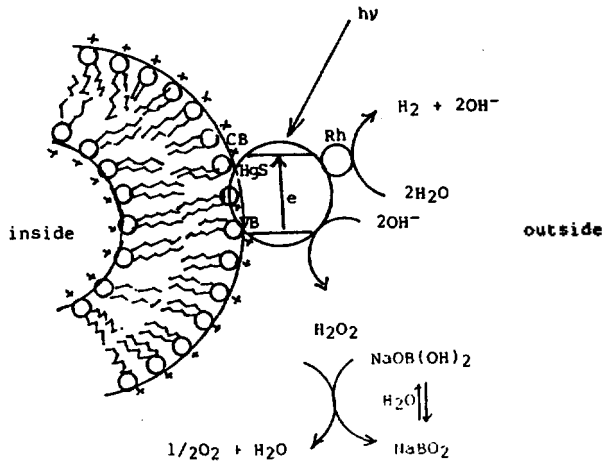
Table 1. Amount of H_2 and O_2 Produced in HgS Colloid System with Rh and Sodium Metaborate

Irradiation time (min)	H_2 (1×10^{-7} mole)		O_2 (1×10^{-7} mole)	
	1st run	2nd run*	1st run	2nd run*
30	0.92	1.78	0	0
50	2.26		0.79	
70	2.98		0.70	
90	4.20	2.74	1.12	0.90
110	4.66		0.91	
130	4.90		2.41	
150	5.20	3.45	1.34	1.76

*After 150 min irradiation.



Scheme 1. Generation of hydrogen and oxygen from water using vesicle-stabilized HgS colloid with Rh particles, and $NaBO_2$. VB: valence band, CB: conduction band.

gen (0.5 ml/l·soln) was generated for 150 min irradiation. The vesicle solution degassed after 150 min irradiation produced hydrogen and oxygen again. Even though hydrogen generation is somewhat higher than oxygen in the first rnn, one volume of hydrogen and half volume of oxygen were produced in the second run.

No hydrogen and oxygen productions were observed without illumination. The following scheme is drawn not because we have firm conviction that it is entirely correct, but rather because it affords a rationale for the process (see Scheme 1). Light absorption leads to the promotion of an electron from the valence to the conduction band of HgS to given e^-h^+ pair[15]. Water is reduced to given hydrogen and hydroxide anion on Rh catalyst holding negative charge that is injected from the conduction band of HgS[5,9-11]. The hydroxide anion is oxidized to give hydroxyl radical[16] which in turn produces then hydrogen peroxide on electron hole of the HgS semiconductor. Oxygen probably is generated by reacting hydrogen peroxide and sodium borate which is equilibrated with sodium metaborate[17]. It is significant that hydrogen peroxide has been detected with ferrous chloride and potassium manganate solution upon irradiation of the vesicle systems. We are currently exploring the optimum conditions for the water photolysis and will report on them in due course.

Acknowledgement. We acknowledge the financial support of this work by the Ministry of Science and Technology, Korea.

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Functionalization of *p*-1,3-Diallylcalix[4]arene

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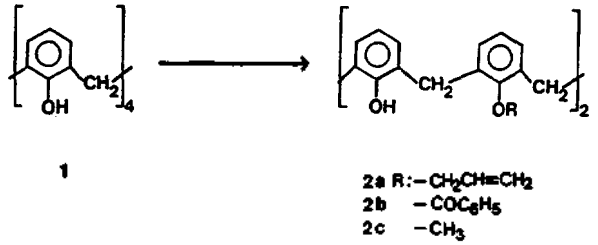
Received November 30, 1992

Host-guest or biomimetic chemistry[1] comprises a variety of types of investigations which attempt the *in vitro* simulation of processes that occur *in vivo*. Particularly interesting among these are reactions involving enzymes, and an important and expanding area of current investigation deals with compounds that have been called "enzyme models". Functionalization is essential to the enzyme model studies of calixarene compounds[2]. Functionalization can be carried out both

