

per-Hydroxylated Prism[*n*]arenes: Supramolecularly Assisted Demethylation of Methoxy-Prism[5]arene

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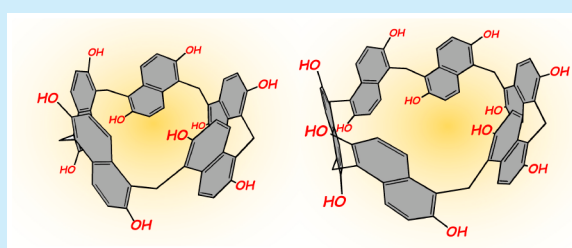
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ABSTRACT: Methoxy-prism[5]arene $\text{PrS}[5]^{\text{Me}}$ is demethylated by a supramolecularly assisted reaction. In the presence of a tetramethylammonium cation, $\text{PrS}[5]^{\text{Me}}$ is demethylated by BBr_3 in high yield, while in its absence a 55/40 mixture of $\text{PrS}[5]^{\text{OH}}/\text{PrS}[6]^{\text{OH}}$ is formed. The dealkylation of prismarenes, such as $\text{PrS}[6]^{\text{R}}$ ($\text{R} = \text{Et}, n\text{Pr}$) and *c*- $\text{PrS}[5]^{\text{Me}}$, can be easily obtained in high yields in the presence of BBr_3 .



In the past few years, growing interest has been directed toward the synthesis of novel macrocycles^{1a} starting with naphthalene^{1b–e} or anthracene² monomers. Oxatubarenes,³ naphcages,⁴ zorbarenes,⁵ naphthotubes,⁶ calix[2]naphth[2]-arenes,⁷ and prismarenes^{8–10} are naphthalene-based emerging macrocycles, which are of great interest in supramolecular chemistry due to their peculiar structural properties and π -rich deep cavities. Recently, our group reported the prism[*n*]arenes^{8–10} ($\text{PrS}[n]^{\text{R}}$, $n = 5$ and 6 , $\text{R} = \text{Me}, \text{Et}, n\text{Pr}$, Figure 1), a

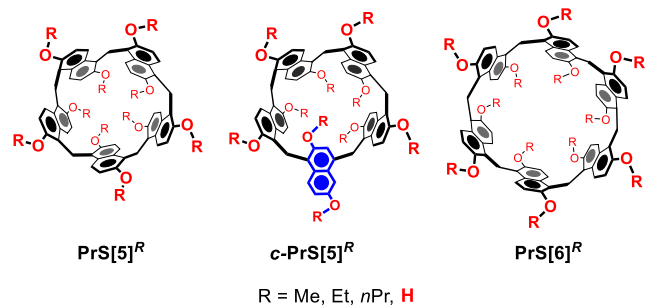


Figure 1. Prism[*n*]arene macrocycles.

novel class of macrocyclic hosts constituted by 1,5-methylene-bridged naphthalene units, obtained by one-pot condensation of 2,6-dimethoxynaphthalene and paraformaldehyde in the presence of TFA.¹¹ Very recently¹² the saucer[*n*]arene macrocycles were reported by the one-pot condensation of 2,7-dimethoxynaphthalene and paraformaldehyde.¹²

Phenol and resorcinol-based macrocycles, such as calixarenes,¹³ resorcinarenes,¹⁴ and pillararenes,¹⁵ have become highly studied and attractive synthetic hosts in supramolecular chemistry because of their easy functionalization. In particular, the procedure of functionalization of pillararenes starts

primarily by the dealkylation of alkoxy-substituted ($-\text{OR}$) aromatic units.¹⁶ In fact, *per*-hydroxylated macrocycles are considered as useful synthetic precursors to obtain chemically modified hosts with novel supramolecular properties with respect to the parent macrocycles.^{16,17} Based on these considerations, and with the aim to expand the potentialities of prismarene macrocycles as supramolecular hosts, we decided to investigate a convenient procedure for the synthesis of *per*-hydroxylated prism[*n*]arenes $\text{PrS}[n]^{\text{OH}}$ ($n = 5$ and 6 , Figure 1).

