[Note]

Selective Epoxidation of Cyclohexene Catalyzed by Lacunary Heteropolyanion Combined with a Ruthenium Complex

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The oxidation of cyclohexene produced cyclohexene oxide in much higher yields (90-97% selectivity at 89-94% conversion) when a catalytic system combining $\text{RuCl}_2(\text{PPh}_3)_3$ with lacunary heteropolyanion, $\text{SiW}_{11}\text{O}_{39}^{8-}$, was used in the presence of dioxygen (1 atm) and aldehyde at room temperature than when the single components or the combination of the Ru complex and non-lacunary heteropolyanion, $\text{SiW}_{12}\text{O}_{40}^{4-}$, were used. Lacunary heteropolyanion was stable under the present reaction conditions.

1. Introduction

Selective catalytic epoxidation has attracted considerable attention. Recently, epoxidation of simple alkenes has been achieved with dioxygen in the presence of aldehydes under mild reaction conditions by using porphyrin or salen complexes of Co^{II} , Mn^{II} , and Ni^{II} as well as heteropolyacids^{4),5)}. Besides, it has been reported that lacunary heteropolyacids substituted by transition metals catalyzed oxidation of organic substrates with peroxide⁶⁾. We investigated oxidation of cyclohexene focusing on the effect of combining complex ($\text{RuCl}_2(\text{PPh}_3)_3$) with lacunary heteropolyanions, possible “ π -acceptor ligands”^{6a)}, under co-oxidation of dioxygen and aldehyde⁷⁾, and found that epoxides were obtained from the corresponding olefins in high selectivity.

2. Experimental

Lacunary heteropolyanions, $\text{K}_8\text{SiW}_{11}\text{O}_{39} \cdot n\text{H}_2\text{O}$ and $\text{K}_7\text{PW}_{11}\text{O}_{39} \cdot n\text{H}_2\text{O}$ were prepared as in the literature⁸⁾. $\text{K}_2\text{TPA}_6\text{SiW}_{11}\text{O}_{39}$ (TPA=tetra-*n*-pentylammonium) (1) was prepared by vigorously mixing 5 g of $\text{K}_8\text{SiW}_{11}\text{O}_{39} \cdot n\text{H}_2\text{O}$ dissolved in 100 ml of water and 3.24 g of $(\text{C}_5\text{H}_{11})_4\text{NBr}$ in 30 ml of water. The resultant precipitate was filtered off and washed with water and ether, and then dried *in vacuo*. $\text{K}_2(\text{TBA})_5\text{PW}_{11}\text{O}_{39}$ (TBA=tetra-*n*-butylammonium) and $\text{K}_2(\text{TPA})_6\text{SiW}_{11}\text{O}_{39}$ were also prepared similarly. A typical procedure for oxidation reaction was as follows. $\text{K}_2\text{TPA}_6\text{SiW}_{11}\text{O}_{39}$

(0.025 mmol) and CH_2Cl_2 (6 ml) were introduced into a 30 ml, two-necked, round-bottomed flask equipped with a magnetic stirrer under a dry argon atmosphere. After several freeze-pump-thaw cycles $\text{RuCl}_2(\text{PPh}_3)_3$ (2) (0.025 mmol) was added to the solution. After stirring the mixture for *ca.* 20 min, 1 atm of O_2 gas was introduced into the system, and then olefin (1 mmol) and aldehyde (2.5 mmol) were added dropwise to the mixture. The products were analyzed by a gas chromatograph (Shimadzu GC-8A) equipped with a Gaskuropak 55 (4 m) and a thermal conductivity detector.

3. Results and Discussion

Typical results under various reaction conditions are collected in Table 1. Products from cyclohexene contained, besides cyclohexene oxide, cyclohexenone and cyclohexenol but not cyclohexanol, cyclohexanone, adipic acid, and 1,2-cyclohexandiol. In the case of the combination of aldehyde, ruthenium complex (2), and lacunary heteropolyanion (run 1), the epoxide was obtained in over 90% selectivity. The yield after 8-12 h was 80-91%, but a quite high yield (77%, run 1') was obtained within 2 h. The performance was much better in CH_2Cl_2 than in CH_3CN (runs 1 and 2). In the absence of aldehyde the epoxide was not formed (run 6). Although the reaction proceeded without a catalyst (run 5) or with the ruthenium complex (2) in the absence of heteropolyanion (run 7), the yield of epoxide was much higher when the complex was combined with lacunary heteropolyanion (run 1). In the case of lacunary

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Table 1 Oxidation of Cyclohexene in the Presence of Oxygen and Aldehyde^{a)}

Run	Catalyst	Time [h]	Solv.	Conv. [%]	Yield [%] ^{b)}	Select. [%] ^{c)}
1	2+QSiW ₁₁ O ₃₉	8-12	CH ₂ Cl ₂	89-94	80-91	90-97
1'	2+QSiW ₁₁ O ₃₉	2	CH ₂ Cl ₂	82	77	93
2	2+QSiW ₁₁ O ₃₉	19	CH ₃ CN	95	34	36
3	2+Q'SiW ₁₂ O ₄₀	12	CH ₂ Cl ₂	96	58	60
4	QSiW ₁₁ O ₃₉	21	CH ₂ Cl ₂	39	18	47
5	No catalyst	24	CH ₂ Cl ₂	28	17	61
6	2+Q'SiW ₁₁ O ₃₉ ^{d)}	24	CH ₃ CN	19	0	0
7	RuCl ₂ (PPh ₃) ₃	10	CH ₂ Cl ₂	97	64	65
	Ni(dmp) ₂ ^{e)}	1	CH ₃ CN	31	20	65
	PW ₁₁ CoO ₃₉ ^{f-e)}	1	CH ₃ CN	41	33	80
	(NH ₄) ₅ H ₄ PV ₆ Mo ₆ ^{f)}	4	CH ₂ Cl ₂	83	78	94

a) Reaction conditions; catalyst (0.025 mmol), cyclohexene (1 mmol), aldehyde (2.5 mmol) temperature (room temp.) and reaction time (10-24 h). b) By GC analysis. c) Selectivity to cyclohexene oxide. d) Without aldehyde. e) Ref. 4. dmp=1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato). f) Ref. 5. 2: RuCl₂(PPh₃)₃, Q: K₂(TBA)₆, Q': K₂(TPA)₆, Q'': K₂(TBA)₅.