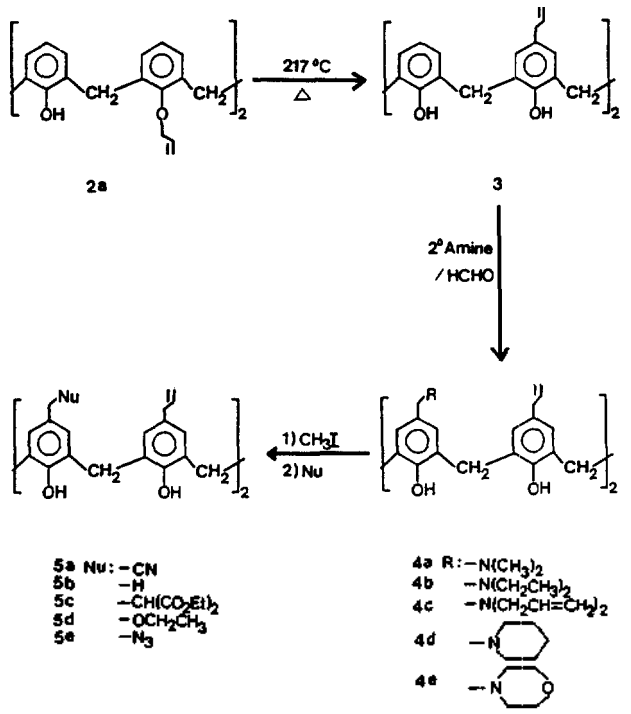


Scheme 1.

at the lower rim and the upper rim of calix[4]arene moieties. At the lower rim four hydroxyl groups can be manipulated as ester and ether groups, which often fixed calix[4]-arene in a cone conformation, giving sodium cation selective binding ligands[3]. At the upper rim the empty four para positions of the phenols of the calix[4]arene can be functionalized as a variety aromatic electrophilic substitution reactions such as nitration[4], chloromethylation[5], and aminomethylation[6] and also Claisen Rearrangement[7] reaction can provide the various functionalized calix[4]arenes.

Most calixarenes so obtained are symmetrically substituted. Besides the stepwise synthesis[8], less symmetrical calixarenes have been synthesized by the direct condensation[9] of two different phenolic units. Recently Reinhoudt[10] developed the very useful methods for the preparation of the less symmetrical calix[4]arene based on the selective dialkylation followed by the Claisen Rearrangement and ozonolysis reaction. To extend the dialkylation techniques for the selective functionalization we combine the Claisen Rearrangement reaction and aminomethylation of the diallylated calix[4]-arene (**2a**). Those reactions provide the ABAB type (where A and B symbolized two different phenolic units) calix[4]-arene which can be further functionalized as a separate reaction sequence, that is, one quinone methide route for the aminomethyl groups and the other ozonolysis of the allyl double bonds. In the present study aminomethylation and quinone methide reactions of the diallylated calix[4]arene (**2a**) are investigated.

Lower rim functionalization can be achieved by aroylation and alkylation of calixarene **1** (Scheme 1). Aroylation[11] of **1** with two equivalent of benzoyl chloride in pyridine at 0℃ yields a dibenzoylate calix[4]arene **2b**. But the following aminomethylation[6] (Mannich reaction) of **2b** with the dimethyl amine and formaldehyde which can functionalize the upper rim did not occur even at 140℃. Alkylation of[10] **1** with allyl bromide in the presence of K_2CO_3 yields a diallylate calix[4]arene **2a** which was tried to aminomethylation with a secondary amine and formaldehyde even at the very vigorous conditions but only to recover the unreacted starting material **2a**. But 1,3-*p*-diallylcalix[4]arene **3** prepared by the Claisen Rearrangement[7] of **2a** reacts with the various secondary amines such as dimethyl amine, diethyl amine, diallyl amine, piperidine and morphorine in the presence of formaldehyde to yield a 70-90% *p*-aminomethylcalix[4]-arene (Mannich bases **4a-4e**) even at the room temperature (Scheme 2). Though Reinhoudt[10] succeeded the Mannich reaction with the O-dimethylated calix[4]arene **2c** with excess of dimethyl amine and formaldehyde with reflux in dioxane/H_2O for 3 days, **2b** and **2c** which has two free OH and two large substituents on the lower rim of calix[4]arene



