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Catalytic Ability of Octopus-Type Calixarene in the Formation of Ethers from Phenols and Alkyl Halides or 1-Chloro-4-nitrobenzene

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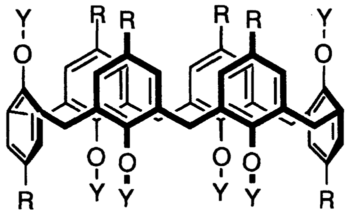
The formation of ethers was catalyzed by 5,11,17,23,29,35-hexa-*p*-*t*-butyl-37,38,39,40,41,42-hexakis(3,6,9-trioxadecyloxy)calix[6]arene (**1**). It was found that the calixarene-catalyzed reaction of phenol with benzyl bromide in the presence of KOH in CH_2Cl_2 yields only the *O*-alkylated product and this reaction proceeds according to Michaelis–Menten type kinetics. The calixarene **1** also catalyzed the reactions of phenols with dichloromethane and 1-chloro-4-nitrobenzene.

Calixarenes are macrocyclic oligomers that can be obtained by the base-catalyzed condensation of para-substituted phenols with formaldehyde, and various types of their functionalized derivatives have been synthesized.[1)] Their properties are now finding many applications in various fields of chemistry. For example, these compounds serve as a host of inclusion compounds,[2)] selective complexing agents for metal ions,[3)] and catalysts for chemical reactions.[4—8)]

Previously, we have reported that *p*-*t*-butylcalix[6]arene derivative **1**, which has six trioxadecyl substituents on the phenolic oxygens, serves as a catalyst for the ester-forming reaction from alkyl halides and alkali metal carboxylates[5,6)] and for the generation of dichlorocarbene from $CHCl_3$ and solid KOH.[7)] An important structural feature of **1** is that this molecule contains both a hydrophobic functionality composed of six aromatic groups and a hydrophilic functionality composed of six trioxadecyl groups. We have also demonstrated that calixarene **1** has a 1,4-*anti* conformation in CD_2Cl_2 at -20 °C[6)] (see Fig. 1) and its catalytic ability for these reactions strongly depends on the nature of solvents through the variation in the binding ability for alkali metal ions.[4—7)] Furthermore, on the dichlorocarbene addition reaction with alkadienes having isolated double bond, monoadducts formation predominated.[7)]

In a previous communication, we showed that **1** acts as a catalyst for the ether-forming reaction from alkyl halides and phenols in the presence of potassium hydroxide.[4)] From the standpoint described above, we reexamined our previous work.[4)] This paper deals with the following subjects: 1) the catalytic ability of **1** for the ether forming reaction of phenols with alkyl halides in the presence of potassium hydroxide. 2) application of the Michaelis–Menten model to the reaction of potassium phenoxide with benzyl bromide. 3) the catalytic ability of **1** for the diphenyl ether-forming reaction of phenol with 1-chloro-4-nitrobenzene in the presence of potassium hydroxide.



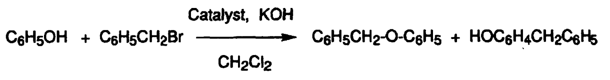
R = *t*-butyl

Y = $(CH_2CH_2O)_3CH_3$

Fig. 1. A representative 1,4-*anti* conformation of **1** in CD_2Cl_2 at -20 °C.

Results and Discussion

Reaction of Phenol with Benzyl Bromide. To assess the catalytic ability of **1** and to compare **1** with various other catalysts, we at first examined the reaction of phenol with benzyl bromide in the presence of potassium hydroxide. Most recently, the mechanism of this reaction has been investigated in detail in some solid–solid–liquid reaction systems using polymer-bound phase transfer catalysts to find that *C*/*O*-alkylation takes place.[9)]



$$\underset{\mathbf{2a}}{C_6H_5OH} + \underset{\mathbf{3}}{C_6H_5CH_2Br} \xrightarrow[CH_2Cl_2]{\text{Catalyst, KOH}} \underset{\mathbf{4}}{C_6H_5CH_2\text{-}O\text{-}C_6H_5} + \underset{\mathbf{5}}{HOC_6H_4CH_2C_6H_5} \qquad (1)$$

