposition. *ortho* Substituents inhibit the reaction, presumably by steric hindrance. The last two entries contain strong electron withdrawing substituents. In these cases the oxidation of the arsine to arsine oxide is very slow and epoxidation only starts after an induction period or does not start at all. The encouragingly high selectivity obtained with triarylsines containing electron donating groups prompted us to investigate mixed alkylarylarsines. Alkyl groups are more electron donating than (substituted) phenyl rings. Table 4 shows the results of the cocatalysis by the mixed alkylarylarsines for some substrates. The best cocatalyst with regard to both activity and selectivity was diphenylmethylarsine. Preformed diphenylmethylarsine oxide gave identical results, indicating that the oxidation of the arsine proceeds quickly and selectively. The other arsines, dibutylphenylarsine and tributylarsine, gave a much slower reaction resulting in lower yields even after prolonged reaction times.

Other alkyldiphenylarsines were prepared to investigate the effect of the alkyl group on the efficiency of the cocatalysis. As shown in Table 5 only small differences were observed and yields were high for all alkyldiphenylarsines studied. The initial rate decreases with increasing length of the alkyl group or a higher degree of substitution. The best results were again obtained with diphenylmethylarsine.

Effect of solvent

Preliminary solvent screening in the HReO_4 - Ph_3As catalysed epoxidation of dec-1-ene showed that the best solvents were halogenated hydrocarbons such as CH_2Cl_2 or CHCl_3 . Other more environmentally friendly solvents such as esters, ethers, alcohols or hydrocarbons showed much slower reactions and attempts to increase the rate by performing the reactions at higher temperatures resulted in a fast hydrolysis of the epoxides. Having optimised the structure of the arsine, we repeated this solvent screening using diphenylmethylarsine and HReO_4 at a higher temperature. Table 6 shows the results for several solvents at reflux temperature or at 80 °C. The only solvents that afforded a yield higher than 20% were polar, non-coordinating solvents. Apolar solvents or polar, coordinating solvents give inferior yields. Trifluoroethanol gave not only high yields of epoxide, but the rate of the reaction was also much higher than in chlorinated hydrocarbons.

Scope and limitations

Based on the above results, we tested several alkenes to investigate the scope and limitations of the catalytic system. Table 7 shows the initial rates and the epoxide yields for several olefins. Terminal alkenes gave yields in the range of 70–80%. As shown in Table 6 this yield could be improved to 85% by using double the amount of catalyst. Very unreactive alkenes, such as allyl ethers and esters, show low yields. In this case the epoxidation was slow compared to the decomposition of the epoxide. Disubstituted alkenes reacted about 30 times faster than terminal

Table 5 Cocatalysis by diphenylalkylarsines in the epoxidation of dec-1-ene^a

Cocatalyst	Initial rate ^b /h ⁻¹	Yield (%) ^c
Ph ₂ As	1.71	62
Ph ₂ AsMe	1.79	83
Ph ₂ AsEt	1.5	77
Ph ₂ AsPr	1.54	79
Ph ₂ AsBu	1.5	77
Ph ₂ AsCH ₂ CMe ₃	1.42	74
Ph ₂ AsCH ₂ SiMe ₃	1.17	78

^a Conditions: 5 mmol dec-1-ene, 1 mmol undecane, 0.05 mmol HReO₄ (1 mol%), 0.075 mmol cocatalyst (1.5 mol%), 10 mmol 60% H₂O₂ in 5 ml CH₂Cl₂. Stirring at room temperature. ^b Rate in first 24 h; induction period of ~3 h is sometimes observed. ^c After 168 h.

Table 6 Solvent screening for high temperature epoxidation of dec-1-ene catalysed by HReO₄ and Ph₂AsMe^a

Solvent	T/°C	Initial rate/h ⁻¹	Yield (%) (t/h)
CHCl ₃	60	14	37 (4)
CICH ₂ CH ₂ Cl	75	56	72 (2)
C ₆ H ₅ Cl	83	9	18 (3)
EtOAc	73	9	16 (4)
BuOAc	81	16	18 (3)
Bu ₃ PO ₄	85	10	5 (3)
MeOCH ₂ CH ₂ OMe	80	4	11 (4)
Toluene	80	0 ^b	13 (4)
^t BuOH	78	21	17 (2)
CF ₃ CH ₂ OH ^c	75	360	79 (0.5)
CF ₃ CH ₂ OH ^{c,d}	70	240	85 (0.75)

^a Conditions: 5 mmol dec-1-ene, 1 mmol undecane, 0.05 mmol HReO₄ (1 mol%), 0.075 mmol Ph₂AsMe (1.5 mol%), 10 mmol 60% H₂O₂ in 10 ml solvent. Stirring at the indicated temperature under reflux. ^b Induction period of 2 h. ^c 5 ml of solvent. ^d 2 mol% of cocatalyst.

