Heteropoly Blue as a Reaction-Controlled Phase-Transfer Catalyst for the Epoxidation of Olefins

Li Mingqiang*^,[1,2] **and Jian Xigao**[1]

[1]Department of Polymer Science and Materials, Dalian University of Technology, Dalian 116012, P. R. China

[2]303group, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

Received March 3, 2005; E-mail: limingqiang@dicp.ac.cn

A new reaction-controlled phase-transfer catalyst system has been designed and synthesized. In this system, heteropoly blue, $[C_7H_7N(CH_3)_3]_3PMo_4O_{16}$, is used for the catalytic epoxidation of olefins with H_2O_2 as the oxidant. In this system, the catalyst not only can be recovered, like heterogeneous catalyst, but also acts as a homogeneous catalyst. The main products are epoxide of olefins and H_2O; no co-product forms. The system exhibits high conversion and selectivity as well as excellent catalyst stability. ^{31}P NMR spectra, UV–vis spectra, and infrared spectra are used to analyze the reason for the phase transfer of the catalyst, indicating that the change of structure leads to the formation of reaction-controlled phase-transfer catalyst.

Epoxidation—oxygenation of olefins to form cyclic epoxide groups—is an important industrial process.[1–3] Although a number of epoxidation processes that use various catalysts and oxidants have been developed, a chlorine-using noncatalytic process (the chlorohydrin process) and catalytic processes based on expensive oxidants are still used extensively.[4] In contrast to such classical "nongreen" processes, H_2O_2-based catalytic epoxidation is of great advantage to the environment and industry because it generates H_2O as a sole by-product, and it is rather inexpensive compared with organic peroxides and peracids.[5] Recently, a reaction-controlled phase-transfer catalyst system has been developed.[6,7] In this catalyst system, the catalyst, which is insoluble in the reaction medium, forms soluble active species by the action of one of the reactants. This kind of catalyst not only can be recovered, like a heterogeneous catalyst, but also acts as a homogeneous catalyst. Since the reaction-controlled phase-transfer catalyst system possesses the above advantages, it is significant to design and synthesize.

There has been a great deal of interest in the redox behavior of heteropolyoxometalates and their ability to form "heteropoly blues" upon reduction. In the presence of an acid, electrons are usually transferred in even numbers due to stabilization of these species by protonation. Numerous heteropoly complexes can be reduced by the addition of various numbers of electrons. The reduction products, which typically retain the general structures of their oxidized parents, and are frequently deep blue in color, comprise a potentially important large group of complexes, generally known as heteropoly blues. The added ("blue") electrons are "delocalized", according to various time scales, over certain atoms or regions of the heteropoly blues, corresponding to class **II** systems in the Robin and Day classification of mixed-valence compounds.

In the present work, we designed and synthesized a reaction-controlled phase-transfer catalyst comprised of heteropoly blue, $[C_7H_7N(CH_3)_3]_3PMo_4O_{16}$, for the catalytic epoxidation olefins with 30% H_2O_2 as the oxidant. In same time, we investigated the reason of solid–liquid–solid phase cycle of the catalyst. The catalyst has high efficiency of H_2O_2 utilization and selectivity. Moreover, the reason for the solid–liquid–solid phase cycle of the catalyst heteropoly blue, $[C_7H_7N(CH_3)_3]_3PMo_4O_{16}$, is different from that of others catalyst.

Experimental

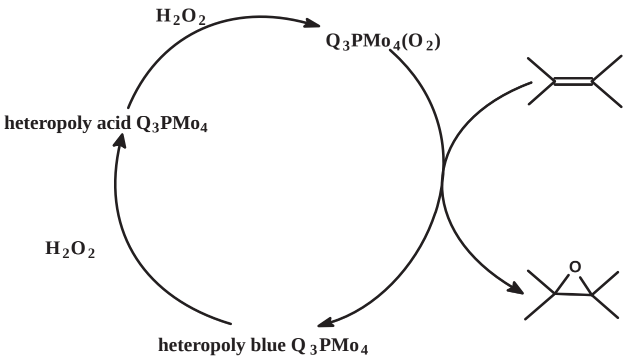
Unless specially mentioned, the chemicals used in this work were at least of C. P. grade and were used as purchased.

