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# Calixarene-Catalyzed Generation of Dichlorocarbene and Its Application to Organic Reactions: The Catalytic Action of Octopus-Type Calix[6]arene

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The dichlorocarbene generation reaction from $CHCl_3$ and solid KOH in $CH_2Cl_2$ was catalyzed by the *p*-*t*-butylcalix[6]arene derivative **1** which bears six 3,6,9-trioxadecyl substituents on the phenolic oxygens. Dichlorocarbene generated by this method reacted efficiently with alkenes and amides to give dichlorocyclopropane derivatives and nitriles, respectively, in high yields. The reaction with alkadiene having isolated double bonds gave mixtures of the mono- and bis-dichlorocarbene adducts, but the monoadduct formation always predominated. The catalytic action of the calixarene and the reactivity features of dichlorocarbene generated by the above procedure are discussed on the basis of kinetic measurements. They are also compared with those of the 18-crown-6-catalyzed reactions.

The chemistry of calixarenes has received a great deal of attention in recent years.[1)] Their properties are now finding wide chemical applications in various fields of chemistry; for example, as hosts of inclusion compounds,[2)] selective complexing agents for metal ions,[3)] and also as catalysts for chemical reactions.[4—7)]

Previously, we have reported that the *p*-*t*-butylcalix[6]arene derivative **1**, which has six trioxadecyl substituents on the phenolic oxygens, serves as a catalyst for the ether-forming reaction from alkyl halides and phenols in the presence of KOH[4)] and also for the ester-forming reaction from alkyl halides and alkali metal carboxylates.[5,6)] We have also demonstrated that the calixarene **1** has a 1,4-*anti* conformation[8)] (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—6)]

We now report that **1** also serves as an effective catalyst for the generation of dichlorocarbene from $CHCl_3$ and solid KOH in $CH_2Cl_2$. It is well-known that the dichlorocarbene generation reaction from $CHCl_3$ and alkali metal hydroxides can be achieved in two-phase systems by utilizing tetraalkylammonium salts[7)] or crown ethers[8)] as phase-transfer catalysts. In this investigation, we focus our attention on the catalytic behavior of **1** and the selectivity in the dichlorocarbene addition reactions to alkenes and alkadienes. We show that the reactivity of dichlorocarbene generated by the calixarene-catalyzed reaction is quite different from that generated by the crown ether-catalyzed reaction. We also show that the dichlorocarbene generation reaction can be applied to dehydration of amides.

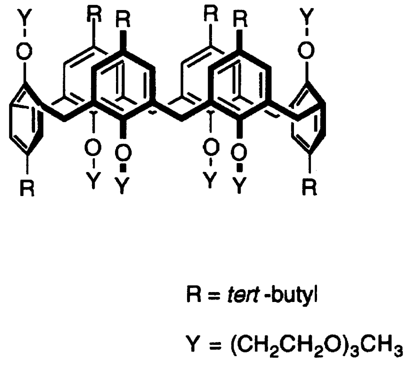
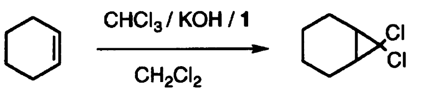


Fig. 1. A schematic illustration of the 1,4-*anti* conformation of **1**.

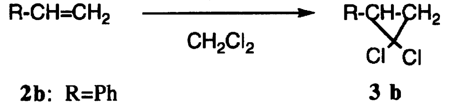
## Results and discussion

**Addition of Dichlorocarbene to Alkenes.** Treatment of cyclohexene (**2a**) with excess $CHCl_3$ in $CH_2Cl_2$ in the presence of solid, powdered KOH and a catalytic amount of **1** at 40°C gave 7,7-dichlorobicyclo[4.1.0]heptane (**3a**) in high yield. This reaction did not occur appreciably in the absence of **1**. The calixarene-catalyzed dichlorocarbene addition reaction also occurred with styrene (**2b**) and 1-octene (**2c**), giving **3b** and **3c**, respectively, in high yields. The results are summarized in Table 1.



(I)

**2 a** **3 a**



(II)

**2b**: R=Ph **3 b**
**2c**: R=*n*-$C_6H_{13}$ **3 c**

18-Crown-6 served also as an effective catalyst for the dichlorocarbene addition to **2a** under similar conditions. However, there is a practical advantage in the calixarene-catalyzed reaction over the crown ether-catalyzed reaction. In the former reaction, the catalyst could be recovered easily from the reaction mixture, and the recovered catalyst exhibited essentially the same

