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Calixarene-Catalyzed Permanganate Oxidation of Organic Compounds

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Synopsis. The calix[6]arene **1** bearing six trioxadecyl groups on the phenolic oxygens served as an effective catalyst for the oxidation of alkenes, alkynes, and alcohols with $KMnO_4$ in CH_2Cl_2. The reaction of alkenes, alkynes, and primary alcohols gave carboxylic acids in high yields, but that of secondary alcohols gave ketones in high or moderate yields.

Our previous work has shown that the calix[6]arene derivative **1**, which bears six trioxadecyl groups on the phenolic oxygens, serves as effective catalysts for several chemical reactions such as the ether-forming reaction from alkyl halides and potassium phenoxides,[1] the ester-forming reaction from alkyl halides and alkali metal carboxylates,[2,3] and the dichlorocarbene generation reaction from trichloromethane and alkali metal hydroxides.[4] The catalytic ability of **1** in these reactions depended strongly on its binding ability toward alkali metal cations in organic solvents.[3] We now report that **1** also serves as an effective catalyst for the permanganate oxidation of alkenes, alkynes and alcohols (Chart 1).

Results and Discussion

Oxidation of Alkenes and Alkynes. Reactions of alkenes **2a-b** and alkynes **3a-b** with an excess (3 equiv) of $KMnO_4$ in CH_2Cl_2 or CH_2Cl_2–water (10:1) in the presence of a catalytic amount of **1** gave the corresponding carboxylic acids **4a-b** in high yields. The oxidation of stilbene (**2c**) in a similar manner gave **4a** in high yield. The results are shown in Table 1. In the absence of **1**, the oxidation reaction occurred inefficiently and the yields of products were low (<10%) under similar conditions.

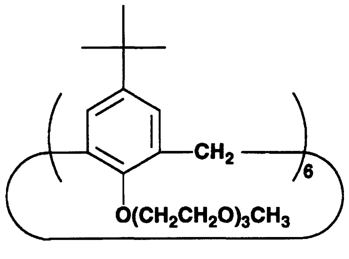

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Chart 1.

$$\begin{array}{l}\mathrm{RCH{=}CH_2}\\ \quad\mathbf{2a\text{-}b}\\ \mathrm{RC{\equiv}CH}\\ \quad\mathbf{3a\text{-}b}\end{array} \xrightarrow{\mathrm{KMnO_4}/\mathbf{1}} \begin{array}{c}\mathrm{RCO_2H}\\ \mathbf{4a\text{-}b}\end{array} \qquad (1)$$

a: R=phenyl, b: R=hexyl

$$\underset{\mathbf{2c}}{\mathrm{RhCH{=}CHPh}} \xrightarrow{\mathrm{KMnO_4}/\mathbf{1}} \mathbf{4a} \qquad (2)$$

The efficiency of the reaction was affected by solvents. The oxidation of alkenes occurred more efficiently in a water-containing CH_2Cl_2 than in nonaqueous CH_2Cl_2. The reverse tendency was observed for the oxidation of alkynes, although the reason for this is unclear at present. In benzene, the oxidation reaction took place inefficiently (Table 1). This may be attributable to the solvent effect on the complexing ability of **1** toward K^+ ion. We have shown from solvent-extraction experiments of metal picrates that the encapsulating or complexing ability of **1** toward K^+ ion in CH_2Cl_2 is much greater than in benzene.[3] Evidence for such a solvent dependence on the complexing ability was obtained also for the oxidation reaction. We recognized that a clear purple solution was obtained when $KMnO_4$ was added into a CH_2Cl_2 solution of **1**, whereas such a color change did not occur when benzene was used as solvent.

The oxidation of alkenes and alkynes with $KMnO_4$ has been shown to be catalyzed by phase-transfer catalysts such as quaternary ammonium salts[5] and crown ethers.[6] The ammonium salt-catalyzed reaction is usually carried out in a liquid(water)–liquid(organic solvent) two phase system. On the other hand, crown ethers and **1** can be used as catalyst for the reaction in a solid($KMnO_4$)–liquid(organic solvent) two phase system. Because of the similarity of the catalytic function of **1** and 18-crown-6 for the permanganate oxidation of **2a** and **3a** was compared under similar conditions. The catalytic ability of **1** was found to be comparable to that of 18-crown-6 (Table 1). However, we found that the use of **1** as a catalyst was more profitable in a practical sense, compared to 18-crown-6. In fact, the products were able to be isolated easily in pure forms without being contaminated by the catalyst when **1** was used as catalyst; note that 18-crown-6 is somewhat soluble, but **1** is little soluble in aqueous solutions.

Oxidation of Alcohols. The oxidation of alcohols with $KMnO_4$ was also catalyzed by **1** in CH_2Cl_2.

Table 1. Calixarene-Catalyzed Oxidation of Alkenes and Alkynes with $KMnO_4$[a)]

Compd	Catalyst	Solvent	Time/h	Temp/°C	Product	Yield/%[b)]
2a	**1**	CH_2Cl_2	4	40	**4a**	54
2a	**1**	CH_2Cl_2 : H_2O (10 : 1)	4	40	**4a**	85
2a	**1**	C_6H_6	4	40	**4a**	12
2a	18-Crown-6	CH_2Cl_2 : H_2O (10 : 1)	4	40	**4a**	82
2b	**1**	CH_2Cl_2	6	40	**4b**	35
2b	**1**	CH_2Cl_2 : H_2O (10 : 1)	6	40	**4b**	69
2c	**1**	CH_2Cl_2	6	40	**4a**	46
2c	**1**	CH_2Cl_2 : H_2O (10 : 1)	6	40	**4a**	86
3a	**1**	CH_2Cl_2	6	30	**4a**	82
3a	**1**	CH_2Cl_2 : H_2O (10 : 1)	6	30	**4a**	63
3a	**1**	C_6H_6	6	30	**4a**	25
3a	18-Crown-6	CH_2Cl_2	6	30	**4a**	74
3b	**1**	CH_2Cl_2	6	30	**4a**	69

a) The reaction was carried out by stirring a mixture containing a substrate (10 mmol), $KMnO_4$ (30 mmol), and a catalyst in an organic solvent (30 cm^3). The molar ratio of the substrate to the catalyst was 36 for **1** and 13 for 18-crown-6. b) Isolated yield.