In this reaction, it has been shown that *C*-alkylation occurs only with solvents capable of strong hydrogenbond formation such as water or phenol or in a "truly heterogeneous" solid–liquid reaction[10] and that selective *O*-alkylation occurs in nonpolar aprotic solvents.[11] Therefore, in this reaction we used CH_2Cl_2 as a solvent to avoid *C*-alkylation. The reaction was done as follows: Equimolecular amounts of phenol and benzyl bromide were dissolved in CH_2Cl_2. To this solution, powdered potassium hydroxide and an appropriate catalyst were added and the mixture was stirred at 40 °C. Table 1 shows the results. The catalyst **1** was the best among the catalysts used. Within only 2 h, the reaction was complete.

Only *O*-alkylation occurred. The reaction system was a solid–liquid two-phase system due to good solubility of **1** in CH_2Cl_2. After the reaction, the yield of **4** was measured by TLC analyses of the reaction mixtures. The calixarene **1** could be easily removed by adsorption of silica gel. Moreover, catalyst **1** could be recovered from the silica gel mass by extracting it with ethanol. The catalytic activity of the recovered calixarene was essentially the same as that of the freshly prepared one. Less efficient appear to be benzyltrimethylammonium chloride, which is a typical phase-transfer catalyst, polyethylene glycol diethyl ether (PEG-DEE), and 18-crown-6. With the quaternary ammonium salt a longer reaction time was required (20 h) than with the catalyst **1**. With PEG-DEE and 18-crown-6 the yield of the ether was lowered (80 and 89%). Also under these reaction systems, *C*-alkylation did not occur. In an uncatalyzed reaction the yield of the ether fell to 31%. In a liquid–liquid, CH_2Cl_2–water, two-phase system the yield of the ether was only 4% and no *C*-alkylation occurred.

The catalytic ability of **1** for this reaction depended on the solvent. The use of benzene as a solvent decreased the yield of the product. This solvent-dependent catalytic ability of **1** was observed in the ester-forming reaction and the generation of dichlorocarbene.[6,7] We had shown that the metal cation extraction ability of **1** depends on the nature of solvents.[6] The high extraction ability toward K^+, Rb^+, and Cs^+ ions was observed in CH_2Cl_2 and $ClCH_2CH_2Cl$. The extraction ability was negligible small in benzene and $CHCl_3$ for all the alkali metal cations. These result shows that the catalytic ability of **1** is based on the ability to capture metal ions.

Application of Michaelis–Menten Model to the Reaction of Potassium Phenoxide with Benzyl Bromide. We had reported that the dichlorocarbene addition to alkadienes catalyzed by **1** obeys the Michaelis–Menten type kinetics.[7] This suggested that the dichlorocarbene addition reaction occurs within the cavity of the calixarene. We now extended this model to the ether-forming reaction of potassium phenoxide with benzyl bromide. A kinetic study was done in CH_2Cl_2 with an excess of potassium phenoxide in the presence of a catalytic amount of **1** at 30 °C. Figure 2 shows the reciprocal plot of the initial rate of the reaction and the initial concentration of benzyl bromide (Lineweaver–Burk plot[12]). This linear plot indicates that this calixarene-catalyzed reaction obeys the Michaelis–Menten type kinetics. The Michaelis constant was calculated to be 1.5×10^{-1} mol dm^{-3}. From this result it can be considered that the calixarene-cat-

