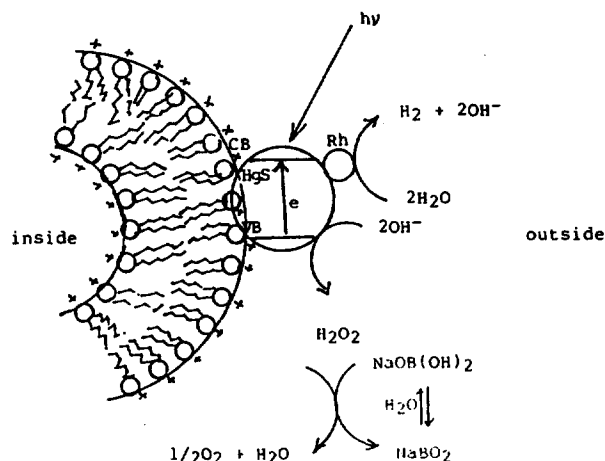


Table 1. Amount of H₂ and O₂ Produced in HgS Colloid System with Rh and Sodium Metaborate

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 NaBO₂. 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 run, 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 give an e⁻h⁺ pair¹⁵. Water is reduced to give hydrogen and hydroxide anion on Rh catalyst holding negative charge that is injected from the conduction band of HgS⁹⁻¹¹. The hydroxide anion is oxidized to give hydroxyl radical¹⁶ 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 metaborate¹⁷. 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.

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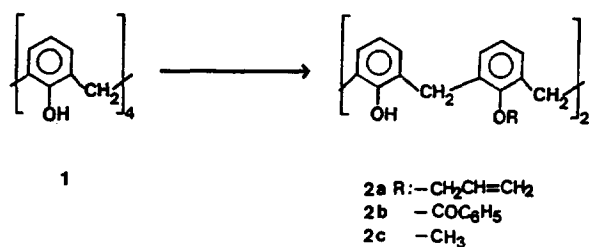
Functionalization of p-1,3-Diallylcalix[4]arene

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Host-guest or biomimetic chemistry¹ 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 compounds². Functionalization can be carried out both

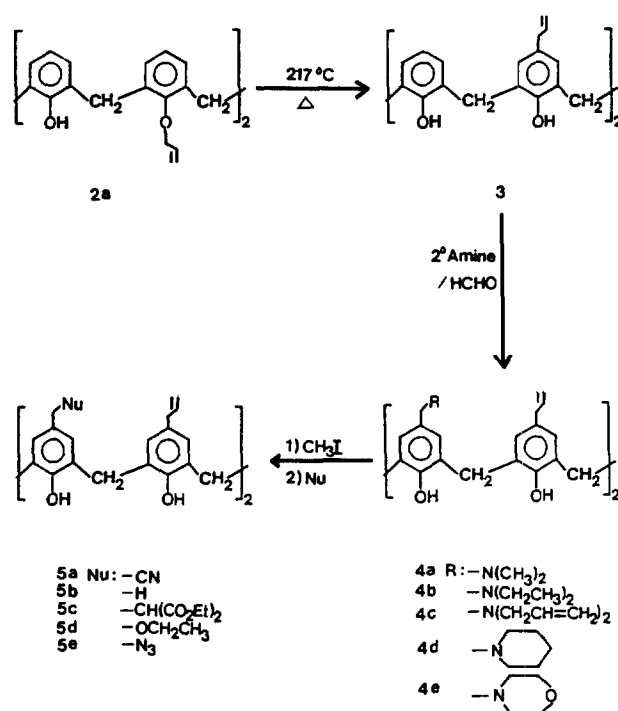


Scheme 1.

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 ligands³. 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 nitration⁴, chloromethylation⁵, and aminomethylation⁶ and also Claisen Rearrangement⁷ reaction can provide the various functionalized calix[4]arenes.

Most calixarenes so obtained are symmetrically substituted. Besides the stepwise synthesis⁸, less symmetrical calixarenes have been synthesized by the direct condensation⁹ of two different phenolic units. Recently Reinhoudt¹⁰ 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 arylation and alkylation of calixarene 1 (Scheme 1). Arylation¹¹ of 1 with two equivalent of benzoyl chloride in pyridine at 0°C yields a dibenzoylate calix[4]arene 2b. But the following aminomethylation⁶ (Mannich reaction) of 2b with the dimethyl amine and formaldehyde which can functionalize the upper rim did not occur even at 140°C. Alkylation of¹⁰ 1 with allyl bromide in the presence of K₂CO₃ 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 Rearrangement⁷ of 2a reacts with the various secondary amines such as dimethyl amine, diethyl amine, diallyl amine, piperidine and morpholine 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 Reinhoudt¹⁰ succeeded the Mannich reaction with the *O*-dimethylated calix[4]arene 2c with excess of dimethyl amine and formaldehyde with reflux in dioxane/H₂O 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 acidities¹² 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 ¹H-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 ¹H-NMR spectra¹³.