Table 1. Reaction of Dichlorocarbene with Alkenes[a)]

| Alkene | Cat. | Molar ratio alkene/cat. | Solvent | Reaction time/h | Product | Yield/% |
|---|---|---|---|---|---|---|
| **2a** | **1** | 23 | $CH_2Cl_2$ | 6 | **3a** | 79 |
| **2a** | **1** | 90 | $CH_2Cl_2$ | 6 | **3a** | 69 |
| **2a** | **1** | 90 | $CH_2Cl_2$:$H_2O$ (50 : 1)[b)] | 6 | **3a** | 68 |
| **2a** | **1** | 90 | $CH_2Cl_2$:$H_2O$ (10 : 1)[b)] | 6 | **3a** | 40 |
| **2a** | **1** | 90 | $CH_2Cl_2$:$H_2O$ (10 : 3)[b)] | 4 | **3a** | 14 |
| **2a** | **1** | 90 | $C_6H_6$ | 6 | **3a** | 13 |
| **2a** | **1** | 90 | $ClCH_2CH_2Cl$ | 6 | **3a** | 67 |
| **2a** | **1** | 90 | $CH_3CN$ | 6 | **3a** | 85 |
| **2a** | **1** | 90 | None | 6 | **3a** | 38 |
| **2a** | **4** | 14 | $CH_2Cl_2$ | 6 | **3a** | 27 |
| **2a** | 18-Crown-6 | 10 | $CH_2Cl_2$ | 6 | **3a** | 98 |
| **2a** | None | — | $CH_2Cl_2$ | 20 | **3a** | 2 |
| **2b** | **1** | 18 | $CH_2Cl_2$ | 6 | **3b** | 82 |
| **2b** | **1** | 18 | $CH_2Cl_2$:$H_2O$ (10 : 1)[b)] | 6 | **3b** | 58 |
| **2b** | None | — | $CH_2Cl_2$ | 6 | **3b** | 11 |
| **2c** | **1** | 34 | $CH_2Cl_2$ | 6 | **3c** | 71 |
| **2c** | None | — | $CH_2Cl_2$ | 6 | **3c** | <1 |

a) Reaction conditions: alkene, 10 mmol; $CHCl_3$, 50 mmol; KOH, 50 mmol solvent, 5 $cm^3$; temp, 40 °C. b) vol%.

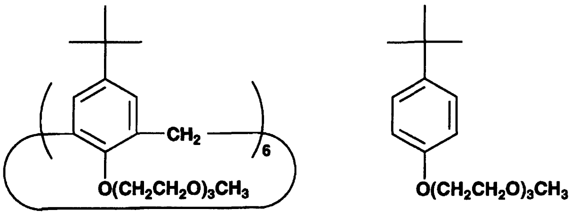
catalytic activity as did the freshly prepared one. On the other hand, the crown ether turned the reaction mixture black immediately after the reaction started and the catalyst was difficult to recover from the reaction mixture.

The *p*-*t*-butylphenol derivative **4**, which is a monomer model of **1**, showed a catalytic ability for the dichlorocarbene generation reaction, but its catalytic activity was smaller than that of **1** (Chart 1). This implies that the catalytic activity of **1** comes from its molecular architecture (see Fig. 1).

The catalytic ability of **1** for the generation of dichlorocarbene depended on the amount of water in the solvent. An increase in the water content of $CH_2Cl_2$ resulted in a decrease in the yield of the product. A similar tendency for the effect of water content in solvent on the catalytic ability of **1** was also observed in the ether- and ester-forming reactions.[4—6)] The results of Table 1 also indicate that the reaction proceeds much more efficiently in polar solvents than in less polar solvents.

The catalytic ability of **1** also depended on the alkali metal cation in metal hydroxide employed as base for the generation of dichlorocarbene. Figure 2 shows the effect of the alkali metal cations on the catalytic activity of **1** for the formation of **2a**. Higher yields of **3a** were obtained when alkali metal cations with larger ionic radii, such as $K^+$ and $Rb^+$ ions, were used.

It was shown previously that the alkali metal cation extraction ability of **1** from aqueous solution to $CH_2Cl_2$ increases in the order: $Li^+ < Na^+ \ll K^+$, $Cs^+ < Rb^+$.[6)] The metal cation extraction ability depended also on solvents. The high extraction ability toward $K^+$, $Rb^+$, and $Cs^+$ ions was observed in $CH_2Cl_2$ and $ClCH_2CH_2Cl$, while the extraction ability toward $Li^+$ and $Na^+$ ions was low even in these solvents. The extraction ability was negligibly small in benzene and $CHCl_3$ for all the alkali metal cations. The tendency for the metal cation extraction ability of **1** was parallel with



**1** **4**

Chart 1.