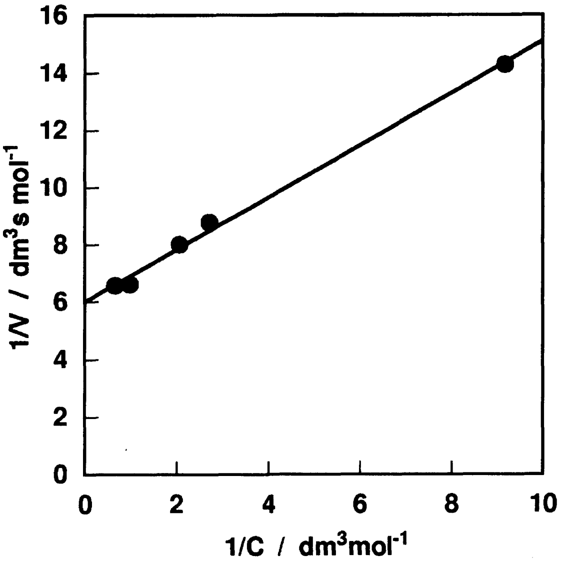


Fig. 2. Lineweaver–Burk plot for the reaction of potassium phenoxide with benzyl bromide catalyzed by **1**.

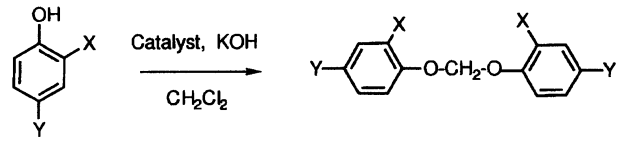
Table 1. Reaction of Phenol with Benzyl Bromide[a)]

Reaction	Catalyst	2/Cat[b)]	Solvent[c)]	Time	Recovery/%	Yield/%	
system				h	**3**	**4**	**5**
S–L	**1**	35	CH_2Cl_2	2	0	100	0
S–L	BTMAC[d)]	4.8	CH_2Cl_2	20	0	100	0
S–L	PEG-DEE[e)]	5.8	CH_2Cl_2	3	Trace	80	0
S–L	18-crown-6	5.0	CH_2Cl_2	2	8	89	0
S–L	None	—	CH_2Cl_2	20	69	31	0
S–L	**1**	35	C_6H_6	2	61	35	0
L–L	None	—	CH_2Cl_2–H_2O[f)]	24	87	4	0

a) Phenol (1.2 g, 12.8 mmol), benzyl bromide (2.2 g, 12.5 mmol), KOH (2.5 g), temp at 40 °C. b) Molar ratio. c) Guaranteed grade 15 cm^3. d) Benzyltrimethylammonium chloride. e) Polyethylene glycol diethyl ether (mol wt=456). f) CH_2Cl_2 (15 cm^3)–H_2O (5 cm^3).

alyzed ether-forming reaction occurs within the cavity of the calixarene, like the calixarene-catalyzed dichlorocarbene addition reaction.[7)]

Reaction of Phenols with Dichloromethane. Quaternary ammonium salts are already known to be good catalysts for the formation of bis(aryloxy)methanes.[13)] We next applied calixarene **1** as a catalyst to the formation of bis(aryloxy)methanes to assess its catalytic activity.



2a: X=Y=H

2b: X=H, Y=Cl

2c: X=Y=Cl

6a: X=Y=H

6b: X=H, Y=Cl

6c: X=Y=Cl

(2)

