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Highly effective peroxidic epoxidation of olefins using hexathiocyanatorhenate(IV) as catalyst and bicarbonate as co-catalyst

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Abstract—In the presence of bicarbonate as co-catalyst hexathiocyanatorhenate(IV) functions as an extremely effective catalyst in the epoxidation of olefins using aqueous hydrogen peroxide as the terminal oxidant.

Homogeneous epoxidation of olefins using hydrogen peroxide as terminal oxidant[1–5] in conjunction with a trace amount of a metal complex as catalyst in the presence of a suitable additive is potentially viable for large-scale production. Much work has already been done in this area,[6] but still the % yield and turnover number are far from efficient. Methyltrioxorhenium (MTO)[7] in the presence of amine derivatives as additives, as introduced by Sharpless and co-workers,[8] may be regarded as the best olefin epoxidation method available to date for *fairly unreactive substrates* with H_2O_2 as terminal oxidant. However, MTO is difficult to prepare, which makes it highly expensive and in-house synthesis takes a long time. This motivated us to examine whether an easily and readily synthesizable Re complex as catalyst could be used instead of MTO. In this communication we describe the one-pot, single-step synthesis[9] of the rhenium compound, $(Ph_4P)_2[Re(NCS)_6]$ **1**, which when used in tandem with $NaHCO_3$ as a co-catalyst and H_2O_2 as the terminal oxidant results in excellent catalytic efficiency towards the epoxidation of olefins with respect to selectivity, % yield, time required, amount of catalyst loading and catalyst turnover (TON = ratio of moles of product obtained to moles of catalyst used). In addition, the low cost (compared to MTO) and the environmentally benign nature of the described method lead us to claim that this method along with another method using a Mn(III)–porphyrin system as catalyst[10] displays excellent efficiency in the catalytic epoxidation of olefinic compounds.[11]

The experimental conditions for the epoxidation involving a wide variety of olefins are as follows: substrate (between 400 and 2000 and the co-catalyst between 100 and 500 M equiv per molar equivalent of catalyst), were dissolved with stirring in acetonitrile (≈20–25 M equiv per molar equivalent of substrate) in a two-neck, flat-bottomed flask (one neck fitted with a reflux condenser). Reaction solutions were stirred at room temperature and after every 15 min, 0.1 mL of the solution was withdrawn, quenched at −10 °C and extracted with ether (several extractions were necessary in most cases). The ether extract was concentrated and analyzed by GC The retention times were compared with those of commercial standards and for quantitative estimation of the products, nitrobenzene was used as an internal standard. Control experiments indicated that the desired epoxidation failed to occur even after 24 h when both the catalyst **1** and $NaHCO_3$ were omitted. Interestingly, the epoxidation reaction occurred if catalyst **1** was omitted but $NaHCO_3$ was present. The results are shown in Table 1. It was observed that under the above conditions a stoichiometric (but not catalytic, when the % conversion was found to be negligible) amount of $NaHCO_3$

Keywords: Hexathiocyanatorhenate(IV); Catalyst; Co-catalyst; Efficient epoxidation; Sodium bicarbonate.

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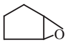
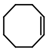
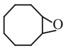
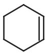
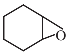
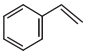
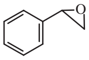
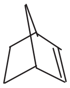
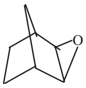
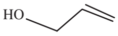
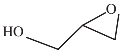
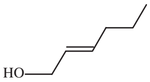
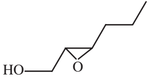
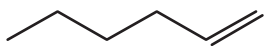
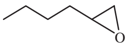
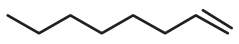
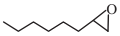
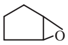
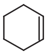
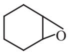
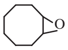
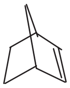
Table 1. Details of the catalytic epoxidation of olefinic compounds

$$\text{Alkene} \xrightarrow[\text{7-8 eq. } H_2O_2\text{, 25 mol\% } NaHCO_3\text{, Room temp.}]{\text{0.25/0.05 mol\% } (PPh_4)_2[Re(NCS)_6]\text{, acetonitrile}} \text{Epoxide}$$