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 displacement⁶ 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 nucleophiles¹⁴ 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°C in an atmosphere of N₂. 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 CHCl₃-hexane) to yield 0.50 g (57%) of colorless powder **5a**. ¹H-NMR (CDCl₃) 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, =CH₂), 3.3-4.2 (br s, 8, ArCH₂Ar), 3.5 (s, 4, ArCH₂CN), 3.2 (d, 4, ArCH₂C=). IR of **5a** (KBr) 2250 cm⁻¹ (-CN, weak). Spectroscopic data of **5b**, **5c**, **5d**, **5e** are listed on the reference¹⁵.

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13. ¹H-NMR of **4b** (CDCl₃) 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, =CH₂), 3.5-4.2 (br s, 8, ArCH₂Ar), 3.3 (s, 4, ArCH₂N-), 3.1 (d, 4, ArCH₂C=), 2.4 (q, 8, -NCH₂-), 1.0 (t, 12, =CH₃). ¹H-NMR of **4c** (CDCl₃) 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, =CH₂), 3.3-4.2 (br s, 8, ArCH₂Ar), 3.3 (s, 4, ArCH₂N-), 2.9-3.2 (m, 12, ArCH₂N- and -NCH₂C=). ¹H-NMR of **4d** (CDCl₃) 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, =CH₂), 3.3-4.2 (br s, ArCH₂Ar), 3.3 (s, 4, ArCH₂N-), 3.2 (d, 4, ArCH₂C=), 2.3 (m, 8, -NCH₂-), 1.5 (m, 12, -CH₂CH₂CH₂-). ¹H-NMR of **4e** (CDCl₃) 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, =CH₂), 3.5-4.2 (br s, 8, ArCH₂Ar), 3.7-3.8 (m, 8, -CH₂OCH₂-), 3.3 (s, 4, ArCH₂N-), 3.2 (d, 4, ArCH₂C=), 2.3-2.6 (m, 8, -CH₂NCH₂-).
14. Nucleophiles for **5a**, **5b**, **5c**, **5d**, and **5e** are NaCN, NaBH₄, NaCH(CO₂Et) prepared from CH₂(CO₂Et) and Na, NaOEt, and NaN₃.
15. ¹H-NMR of **5b** (CDCl₃) δ 10.0 (s, 4, OH), 6.7 (s, 8, ArH), 5.5-6.0 (m, 2, -CH=), 4.8-5.2 (m, 4, =CH₂), 3.3-4.2 (br s, 8, ArCH₂Ar), 3.2 (d, 4, =CH₂), 2.1 (s, 6, -CH₃). ¹H-NMR of **5c** (CDCl₃) 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, =CH₂), 3.9 (q, 8, -OCH₂-), 3.3-4.0 (br s, 8, ArCH₂Ar), 2.9-3.6 (m, 10, ArCH₂C= and ArCH₂CH-), 0.9 (t, 12, -CH₃). IR of **5c** (KBr) 1720 cm⁻¹ (-COO-). ¹H-NMR of **5d** (CDCl₃) 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, =CH₂), 4.2 (s, 4, ArCH₂O-), 3.3-4.2 (br s, 8, ArCH₂Ar), 3.5 (q, 4, -OCH₂-), 3.2 (d, 4, =CH₂), 1.2 (t, 6, -CH₃). ¹H-NMR of **5e** (CDCl₃) 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, ArCH₂N₃), 3.3-4.2 (br s, 8, ArCH₂Ar), 3.2 (d, 4, ArCH₂C=). IR of **5e** (KBr) 2100 cm⁻¹ (-N₃).

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

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The MoCl₅-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 MoCl₅ for the polymerization of HC≡CCH₂OH to give a quantitative yield of polymer.^{6,7} To our knowledge, molybdenum alkoxides such as Mo(OEt)₅/Al₂O₃/SiO₂,⁸ Mo(OEt)₂Cl₂/Et₃B,⁹ Mo(OEt)₂Cl₃/Me₂AlCl₃,¹⁰ and Mo(O-t-Bu)₂(CH-t-Bu)(N-2,6-C₆H₃-i-Pr₂)^{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≡CCH₂OH for the polymerization of acetylenic monomer, especially phenylacetylene. Unless otherwise specified, the polymerizations