Preparation of Heteropoly Acid $[C_7H_7N(CH_3)_3]_3PMo_4O_{16}$. Preparation method according to the literature:[8] 10 mmol $Na_2MoO_4 \cdot 2H_2O$ was dissolved in 30 mL of water. To this solution was added dropwise 2.5 mmol of 85% H_3PO_4, and added with stirring the required amount of ice acetic acid to adjust the pH to 4. To the resultant solution, 5 mmol of benzyltrimethylammonium chloride in water (15 mL) was added dropwise with stirring over about 30 min at 60 °C. The precipitate, being the product, was filtered, washed with water, and air-dried at room temperature. The yield was 83%. Anal. Calcd for $[C_7H_7N(CH_3)_3]_3PMo_4O_{16}$: C, 32.09; H, 4.28; N, 3.70; Mo, 34.28; P, 2.79%. Found: C, 32.13; H, 4.31; N, 3.75; Mo, 34.22; P, 2.76%. IR (neat, KBr plates): 3433, 3034, 1629, 1456, 1217, 1063, 1038, 938, 889, 812, 780, 703, 517 cm^{-1}.

Preparation of $[C_7H_7N(CH_3)_3]_3PO_4\{MoO(O_2)_2\}_4$. The $[PO_4\{MoO(O_2)_2\}_4]^{3-}$ was reported in the literature,[9] and converted to the corresponding tetrabutylammonium salts by a cation-exchange reaction with benzyltrimethylammonium. The yield was 71%. Anal. Calcd (found) for $[C_7H_7N(CH_3)_3]_3PMo_4O_{24}$: C, 28.75; H, 3.81; N, 3.28; Mo, 30.77; P, 2.53%. Found: C, 28.84; H, 3.87; N, 3.36; Mo, 30.71; P, 2.48%. IR (neat, KBr plates): 3436, 3037, 1619, 1474, 1217, 1072, 1034, 964, 869, 780, 727, 702, 658, 588, 541 cm^{-1}.

General Procedure for the Benzalcohol Oxidation. After 20 mmol of olefins was dissolved in 40 mL of CH_3CN solvent; 15 mmol of 30% H_2O_2 and 0.1 mmol of catalyst were added. The reaction was maintained at 70 °C with vigorous stirring until the

Published on the web August 4, 2005; DOI 10.1246/bcsj.78.1575



Scheme 1. Cycle process of the catalytic olefins oxidation.

catalyst precipitated. The products were analyzed by GC-MS and gas chromatography (GC) with the internal standard method. The remaining H_2O_2 after the reaction was estimated by the potential-difference titration of Ce^{3+}/Ce^{4+} (0.1 M aqueous $Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$).

The catalyst was recovered by centrifugation and used in the next reaction without adding any fresh catalyst.

Results and Discussion

Phase Transfer of Catalyst in the Reaction. Scheme 1 shows the cycle progress of the catalytic olefins epoxidation. Under the action of H_2O_2, insoluble heteropoly blue, $[C_7H_7N(CH_3)_3]_3PMo_4O_{16}$, firstly forms a yellow heteropoly acid, $[C_7H_7N(CH_3)_3]_3PMo_4O_{16}$, which subsequently reacts with H_2O_2 to form $[C_7H_7N(CH_3)_3]_3PO_4\{MoO(O_2)_2\}_4$, named as $Q_3PMo_4(O_2)$, and transfers from the solid phase to the liquid phase. The yellow $Q_3PMo_4(O_2)$ is dissolved in the medium of reaction and gives olefins homogeneous catalytic epoxidation with the help of hydrogen peroxide. When the hydrogen peroxide is exhausted, the yellow $Q_3PMo_4(O_2)$ is reduced to heteropoly blue, Q_3PMo_4, which is then separated out of the liquor as a diposit. This makes it easier for the heteropoly blue to be recovered. This is a solid–liquid–solid phase cycle of the catalyst, which is controlled by the reaction. In this reaction-controlled phase-transfer catalyst system, the reaction can also start from $Q_3PMo_4(O_2)$ or heteropoly acid, Q_3PMo_4, reacting with H_2O_2. In this catalyst system, we do not observe the precipitate of Q_3PMo_4 until the H_2O_2 is used up. This is because the reaction between Q_3PMo_4 and H_2O_2 is faster than the reaction between $Q_3PMo_4(O_2)$ and olefins. In this reaction-controlled phase-transfer catalyst system, the reaction rate is dominated by the reaction between $Q_3PMo_4(O_2)$ and olefins.