Entry	Substrate	Product	Time (h)	Conversion (%)	Yield[a] (%)		Yield[b] (%)	TON (TOF)[c]
					Chromatographic	Isolated		
Molar ratio of substrate:catalyst = 400:1 (0.25 mol%)								
1			1.5	99	99	—	50	396 (264)
2			0.5	88	88	80	25	352 (704)
3			1	96	96	—	24	384 (384)
4			4	80	80	—	36	320 (80)
5			1	99	99	88	37	396 (396)
6			4	99	99	—	45	396 (99)
7			2.5	93	93	—	48	372 (149)
8			4.5	90	90	70	53	360 (80)
9			3	80	80	—	38	320 (107)
Molar ratio of substrate:catalyst = 2000:1 (0.05 mol%)								
1			3	99	99	—	75	1980 (660)
2			4	57	51	—	41	1140 (285)
3			2	77	77	—	52	1540 (770)
4			3	95	95	—	64	1900 (633)

The methods for the determination of isolated yield and for calculation of the GC yield are enclosed as Supplementary material.

[a] % Yield of the control experiment without using the catalyst and $NaHCO_3$ is zero.

[b] % Yield of the control experiments excluding the catalyst only but in the presence of $NaHCO_3$ (25 mol%).

[c] Figures in the parentheses indicate TOF (turnover frequency; TON h^{-1}).

was necessary for the reactions to provide the products. Also, in the absence of the co-catalyst, **1** functions less efficiently, with % yield and TON being much lower and the conversion time much higher.

Richardson[12] has shown that hydrogen peroxide and bicarbonate react to give peroxymonocarbonate,[13] (HCO_4^-) and this was considered to be the oxidizing species present. Interestingly, the catalyst functions poorly on its own and the co-catalyst much more poorly, but both together (with the former even in microamounts) make the reaction extremely facile. It is quite interesting to note that a catalyst, which contains Re^{IV} is more effective than MTO, which contains Re^{VII}. This can be easily rationalized on the basis that H_2O_2 as oxidant easily oxidizes Re^{IV} to Re^{VII} (to the putative compound $[Re^{VII}O_3NCS]$ **2**). Evidently **2**[14] is a more efficient catalyst precursor than MTO for epoxidation when using H_2O_2 as a terminal oxidant. An oxo bridged di-iron(II) compound has recently been found to be an epoxidation catalyst[6k] in the presence of H_2O_2 and it has been suggested that here also the $Fe^{V}{=}O$ (oxoferryl) moiety is the active species for catalysis. Furthermore, in the case of MTO and subsequent to their first report, Hermann et al.[15] were able to isolate and structurally characterize $[ReO(O_2)_2(CH_3)(H_2O)]$ **3** by conducting the synthetic reaction ($MTO+H_2O_2$) at 0 °C and crystallization at −30 °C and claimed that **3** was the active catalyst. Since the rhenium oxo diperoxo system is very unstable at rt, one cannot be confident in concluding that this is the active form of the catalyst. We also suggested[16] an active catalyst system for the oxidation of methyl benzenes using $[MoO(O_2)(QO)]$ (QO = 8-quinolinol) as catalyst and H_2O_2 as oxidant. However, it is very difficult to prove the composition of the catalyst at the moment of reaction with the substrate and all suggestions are tentative. In the present case we were not able to isolate any peroxorhenium compound by conducting a preparative reaction at −20 °C. Hence at this moment we cannot suggest a mechanism for this epoxidation reaction involving $[Re(NCS)_6]^{2-}$, HCO_3^-, HCO_4^-, H_2O_2 and olefins.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.10.163.

