CHEMISTRY LETTERS, pp. 2167-2170, 1991.

Catalytic Ability of Octopus-Type Calixarene in the Formation of Esters from Alkyl Halides and Alkali Metal Carboxylates

Eisaku NOMURA, Hisaji TANIGUCHI,* Kouichi KAWAGUCHI,† and Yoshio OTSUJI††

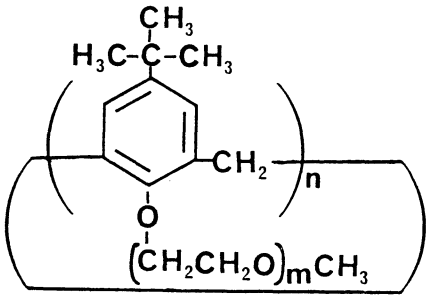
Industrial Technology Center of Wakayama Prefecture, 60 Ogura, Wakayama 649-62

†Mikiriken Industrial Co., Ltd, 13-1 Sakaedani, Wakayama 640

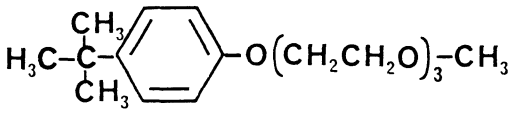
††Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591

5,11,17,23,29,35-Hexa-p-tert-butyl-37,38,39,40,41,42-hexakis(3,6,9-trioxadecyloxy)calix[6]arene efficiently catalyzes the reaction of alkyl halides with alkali metal carboxylates to produce esters.

Calixarenes are macrocyclic oligomers that can be obtained by the base-catalyzed condensation of p-substituted phenols with formaldehyde, and various types of their functionalized derivatives have been synthesized.[1,2] An important feature of this class of compounds is their cylindrical molecular architecture. This structural feature is now finding wide applications in various fields of chemistry. For example, these compounds serve as a host of inclusion compounds,[3] selective complexing agents for metal ions,[4] and catalysts for chemical reactions.[5] It has been shown that the hexakis(2,5,8-trioxadecanyl)derivative of p-t-butylcalix[6]arene (**1**),[6] which we call an "octopus-type calixarene", forms complexes with alkali metal cations. This calixarene has also a cylindrical molecular architecture. We have, therefore, anticipated that



1 n=6 m=3

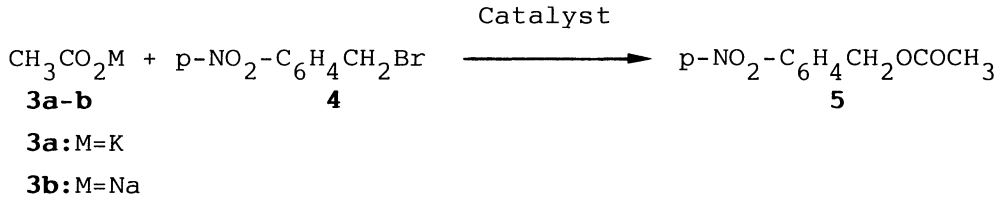


2

this molecule may serve as catalyst for organic reactions. 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.[7] We now report that **1** also serves as an effective catalyst for the condensation of alkali metal carboxylates with alkyl halides to form esters.

The catalytic abilities of **1** for the reaction of alkali metal acetates (**3**) with p-nitrobenzyl bromide (**4**) were first studied, in comparison with those of benzyltrimethylammonium chloride, which is a typical phase-transfer catalyst, and also of 18-crown-6. The reactions were carried out under solid-liquid phase-transfer conditions. A typical procedure was as follows: A mixture of **3a** (5.6 mmol), **4** (5.0 mmol), and a catalytic amount (0.132 mmol) of **1** in CH_2Cl_2 containing a small quantity of water was stirred at 40 °C for 24 h. The resulting mixture was poured onto a Büchner funnel paved with silica gel (10 g) and washed with CH_2Cl_2 (100 cm^3). The calixarene **1** was absorbed by silica gel in the funnel. Evaporation of the filtrate left a mixture of p-nitrobenzyl acetate (**5**) and the unreacted **4**. These two compounds were separated by chromatography on silica gel with hexane-benzene (1:1) to give **5** in its pure form. This reaction was studied under various conditions. The results are summarized in Table 1.

The yield of **5** was determined by TLC analyses of the reaction mixtures. In every case, the calixarene **1** could be recovered from the silica gel mass in the Büchner funnel by extracting with ethanol. The catalytic activity of the recovered calixarene was essentially the same as that of the freshly prepared one.



The catalytic ability of 1-(p-t-butylphenyl)-1,4,7,10-tetraoxaundecane (**2**), a monomer model of **1**, for the same esterification reaction was also examined under the similar conditions. The results are also given in Table 1.