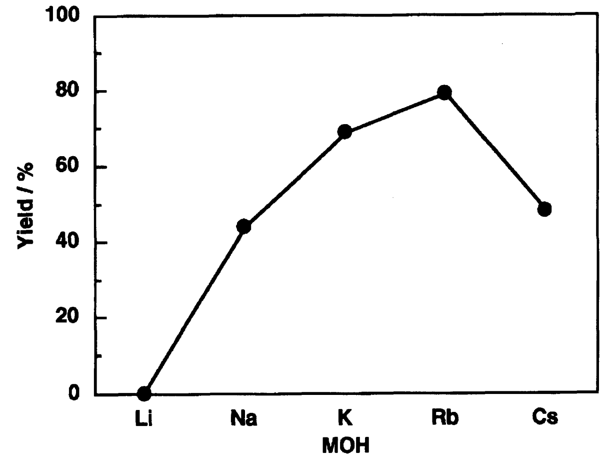
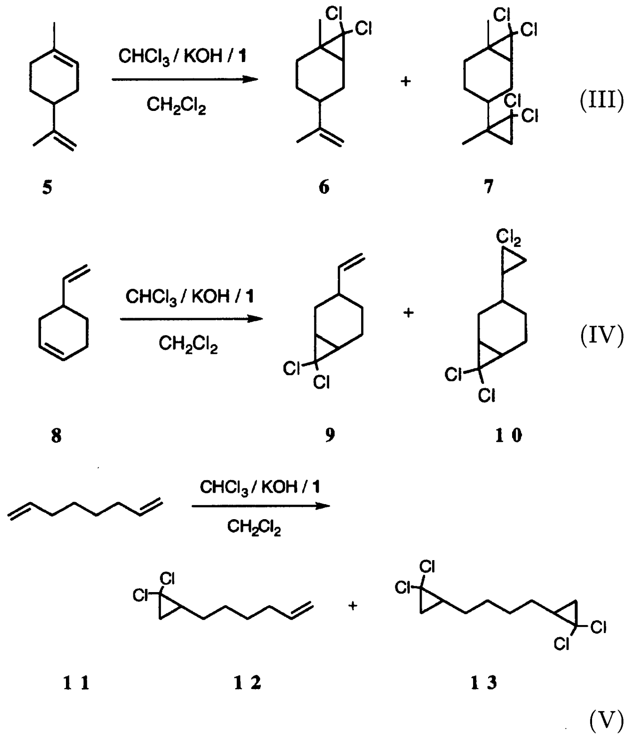


Fig. 2. Effect of alkali metal cations in metal hydroxides on the yields of **3a**. The amount of metal hydroxides was 50 mmol. The other reaction conditions are the same as those described in the footnotes of Table 1.

that for its catalytic activity with respect to both the solvent and metal cation effects. These results indicate that the catalytic ability of **1** is determined primarily by the ability to capture metal cations from the metal hydroxide. A plausible model for capturing K$^+$ ion by **1** is illustrated in Fig. 3. The trioxadecyl moieties of **1** forms a complex with K$^+$ ion.

**Addition of Dichlorocarbene to Alkadienes.** The dichlorocarbene addition to alkadienes having isolated carbon–carbon double bonds was studied using **1** as catalyst. The product distributions were analyzed after carrying out the reactions for a given period of time, usually for 4 h. The results are summarized in Table 2.



From *d*-limonene (**5**), 4-vinylcyclohexene (**8**), and 1,7-octadiene (**11**), the monoadducts **6**, **9**, and **12** were obtained, respectively, as major products along with small amounts of the bisadducts **7**, **10**, and **13**. However, when 18-crown-6 was used as catalyst, the bisadducts **7**, **10**, and **13** were obtained as the major products. The selective formation of the monoadducts **6**, **9**, and **12** was also observed in the reactions of **5**, **8**, and **11** with dichlorocarbene generated from CHCl$_3$ and aqueous NaOH solution using certain tertiary amines[11] and quaternary ammonium salts[12,13] as phase-transfer catalysts.

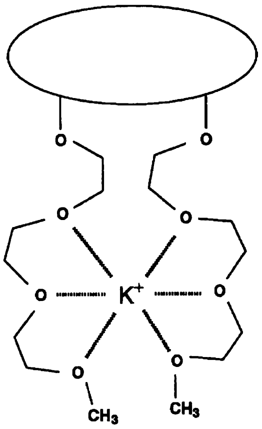


Fig. 3. A schematic illustration of complexation of the potassium cation with **1**.

Table 2. Reaction of Dichlorocarbene with Alkadienes[a]

| Diene | Catalyst | Molar ratio diene/cat. | Yield/% | |
|---|---|---|---|---|
| | | | Monoadduct | Bisadduct |
| 5 | 1 | 200 | 45[b] | 7[b] |
| 5 | 1 | 50 | 55[b] | 17[b] |
| 5 | 1 | 14 | 55[b] | 14[b] |
| 5 | 18-Crown-6 | 50 | <1[b] | 80[b] |
| 5 | 18-Crown-6 | 10 | <1[b] | 84[b] |
| 5 | None | — | 19[b] | <1[b] |
| 8 | 1 | 50 | 61[b] | 9[b] |
| 8 | 18-Crown-6 | 50 | 9[b] | 70[b] |
| 8 | None | — | 16[b] | 0 |
| 11 | 1 | 50 | 45 | 21 |
| 11 | 18-Crown-6 | 50 | 10 | 77 |
| 11 | None | — | 6 | 0 |

a) Reaction conditions; alkadiene, 10 mmol; CHCl$_3$, 60 mmol; KOH, 60 mmol; reaction time, 4 h; other reaction conditions are the same as those described in the footnote in Table 1. b) Total yield of the two stereoisomers.