Scheme 2.

did not react with secondary amine and formaldehyde under the same reaction conditions applied by Reinhoudt. On the other hand calixarene **3** which has no substituents on the hydroxy groups proceeds the Mannich reaction even at the room temperature like calixarene **1**. This indicates that the substituents larger than methyl groups on the lower rim of the calix[4]arene prevent the Mannich reaction of the calix-[4]arene. This phenomena might be explained by the acidities[12] of phenols, the phenols of **1** and **3** are more acidic than **2a** and **2b**, and also the steric hindrance of the substituents, benzoyl and allyl groups are larger than hydrogen and methyl groups. The Mannich bases **4a** can be identified by the ^{1}H-NMR spectrum; two singlet at 7.0 and 6.8 ppm in equal intensity for the aromatic protons and two multiplet at 5.5-6.1, 5.0-5.2, and a doublet at 3.0 ppm for the allyl protons and a broad singlet at 3.7 ppm for the bridged methylene protons and a singlet at 3.0 ppm for methylene protons between aromatic and amine, and a singlet at 2.4 ppm for the *N*-methyl protons, indicating that Mannich reaction did occur on the 1,3-para position of calix[4]arene. Other Mannich products such as **4b**, **4c**, **4d**, and **4e** show also similar pattern of ^{1}H-NMR spectra[13].

Those reactions provide the various ABAB type calix[4]-arene which can be further functionalized as a separate reaction sequence. One of the principal synthetic applications of Mannich bases involves their conversion to the corresponding quaternary ammonium salt followed by treatment with a nucleophile to effect an S_N2 displacement[6] of the amino moiety. The Mannich bases (**4a**) were treated with methyl iodide to produce the quaternary ammonium salt, which were not isolated but allowed to react directly a nucleophile, yielding the substitution products (**5a-5e**). Those for the successfully applied nucleophiles[14] are cyano, hydride, ethyl malonate, ethoxy, and azide. **5a** and **5e** can be reduce to the corresponding aminocalixarenes and **5c** be hydrolyzed

followed by decarboxylation to yield the acid calixarene.

The typical procedure for the synthesis of **5** is as follows; To a solution containing 0.92 g (1.5 mmole) of **4a** in 20 ml of DMSO was slowly added 0.47 g (3.3 mmole) of methyl iodide. After the reaction mixture was stirred for 30 min at the room temperature, 0.4 g (4 mmole) of NaCN was added and the mixture heated for 4 h at 80℃ in an atmosphere of N_2. The solution was cooled, treated with 50 ml of ice water, acidified with 2 N HCl, filtered, and air dried. The crude product was purified by column chromatography (eluent, 1 : 1 $CHCl_3$-hexane) to yield 0.50 g (57%) of colorless powder **5a**. ^{1}H-NMR ($CDCl_3$) δ 9.2 ppm (br s, 4, OH), 6.9 and 6.8 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.5 (s, 4, $ArCH_2CN$), 3.2 (d, 4, $ArCH_2C=$). IR of **5a** (KBr) 2250 cm^{-1} (-CN, weak). Spectroscopic data of **5b**, **5c**, **5d**, **5e** are listed on the reference[15].

Acknowledgement. This paper was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1992.