The catalytic ability of **1** strongly depended on the water content in CH_2Cl_2 and alkali metal ions. In the case of **3a**, the yield of **5** reached a maximum value (≈100%) when the water content was 0.0398% and decreased with

Table 1. Reaction of potassium acetate with p-nitrobenzyl bromide[a)]

CH_3COOM	Catalyst	Molar ratio **4**/Catalyst	Solvent	Water content/wt %[b)]	Reaction time/h	Yield of **5**/%
3a	none	--	CH_2Cl_2[c)]	0.0846	24	trace
3a	**1**	38	CH_2Cl_2[d)]	0.0193	24	72
3a	**1**	38	CH_2Cl_2[e)]	0.0398	24	100
3a	**1**	38	CH_2Cl_2-H_2O(100:1)[f)]		24	38
3a	**1**	38	CH_2Cl_2-H_2O(20:1)[f)]		24	27
3a	**2**	6	CH_2Cl_2[c)]	0.0846	6	trace
3a	$PhCH_2(Me)_3N^+Cl^-$	2.3	CH_2Cl_2[c)]	0.0846	24	94
3a	18-Crown-6	4.4	CH_2Cl_2[c)]	0.0846	6	99
3b	**1**	38	CH_2Cl_2[e)]	0.0398	24	6.1
3b	**1**	38	CH_2Cl_2-H_2O(50:1)[f)]		24	12
3b	**1**	38	CH_2Cl_2-H_2O(20:1)[f)]		24	7.7

a) Reaction conditions: Solvent, 10 cm^3; temp, 40 °C; b) The water content in the solvent was determined by the Karl-Fischer method before use; c) Garanteed reagent grade solvent; d) CH_2Cl_2 was dried over $CaCl_2$ for one week and then over molecular sieves 4A; e) CH_2Cl_2 was dried over molecular sieves 4A; f) Volume ratio.

increasing the water content. Under the best conditions, the catalytic ability of **1** was comparable to those of benzyltrimethylammonium chloride and 18-crown-6. Compound **2** exhibited no catalytic activity. In the case of sodium acetate (**3b**), the reaction occurred inefficiently and the yield of **5** significantly decreased (6.1%). This may be attributable in part to the extractability of metal ions by **1**: the extractability of K^+ by **1** is much larger than that of Na^+.[6)]

Crown ethers catalyze the reaction of benzyl halides with potassium cyanide. It has been shown that in this reaction, the addition of a minute quantity of water causes a dramatic increase in the reaction rate.[8)] Although the mechanism is unclear at present, it is of interest that the efficiency of our reaction is also remarkably affected by the water content in solvent.

We also found that the esterification of potassium benzoate and potassium 3-(4-hydroxy-3-methoxyphenyl)-2-propenoate (potassium ferulate) with alkyl halides was catalyzed by **1**. For example, the reaction of potassium benzoate with **4** in CH_2Cl_2-H_2O (20:1, v/v) in the presence of a

catalytic amount of **1** at 40 °C for 20 h gave p-nitrobenzyl benzoate in 84% yield. Under the similar conditions, p-nitrobenzyl ferulate was obtained in 88% yield from potassium ferulate and **4**. Aromatic halides such as 4-chloronitrobenzene did not react with potassium benzoate under the similar conditions.

References

1) C. D. Gutsche, "Calixarenes, Monographs in Supramolecular Chemistry," ed by J. F. Stoddart, the Royal Society of Chemistry, Cambridge(1989), Vol. 1.
2) E. Nomura, H. Taniguchi, and S. Tamura, Chem. Lett., 1989, 1125; Y. Morita, T. Agawa, Y. Kai, N. Kanehisa, N. Kasai, E. Nomura, and H. Taniguchi, Chem. Lett., 1989, 1349; S. Shinkai, K. Araki, M. Kubota, T. Arimura, and T. Matsuda, J. Org. Chem., 56, 295(1991); S. Shinkai, K. Araki, J. Shibata, D. Tsugawa, and O. Manabe, J. Chem. Soc., Perkin Trans. 1, 1990, 3333; S. Shinkai, T. Arimura, K. Araki, and H. Kawabata, ibid., 1989, 2039; S. Shinkai, K,Araki, and O. Manabe, J. Am. Chem. Soc., 110, 7214(1988); T. Arimura, T. Nagasaki, S. Shinkai, and T. Matsuda, J. Org. Chem., 54, 3776(1989).
3) T. Komoto, I. Ando, Y. Nakamoto, and S. Ishida, J. Chem. Soc., Chem. Commun., 1988, 135.
4) S. Shinkai, H. Koreishi, K. Ueda, T. Arimura, and O. Manabe, J. Am. Chem. Soc., 109, 6371(1987).
5) S. Shinkai, S. Mori, H. Koreishi, T. Tshubaki, and O. Manabe, J. Am. Chem. Soc., 108, 2409(1986).
6) H. Funada, Y. Nakamoto, and S. Ishida, Polymer Preprints, Japan, 34, 368(1985).
7) H. Taniguchi and E. Nomura, Chem. Lett., 1988, 1773.
8) C. L. Liotta, E. M. Burgess, C. C. Ray, E. D. Black, and B. E. Fair, "Phase-Transfer Catalysis - New Chemistry, Catalysts, and Applications," ed by C. M. Starks, American Chemical Society, Washington, DC(1987), Chap.3.

(Received August 29, 1991)