Initially, we investigated the demethylation of $\text{PrS}[5]^{\text{Me}}$ under the conditions previously reported¹⁵ for methoxypillar[5]arene. Thus, $\text{PrS}[5]^{\text{Me}}$ was treated with BBr_3 in dry CH_2Cl_2 at 25°C for 12 h. The FT ICR MALDI mass spectrum of the crude product of this reaction unambiguously revealed the presence of a mixture of *per*-hydroxylated $\text{PrS}[5]^{\text{OH}}$ and $\text{PrS}[6]^{\text{OH}}$ derivatives. $\text{PrS}[6]^{\text{OH}}$ was separated in 40% yield from $\text{PrS}[5]^{\text{OH}}$ (55%) by precipitation from ethyl acetate.

With this result in hand, we attempted the demethylation of $\text{PrS}[5]^{\text{Me}}$ by lowering the reaction temperature. Thus, $\text{PrS}[5]^{\text{Me}}$ was reacted with BBr_3 under the conditions reported in Scheme 1, at -78°C for 1 h and 0°C for 3 h, but analogously, a mixture of *per*-hydroxylated $\text{PrS}[5]^{\text{OH}}$ (55%) and $\text{PrS}[6]^{\text{OH}}$ (40%) derivatives was obtained. Chromatographic analysis and HR FT ICR mass spectrometry evidenced that, during the demethylation of $\text{PrS}[5]^{\text{Me}}$ in the presence of BBr_3 , the hexamer $\text{PrS}[6]^{\text{Me}}$ started to appear after 15 min through the formation of linear oligomers (Figure 2), and

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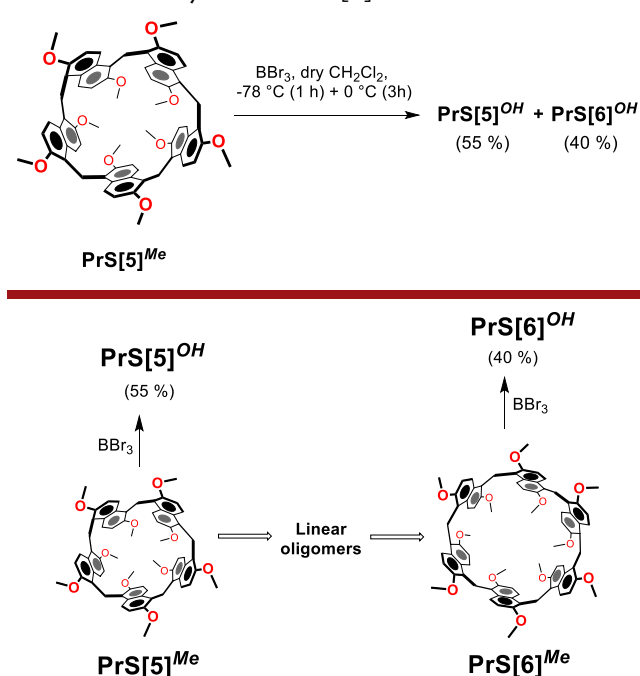
Scheme 1. Dealkylation of PrS[5]^{Me}

Figure 2. Proposed mechanism for the conversion of PrS[5]^{Me} to PrS[6]^{Me} and their demethylation. Reaction conditions in Scheme 1: BBr₃, dry CH₂Cl₂, 1 h at −78 °C and 3 h at 0 °C.