In order to gain an insight into the mechanistic aspect of the characteristic regioselectivity in the dichlorocarbene addition reactions, kinetic studies were carried out by using **5** as a substrate. The catalytic action of **1** and 18-crown-6 were compared under the same reaction conditions. The reactions of **5** with dichlorocarbene were performed in CH$_2$Cl$_2$ by using excess CHCl$_3$ and KOH in the presence of catalytic amounts of the two catalysts at 30°C. The results are shown in Figs. 4 and 5. The results of Fig. 4 indicate that in the calixarene-catalyzed reaction, the monoadduct and bisadduct forming reactions occur competitively (Scheme 1). The pseudo-first-order rate constants $k_1$ and $k_2$ for the formation of **6** and **7** were estimated from the slopes of straight lines (Fig. 6) that were obtained by the use of the usual first-order rate expression (Eqs. 1, 2, and 3)[14] at the initial stage of the reaction (conversions of **5**; <20%). The reaction of **6** with dichlorocarbene generated under the same reaction conditions also gave **7** as shown in Fig. 7. The pseudo-first-order rate constant $k_3$ for the formation of **7** from **6** was estimated in a similar manner as above (Eq. 4).

The results are given in Scheme 1. Interestingly, the $k_3$ value was much larger than the $k_2$ value.

On the other hand, the results of Fig. 5 indicate that the crown ether-catalyzed reaction of **5** occurs in a con-

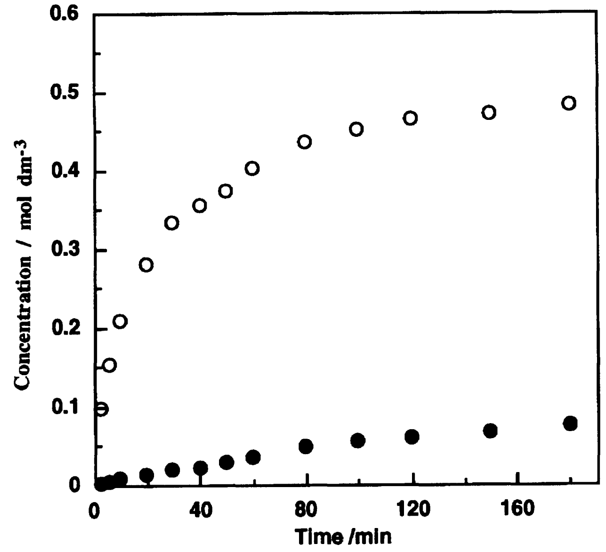


Fig. 4. Time-course for the formation of the monoadduct **6** (○) and the bisadduct **7** (●) in the calixarene-catalyzed dichlorocarbene addition to **5**.

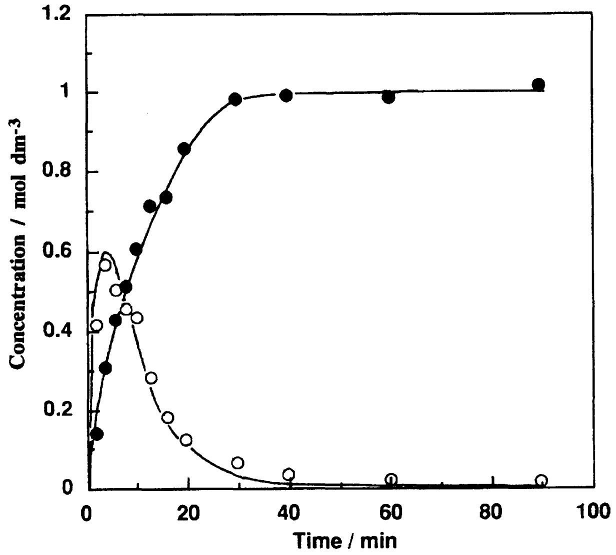
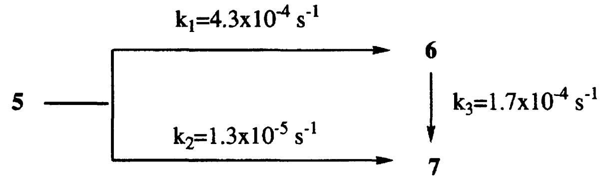


Fig. 5. Time-course for the formation of the monoadduct **6** (○) and the bisadduct **7** (●) in the 18-crown-6-catalyzed dichlorocarbene addition to **5**. The curves were drawn by using Eqs. 5, 6, and 7 and the $k_4$ and $k_5$ values shown in the text.