Table 7 High temperature epoxidation catalysed by HReO₄ and Ph₂AsMe^a

Substrate	S:C	As:Re	Initial rate/h ⁻¹	Yield (%) (t/min)
Oct-1-ene	200	2	600	72 (45)
Dec-1-ene	200	2	650	78 (60)
Vinylcyclohexane	200	2	700	76 (45)
Allylbenzene	200	2	260	72 (120)
Allyl phenyl ether	50	2	95	26 (60)
Cyclohexene	1000	20	13500	64 (20)
Cyclooctene	1000	2	18600	99 (30)
2-Methylundec-1-ene	500	2.5	20100	61 (20)

^a Conditions: 5 mmol alkene, 1 mmol dibutyl ether, indicated amount of HReO₄ and Ph₂AsMe, 10 mmol 60% H₂O₂ in 5 ml trifluoroethanol. Reflux under N₂ (ca. 75 °C).

alkenes which is comparable to the ratio observed in oxidations with peracids or early transition metals and hydroperoxides (peroxo-metal mechanism) indicating that the rate determining step is the electrophilic epoxidation of the alkene¹¹ and not the other steps in the catalytic cycle (e.g. regeneration of the catalyst).

In the case of cyclohexene a very acid sensitive epoxide is formed and under normal conditions only small amounts of epoxide were formed. Addition of a large excess of the arsine relative to rhenium gave a much more selective reaction. In this case the excess arsine (in the form of the basic arsine oxide) neutralises the traces of acid that are responsible for the decomposition of the epoxide.

Recently, simple triarylsarsine oxides were claimed to be active as catalysts in the epoxidation of olefins with hydrogen peroxide.¹² However, at room temperature triphenylarsine was

virtually inactive in the epoxidation of cyclooctene in CH₂Cl₂ (the reaction was 3600 times slower than the rhenium–arsine system). In refluxing trifluoroethanol the catalytic activity of Ph₂AsMe alone in the epoxidation of cyclooctene was still 200 times slower^{12b} than that of the combination of HReO₄ and Ph₂AsMe. Hence, the catalytic activity of our system cannot be attributed to the tertiary arsine alone.

Similarly, the epoxidation of cyclooctene in the presence of 0.1 mol% HReO₄ alone proceeded only slightly faster than the blank reaction (without rhenium and arsine). Addition of 0.2 mol% of arsine resulted in a ten-fold increase of the reaction rate, comparable to the normal catalytic experiment with both catalyst and cocatalyst present at the beginning of the reaction.

We are currently investigating the immobilisation of the arsine cocatalyst to facilitate its recovery.

Conclusion

The combination of HReO₄ with tertiary arsines (e.g. Ph₂AsMe) gives a versatile catalytic system for the epoxidation of alkenes with aqueous hydrogen peroxide.

Experimental

Triphenylphosphine, triphenylarsine, triphenylarsine oxide, triphenylstibine, triphenylbismuth and dibutyltin oxide were obtained from Aldrich. Tris(4-methylphenyl)arsine,¹³ tris(4-methoxyphenyl)arsine,¹⁴ tris(3-methoxyphenyl)arsine,¹⁴ tris(2-methoxyphenyl)arsine,¹⁵ tris(4-fluorophenyl)arsine,¹² tris(pentafluorophenyl)arsine,¹⁶ tris[3,5-bis(trifluoromethyl)phenyl]arsine and tributylarsine¹⁵ were prepared from the corresponding Grignard or organolithium reagent and AsCl₃. Diphenylmethylarsine,¹⁴ diphenylethylarsine,¹⁷ diphenylpropylarsine,¹⁸ butyldiphenylarsine,¹⁸ (2,2-dimethylpropyl)diphenylarsine¹⁹ and diphenyl(trimethylsilylmethyl)arsine²⁰ were prepared by the reaction of the corresponding alkyl iodide with sodium diphenylarsenide, prepared by reductive cleavage of triphenylarsine. Dimethylphenylarsine¹⁸ and dibutylphenylarsine²¹ were prepared from methylmagnesium iodide or butyllithium and dichlorophenylarsine. Dibutylgermanium oxide²² was prepared by hydrolysis of dibutylgermanium dichloride. GLC analysis was performed on a Varian Star 3600 with a CP Sil 5 CB column of 50 m length and 0.53 mm inner diameter. NMR measurements were conducted using a Varian Unity Inova 300. MS measurements were conducted using a VG 70 SE spectrometer working at 70 eV.