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13. ^{1}H-NMR of **4b** ($CDCl_3$) δ 8.9 (s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.7-5.0 (m, 4, $=CH_2$), 3.5-4.2 (br s, 8, $ArCH_2Ar$), 3.3 (s, 4, $ArCH_2N$-), 3.1 (d, 4, $ArCH_2C=$), 2.4 (q, 8, $-NCH_2$-), 1.0 (t, 12, $=CH_3$). ^{1}H-NMR of **4c** ($CDCl_3$) δ 8.9 (br s, 4, OH) 6.9 and 6.7 (two s, 8, ArH), 5.4-6.0 (m, 6, -CH=), 4.8-5.2 (m, 12, $=CH_2$), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.3 (s, 4, $ArCH_2N$-), 2.9-3.2 (m, 12, $ArCH_2N$- and $-NCH_2C=$). ^{1}H-NMR of **4d** ($CDCl_3$) δ 7.2 (br s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.3-4.2 (br s, $ArCH_2$ Ar), 3.3 (s, 4, $ArCH_2N$-), 3.2 (d, 4, $ArCH_2C=$), 2.3 (m, 8, $-NCH_2$-), 1.5 (m, 12, $-CH_2CH_2CH_2$-). ^{1}H-NMR of **4e** ($CDCl_3$) δ 9.3 (s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.5-4.2 (br s, 8, $ArCH_2Ar$), 3.7-3.8 (m, 8, $-CH_2OCH_2$-), 3.3 (s, 4, $ArCH_2$ N-), 3.2 (d, 4, $ArCH_2C=$), 2.3-2.6 (m, 8, $-CH_2NCH_2$-).
14. Nucleophiles for **5a**, **5b**, **5c**, **5d**, and **5e** are NaCN, $NaBH_4$, $NaCH(CO_2Et)$ prepared from $CH_2(CO_2Et)$ and Na, NaOEt, and NaN_3.
15. ^{1}H-NMR of **5b** ($CDCl_3$) δ 10.0 (s, 4, OH), 6.7 (s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.2 (d, 4, $=CH_2$), 2.1 (s, 6, $-CH_3$). ^{1}H-NMR of **5c** ($CDCl_3$) δ 9.9 (s, 4, OH), 6.9 and 6.8 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 3.9 (q, 8, $-OCH_2$-), 3.3-4.0 (br s, 8, $ArCH_2Ar$), 2.9-3.6 (m, 10, $ArCH_2C=$ and $ArCH_2CH$-), 0.9 (t, 12, $-CH_3$). IR of **5c** (KBr) 1720 cm^{-1} (-COO-). ^{1}H-NMR of **5d** ($CDCl_3$) δ 6.9 (br s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, $=CH_2$), 4.2 (s, 4, $ArCH_2O$-), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.5 (q, 4, $-OCH_2$-), 3.2 (d, 4, $=CH_2$), 1.2 (t, 6, $-CH_3$). ^{1}H-NMR of **5e** ($CDCl_3$) δ 8.7 (br s, 4, OH), 6.9 and 6.7 (two s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.0 (s, 4, $ArCH_2N_3$), 3.3-4.2 (br s, 8, $ArCH_2Ar$), 3.2 (d, 4, $ArCH_2C=$). IR of **5e** (KBr) 2100 cm^{-1} ($-N_3$).

Polymerization of Phenylacetylene by Molybdenum Pentachloride/2-Propyn-1-ol Catalyst Systems

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Received December 15, 1992

The $MoCl_5$-catalyzed polymerization of some acetylene derivatives such as phenylacetylene,[1,2] 2-hexyne,[3] 2-ethynylthiophene,[4] 1-chloro-2-thienylacetylene,[5] *etc.* have been carried out. In these cases, the cocatalyst (as activator) was mainly restricted to some cases such as organotin- and organoaluminum compounds.[1,3-5] Recently, we found the very active catalytic activity of $MoCl_5$ for the polymerization of $HC{\equiv}CCH_2OH$ to give a quantitative yield of polymer.[6,7] To our knowledge, molybdenum alkoxides such as $Mo(OEt)_5/Al_2O_3/SiO_2$,[8] $Mo(OEt)_2Cl_2/Et_3B$,[9] $Mo(OEt)_2Cl_3/Me_2Al_2Cl_3$,[10] and $Mo(O\text{-}t\text{-}Bu)_2(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)$[11,12] were used as catalyst systems for the olefin metathesis reaction and the metathesis polymerization of cycloolefins.

We now report a cocatalytic effect of $HC{\equiv}CCH_2OH$ for the polymerization of acetylenic monomer, especially phenylacetylene. Unless otherwise specified, the polymerizations