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9. $KReO_4$ (0.21 g; 0.74 mmol) was dissolved in 25 mL of 4 M HCl and then 0.50 g (6.60 mmol) of solid NH_4SCN was added to the solution with stirring and the temperature was maintained at 60 °C. The resulting solution was stirred for 3 h when a deep red solution was obtained. PPh_4Cl (0.78 g; 2.11 mmol), dissolved in a minimum volume of water was added to the red solution with stirring leading to an orange-red solid precipitate. The solid was filtered off, washed with water and ethanol and dried over fused $CaCl_2$ in vacuo. The crude compound (yield = 0.70 g; 46%) was crystallized from acetone to give fine orange red crystals. Calcd for, $C_{54}H_{41}N_6O_{0.50}P_2S_6Re$, C, 53.5, H, 3.3; N, 6.9, S, 15.8. Found C, 53.1, H, 3.4, N, 7.2, S, 15.4%. IR (KBr disc): ν (CN), 2080 (s), 2060 (m); ν (CS), 760 (sh), δ(NCS), 480 (w) and ν (M–N) at 445 cm^{-1}. UV–vis (acetonitrile solution): 345 (sh) and 452 (ε = 1230 $M^{-1}cm^{-1}$) nm. Besides the physico-chemical characterization the compound was also structurally characterized and found to consist of discrete monomeric anions, $[Re(NCS)_6]^{2-}$ and PPh_4^+ cations, the anion (the catalyst precursor) having an octahedral geometry.
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11. Besides the Mn^{III}–porphyrin work, which shows a TOF (turnover frequency = h^{-1}) of 20,000 h^{-1} with cyclooctene as the only substrate, all other work, to the best of our knowledge, shows much lower TOFs than we obtained with **1**. The next best TOFs are: (i) Thiel et al. (Thiel, W. R.; Eppinger, J. *Chem. Eur. J.* **1997**, *3*, 696–705) who observed that cyclooctene could be epoxidized with TOF = 6470 h^{-1} with the Mo-complex used as catalyst only when *t*-butyl hydroperoxide (but not H_2O_2, which failed to effect oxidation) was used as oxidant. (ii) W: TOF = 100 h^{-1}, see Ref. 3, p 355; (iii) Re(MTO): TOF = 38 h^{-1} (for styrene); this catalyst exhibited the highest TOF (190 h^{-1}) for the epoxidation of 1-phenyl cyclohexene.
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13. Lane, B. S.; Vogt, M.; de Rose, V. J.; Burgess, K. *J. Am.Chem. Soc.* **2002**, *124*, 11946–11954.
14. Complex **2** was obtained by treating **1** (0.1 g, 0.082 mmol) with excess H_2O_2 (10 mL, 98 mmol) in acetonitrile (20 mL) and stirring for 30 min upon which an orange powder precipitated (yield = 0.09 g, 79%). The powder was dissolved in acetonitrile and concentrated, when 75% of the product precipitated as powdery material. Complex **2** was characterized by elemental analysis [C (found, 3.56; calcd, 4.11), N (found, 4.01; calcd, 4.79), S (found, 9.86; calcd, 10.96) and Re (found, 65.17; calcd, 63.70)]. The elements C and N were analyzed using a Perkin Elmer 240C elemental analyzer, for S and Re, about 0.1 g of the respective compounds were separated by fusion with alkali peroxide and the former was estimated as $BaSO_4$ (Vogel, A. I. *A Textbook of Quantitative Inorganic Analysis*, 3rd ed.; ELBS and Longmans, Green and Co.: London, 1964) and the latter as Nitron perrhenate (Geilmann, W.; Voight, A. *Z. Anorg. Allgem. Chem.* **1930**, *193*, 311). IR (KBr disc) [ν(CN) at 2080 cm^{-1} (w), ν(Re=O) at 896 (s), 912 (m) and 932 cm^{-1} (sh)]; UV–vis in acetonitrile [472 (ε = 880 $M^{-1}cm^{-1}$) and 321 (ε = 2120 $M^{-1}cm^{-1}$) nm]. The band at 472 nm may be assigned as the $SCN^-(p\pi^*)\rightarrow Re(5d\pi)$ LMCT transition.
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