UV–Vis Spectra. Figure 1 shows the UV–vis spectra of the catalysts. There is a wide absorption band near 700–800 nm, appearing in the UV–vis spectra of heteropoly blue, Q_3PMo_4 (C). This is the electronic transfer of Mo–Mo in Q_3PMo_4, which is an important sign of the heteropoly anion being reduced to heteropoly blue. Another new absorption band near 450 nm is the transfer absorption band of O–Mo in Q_3PMo_4, which shifts after the heteropoly anion is reduced.

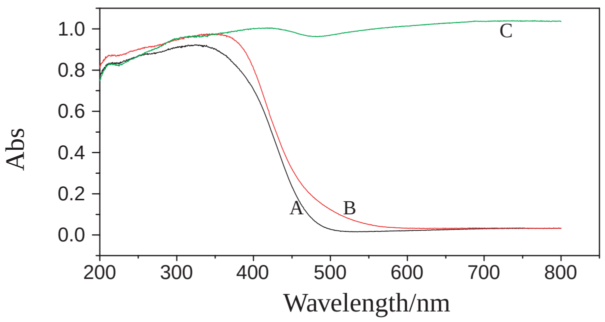


Fig. 1. UV–vis spectra of heteropoly acid Q_3PMo_4 (A), $Q_3PMo_4(O_2)$ (B), and heteropoly blue Q_3PMo_4 (C).

^{31}P NMR Studies. Because ^{31}P NMR has high sensitivity and a wide chemical shift range, it is very sensitive to the valence of the P atom and the change of type, quantity, and structural type of atoms or groups associated with P atom directly.[10] We used it to study the structure of polyoxometalate Q_3PMo_4 and polyoxometalate $Q_3PMo_4(O_2)$. Figure 2 shows the ^{31}P NMR spectra of the catalysts in *N*,*N*-dimethylformamide. The spectrum of heteropoly acid, Q_3PMo_4, shows a peak with a chemical shift of -2.459 ppm. However, for $Q_3PMo_4(O_2)$, the spectrum shows a peak with a chemical shift of 8.067 ppm. This change of the chemical shift is because the number of the oxygen atoms in $Q_3PMo_4(O_2)$ is more than in heteropoly acid, Q_3PMo_4, which makes the electron density surrounding the phosphorus atom decrease and makes the chemical shift change. For the $Q_3PMo_4(O_2)$, the spectrum shows a peak with a chemical shift of 1.698 ppm. The change of the chemical shift based on heteropoly acid Q_3PMo_4 results the aberration of the structure of the MoO_6 octahedron.

IR Spectra. The reason for the solid–liquid–solid phase cycle of the catalyst can be explained according to the change in the infrared spectra of catalyst, as shown in Fig. 3.

Figure 3 shows the infrared spectra of heteropoly acid Q_3PMo_4 (A), $Q_3PMo_4(O_2)$ (B), and heteropoly blue Q_3PMo_4 (C).

There appears in the infrared spectra of heteropoly acid Q_3PMo_4 the characteristic vibration band of P=O (1063 cm^{-1}), the characteristic vibration band of Mo=O (938 cm^{-1}), the characteristic vibration band of Mo–O_b–Mo (889 cm^{-1}), and the characteristic vibration band of Mo–O_c–Mo (812 cm^{-1}).[11–13] There appears in the IR of the recycled heteropoly blue the characteristic vibration band of P=O (1057 cm^{-1}), the characteristic vibration band of Mo=O (937 cm^{-1}), the characteristic vibration band of Mo–O_b–Mo (884.8 cm^{-1}), and the characteristic vibration band of Mo–O_c–Mo (803 cm^{-1}). The great similarity of the two reveals that the structure of heteropoly acid remains almost unchanged in heteropoly blue. However, the vibration effect of Mo–O_c–Mo weakened in heteropoly blue, and its characteristic vibration band is not as distinct as that in heteropoly acid. This is because the number of negative electric charges increases after reduction, which causes an aberration of the MoO_6 octahedron. It is this aberration of the structure of the MoO_6 octahedron that makes the heteropoly blue hard to dissolve in organic solvents.