successively the mixture of PrS[5]^{Me} and PrS[6]^{Me} was demethylated. This is not a surprising result for us; in fact, previously^{8,10} we reported examples of conversion processes between pentamer and hexamer, upon treatment with trifluoroacetic acid (TFA) at 70 °C in 1,2-dichloroethane (1,2-DCE) as solvent, in which the conversions occurred by an acid-catalyzed ring opening and macrocyclization mechanism.^{8,10} With the aim to study this conversion under the conditions of solvent and temperature reported in Scheme 1, PrS[5]^{Me} was treated in CH₂Cl₂ at −78 °C for 1 h at 0 °C and for 3 h in the presence of TFA. ¹H NMR analysis of the crude product revealed the presence of PrS[6]^{Me} and PrS[5]^{Me} in a 1:1 ratio (Figure S16).¹⁸ On the basis of these results, we can assume that, under the conditions reported in Scheme 1, PrS[5]^{Me} was first converted to PrS[6]^{Me} (Figure 2) and finally, the mixture of pentamer and hexamer was demethylated.¹⁹ In other words, the conversion of PrS[5]^{Me} to PrS[6]^{Me} is kinetically favored with respect to its dealkylation.¹⁹ To confirm the role of BBr₃ in promoting the interconversion in Figure 2, we observed that, in its absence, PrS[5]^{Me} was stable under the conditions of demethylation in Scheme 1.

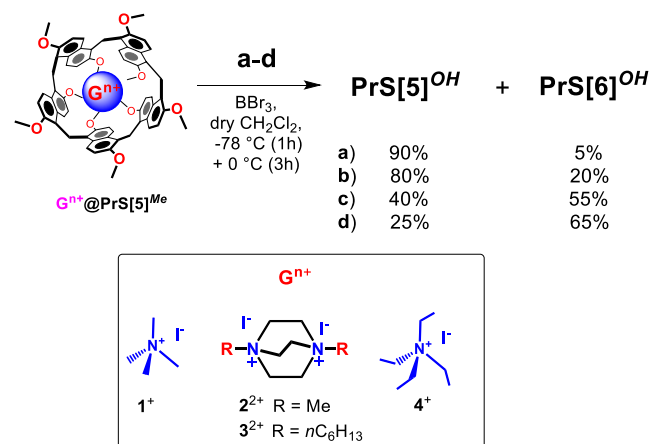
At this point we studied the stability of PrS[5]^{OH} under acid conditions. Interestingly, *per*-hydroxylated PrS[5]^{OH} was stable up to 24 h in the presence of TFA in 1,2-DCE as solvent (at 70 °C), while polymeric insoluble products were formed in the presence of BBr₃ in dichloromethane (1 h at −78 °C and 3 h at 0 °C). In both instances, no hint of hexamer PrS[6]^{OH} was detected in the reaction mixtures, and this result clearly indicated that the conversion of pentamer to hexamer in Figure 2 occurred in the presence of BBr₃, through the methylated macrocycle, while *per*-hydroxylated PrS[5]^{OH} did not convert to hexamer PrS[6]^{OH}.

As known,^{8,10} under acid equilibrium conditions the distribution of prismarene macrocycles (pentamer or hexamer) is influenced by the presence of ammonium guests: in the literature this process is named, in a general way, as thermodynamic template effect.²⁰

In detail, starting with 2,6-dimethoxynaphthalene and paraformaldehyde, in the presence of TFA in 1,2-DCE as solvent at 70 °C, *c*-PrS[5]^{Me} (Figure 1) was obtained in 40% yield (thermodynamic adduct), while its *D*₅-isomer PrS[5]^{Me} and hexamer PrS[6]^{Me} were isolated from the equilibrium mixture by adding as template 1⁺ and 4⁺, respectively.⁸ An analogous effect was observed by Chen and co-workers with saucerarenes; in fact, by adding 1,1-dimethylpiperidin-1-ium as the template, saucer[4]arene was selectively obtained.¹²

On this basis, we envisioned studying the demethylation of PrS[5]^{Me} in the presence of ⁿN(Me)₄ cation 1⁺.⁸ In particular, we speculated that the formation of the 1⁺@PrS[5]^{Me} complex can affect the PrS[5]^{Me}/PrS[6]^{Me} ratio and the successive demethylation with BBr₃.⁸ Thus, PrS[5]^{Me} was treated (Scheme 2) with BBr₃ in dry CH₂Cl₂ (1 h at −78 °C and 3

