Cobalt tetraarylporphyrin-catalysed epoxidation of alkenes by dioxygen and 2-methylpropanal under fluorous biphasic conditions

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The aerobic epoxidation of alkenes with 2-methylpropanal can be carried out under fluorous biphasic conditions, in the presence of the perfluorocarbon soluble cobalt complex of tetraarylporphyrin 3 as catalyst.

Catalysis under homogeneous two-phase conditions has been recognized as a viable alternative for many important chemical processes.[1] Several approaches to liquid–liquid biphasic catalytic reactions have been proposed, and among them the so-called 'fluorous biphase system' (FBS)[2] stands out for its peculiar characteristics. In this approach the low miscibilities of fluorocarbons with most organic solvents allows segregation of a catalyst soluble in the fluorocarbon phase from substrates and products dissolved in the organic phase. The FBS method shows appealing general features, such as the employment of nontoxic, reusable perfluorocarbons and the easy separation of catalyst from reactants and products.[3] Moreover, the inertness of perfluorocarbons and the high solubility of oxygen in these fluids would be particularly helpful in oxidation reactions.[4] In spite of this, the only examples of true FBS oxidation reported so far concern some simple reactions of phosphines and sulfides,[5] and the photooxidation of alkenes to hydroperoxides in the presence of a perfluorocarbon-soluble sensitizer.[6] The availability of efficient oxidation catalysts soluble in fluorocarbons is essential for applying the FBS concept to other synthetically useful reactions, such as the epoxidation of alkenes and hydroxylation of alkanes. These last reactions can be carried out under mild condition using a combination of molecular oxygen and reducing agent in the presence of transition metal complexes.[7] Here we report the synthesis of the perfluorocarbon-soluble tetraarylporphyrin **3**, bearing eight C_8F_{17} chains, and the use of its cobalt complex Co-**3** as epoxidation catalyst under fluorous biphasic conditions.‡

All attempts to apply well-established synthetic procedures[8] to the preparation of **3** failed, as was found in the case of *meso*-perfluoroalkylporphyrins.[9] The synthesis of **3**, outlined in Scheme 1, was thus carried out by condensation of the pyrrole derivative **2**, according to a procedure originally devised by Kuroda and Ogoshi,[10] The presence of Zn(OAc)₂ as templating agent in the cyclisation step turned out to be essential for obtaining the porphyrin in reasonable yield. After removal of zinc, the free-base porphyrin **3** was metalated to form the cobalt complex Co-**3** according to a classical procedure.[11],§ Both **3** and Co-**3** were insoluble in common organic solvents, whereas they were easily dissolved in perfluorocarbons.¶

It is known that Co^{II}-tetraarylporphyrins are capable of binding dioxygen reversibly yielding oxygenated Co^{III}-complexes.[12] The UV-VIS spectra of Co-**3** in $CF_2ClCFCl_2$ and perfluorohexane both showed a broad Soret band with two maxima at 405 and 427 nm. The splitting of the Soret band as well as its breadth were consistent with the coexistence of Co^{II} and Co^{III} species in the aerated solutions.[13]

Co-**3** proved to be an efficient catalyst for the fluorous biphasic epoxidation of alkenes by molecular oxygen and 2-methylpropanal as reducing agent. Reaction conditions and results are detailed in Table 1.

Reactions were carried out at room temperature in flasks carefully shielded from direct sunlight. A solution of Co-**3** in
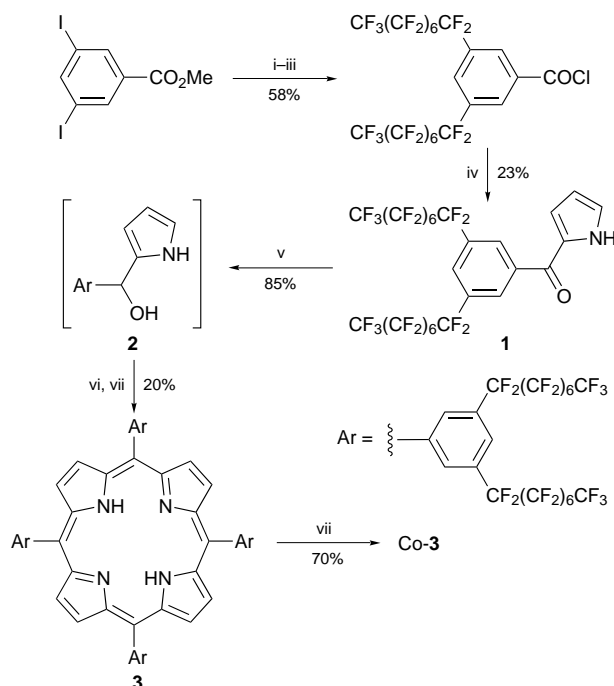
Scheme 1 *Reagents and conditions*: i, $C_8F_{17}I$, Cu, DMF, 125 °C; ii, KOH, H₂O–MeOH, reflux; iii, SOCl₂, reflux; iv, pyrrole, EtMgBr, Et₂O, 0 °C; v, LAH, THF; vi, Zn(OAc)₂.2H₂O, propanoic acid, reflux, then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; vii, CF₃CO₂H, reflux, then aqueous NaHCO₃; viii, Co(OAc)₂.4H₂O, DMF, reflux

Table 1 Epoxidation of alkenes under fluorous biphasic conditions catalysed by Co-**3**[a]