The infrared spectra of $Q_3PMo_4(O_2)$ (B) show P–O stretching bands (1073.35 cm^{-1}), Mo=O band (947.8 cm^{-1}),[14] an O–O absorption peak (868.8 cm^{-1}), and Mo–O–O vibration bands (657.1, 586.9 cm^{-1}).[15] The form of the Mo–O–O structure makes $Q_3PMo_4(O_2)$ more easily to dissolve in organic solvents than heteropoly acid Q_3PMo_4.

X-ray Diffraction of Catalyst. X-ray diffraction was used

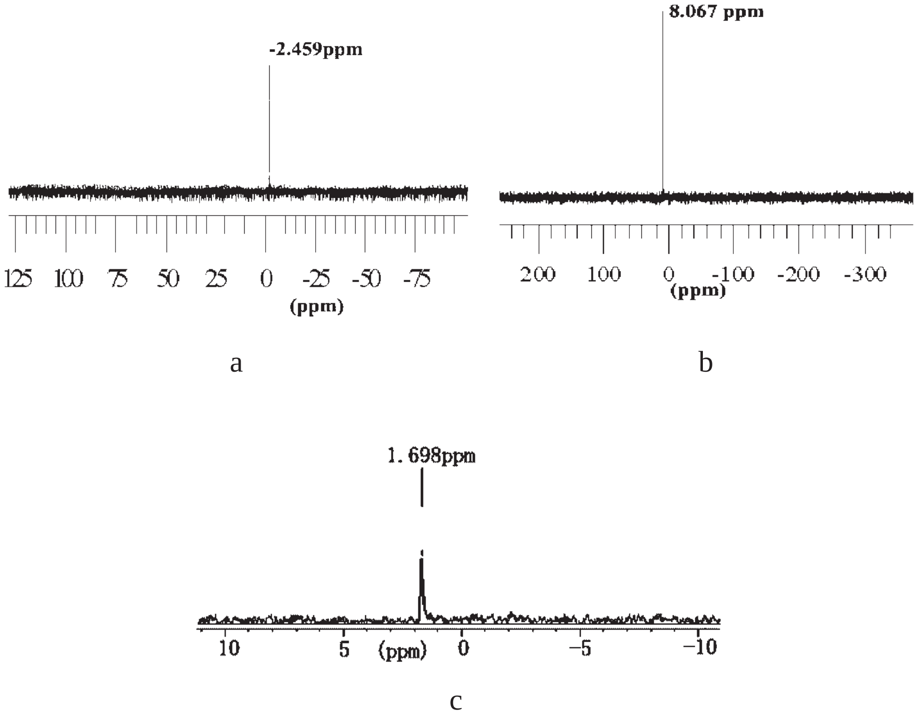


Fig. 2. ^{31}P NMR of heteropoly acid Q_3PMo_4 (a), $Q_3PMo_4(O_2)$ (b), and heteropoly blue Q_3PMo_4 (c).

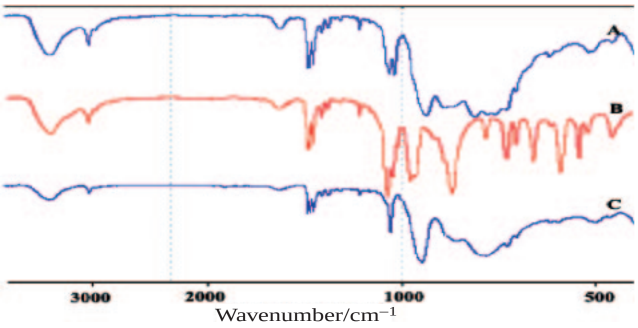


Fig. 3. Infrared spectra of heteropoly acid Q_3PMo_4 (A), $Q_3PMo_4(O_2)$ (B), and heteropoly blue Q_3PMo_4 (C).

extensively in heteropoly acid structure research. Figure 4 shows the X-ray diffraction of catalyst ($5^\circ \leqslant 2\theta \leqslant 80^\circ$). For heteropoly acid Q_3PMo_4 and heteropoly blue Q_3PMo_4, the peaks of X-ray diffraction mostly lies in four regions, where 2θ is 7–8°, 19–24°, 26–31°, and 45–46°. The peaks in 7–8° are the most intense ($d = 12.336$). The similar post and intensity of peaks indicate the basic structure of heteropoly acid remains almost unchanged in heteropoly blue.