For the calixarene **1**-catalyzed reaction:



$$[5]=[5]_0\cdot e^{-kt} \qquad (1)$$

$$k=k_1+k_2$$

$$[6]=k_1\cdot\frac{[5]_0}{k}(1-e^{-kt}) \qquad (2)$$

$$[7]=k_2\cdot\frac{[5]_0}{k}(1-e^{-kt}) \qquad (3)$$

$$[6]=[6]_0\cdot e^{-k_3t} \qquad (4)$$

For the 18-crown-6-catalyzed reaction:

$$5 \xrightarrow{k_4=6.9\mathrm{x}10^{-3}\ s^{-1}} 6 \xrightarrow{k_5=2.1\mathrm{x}10^{-3}\ s^{-1}} 7$$

$$[5]=[5]_0\cdot e^{-k_4t} \qquad (5)$$

$$[6]=[5]_0\cdot\frac{k_4}{k_5-k_4}(e^{-k_4t}-e^{-k_5t}) \qquad (6)$$

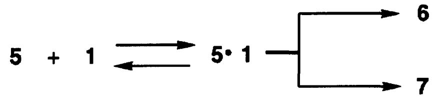
$$[7]=[5]_0(1-\frac{k_4}{k_5-k_4}e^{-k_4t}-\frac{k_4}{k_5-k_4}e^{-k_5t}) \qquad (7)$$

Scheme 1.

secutive manner (Scheme 1). In this case, the pseudo-first-order rate constants $k_4$ and $k_5$ were calculated by using Eqs. 5, 6, and 7.[14] shown in Scheme 1. The rate constant $k_4$ was determined from the slope of the straight line of the first-order rate plot at the initial stage of the reaction (conversion of **5**;<20%). The rate constant $k_5$ was determined by a curve-fitting method using Eqs. 5, 6, and 7. The results are also given in Scheme 1. In this case, the maximum concentration of the monoadduct **6**, $[\mathbf{6}]_{\mathrm{max}}$, is reached at the time, $t_{\mathrm{max}}$. These values were calculated to be: $[\mathbf{6}]_{\mathrm{max}}=0.594$ mol dm$^{-3}$ and $t_{\mathrm{max}}=247$ s. After the $t_{\mathrm{max}}$ time, the formation of the bisadduct increased spontaneously.

The above results strongly suggest that the catalytic functions of **1** and 18-crown-6 are different. Figures 8a and 8b show Lineweaver–Burk plots[15] for the formation of the monoadduct and the bisadduct, respectively, in the calixarene-catalyzed dichlorocarbene addition to **5**. The linear plots indicate that both the mono and bisadduct forming reactions obey Michaelis–Menten type kinetics as shown in Scheme 2. The Michaelis constants were calculated to be: $K_{\mathrm{m}}(\mathrm{mono})=6.5\times10^{-2}$ mol dm$^{-3}$ for the monoadduct formation and $K_{\mathrm{m}}(\mathrm{bis})=6.4\times10^{-2}$ mol dm$^{-3}$ for the bisadduct formation. Both the $K_{\mathrm{m}}$ values coincide with each other in magnitude. This result suggests that the calixarene-catalyzed dichlorocarbene addition to **5** occurs within the cavity of the calixarene.

Under these circumstances, the movement of the substrate molecule may be largely restricted and the mono



Scheme 2.

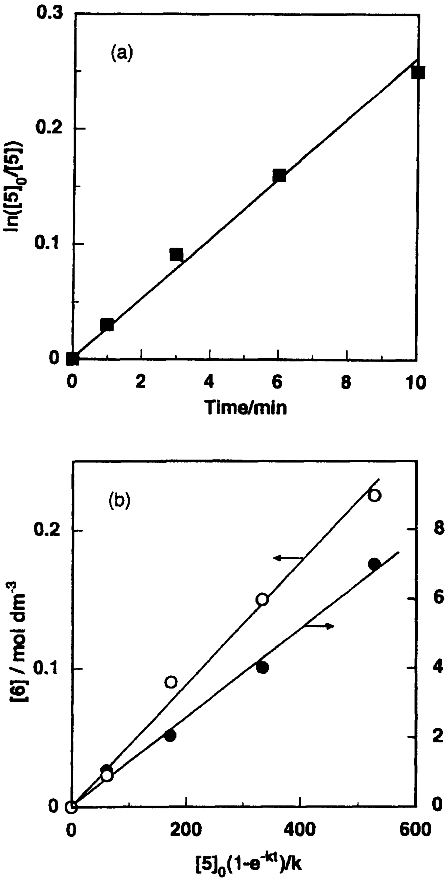


Fig. 6. First-order plots for competitive reactions in the calixarene-catalyxed dichlorocarbene addition reaction to **5**: (a) time-course for the decrease in the concentration of **5**, (b) time-courses for the formation of the monoadduct **6** (○) and the formation of the bisadduct **7** (●).

and bisadduct forming reactions would occur in a competitive manner. The high regioselectivity in this reaction arises from the large difference in the $k_1$ and $k_2$ values. If the mono- and bis-adduct forming reactions occur in a consecutive manner, the proportion of the bisadduct should increase more markedly with increasing reaction time: Note that $k_3 > k_2$. As can be seen from Fig. 4, this is not the case.