Entry	Substrate	t/h	Conversion (%)[b]	Selectivity (%)[b,c]
1	*cis*-Cyclooctene[d]	6	—	—
2	*cis*-Cyclooctene	3	100	> 95
3	*cis*-Cyclooctene[e]	3	100	> 95
4	Norbornene	5	95	> 95
5	1-Methylcyclohexene	3	100	> 95
6	2-Methylundec-1-ene	5	80	90
7	Dodec-1-ene	14	48	92
8	Dodec-1-ene[f]	14	60	87

[a] Conditions: [substrate] = 0.1 mol dm⁻³ in MeCN; [2-methylpropanal] = 0.2 mol dm⁻³ in MeCN; [Co-**3**] = 0.0001 mol dm⁻³ in perfluorohexane; volume of MeCN = 1 ml; volume of perfluorohexane = 1 ml; stirring rate = 1300 rpm; T = 25 °C. Reactions were carried out in the dark. [b] Determined by GC using the internal standard method. [c] Selectivity = (moles of epoxide)/(moles of substrate converted). Epoxides were identified by comparison with authentic samples or by GC–MS. [d] Reaction carried out in the absence of Co-**3**. [e] Using the perfluorohexane layer recovered from entry 2. [f] Using 3-methylbutanal instead of 2-methylpropanal.

perfluorohexane was added to a solution of alkene in MeCN containing a twofold excess of aldehyde with respect to the substrate. The resulting biphasic mixture was vigorously stirred under atmospheric pressure of dioxygen. Co-**3** was completely partitioned in the fluorous phase, as shown by the UV–VIS spectra of the two layers. At the end of the reaction, the two phases were easily separated and the MeCN layer was analysed by gas chromatography (GC). It is worthwhile noting that under these conditions, but in the absence of Co-**3**, alkenes did not react (Table 1, entry 1). In the presence of the perfluorocarbon soluble catalyst, high alkene conversions were generally obtained, epoxides being the major products.‖

As reported for reactions carried out under homogeneous conditions, the present procedure is less suited for unsubstituted terminal alkenes such as dodec-1-ene (entry 7) than for other substrates. Nevertheless, epoxide yields were still satisfactory, and could even be increased by raising the aldehyde–alkene ratio[7] or by choosing different aldehydes (entry 8).

Cobalt complexes of *meso*-tetraarylporphyrins have been recently used as homogeneous catalysts for the aerobic oxidation of organic substrates in the presence of 2-methyl-propanal.[14] The positive effect of running the reaction under fluorous biphasic conditions can be appreciated by comparing the present results with those reported in the cited reference. We were able to use a much higher substrate–catalyst ratio (1000 : 1) than that previously reported (20 : 1). Moreover, after complete conversion of cyclooctene the perfluorocarbon layer, recovered by simple phase separation, could be used as such for a second run, without decreasing either the substrate conversion or the selectivity for cyclooctene oxide (entry 3).

Our current efforts are aimed at the synthesis of metal complexes of non-porphyrinic perfluorocarbon-soluble ligands, to be used as catalysts for hydrocarbon oxygenations in the presence of simple oxygen atom donors.

Footnotes

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‡ Introduction of one perfluoroalkyl tail on each *meso*-aryl group is not sufficient to impart solubility in perfluorocarbons (G. Pozzi and M. Miglioli, unpublished results).

§ *Selected data* for **1**: ^{1}H NMR (CDCl$_3$): δ 9.64 (br s, 1 H), 8.30 (s, 2 H), 7.95 (s, 1 H), 7.22 (m, 1 H), 6.78 (m, 1 H), 6.39 (m, 1 H); ^{19}F NMR (CDCl$_3$; CFCl$_3$): δ −81.3 (t, *J* 9 Hz, 3 F), −111.5 (t, *J* 13 Hz, 2 F), −121.6 (br s, 2 F), −122.3 (m, 6 F), −123.3 (br s, 2 F), −126.7 (br s, 2 F); ^{13}C NMR (CDCl$_3$): δ 105–118 (m, C$_8$F$_{17}$), 112.0, 119.9, 126.6, 128.2, 130.2, 130.5, 130.8, 139.7, 181.2. For **3**: ^{1}H NMR (CF$_2$ClCFCl$_2$, C$_6$D$_6$): δ 8.77 (s, 8 H), 8.72 (s, 8 H), 8.36 (s, 4 H), −2.85 (s, 2 H); λ$_{max}$ (CF$_2$ClCFCl$_2$) 413 nm (ε 7.2 × 10^4 dm^3 mol^{-1} cm^{-1}). (Calc. for C$_{108}$H$_{22}$F$_{136}$N$_4$: C, 32.76; H, 0.56; N, 1.41; F, 65.27. Found: C, 32.72; H, 0.60; N, 1.34; F, 64.24%). For Co-**3**: λ$_{max}$ (CF$_2$ClCFCl$_2$) 405 nm (ε 1.6 × 10^4 dm^3 mol^{-1} cm^{-1}), 427 (ε 1.6 × 10^4). The acid-sensitive alcohol **2** was not purified and it was used directly for the cyclisation step.

¶ The following perfluorocarbons, available from 3 M, were tested as solvents: FC-72 (mainly perfluorohexane, bp 56 °C), FC-75 (mainly perfluorobutyltetrahydrofuran, bp 102 °C), FC-43 (mainly perfluorotributylamine, bp 174 °C).

‖ Although the exact role of the metal complex in the epoxidation of alkenes by dioxygen with co-oxidation of aldehydes is still a matter of debate (see W. Nam, H. J. Kim, S. H. Kim, R. Y. N. Ho and J. S. Valentine, *Inorg. Chem.*, 1996, **35**, 1045), consistent literature data demonstrate that its presence is crucial for ensuring conversion of linear alkenes and for obtaining high epoxide yields without using large amounts of aldehyde.

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