The substrates used in this investigation are **2a**, **2b**, and **2c**. Table 2 shows the results. When **2a** was used, in the non-catalyzed reaction the yield of diphenoxymethane, **6a**, is only 0.3%. The use of a liquid–liquid two-phase reaction system let to a very small yield, 1.4%, even if benzyltrimethylammonium chloride was used as a catalyst. Therefore, a solid–liquid reaction system was chosen to afford **6a** in a good yield. The calixarene **1** catalyzed the reaction best among the catalysts used to form **6a** in quantitative yield. The ability of the calixarene **1** was better than that of benzyltrimethylammonium chloride and 18-crown-6. When polyethylene glycol (PEG), which has an average molecular weight of 600, was used as a catalyst, **6a** was given in a low yield in a prolonged reaction time (195 h). It was found that PEG-diethyl ether had also a catalytic ability toward this reaction, but its ability was weaker than that of **1**. When the substrate was **2b** and the calixarene **1** was used as a catalyst, the yield of **6b** varied with reaction systems. In a liquid–liquid two-phase reaction system, i.e., in CH_2Cl_2–water, **6b** produced in a low yield (19%) at a reaction time longer than 100 h. And also when dried CH_2Cl_2, which was dried over molecular sieve 4A was used, the yield of **6b** was low (31%). When CH_2Cl_2 saturated with water was used as the solvent, the calixarene catalyzed the reaction as well as benzyl-trimetylammonium chloride, tetrabutylammonium bromide, and 18-crown-6, to form the corresponding diphenoxymethane **6b** in a quantitative yield. A similar tendency for the effect of water content in solvent on the catalytic ability of **1** was observed in the ester-forming reactions and the generation of dichlorocarbene.[6,7)] In this reaction, water adsorbed on the surface of potassium hydroxide or potassium phenoxide would facilitate formation of a partially dissociated ion pair $[K^+\cdots PhO^-]$ that may transfer to the organic phase where the reaction takes place. In the organic phase, a potassium cation is captured by forming a complex probably with trioxadecyl groups. The phenoxide anion then reacts with alkyl halide in CH_2Cl_2 in

Table 2. The Reaction of Phenol with Dichloromethane[a)]

Reaction system	Phenol	Catalyst	PhOH/Cat[b)]	Solvent	Time / h	Yield of **6**/%
S–L	**2a**	None	—	CH_2Cl_2[c)]	24	0.3
L–L	**2a**	BTMAC[d)]	4.7	CH_2Cl_2–H_2O (5 : 1)	24	1.4
S–L	**2a**	1	24	CH_2Cl_2[c)]	24	100
S–L	**2a**	PEG-DEE[e)]	5.8	CH_2Cl_2[c)]	24	85
S–L	**2a**	PEG-600[f)]	0.77	CH_2Cl_2[c)]	195	23
S–L	**2a**	BTMAC	4.7	CH_2Cl_2[c)]	24	86
S–L	**2a**	18-crown-6	5.0	CH_2Cl_2[c)]	24	96
S–L	**2b**	1	48	Wet CH_2Cl_2[g)]	96	100
S–L	**2b**	1	48	Dry CH_2Cl_2[h)]	96	31
L–L	**2b**	1	48	CH_2Cl_2–H_2O (10 : 1)	144	19
S–L	**2b**	BTMAC	4.7	CH_2Cl_2[c)]	72	100
S–L	**2b**	Bu_4NCl	3.5	CH_2Cl_2[c)]	74	100
S–L	**2b**	18-crown-6	5.0	CH_2Cl_2[c)]	75	100
S–L	**2c**	1	48	CH_2Cl_2[c)]	168	Trace
S–L	**2c**	BTMAC	2.3	CH_2Cl_2[c)]	77	99
S–L	**2c**	18-crown-6	5.0	CH_2Cl_2[c)]	75	90

a) Phenol (12.8 mmol), KOH (2.5 g), CH_2Cl_2 (50 cm^3), temp at 40 °C. b) Molar ratio. c) Guaranteed grade; water content: 0.0846 wt% d) Benzyltrimethylammonium chloride. e) Polyethylene glycol diethyl ether (mol wt=456). f) Polyethylene glycol (mol wt=600). g) Dichloromethane saturated with water. h) Dichloromethane dried over molecular sieve 4A: 0.0398 wt%.

Table 3. Reaction of Metal Phenolate with 1-Chloro-4-nitrobenzene[a)]

