Calixarenes containing modified *meso* bridges

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Abstract
In the first part of this review calixradialenes and homocalixarenes are described showing their syntheses and application possibilities. The second part concerns the use of compounds related to spirodienonecalixarenes in the synthesis of wide rim functionalized calixarenes.

Keywords: Calixradialenes, homocalixarenes, ketocalixarenes

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1. Introduction

Calixarenes and their derivatives are cage macrocycles important as scaffolds upon which receptors of organic compounds and metal ions have been designed. They are intensively studied due to the wide range of their applications, *e.g.* they form inclusion complexes useful in various fields,[1] form calixarene capsules,[2] are promising as chiral NMR solvating agents,[3] form gold[4]

and silver[5] nanoparticles, are useful as catalysts[6] and as liquid crystals,[7] serve for design of sensors[8-10] and are promising as therapeutic agents.[11,12]

Calixarenes belong to the family of cage macrocycles, including besides them cyclodextrins,[13-15] cucurbiturils[16,17] and pillararenes.[18] All macrocycles of this family are useful in the field of supramolecular chemistry for formation of inclusion complexes[1,19-21] and rotaxanes in which they serve as rings.[22-25]

One should note also heteracalixarenes, *i.e.* thia-, aza- and homooxa-calixarenes containing S, N and O heteroatoms in their structures,[26-28]. They have recently attracted considerable attention due to their easy accessibility and versatile receptor properties. Related to calixarenes are resorcinarenes and pyrogallolarenes, which recently are being intensively studied.[29,30]

Attention should be paid also to pillararenes, a new class of cage macrocycles interesting for their receptor properties,[31] reactivity[32] and promising therapeutic applications,[33,34] as well as the formation of rotaxanes,[35] supramolecular polymers,[36] gold nanoparticles,[37] artificial transmembrane channels,[38] vesicles[39] and liquid crystals.[40]

The present paper is a continuation of our earlier review on calixarenes functionalized at *meso* positions,[41] as well as of other papers dealing with rotaxanes containing calixarene macrocycles as rings,[22] functionalized calixarenes,[42] covalently and noncovalently bound assemblies of calixarenes[43] and calixarene complexes with metal ions;[44,45] calixarenes and resorcinarenes were described in ref. 30.

Calixarenes containing modified *meso* bridges [46-48] are synthesized *via* substitution of methylene bridges [49-52] or *via* their oxidation to keto groups; [53,54] they have not been as intensively studied as calixarenes functionalized at wide [55,56] or narrow [57.58] rims. Therefore it seems of interest to describe several selected examples of this class of compounds, showing their possible applications.

In the present review, calixradialenes which are new species promising as synthons for reactions performed at *meso* positions, will be presented first. Homocalixarenes will then also be briefly described; these compounds deserve an attention due to their receptor properties.

In the previous paper on *meso* functionalized calixarenes[41] we showed the oxidation of *p-t*-butylcalix[4]arene into *bis*(spirodienone)calix[4]arene. In this review compounds related to spirodienone calixarenes will be described as synthons of wide-rim functionalized calixarenes obtained by the acid-mediated bis(spirodienone) route and by a silver-mediated *p*-bromodienone route.