However, for heteropoly acid, $Q_3PMo_4(O_2)$, the peaks of X-ray diffraction mostly lie in three regions that 2θ is 6–12°, 13–25°, and 25–33°. The peak in 6.960° is the most intense ($d = 12.336$). The different post and intensity of the peaks indicate that the structure of $Q_3PMo_4(O_2)$ is very different from Q_3PMo_4.

Epoxidation of Olefins. Epoxidation of olefins catalyzed by Q_3PMo_4 with 30% H_2O_2 at 70 °C are shown in Table 1. Under the reaction conditions employed, no epoxidation reaction occurred, even after 18 h when allyl chloride was used as the substrate (Entry 5). Since the molar ratio between the substrate and H_2O_2 was 4:3, the theoretical maximum conversion of the olefins was 75%. Thus, the resulting conversions of the olefins based on the olefins (67–72%) were high.[15,16] At the same time, good epoxide selectivities (94–99%) and high olefin selectivity based on H_2O_2 (>99%) were obtained. Thus, high yields of the epoxides based on H_2O_2 (90–93%) were achieved in this epoxidation system. This is one characteristic of this new epoxidation system, with which a high utilization efficiency of the reductant, which is much higher than 50%, could generally be obtained.[17] Moreover, the epoxidation of butadiene performs the selectivity at the 99% level (The operation pressure is 0.05 MPa). This high selectivity of epoxidation is another characteristic of this new epoxidation system.

The catalyst is recovered by centrifugation, and is used in the epoxidation of cyclohexene and 1-octene with 87% recovery yield (by weight). By 3-time recycle reaction, the catalytic activity and the selectivity of the recovered catalyst is practically the same as those of the fresh catalyst, indicating the excellent stability of the catalyst.

In the present work, we proved by experiments 1 mol of H_2O_2 was consumed during the formation of 1 mol of epoxide. By experiments, we found that hetero acid consisting of Mo(+6) is very easily to form hetero blue in an organic solvent. For example, the hetero acid $H_3PMo_{12}O_{40}$ in *N*,*N*-dimethylacetamide (DMAC) solution becomes hetero blue if it is heated for 1 h at 60 °C. Heteropoly acid Q_3PMo_4 in a CH_3CN solution will become hetero blue Q_3PMo_4 if it is heated for 4 h at 70 °C. These facts tell us that the formation of hetero blue does not need a reducer.

Conclusion

In this work, we designed and synthesized a new reaction-controlled phase-transfer catalyst system, heteropoly blue