Scheme 2. Supramolecularly Assisted Dealkylation of PrS[5]^{Me} in the Presence of Template Agent 1⁺–4⁺ as Iodide Salts^a



^aReaction conditions: BBr₃, dry CH₂Cl₂, 1 h at −78 °C and 3 h at 0 °C: (a) 1⁺; (b) 2²⁺; (c) 3²⁺; (d) 4⁺.

h at 0 °C) in the presence of 1⁺ as iodide salt (1 equiv), and under these conditions PrS[5]^{OH} was selectively obtained in 90% yield. This result is particularly surprising; in fact, the presence of 1⁺ strongly improves the selectivity of the demethylation reaction of PrS[5]^{Me}. Probably the formation of 1⁺@PrS[5]^{Me} complex kinetically favors the demethylation of PrS[5]^{Me} with respect to its conversion to PrS[6]^{Me}. In fact, as previously reported by us,¹⁰ upon inclusion of the guest 1⁺, the PrS[5]^{Me} macrocycle adopts an open conformation, in which the methoxy groups are sterically more accessible with respect to the closed conformation¹⁰ of PrS[5]^{Me} in the free state (Figure S20). These results clearly indicated that the demethylation of PrS[5]^{Me} is supramolecularly driven by the tetramethylammonium guest, which forms the complex 1⁺@PrS[5]^{Me} that is easily demethylated.²¹

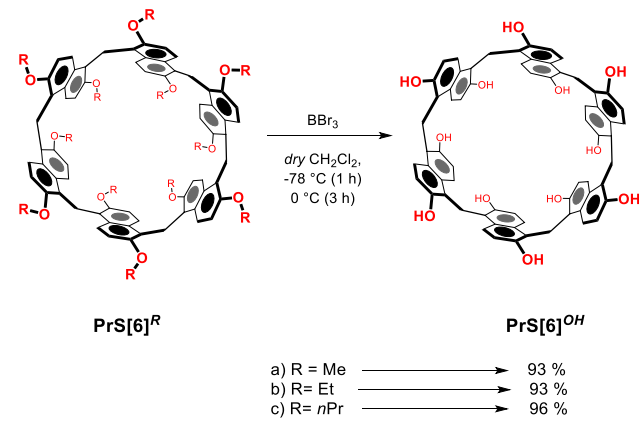
With these results in hand we attempted the demethylation of PrS[5]^{Me} in the presence of 1,4-dihexyl-DABCO 3²⁺, as iodide salt (Scheme 2). As previously reported,⁸ the 3²⁺@PrS[5]^{Me} complex shows an association constant value of 3.9 × 10⁷ M^{−1} which is significantly higher than that for 1⁺@

$\text{PrS}[5]^{Me}$ ($6.4 \times 10^4 \text{ M}^{-1}$). When $\text{PrS}[5]^{Me}$ was reacted with BBr_3 in dry CH_2Cl_2 (1 h at -78°C and 3 h at 0°C) in the presence of 3^{2+} as iodide salt (1 equiv), the hexamer $\text{PrS}[6]^{OH}$ was obtained in 55% yield, while the pentamer $\text{PrS}[5]^{OH}$ was obtained in 40% yield (Scheme 2). This result clearly indicates that in the presence of $3^{2+}@\text{PrS}[5]^{Me}$ complex the demethylation is kinetically underdog with respect to the conversion of $\text{PrS}[5]^{Me}$ to $\text{PrS}[6]^{Me}$, probably due to steric reasons. In fact, inspection of a $3^{2+}@\text{PrS}[5]^{Me}$ model (Figure S21) suggests that the two methoxy-rims are hindered by the presence of hexyl chains.⁸ To confirm this assumption, $\text{PrS}[5]^{OH}$ was again the favored product (80%, Scheme 2) when the demethylation was performed in the presence of 1,4-dimethyl-DABCO 2^{2+} bearing less encumbering methyl groups.