Table 2. Calixarene-Catalyzed Oxidation of Alcohols with $KMnO_4$[a)]

Alcohol	Catalyst	Molar ratio [Alcohol]/[Catalyst]	Time/h	Product	Yield/%	Recovery of alcohol/%[b)]
5a	**1**	38	6	**6a**	100[c)]	—
5b	**1**	38	6	**6b**	92[c)]	—
5b	18-Crown-6	13	6	**6b**	88[c)]	—
7a	**1**	38	8	**8a**	96	0
7a	18-Crown-6	38	8	**8b**	96	0
7b	**1**	38	7	**8b**	45	36
7b	18-Crown-6	13	7	**8b**	48	22
7c	**1**	38	6	**8c**	21	78
7c	18-Crown-6	13	6	**8c**	28	65

a) The reaction was carried out by stirring a mixture containing an alcohol (10 mmol), $KMnO_4$ (30 mmol) and a catalyst in CH_2Cl_2 at 30 °C. The amount of the catalyst used was same as Table 1.
b) The recovery of the starting alcohol was determined by the GLC analysis of the reaction mixture.
c) Isolated yield.

Primary alcohols **5a-b** gave carboxylic acids **6a-b** practically in quantitative yield. Secondary alcohols **7a-c** afforded ketones **8a-c**, but the yields depended on the structure of alcohols. The results are shown in Table 2.

$$\underset{\textbf{5a-b}}{RCH_2OH} \xrightarrow[CH_2Cl_2]{KMnO_4/\textbf{1}} \underset{\textbf{6a-b}}{RCO_2H} \qquad (3)$$

a: R=phenyl, b: R=heptyl

$$\underset{\textbf{7a-c}}{R^1CH(OH)R^2} \xrightarrow[CH_2Cl_2]{KMnO_4/\textbf{1}} \underset{\textbf{8a-c}}{R^1COR^2} \qquad (4)$$

a: R^1=R^2=phenyl, b: R^1-R^2=$-(CH_2)_5-$
c: R^1=methyl, R^2=hexyl

18-Crown-6 acted also as catalyst for these reactions, and its catalytic activity was almost the same as that of **1**. Furthermore, the reactivity of alcohols in both the catalyzed reactions was parallel and decreased in the order: **7a** (an aromatic alcohol) >**7b** (an alicyclic alcohol) >**7c** (an aliphatic alcohol).

Experimental

Materials. Calix[6]arene **1** was prepared as described previously.[3)] Organic solvents were purified by distillation after drying over molecular sieve 3A or 4A. All other organic reagents were of reagent grade and used without further purification.

General Procedure for Oxidation. To a stirred mixture of an alkene (10 mmol) and **1** (0.3 mmol) in CH_2Cl_2 (30 cm^3) was added $KMnO_4$ (30 mmol). The mixture was further stirred at 40 °C for 4 h and cooled. Water (30 cm^3) and $NaHSO_3$ (5 g) were then added to reduce excess $KMnO_4$. The resulting mixture was acidified with aqueous HCl solution, treated with $NaHSO_3$ to reduce MnO_2, and extracted three times with ether (30 cm^3). The combined ether solution was extracted three times with 0.1 $mol\,dm^{-3}$ aqueous NaOH (30 cm^3) to separate out the catalyst **1** from the reaction mixture. The aqueous layer was filtered, acidified with aqueous HCl solution, and extracted three times with ether (30 cm^3). The combined organic layer was dried ($MgSO_4$) and evaporated to give a carboxylic acid.

Alkynes and alcohols were oxidized in a similar manner. In the case of the oxidation of secondary alcohols, the products were usually obtained as oil. The oily products were analyzed by GLC on PEG 20M (10%, 60/80 mesh). When 18-crown-6 was used as a catalyst, the aqueous layer was washed with ether to remove the crown ether after the extraction with aqueous NaOH solution.

The products were identified by comparison of IR and NMR data with those of the authentic samples which were purchased from Wako Pure Chemical Industries, Ltd.

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References

1) H. Taniguchi and E. Nomura, *Chem. Lett.*, **1988**, 1773.

2) E. Nomura, H. Taniguchi, K. Kawaguchi, and Y. Otsuji, *Chem. Lett.*, **1991**, 2167.

3) E. Nomura, H. Taniguchi, K. Kawaguchi, and Y. Otsuji, *J. Org. Chem.*, **58**, 4709 (1993).

4) E. Nomura, H. Tahiguchi, and Y. Otsuji, *Bull. Chem. Soc. Jpn.*, in press.

5) D. G. Lee and V. S. Chang, *J. Org. Chem.*, **44**, 2726 (1979).

6) D. J. Sam and H. E. Simmons, *J. Am. Chem. Soc.*, **94**, 4024 (1972); D. Landini, A. M. Maia, F. Montanari, and F. M. Pirisi, *Gazz. Chim. Ital.*, **105**, 863 (1975).