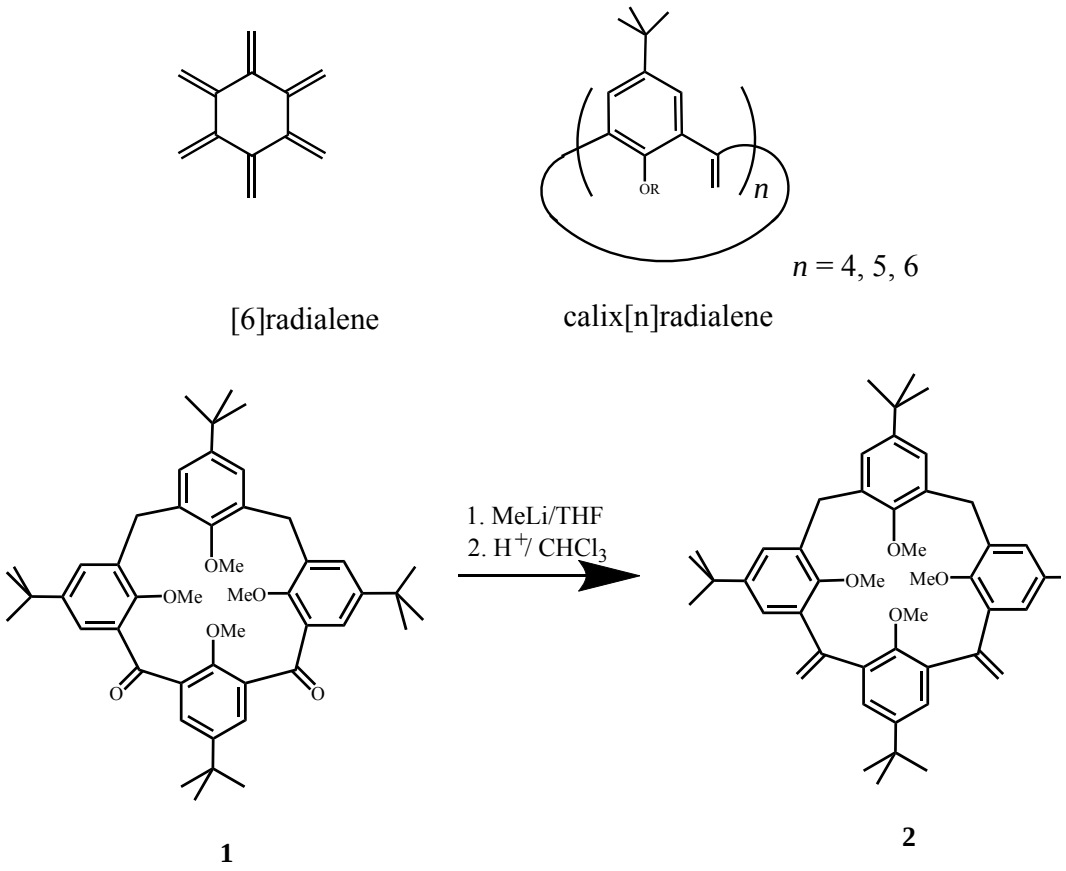
Calixarenes containing modified *meso* bridges may be considered as a supplement to numerous reports dealing with functionalized calixarenes, especially those functionalized at their wide rims.

2. Calixradialenes

Calixradialenes are calixarene derivatives with exocyclic double bonds. The name calixradialenes is connected with their formal similarity to radialenes, in which double bonds

radiate from the centre of the macrocycle. Structures of [6]radialene and calix[n]radialene are shown in Scheme 1.

Calixradialenes are obtained from ketocalixarenes by reaction with MeLi followed by water elimination.[59] Treatment of ketocalix[4]arene **1** containing two keto groups at adjacent *meso* positions with MeLi, and subsequent elimination of water, affords calixradialene **2** with two exocyclic double bonds at adjacent *meso* positions. (Scheme 1)