Among the ammonium guests so far explored for the endocavity complexation with prismarene hosts,^{8,10} tetraethylammonium 4^+ shows the higher $\text{PrS}[6]^{Me}/\text{PrS}[5]^{Me}$ selectivity ratio ($S = K_{2@6}/K_{2@5} = 2700/90 = 30$).⁸ For this reason, we studied the demethylation of $\text{PrS}[5]^{Me}$ in the presence of tetraethylammonium 4^+ (Scheme 2), which shows low affinity for $\text{PrS}[5]^{Me}$.⁸ When the demethylation reaction of $\text{PrS}[5]^{Me}$ was performed with BBr_3 in dry CH_2Cl_2 (Scheme 2) in the presence of 4^+ as iodide salt, $\text{PrS}[6]^{OH}$ was favored (65%) over $\text{PrS}[5]^{OH}$ (25%). Under these conditions (d in Scheme 2), initially the conversion of $\text{PrS}[5]^{Me}$ in $\text{PrS}[6]^{Me}$ was kinetically favored with respect to its demethylation. Then the $4^+@\text{PrS}[6]^{Me}$ complex was formed and quickly demethylated.

Considering these results, the question arises as to whether $\text{PrS}[6]^{Me}$ itself can be easily demethylated: in other words, does demethylation of $\text{PrS}[6]^{Me}$ lead to the formation of a mixture of $\text{PrS}[6]^{OH}/\text{PrS}[5]^{OH}$? To investigate this aspect, $\text{PrS}[6]^{Me}$ was reacted with BBr_3 in dry CH_2Cl_2 (Scheme 3, 1 h

Scheme 3. Dealkylation of $\text{PrS}[6]^R$



at -78°C and 3 h at 0°C), and $\text{PrS}[6]^{OH}$ was obtained in 93% yield. No hint of $\text{PrS}[5]^{OH}$ was detected in the reaction mixture, and this result suggests that no conversion of $\text{PrS}[6]^{Me}$ to $\text{PrS}[5]^{Me}$ occurs. In order to confirm this assumption, $\text{PrS}[6]^{Me}$ was treated with TFA under the usual conditions of solvent and temperature reported in Scheme 3. Thin layer chromatography and ^1H NMR analysis (Figure S18) clearly indicated the absence of $\text{PrS}[5]^{Me}$, while confused $c\text{-PrS}[5]^{Me}$ began to appear by prolonging the reaction time.²² In conclusion, in the presence of TFA in CH_2Cl_2 , $\text{PrS}[5]^{Me}$ is first converted to $\text{PrS}[6]^{Me}$ and, in the long-run, to $c\text{-PrS}[5]^{Me}$,⁸ while when starting with $\text{PrS}[6]^{Me}$ its slow

conversion to $c\text{-PrS}[5]^{Me}$ occurs (Figure S19), and no $\text{PrS}[5]^{Me}$ is formed. These results are in full accord with the data previously reported by us⁸ that indicated $\text{PrS}[6]^{Me}$ as a kinetic intermediate and $c\text{-PrS}[5]^{Me}$ as the thermodynamic macrocycle (Figure 1). Accordingly, when $c\text{-PrS}[5]^{Me}$ was demethylated in the presence of BBr_3 in CH_2Cl_2 , $c\text{-PrS}[5]^{OH}$ was formed in 93% yield and no conversion to other prismarenes was observed.

With these results in hand, we attempted the synthesis of *per*-hydroxylated prismarenes starting with ethoxy $\text{PrS}[n]^{Et}$ and propoxy $\text{PrS}[n]^{nPr}$ derivatives. As previously reported, $\text{PrS}[6]^{Et}$ and $\text{PrS}[6]^{nPr}$ are obtained in high yields,¹⁰ and could be very convenient to investigate a procedure of dealkylation starting with these derivatives. When $\text{PrS}[6]^{Et}$ and $\text{PrS}[6]^{nPr}$ were dealkylated in the presence of BBr_3 in CH_2Cl_2 , under the conditions reported in Scheme 3, *per*-hydroxylated $\text{PrS}[6]^{OH}$ was selectively obtained in 93% and 96% yield, respectively. The selectivity observed in the dealkylation reactions of $\text{PrS}[6]^{Et}$ and $\text{PrS}[6]^{nPr}$ in the presence of BBr_3 can be reasonably explained on the basis of their thermodynamic stability in solution under acid conditions.^{8,10} As previously shown,¹⁰ the crucial factor which determines the stability of ethoxy- and propoxy-prismarenes under acid conditions is the self-filling of their cavity by intramolecular effects of the alkyl chains.¹⁰ Consequently, in the presence of BBr_3 in CH_2Cl_2 , $\text{PrS}[6]^{Et}$ and $\text{PrS}[6]^{nPr}$ were efficiently dealkylated and no hint of other cyclooligomers was present in the reaction mixture.