heteropolyanion without the ruthenium complex (2) (run 4), the selectivity was lower than in the case without a catalyst (run 5). Combination with the Keggin-type heteropolyanion (run 3), instead of lacunary anions, showed performance similar to that of the Ru-complex alone (run 7). Therefore, the high selectivity at high conversion levels was brought about by a synergistic effect of lacunary heteropolyanion (1) and Ru-complex (2). The high yields observed in run 1 is remarkable as compared with those in the literature (last three lines in Table 1)^{4),5)}.

The stability of polyanions and the possible complexation were examined by IR and ³¹P-NMR. The IR spectrum of 1 in CH₂Cl₂ showed absorption bands at 1014 cm⁻¹ for terminal W=O, 963 cm⁻¹ for Si-O, and 902 and 793 cm⁻¹ for the two types of bridging W-O-W as in the literature^{6b)}. Since, these IR bands little changed after run 1, the framework of heteropolyanion structure remained essentially intact during the *in-situ* preparation and reaction of run 1. The ³¹P-NMR signal for the heteroatom of K₂TBA₅PW₁₁O₃₉ shifted downfield by 0.2 ppm (-12.16 to -11.94 ppm with reference to tri-*n*-butylphosphate) and the linewidth increased slightly by the addition of Ru-complex (2). The changes were small but still greater than those in the case of nonlacunary TBA₃PW₁₂O₄₀ (0.06 ppm, from -14.68 to -14.62 ppm). If one considers the shift to be usually very small^{6a),9)}, the present observation suggests the presence of interaction between the lacunary heteropolyanion and the Ru-complex.

Now, the reaction mechanism will be briefly discussed. The catalytic system for epoxidation may be classified into two major types. One is the oxygen transfer processes involving oxometal (or peroxometal) complexes as the active oxidants¹⁰⁾. The other is the radical chain reactions initiated by metal complexes¹¹⁾. In the latter case, the role of

aldehyde usually is to generate an acyl radical by reacting with a metal complex (Eq. (2)). Three possible active species may be derived from the acyl radical: acylperoxy radical (Eq. (3))¹¹⁾, peracid (Eq. (4))¹²⁾, and oxometal complex (Eq. (5))^{11),13)}. The relative importance of these changes in the reaction depends on the reaction systems and conditions^{13),14)}. Murahashi *et al.*¹⁵⁾ have indicated that oxometal species is the more important species for the reaction of aldehyde and dioxygen with Ru complex (2). Nam *et al.* have recently reported that in the case of oxidation by dioxygen plus aldehyde in the presence of Fe, Co, Ni, Cr, and Mn complexes, the principal role of metal complexes is to aid the formation of acyl radical and that the active species are acylperoxy radicals (Eq. (6a)) rather than peracids (Eq. (8)) or oxometal complexes (Eq. (7))¹³⁾.

We carried out oxidation of *cis*-stilbene with the present catalytic system and observed non-stereospecific formation of the corresponding

epoxides. The *trans/cis* ratio of epoxide was 79/21, the isolated yield after 4 h at room temperature was 65%. This indicates that the epoxidation proceeded mainly *via* a radical reaction (probably *via* acyl peroxy radical) rather than *via* peracid as discussed by Nam *et al.*¹³⁾. The oxidation of styrene carried out under the our present reaction conditions formed benzaldehyde and styrene epoxide (aldehyde/epoxide=77/23). The formation of benzaldehyde indicates the radical path¹⁶⁾, but the formation of epoxide shows that there is a path *via* peracid (Eq. (8))¹⁷⁾ or oxoruthenium (Eq. (7)).

In summary, by using a combination of $\text{RuCl}_2(\text{PPh}_3)_3$ and lacunary Keggin-type heteropolyanions as catalysts in CH_2Cl_2 , cyclohexene was oxidized to epoxides with high selectivity and yield in the presence of dioxygen and aldehyde at ambient temperature; for example, cyclohexene was epoxidized with 90-97% selectivity.

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要 旨

欠損型ヘテロポリアニオンとルテニウム化合物の複合触媒系によるシクロヘキセンの選択的エポキシ化

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欠損型ヘテロポリアニオン ($\text{SiW}_{11}\text{O}_{39}^{8-}$) とルテニウムホスフィン錯体 ($\text{RuCl}_2(\text{PPh}_3)_3$) の複合系を触媒とすると, 室温, 酸素 (1 atm), イソブチルアルデヒド存在下において, 各単独系ならびに非欠損型ヘテロポリアニオン ($\text{SiW}_{12}\text{O}_{40}^{4-}$) と Ru

錯体の複合系に比較し, 高い収率 (転化率 89~94%, 選択率 90~97%) でシクロヘキセンがエポキシ化することを見出した。欠損型ヘテロポリアニオンは反応前後で安定である。

Keywords

Epoxidation, Lacunary heteropolyanion, Ruthenium catalyst, Selectivity, Dioxygen, Aldehyde