Tris[3,5-bis(trifluoromethyl)phenyl]arsine

Magnesium turnings (0.50 g; 20.6 mmol) were activated by addition of I₂ (10 mg) in anhydrous THF (25 ml). To this solution 3,5-bis(trifluoromethyl)-1-bromobenzene (5.90 g; 20.1 mmol) was added dropwise over 10 min. The mixture was stirred for 30 min under cooling in a water bath. AsCl₃ (0.97 g; 5.4 mmol) was added dropwise to the dark solution. The solution was stirred for 2 h at room temperature. The excess Grignard reagent was destroyed by subsequent addition of methanol (1 ml), aqueous NH₃ (10 ml; 2 M) and water (20 ml). The organic layer was separated and the water layer was extracted with ether (2 × 50 ml). The combined organic layers were washed with water (25 ml) and saturated NaCl solution (25 ml) and dried on Na₂SO₄. Evaporation of the solvent gave a brown oil. This oil was crystallised from hexane to give a light-brown powder (2.82 g; 73%). This powder was distilled on a Kugelrohr apparatus (0.2 mmHg; bath temperature 120 °C). A white solid was obtained (2.72 g, 71%).

Mp 97–98 °C; GLC: 99.9% purity; δ_H(300 MHz; CDCl₃; Me₄Si) 7.785 (m, 6H), 7.97 (m, 3H); δ_C(75 MHz; CDCl₃; Me₄Si) 117.3, 121.0, 124.1, 124.1, 124.2, 124.6, 128.2, 132.2, 132.7, 133.1, 133.3, 133.6, 139.9; *m/z* (EI) 713.9629 (M⁺, C₂₄H₉AsF₁₈

requires 713.9633), 695 (33%), 501 (26), 407 (92), 319 (56), 288 (100).

General procedure for epoxidation at room temperature

A 10 ml flask was charged with 5 mmol substrate, 1 mmol of internal standard (*n*-alkane), 10 mmol of 60% H₂O₂, the appropriate amount of HReO₄ and cocatalyst and 5 ml of solvent. The flask was stirred at room temperature with a magnetic stirring bar (1000 rpm). Aliquots of the reaction mixture (~0.05 ml) were diluted with 2 ml ethyl acetate. 10 mg of MnO₂ was added to the solution to decompose the H₂O₂. The suspension was filtered and analysed by GLC.

General procedure for epoxidation at a higher temperature

A 10 ml round-bottom flask, equipped with a reflux condenser and maintained under an inert atmosphere, was charged with 5 mmol substrate, 1 mmol of internal standard (*n*-alkane or dibutyl ether), 10 mmol of 60% H₂O₂, the appropriate amount of HReO₄ and cocatalyst and 10 ml of solvent. The reaction mixture was heated with an oil bath to the indicated temperature and stirred with a magnetic stirring bar at 1000 rpm. Aliquots of the reaction mixture (~0.05 ml) were diluted with 2 ml ethyl acetate. 10 mg of MnO₂ was added to the solution to decompose the H₂O₂. The suspension was filtered and analysed by GLC.

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References

- (a) S. E. Jacobson, F. Mares and P. M. Zambri, *J. Am. Chem. Soc.*, 1979, **101**, 6946; (b) H. J. Reich, F. Chow and S. L. Peake, *Synthesis*, 1978, 299; (c) G. Strukul and R. A. Michelin, *J. Chem. Soc., Chem. Commun.*, 1984, 1538; (d) C. Venturello and R. D'Aloisio, *J. Org. Chem.*, 1988, **53**, 1553; (e) Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida and M. Ogawa, *J. Org. Chem.*, 1988, **53**, 3587; (f) R. Neumann and M. Gara, *J. Am. Chem. Soc.*, 1995, **117**, 5066; (g) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, *J. Org. Chem.*, 1996, **61**, 8310; (h) T. Kamiyama, M. Inoue, H. Kashiwagi and S. Enomoto, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1559; (i) P. L. Anelli, S. Banfi, F. Montanari and S. Quici, *J. Chem. Soc., Chem. Commun.*, 1989, 779; (j) D. de Vos and T. Bein, *Chem. Commun.*, 1996, 917; (k) M. G. Clerici and P. Ingallina, *J. Catal.*, 1993, **140**, 71.