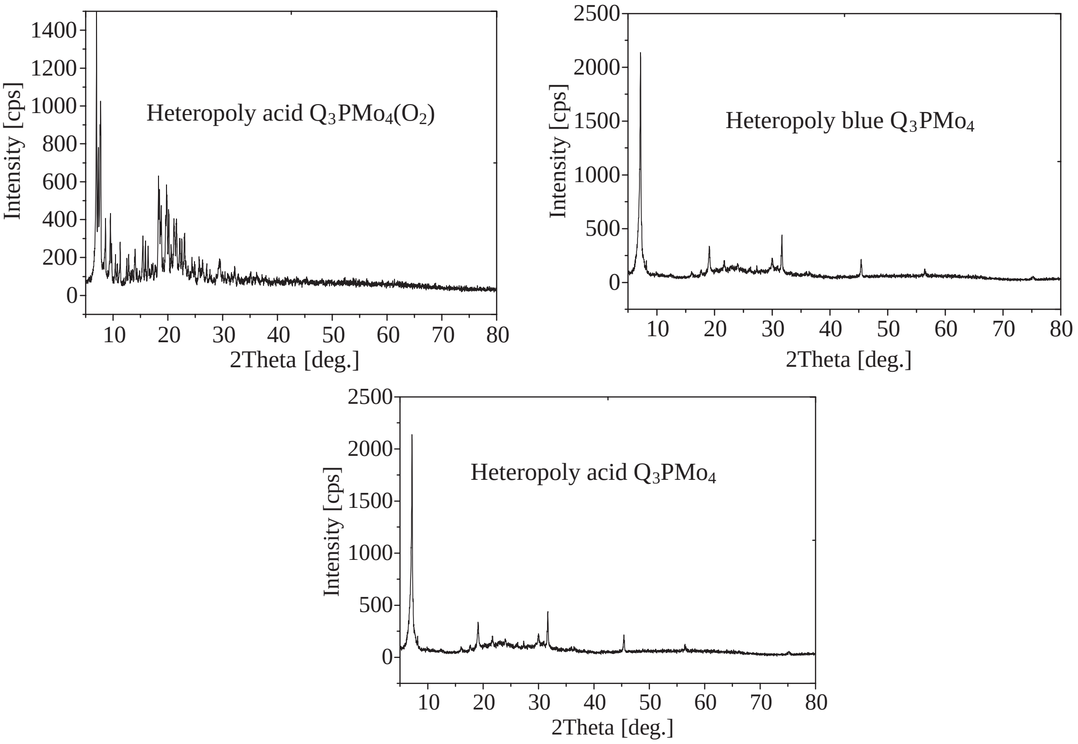


Fig. 4. X-ray diffraction of heteropoly acid Q_3PMo_4, $Q_3PMo_4(O_2)$, and heteropoly blue Q_3PMo_4.

Table 1. Epoxidation of Olefins Catalyzed by Q_3PMo_4 with 30% H_2O_2 at 70 °C

Entry	Substrate	Time/h	Based on olefin		Based on H_2O_2	Yield/%
			Conversion/%	Selectivity/%	Selectivity/%	
1	Butadiene (0.05 MPa)	4	72	99	>99	93
2	Cyclohexene	5	71.5	94	>99	91
3	1-Octene	12	70.2	99	>99	90
4	1-Decene	18	67	96	>99	90
5	Allyl chloride	18	0	0	0	0

Q_3PMo_4, for the catalytic epoxidation of olefins with H_2O_2 as the oxidant. The system exhibits high conversion and selectivity as well as excellent catalyst stability. In this system, the catalyst can act as a homogeneous catalyst and can be easily filtered and reused, like a heterogeneous catalyst. The ^{31}P NMR spectra and infrared spectra are used to analyze the phase transfer of the catalyst, because an increase in the number of oxygen atoms in the molecule makes the $Q_3PMo_4(O_2)$ dissolve in the organic solvent. This is the reason for the catalyst transfer between the solid phase and the liquid phase. In this catalyst system, the consumed materials are olefin and H_2O_2. The main products are epoxide and H_2O, and no co-product forms. All of these results show that the system is very environmentally friendly and economical.

References

1 R. A. Sheldon, J. K. Kochi, "Metal Catalyzed Oxidation of Organic Compounds," Academic Press, New York (1981).

2 C. L. Hill, "Advances in Oxygenated Processes," ed by A. L. Baumstark, JAI, London (1988), Vol. 1, pp. 1–30.

3 M. Hudlucky, "Oxidations in Organic Chemistry," ACS Monograph Series, American Chemical Society, Washington, DC (1990).

4 K. A. Jorgensen, *Chem. Rev.*, **89**, 431 (1989).

5 K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, and N. Mizuno1, *Science*, **300**, 964 (2003).

6 Z. W. Xi, N. Zhou, Y. Sun, and K. L. Li, *Science*, **292**, 1139 (2001).

7 M. Q. Li and X. G. Jian, *Chin. Chem. Lett.*, **15**, 350 (2004).

8 C. Venturello and R. D'Aloisio, *J. Org. Chem.*, **53**, 1553 (1988).

9 F. P. Ballistreri, A. Bazzo, G. A. Tomaselli, and R. M. Toscano, *J. Org. Chem.*, **57**, 7074 (1992).

10 F. Gao, T. Yamase, and H. Suzuki, *J. Mol. Catal. A: Chem.*, **180**, 97 (2002).

11 D. V. Luu and M. Abeaoza, *C. R. Acad. Sci., Ser. B*, **269**, 208 (1969).

12 D. J. Hewkin and W. P. Griffith, *J. Chem. Soc. A*, **1966**, 472.

13 R. M. Wing and R. P. Callahan, *Inorg. Chem.*, **8**, 871 (1969).

14 R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini, and M. Fournier, *Inorg. Chem.*, **16**, 2916 (1977).

15 Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida,

and M. Ogawa, *J. Org. Chem.*, **53**, 3587 (1988).

16 Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, and M. Ogawa, *J. Org. Chem.*, **52**, 1868 (1987).

17 Y. Kurusu, *Bull. Chem. Soc. Jpn.*, **54**, 293 (1981).