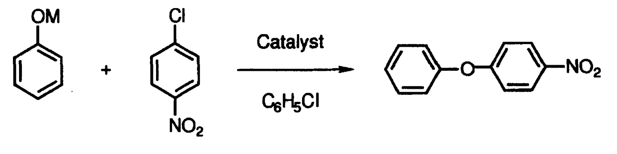
Metal phenolate	Catalyst	**8**/Cat[b)]	Solvent	Temp °C	Time h	Rec/% **8**	Yield/% **9**
7a	None	—	C_6H_5Cl	130	24	86	13
7a	None	—	C_6H_5Cl	130	6		1[c)]
7a	Bu_4NBr	1	C_6H_5Cl	130	6		93[c)]
7a	**1**	24	C_6H_5Cl	130	7	6	93
7a	**1**	24	C_6H_5Cl $+H_2O$ (20 μl)	130	7	5	95
7a	**1**	24	C_6H_5Cl $+H_2O$ (200 μl)	130	7	6	94
7a	**10**	3.7	C_6H_5Cl	130	7	42	56
7a	18-crown-6	5.0	C_6H_5Cl	130	7	5	91
7a	**1**	24	$ClCH_2CH_2Cl$	80	7	94	Trace
7b	**1**	24	C_6H_5Cl	130	7	69	19

a) 1-Chloro-4-nitrobenzene (1.0 g, 6.35 mmol), KOH (1.4 g, 10.6 mmol), solvent (30 cm^3).
b) Molar ratio. c) Ref. 15.

a naked, activated form. When the water content in the reaction system is large, the phenoxide anion would exist in a solvated form in which the reactivity of the phenoxide anion would be greatly decreased.

When **2c** was used, calixarene **1** did not catalyze the reaction, but benzyltrimethylammonium chloride and 18-crown-6 acted as a good catalyst. As described above, it was found that the catalytic ability of calixarene **1** varied with the kind of phenols.

Reaction of Metal Phenoxide with 1-Chloro-4-nitrobenzene. We investigated the preparation of 1-nitro-4-phenoxybenzene (**9**) from potassium phenoxide (**7a**) and 1-chloro-4-nitrobenzene (**8**).



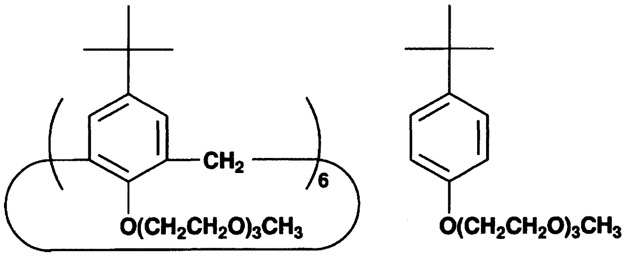
7a: M=K **8** **9**

7b: M=Na

(3)

Nucleophlic substitutions of aromatic halides with phenoxide ions have usually been done in aprotic polar solvents to produce diphenyl ethers.[14)] However, the recovery of these solvents is troublesome because of their good solubility in water. Thus, it is better for those reactions to be done in water-insoluble polar solvents such as chlorobenzene or *o*-dichlorobenzene.

The reaction of potassium phenoxide with 1-chloro-4-nitrobenzene has been done in chlorobenzene in the presence of an equimolar amount of tetrabutylammonium bromide as a phase-transfer catalyst.[15)] In general quaternary ammonium salts which are used in this reaction are easily damaged by heat. However, calixarene **1** is stable to prolonged heating. Therefore, we examined this reaction to assess the catalytic ability of **1**. Table 3 shows the results. Without any catalyst the reaction hardly proceeded. In the presence of **1** the reaction gave **9** in 93—95% yields. In this case the presence of a small amount of water did not have any affect on the product yield. When **10**, which is a unit compound of **1**, was used as a catalyst, the yield of the ether dropped to 56% (Chart 1). When sodium phenoxide was used instead of potassium phenoxide, the yield of the ether significantly decreased (19%). This phenomenon is attributable to the fact that calixarene **1** catches potassium cation more strongly than sodium cation.[6)] The use of 18-crown-6 as the catalyst gave **9** in 91% yield. As described above, calixarene **1** has been demonstrated to be an excellent catalyst as well as 18-crown-6 for the aromatic nucleophilic substitution of phenoxide ions with aromatic halides.



1 **10**

Chart 1.

