Ru(II)-BIPYRIDINE COMPLEX WITH POLYETHER CHAIN AS A BIFUNCTIONAL CATALYST FOR EPOXIDATION OF STILBENE IN A BIPHASIC SYSTEM

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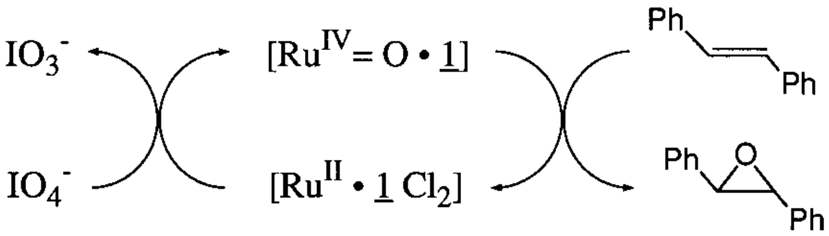
Abstract- Polyether bearing bipyridine moieties at the ends of the chain was found to catalyze not only epoxidation of stilbene but also transfer of periodate salt as an oxidant between two different liquid phases(H_2O - CH_2Cl_2). Metal-ion dependent yield of the epoxide can be modulated by the polyether.

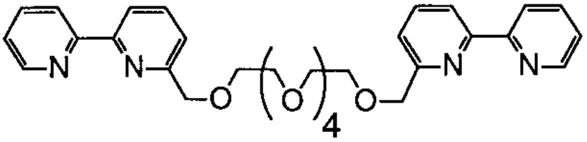
Introduction of *several* molecular functions into *one* molecule seems to be one of the best strategies for construction of sophisticated artificial catalysts to mimic biological ones such as enzymes and to apply to organic synthesis. If the artificial catalysts provide their functions simultaneously during reactions, enhancements of selectivity, specificity, and rate may be accomplished readily. Balavoine et al.[1] have reported a facile and stereospecific oxidation of olefins to afford the corresponding epoxides, very important intermediates for organic synthesis,[2,3] in good yields using a Ru(II)-bipyridine complex as a catalyst. A biphasic system, CH_2Cl_2 - H_2O, was employed for the oxidation, because sodium periodate and hydrophobic olefins were used as the oxidant and the substrates, respectively. These facts led to us an idea to construct a molecule having two functions, catalysis of epoxidation and transfer of the oxidant between the two phases.

We have recently found that a polyether bearing two bipyridines at the ends of the chain is a good ligand for both heavy and alkali metal ions, and the transport selectivity of K^+ across a liquid membrane by the use of the ligand is enhanced dramatically by the addition of Cu(I) into the system due to formation of pseudocrown structure.[4,5] Consequently polyether(1) would be a suitable candidate for the bifunctional catalyst of the epoxidation. Here we report the catalytic ability of 1 for the oxidation and modulation of the reactivity, which depends on alkali metal ion of periodate salt.

Similar conditions[1] to those reported by Balavoine were employed for the epoxidation reaction (Table 1, at 0 - 5°C, CH_2Cl_2(7 ml) *containing trans-stilbene*(1.4 mmol) and a ligand; H_2O(4 ml) containing $RuCl_3 \cdot 3H_2O$(0.034 mmol) and periodate salt(2.8 mmol)). Amount of 1 (0.08 mmol) used as a ligand

Scheme 1





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was half as much as that of 2,2'-bipyridine(0.16 mmol) to make ratio of bipyridine to RuCl$_3$•3H$_2$O the same in both cases. Identification of the products and determination of the yields were carried out by hplc. The epoxidation may proceed via a route shown in Scheme 1. Plausible active species has been proposed to be an oxo compound of a ruthenium-bipyridine complex.[1,6] As reported before, a complex of 2,2'-bipyridine and RuCl$_3$ was found to be a good epoxidation catalyst, when NaIO$_4$ was used as an oxidant (run 1, 70%). KIO$_4$, however, showed less reactivity and a lower yield of the epoxide (run 2, 25%) than NaIO$_4$. In contrast to 2,2'-bipyridine, 1 (bipyridine with polyether chain) revealed reverse sequence of reactivity with respect to alkali metal cation of periodate salt. The potassium salt gave a higher yield (run 4, 52%) of the corresponding trans-epoxide than sodium salt (run 3, 33%). Interestingly, the yield of the epoxide using KIO$_4$ in the presence of 2,2'-bipyridine was increased by addition of 18-crown-6 as a phase transfer catalyst, although the yield is lower (run 6, 58%) than in NaIO$_4$ (run 5, 73%). The high reactivity of the K$^+$ salt for the epoxidation using 1 (run 4) can be attributed to selective recognition of K$^+$, which is in good accordance with high selectivity of transport experiment through a liquid membrane using a complex between Cu(I) and a bipyridine ionophore(2) with a similar structure to 1.[4] We have also found that the pseudocrown of 2 containing