If the calixarene-catalyzed dichlorocarbene addition to **5** occurs within the cavity of **1** in a competitive manner, there is a possibility that the rate of formation of **7** from **6** may be influenced by the presence of **5**. To confirm this possibility, a competitive dichlorocarbene addition reaction to **5** and **6** was studied. The reaction was carried out by stirring a $CH_2Cl_2$ solution containing a 1 : 1 mixture of **5** and **6**, excess $CHCl_3$ and solid KOH in the presence of a catalytic amount of **1** at 30°C. The results are shown in Fig. 9. The time-course of the formation of **7** is different from that shown in Fig. 7. In the case of the competitive reaction (Fig. 9), the rate of formation of **7** at the initial stage (conversion of **5**; <60%) was significantly slower than that observed for

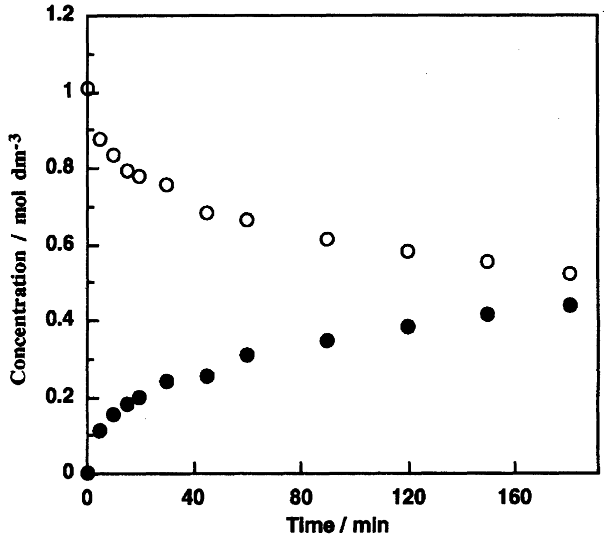


Fig. 7. Time-course for the disappearance of the monoadduct **6** (○) and the formation of the bisadduct **7** (●) in the calixarene-catalyzed dichlorocarbene addition to **6**.

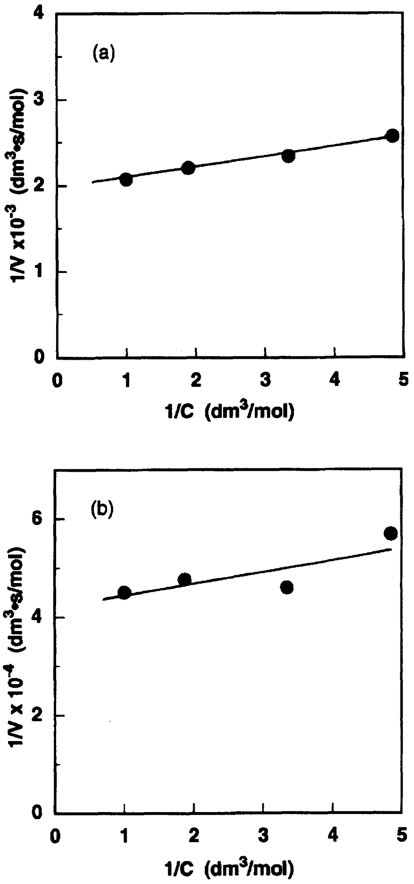


Fig. 8. Lineweaver–Burk plots for (a) the formation of the monoadduct **6** and (b) the formation of the bisadduct **7** in the calixarene-catalyzed dichlorocarbene addition reaction to **5**.

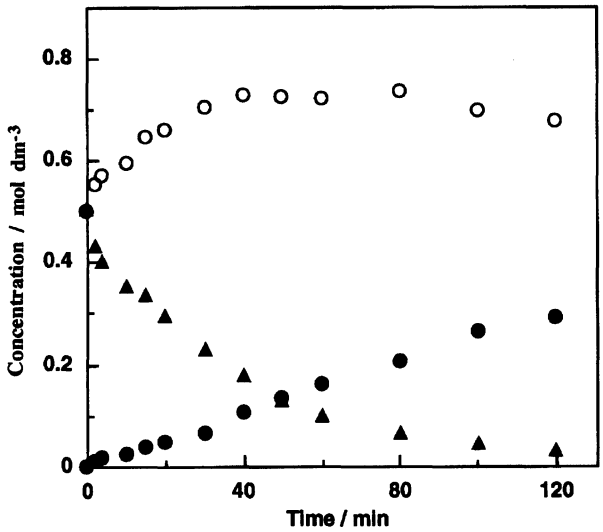


Fig. 9. Time-course for the formation of **6** (○), **7** (●), and the disappearance of **5** (▲) in the calixarene-catalyzed dichlorocarbene addition to a 1 : 1 mixture of **5** and **6**.

the dichlorocarbene addition to **6** in the absence of **5** (Fig. 7). The detailed examination of Fig. 9 shows that the proportion of **7** in the reaction mixture increases significantly after most of **5** is consumed (conversion of **5**;>70%). These results can be interpreted by assuming that the encapsulating ability of **1** toward **5** in the cavity is larger than that toward **6**, and **5** acts as an inhibitor for the formation of **7** from **6**.

On the other hand, in the crown ether-catalyzed reaction, the mono- and bis-adduct forming reactions occur in a consecutive manner as described above. Since the rate constant for the monoadduct formation is only three times larger than that for the bisadduct formation, the selectivity of the bisadduct formation increases with increasing reaction time.