- C. C. Ramão, F. E. Kühn and W. A. Herrmann, *Chem. Rev.*, 1997, **97**, 3197 and references cited therein.
- (a) W. A. Herrmann, R. W. Fischer, M. U. Rauch and W. Scherer, *J. Mol. Catal.*, 1994, **86**, 221; (b) W. A. Herrmann, D. W. Marz, W. Wagner, J. G. Kuchler, G. Weichselbaumer and R. W. Fischer, *Ger. Pat.* 3902357, 1989 to Hoechst AG; (c) G. L. Grocco, W. F. Shum, J. G. Zajacek and H. S. Kesling, Jr., *US Pat.* 5166372, 1992 to Arco.
- (a) J. Rudolph, K. L. Reddy, J. P. Chiang and K. B. Sharpless, *J. Am. Chem. Soc.*, 1997, **119**, 6189; (b) C. Copéret, H. Adolffson and K. B. Sharpless, *Chem. Commun.*, 1997, 1565.
- (a) W. A. Herrmann, R. M. Kratzer, H. Ding, W. R. Thiel and H. Glas, *J. Organomet. Chem.*, 1998, **555**, 293; see also M. Nakajima, Y. Sasaki, H. Iwamoto and S. Hashimoto, *Tetrahedron Lett.*, 1998, **39**, 87.
- (a) W. A. Herrmann, F. E. Kühn, R. W. Fischer, W. R. Thiel and C. C. Romão, *Inorg. Chem.*, 1992, **31**, 4431; (b) W. A. Herrmann, R. M. Kratzer and R. W. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2652.
- Hydrogen peroxide is manufactured as an aqueous solution of 35–70% concentration and can be considered safe at concentrations up to 70%. Higher concentrations (>85%) can decompose with detonation.
- (a) S. Warwel, M. R. Klaas and M. Sojka, *J. Chem. Soc., Chem. Commun.*, 1991, 1578; (b) S. Warwel, M. R. Klaas and M. Sojka, *US Pat.* 5344946, 1994 to Solvay Interox; (c) L. Kim, *US Pat.* 4418203, 1983 to Shell Oil.
- (a) D. Hadži, *J. Chem. Soc.*, 1962, 5128; (b) U. Böhner and G. Zundel, *J. Phys. Chem.*, 1985, **89**, 1408.
- A. M. Rozen, A. S. Skotnikov and E. G. Teterin, *Zh. Neorg. Khim.*, 1982, **27**, 739; *Chem. Abstr.*, 1982, **96**, 206282j.
- J. Sobczak and J. J. Ziolkowski, *J. Mol. Catal.*, 1981, **13**, 11.
- (a) R. A. W. Johnstone en Franciscsne-Czinege, *WO* 98/17640, 1998 to Solvay Interox Limited; (b) M. C. A. van Vliet, I. W. C. E. Arends and R. A. Sheldon, *Tetrahedron Lett.*, 1999, **40**, 5239.
- D. K. Srivastava, L. K. Krannich and C. L. Watkins, *Inorg. Chem.*, 1990, **29**, 3502.
- F. F. Blicke and E. L. Cataline, *J. Am. Chem. Soc.*, 1938, **60**, 419.
- W. R. Cullen and P. E. Yates, *Can. J. Chem.*, 1963, **41**, 1625.
- A. L. Rheingold, D. L. Staley and M. E. Fountain, *J. Organomet. Chem.*, 1989, **365**, 123.
- W. Steinkopf, H. Donat and P. Jaeger, *Chem. Ber.*, 1922, **55**, 2597.
- W. J. Jones, W. J. C. Byke, G. Davies, D. C. Griffiths and J. H. E. Webb, *J. Chem. Soc.*, 1932, 2284.
- E. R. N. Bornancini, S. M. Palacios, A. B. Peññory and R. A. Rossi, *J. Phys. Org. Chem.*, 1989, **2**, 255.
- E. W. Abel and G. W. Farrow, *J. Chem. Res. (S)*, 1979, 278.
- J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1939, 1622.
- H. H. Anderson, *J. Am. Chem. Soc.*, 1961, **83**, 547.

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