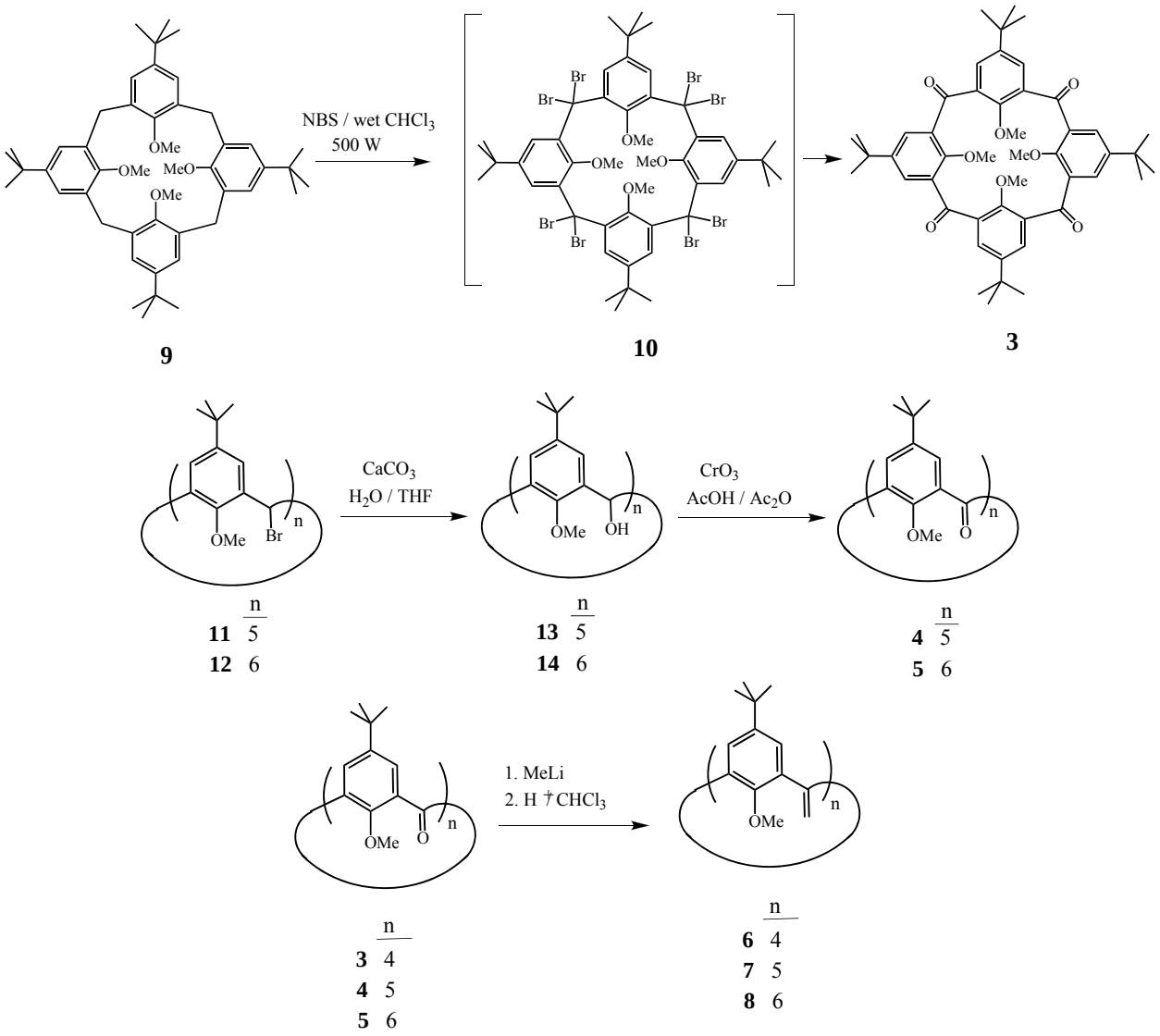


Scheme 1

Similar reactions of ketocalix[n]arenes **3-5** (n=4-6) lead to the respective calix[n]radialenes **6**–**8** (n = 4-6). We describe first the syntheses (Scheme 2) of the ketocalix[n]arenes **3-5**.

Ketocalix[4]arene **3** was synthesized previously from *p*-t-butylcalix[4]arene tetraacetate by CrO_3 oxidation followed by hydrolysis of the acetate groups and methylation of the hydroxy groups.[60] It may be also obtained from calixarene **9** by perbromination with NBS in wet $CHCl_3$ under UV irradiation; the formed octabromo intermediate **10** (not isolated) upon hydrolysis affords **3**.[61] Ketocalix[n]arenes **4** and **5** (n = 5 and 6, respectively) have been synthesized from bromocalixarenes **11** and **12** which upon hydrolysis afforded hydroxy derivatives **13** and **14**. Subsequent oxidation by CrO_3 gave **4** and **5**.[59] The ketocalix[n]arenes **3**–**5** (n = 4-6) upon reaction with MeLi, followed by water elimination yielded calix[n]radialenes **6**–**8** (n = 4-6) with

exocyclic double bonds in all *meso* positions.[59] Calixradialenes are promising as synthons for reactions performed at the *meso* positions of calixarenes.