**Dehydration of Amides with Dichlorocarbene.** It is known that amides can be dehydrated to nitriles by the reaction with dichlorocarbene that is generated from $CHCl_3$ and aqueous NaOH solution by using tetraalkylammonium salts.[16] The catalytic ability of **1** for this reaction was also sudied. The reactions were carried out by stirring $CH_2Cl_2$ solutions containing amides **14a**—**c**, excess $CHCl_3$ and solid KOH in the presence of a catalytic amount of **1** at 40°C. The catalytic ability of **1** was compared with that of 18-crown-6. The results are given in Table 3.

$$\text{R-CONH}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{CHCl}_3\text{/KOH/}\mathbf{1}} \text{R-CN} \qquad \text{(VI)}$$

**14a**: R=Ph **15a**

**14b**: R=*i*-Pr **15b**

**14c**: R=Et **15c**

Table 3. Reactions of Dichlorocarbene with Amides[a)]

| Amide | Catalyst | Molar ratio amide/cat. | Reaction time/h | Product | Yield/% |
|---|---|---|---|---|---|
| **14a** | **1** | 30 | 4 | **15a** | 73 |
| **14a** | None | — | 4 | **15a** | 22 |
| **14a** | 18-Crown-6 | 11 | 4 | **15a** | 65 |
| **14b** | **1** | 43 | 4 | **15b** | 84 |
| **14b** | None | — | 4 | **15b** | 62 |
| **14c** | **1** | 51 | 4 | **15c** | 73 |
| **14c** | None | — | 4 | **15c** | 55 |

a) Reaction conditions are the same as those described in the footnote in Table 1.

All the amides were converted into the nitriles **15a**—**c** in high yields by using **1** as catalyst.

## Experimental

GC analyses were performed using columns (2 m) packed with Silicone SE-30 (20%), Porapak Q and Silicone OV-17 (2%). NMR spectra were obtained at 90 MHz. Chemical shifts are reported as $\delta$ values using $(CH_3)_4Si$ as an internal standard. GC-MS spectra were obtained by applying a chemical ionization (CI) method using isobutane as CI gas.

**Materials.** The calix[6]arene **1** was prepared from *p*-*t*-butylcalix[6]arene and 3,6,9-trioxadecyl *p*-toluenesulfonate by the method previously reported.[4,6] 1-(*p*-*t*-Butylphenyl)-1,4,7,10-tetraoxaundecane (**4**) was prepared from *p*-*t*-butylphenol and 3,6,9-trioxadecyl *p*-toluenesulfonate.[6] Chloroform was dried ($CaCl_2$) and distilled. Other organic solvents were dried over molecular sieve 3A or 4A and purified by distillation. Other organic compounds were purchased and purified by distillation or recrystallization. Alkali metal hydroxides were used after grinding to a powder and drying in a vacuum oven at 110°C for 48 h.

**Reaction of Dichlorocarbene with Alkenes and Alkadienes. A Typical Procedure.** To stirred mixture of cyclohexene (0.82 g, 10 mmol), powdered KOH (2.81 g, 50 mmol), calix[6]arene **1** (0.21 g, 0.11 mmol) in $CH_2Cl_2$ (5 $cm^3$) was added $CHCl_3$ (5.97 g, 50 mmol) dropwise at 40°C. The mixture was stirred at the same temperature for 6 h and extracted with ether. The extract was dried ($MgSO_4$) and analyzed by GC.

The catalyst **1** was recovered from the extract. The extract was subjected to column chromatography on silica gel. The calixarene adsorbed on silica gel column was recovered almost quantitatively by extracting with EtOH and reused for the reaction.

The products were purified by distillation and identified from their IR, NMR, GC-MS, and elemental analysis data.

**3a:** Bp 82°C (17 mmHg, 1 mmHg=133.322 Pa) [lit,[11] bp 79—81°C (15 mmHg)]; IR (neat) 2930, 2848, 1443, 1023, 793 $cm^{-1}$; $^{13}C$ NMR ($CDCl_3$) $\delta$=18.88, 20.23, 25.87, 67.42 ($CCl_2$); MS *m/z* 164 ($M^+$; 100), 166 ($M^+$+2; 64), 168 ($M^+$+4; 11).

**3b:** Bp 113°C (19 mmHg) [lit,[17] 110°C (15 mmHg)]; IR (neat) 3050, 3020, 1604, 1498, 1112, 775, 692 $cm^{-1}$; $^1H$NMR ($CDCl_3$) $\delta$=1.71—2.03 (2H, m, $CH_2$), 2.89 (1H, t, CH), 7.14—7.45 (5H, m, Ar-H); $^{13}C$NMR ($CDCl_3$) $\delta$=25.65, 35.43, 60.73 ($CCl_2$), 127.50, 128.23, 128.80, 134.54.

**3c:**[18] Bp 101°C (18 mmHg); IR (neat) 2950, 2920, 2849, 1460, 1120, 750 cm$^{-1}$; $^{13}$C NMR ($CDCl_3$) $\delta$=14.06, 22.62, 26.82, 28.58, 28.96, 30.39, 30.99, 31.75, 61.70 ($CCl_2$); MS $m/z$ 194 ($M^+$; 100) 196 ($M^+$+2; 67).