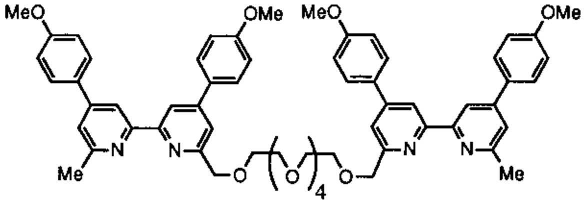

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Table 1 Oxidation of trans-Stilbene by Periodate Salt in the Presence of Ruthenium Catalyst[a]

Run	Ligand	Reaction Time (h)	Oxidant	Products (%) trans-Stilbene Oxide	Benzaldehyde	recovered trans-Stilbene
1	2,2'-bipyridine	50	$NaIO_4$	70	29	0
2	2,2'-bipyridine	50	KIO_4	25	30	35
3	1	50	$NaIO_4$	33	45	10
4	1	50	KIO_4	52	31	14
5	2,2'-bipyridine +18-crown-6[b]	27	$NaIO_4$	73	26	0
6	2,2'-bipyridine +18-crown-6[b]	27	KIO_4	58	38	0
7	None	50	$NaIO_4$	4	88	3
8	None	50	KIO_4	4	17	78

a) organic phase : 7 ml of CH_2Cl_2 containing 2,2'-bipyridine (0.16 mmol) or 1 (0.08 mmol),
and trans-stilbene (1.4 mmol).
aqueous phase : 4 ml of H_2O containing $RuCl_3 \cdot 3H_2O$ (0.034 mmol), and periodate salt (2.8 mmol).
stirring with a magnet (400 rpm) at 0 - 5°C.

b) 0.08 mmol was used.

c) Reproducibility of yields is within 5%.

Cu(I) shows higher preference of K^+ over Na^+ than 18-crown-6 in the transport experiment.[4,7] Consequently the yield of the epoxide in run 4 suggests that a pseudocrown is generated from 1 and $RuCl_3$, and that the cavity works as a selective binding site for phase transfer catalysis. Moreover the decrease of the epoxide and the increase of benzaldehyde by using $NaIO_4$ and 1 (run 3) instead of 2,2'-bipyridine (run 1) imply that the polyether chain as a substituent of 1 inhibits complexation between ruthenium ion and the bipyridine moieties, because the yield of the aldehyde is considered to depend on the amount of the free $RuCl_3$ (vide infra). The yields of the products in run 4 (52% for the epoxide, and 31% for the aldehyde), however, indicate that the Ru(II)-complex is not unstable, suggesting complementary stabilization of the Ru(II)-complex because of specific interaction between K^+ and the polyether moiety to compensate the unfavorable substituent effect. Therefore, the stabilization supports again that the reaction of 1 with Ru(II) should give rise to intramolecular cyclization to afford the corresponding pseudocrown, as in the case of 2 and Cu(I). The most probable stoichiometry, which also suggests formation of the pseudocrown, is 1 : 1 for the complexation between 1 and Ru(II), because (i) bpy_2RuCl_2 has the catalytic activity for the epoxidation but $bpy_3Ru(II)$ not, and (ii) formation of $bpy_3Ru(II)$ type complex with octahedral geometry is prohibited because of steric hindrance of substituent at 6 position of bipyridine ring.[8] Formation of benzaldehyde as undesired product is caused mainly by $RuCl_3$ remained uncomplexed with the ligand, because $RuCl_3$ was reconfirmed to be an excellent catalyst for oxidative cleavage of olefins (run 7).[1] Since trans-stilbene oxide was inert under conditions employed here, benzaldehyde was generated via a different intermediate and the oxidative cleavage of the olefin competed with the epoxidation. From these facts it can be said that product distribution of the oxidation reaction of trans-stilbene stems from the intrinsic effectiveness and specificity of Ru-ligand-MIO_4 (M : alkali metal) systems. In the course of the reaction, the polyether moiety of 1 captures K^+ more advantageously and transfers into the organic layer more efficiently than Na^+. Therefore the anionic oxidant, IO_4^-, as an intimate counter anion in the organic phase should be also transferred, so that in KIO_4 the active species for epoxidation can be generated more promptly than in $NaIO_4$ and epoxidation takes place more smoothly.

In conclusion we have found that 1 simultaneously catalyzes two different phenomena, epoxidation of olefin and transfer of an oxidant in a heterogeneous liquid phase system. This promises a diverse possibility for construction of multifunctional catalysts, which consist of several different ligands for the appropriate metals.

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