Experimental

Column chromatography was done with Wakogel C-300. Thin-layer chromatography was done on a Merck TLC silica gel $60F_{252}$ plates. TLC analysis was done with a Shimadzu dual-wavelength TLC scanner CS-930. Melting points were measured using a Yanako micro melting-point apparatus and are uncorrected. IR spectra were obtained using a JASCO IR-810 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90A spectrometer and chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Elemental analysis was done by a Yanako CHN corder MT-3. Sodium phenoxide[11)] and potassium phenoxide[11)] were prepared by the method in the literature. Preparation of 5,11,17,23,29,35-hexa-*p*-*t*-butyl-37,38,39,40,41,42-hexakis(3,6,9-trioxadecyloxy) calix[6]arene (**1**) and 10-(*p*-*t*-butylphenoxy)-2,5,8-trioxadecane (**10**) were reported previously.[6)]

Reaction of Phenol with Benzyl Bromide Using the Calixarene 1. A mixture of PhOH (1.2 g, 12.8 mmol), benzyl bromide (2.2 g, 12.5 mmol), powdered KOH (2.5 g), and the calixarene **1** (0.7 g) was placed in a flask. To the flask, CH_2Cl_2 (15 cm^3) was added. After stirring for 2 h at 40 °C, the reaction mixture was poured upon a Büchner funnel paved with silica gal (about 10 g). The silica gel was washed with EtOH to extract **1**, which could be used repeatedly. The filtrate was evaporated to dryness to give 2.3 g of **4** as a white solid; mp 39 °C (lit,[10)] 39°C). Yield 100%.

Reaction of Phenol with Benzyl Bromide Using Other Catalysts. A mixture of PhOH (1.2 g, 12.8 mmol), benzyl bromide (2.2 g, 12.5 mmol), powdered KOH (2.5 g), and a catalyst was placed in a flask. Into the flask, 15 cm^3 of CH_2Cl_2 was added and the mixture was stirred at 40 °C for an appropriate hour. Then, the reaction mixture was poured into 100 cm^3 of water. The product was extracted with CH_2Cl_2. With an appropriate treatment the catalyst was removed. The CH_2Cl_2 solution was dried over $MgSO_4$. The CH_2Cl_2 was evaporated to dryness to give the ether **4**.

Kinetic Measurement for the Calixarene-Catalyzed Reaction of Potassium Phenoxide with Benzyl Bromide. A mixture of benzyl bromide (1—15 mmol), **1** (0.10 g, 0.054 mmol) in CH_2Cl_2 (10 cm^3) was stirred at 30 °C. The reaction was started by adding potassium phenoxide (2.64 g, 20 mmol) to the mixture. A sample (0.1 cm^3) was withdrawn every two minutes and diluted with acetone (10 cm^3). The reaction mixture was analyzed by GC using a column packed with OV-17 (2%, 80—100 mesh). Nonane (1 cm^3) was used as an internal standard for GC analyses.

General Procedure of Phenols with Dichloromethane. Into a solution of a phenol (12.8 mmol) in 50 cm^3 of dichloromethane, a catalyst and powdered KOH (2.5 g) were added. The mixture was stirred for an appropriate time at 40 °C. After removing the catalyst as described above, the excess CH_2Cl_2 was evaporated to give a diphenoxymethane. Bisphenoxymethane **6a**; mp 16 °C (lit,[16)] 16 °C). Bis(4-chlorophenoxy)methane **6b**; mp 68 °C (lit,[17)] 67—69 °C). Bis(2,4-dichlorophenoxy)methane **6c**; mp 98 °C (lit,[17)] 96—98 °C).

Reaction of Potassium Phenoxide with 1-Chloro-4-nitrobenzene. A mixture of 1-chloro-4-nitrobenzene (1.0 g, 6.35 mmol), potassium phenoxide (1.4 g, 10.6 mmol), and a catalyst in chlorobenzene (30 cm^3) was stirred for an appropriate time at 130 °C. After removing the catalyst, the solvent was evaporated to dryness to give a mixture of 1-nitro-4-phenoxybenzene and 1-chloro-4-nitrobenzene, which was analyzed by a TLC analytical method. 1-Nitro-4-phenoxybenzene **9**; mp 58—59 °C (lit,[15)] 58—59 °C).

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