**6:** Bp 104°C (10 mmHg); IR (neat) 3070, 2925, 2860, 1642, 1450, 885, 820 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.0—2.4 (14H, m+s (1.42, 1.70)), 4.68 (2H, br s); MS $m/z$ 219 ($MH^+$; 100), 221 ($MH^+$+2; 55), 223 ($MH^+$+4; 8). Found: C, 59.95; H, 7.41%. Calcd for $C_{11}H_{16}C_{12}$: C, 60.28; H, 7.36%.

**7:** Bp 147—148°C (5 mmHg); IR (neat) 2925, 2860, 1450, 1030, 820, 755 cm$^{-1}$; MS $m/z$ 300 ($M^+$; 78), 302 ($M^+$+2; 100). Found: C, 47.41; H, 5.35%. Calcd for $C_{12}H_{16}C_{14}$: C, 47.71; H, 5.34%.

**9:** Bp 88°C (9 mmHg); IR (neat) 3070, 2925, 2848, 1638, 1440, 910, 800 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=0.7—2.4 (9H, m) 4.8—5.2, and 5.5—5.9 (3H, m); MS $m/z$ 191 ($MH^+$; 100), 193 ($MH^+$+2). Found: C, 56.23; H, 6.03%. Calcd for $C_9H_{12}Cl_2$: C, 56.57; H, 6.33%.

**10:** Bp 131—132°C (3 mmHg); IR (neat) 2925, 2848, 1440, 800, 750 cm$^{-1}$; MS $m/z$ 272 ($M^+$; 78), 274 ($M^+$+2; 100), 276 ($M^+$+4; 51), 278 ($M^+$+6; 13). Found: C, 43.71; H, 4.40%. Calcd for $C_{10}H_{12}Cl_4$: C, 43.83; H, 4.41%.

**12:**[13] Bp 78°C (10 mmHg); IR (neat) 3070, 2920, 2849, 1640, 1120, 909, 745 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.0—2.2 (11H, m), 4.8—5.2, and 5.6—6.1 (3H, m); $^{13}$C NMR ($CDCl_3$) $\delta$=26.79, 28.06, 28.52, 30.20, 30.88, 33.59, 61.62 ($CCl_2$), 114.52, 138.66; MS $m/z$ 192 ($M^+$; 100), 194 ($M^+$+2; 72).

**13:** Bp 125—128°C (5 mmHg); IR (neat) 2925, 2850, 1120, 745 cm$^{-1}$; $^{13}$C NMR ($CDCl_3$) $\delta$=26.76, 28.17, 30.18, 30.74, 61.52 ($CCl_2$); MS $m/z$ 274 ($M^+$; 79), 276 ($M^+$+2; 100), 278 ($M^+$+4; 53), 280 ($M^+$+6; 13), 282 ($M^+$+8; 0.7). Found: C, 43.40; H, 5.13%. Calcd for $C_{10}H_{14}Cl_4$: C, 43.51; H, 5.11%.

**Reaction of Dichlorocarbene with Amides. A Typical Procedure.** To stirred mixture of benzamide (1.21 g, 10 mmol), powdered KOH (2.81 g, 50 mmol), the calix[6]arene **1** (0.61 g, 0.33 mmol) in $CH_2Cl_2$ (5 cm$^3$) was added $CHCl_3$ (5.97 g, 50 mmol) dropwise at 40°C. The reaction mixture was further stirred at the same temperature for 4 h and extracted with hexane. The extract was dried ($MgSO_4$) and analyzed by GC.

The products were purified by distillation and identical by comparison of their spectral data (IR, $^1$H NMR and GC) with those of authentic samples.

**Kinetic Measurements for the Addition of Dichlorocarbene to *d*-Limonene (5).** A mixture of **5** (1.36 g, 10 mmol), **1** (0.50 g, 0.27 mmol), $CHCl_3$ (7.16 g, 60 mmol) in $CH_2Cl_2$ (5 cm$^3$) was stirred at 30 °C. The reaction was started by adding powdered KOH (3.37 g, 60 mmol) to the mixture. An aliquot (0.1 cm$^3$) was withdrawn every 2 min and diluted with acetone (5 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.

For the crown ether catalyzed reaction, 18-crown-6 (0.2 g, 0.76 mmol) was used as catalyst. The reaction was carried out under the same conditions as above and was followed in a similar manner.

**Competitive Addition of Dichlorocarbene to 5 and 6.** A mixture of **5** (0.68 g, 0.5 mmol), **6** (1.10 g, 0.5 mmol), **1** (0.50 g, 0.27 mmol), $CHCl_3$ (7.16, 60 mmol), and nonane (1 cm$^3$) in $CH_2Cl_2$ (5 cm$^3$) was stirred at 30 °C. The reaction was started by adding powdered KOH (3.37 g, 60 mmol) to the mixture. The reaction mixture was analyzed by the same procedure as above.

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