Differently, when $\text{PrS}[5]^{Et}$ and $\text{PrS}[5]^{nPr}$ were treated with BBr_3 in CH_2Cl_2 , the hexamer $\text{PrS}[6]^{OH}$ was obtained in very high yield (90%), while $\text{PrS}[5]^{OH}$ was detected in very low yield (<10%), to confirm that, under acid conditions in the presence of BBr_3 , $\text{PrS}[5]^{Et}$ and $\text{PrS}[5]^{nPr}$ convert to the more stable hexamers. Clearly, under these conditions the conversion of pentamers $\text{PrS}[5]^{Et}$ and $\text{PrS}[5]^{nPr}$ to their respective hexamers is kinetically favored with respect to dealkylation of ethyl and propyl chains.

When the dealkylation of $\text{PrS}[5]^{Et}$ with BBr_3 was performed in the presence of 1^+ as iodide salt, then the pentamer $\text{PrS}[5]^{OH}$ was detected in 24% yield, while $\text{PrS}[6]^{OH}$ was formed in 69% yield. This result confirms that the formation of the $1^+@\text{PrS}[5]^{Et}$ complex accelerates the dealkylation with respect to free $\text{PrS}[5]^{Et}$.

In conclusion, here is described the supramolecularly assisted dealkylation of methoxy-prism[5]arene $\text{PrS}[5]^{Me}$. The conversion of the pentamer $\text{PrS}[5]^{Me}$ to hexamer is kinetically favored with respect to the demethylation. Differently, when the complex $1^+@\text{PrS}[5]^{Me}$ is formed then the reaction of demethylation becomes kinetically favored with respect to the conversion pentamer \rightarrow hexamer. The dealkylation of prismarenes, such as $\text{PrS}[6]^R$ ($R = \text{Et}, n\text{Pr}$) and $c\text{-PrS}[5]^{Me}$, can be easily obtained in high yields in the presence of BBr_3 . The *per*-hydroxylated prismarenes described here can be considered as useful synthetic precursors to obtain novel prismarene hosts with intriguing supramolecular properties. Finally, we believe that the procedure of supramolecularly assisted demethylation described here for prism[5]arene could be useful for other macrocycles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.1c02800>.

Detailed synthetic procedures, 1D and 2D NMR spectra of per-hydroxylated prismarenes, HR mass spectra. (PDF)

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Notes

The authors declare no competing financial interest.

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(18) Under conditions of thermodynamic equilibrium, i.e. TFA in CH₂Cl₂ at reflux for 1 h, PrS[5]^{Me} was completely converted to its *c*-PrS[5]^{Me} isomer.

(19) As suggested by a reviewer, probably, in accordance to the Curtin–Hammett principle, the selectivity could be largely determined by the demethylation energy barriers and probably under the reaction conditions, the conversion of PrS[5]^{Me} to PrS[6]^{Me} occurs with a rate constant $k_{\text{conversion}} > k_{\text{dealkylation}}$.

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(21) In other words, $k_{\text{conversion}} < k_{\text{dealkylation}}$ for 1⁺@ PrS[5]^{Me}

(22) Interestingly, when PrS[6]^{Me} was reacted under conditions of thermodynamic equilibrium, in CH₂Cl₂, at reflux in the presence of TFA, its conversion to confused *c*-PrS[5]^{Me} was complete after 2 h.