9 **10** **3**

	n
11	5
12	6

	n
13	5
14	6

	n
4	5
5	6

	n
3	4
4	5
5	6

	n
6	4
7	5
8	6

Scheme 2

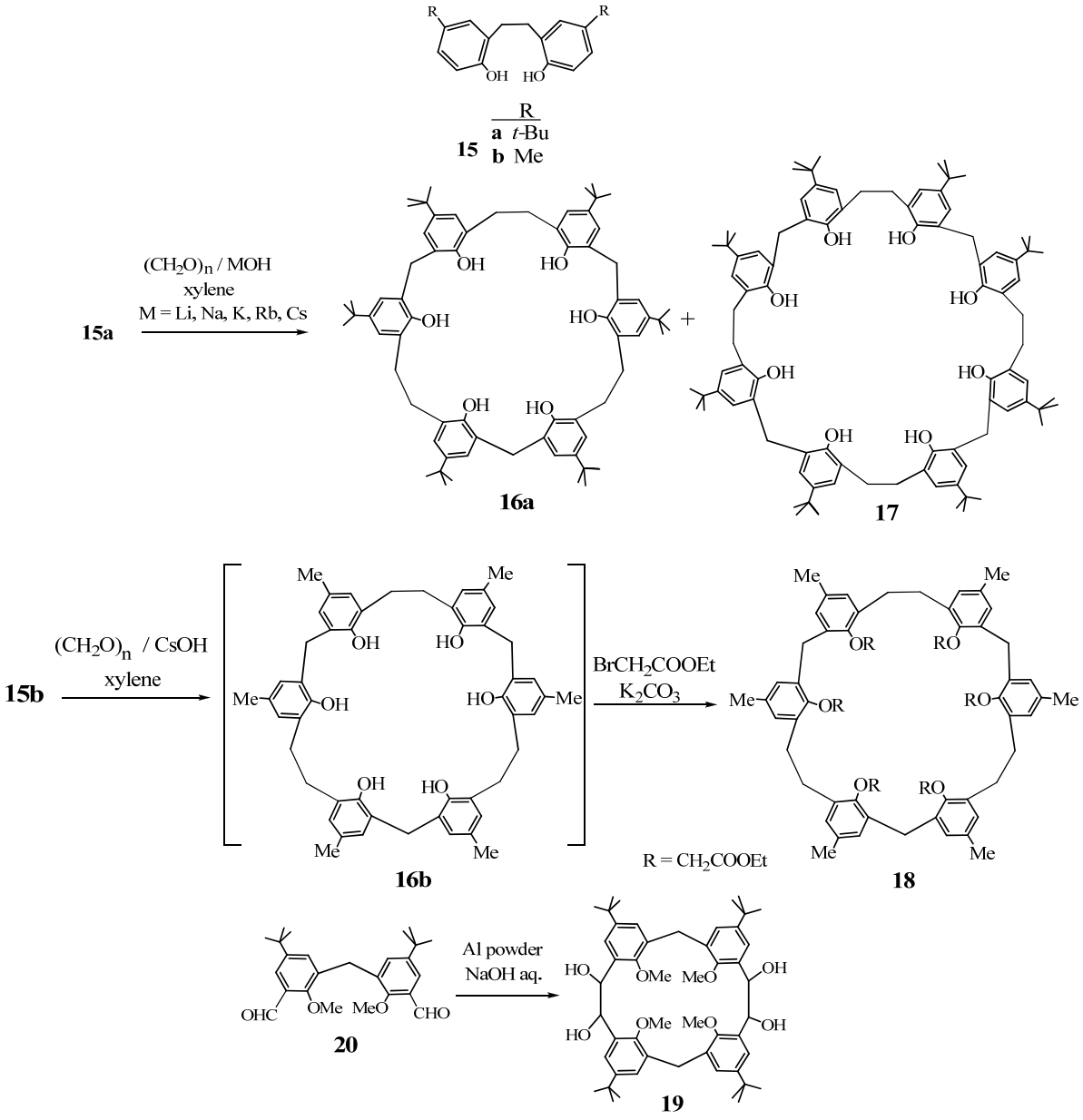
3. Homocalixarenes

Homocalixarenes, *i.e.* calixarenes in which some of the methylene groups in *meso* positions are replaced by more extended bridges, are interesting for their large receptor cavities. The size of the homocalixarenes may be tuned by programming the number of methylene groups which are situated between the aromatic rings.

First the homocalixarenes with ethylene bridges instead of methylene ones will be presented. Then homocalixarenes with all bridges at *meso* positions greater than one carbon atom, here referred to as all-homocalixarenes will be described.

3.1. Homocalixarenes with ethylene bridges at *meso* positions

An example of a synthesis of homocalixarene with ethylene bridges at the *meso* positions is that of the condensation of 2-hydroxyphenylethanes **15a** or **15b** with paraformaldehyde under basic conditions.[62] The reaction of **15a** afforded two homocalixarenes, **16a** and **17**, which were separated by column chromatography. In the case of KOH, RbOH and CsOH, **16a** is the major product, while in the presence of LiOH or NaOH, **17** prevails. The reaction of **15b** performed in the presence of CsOH affords homocalixarene **16b** as the sole product, which without isolation, was treated with ethyl bromoacetate to give homocalixarene **18**.

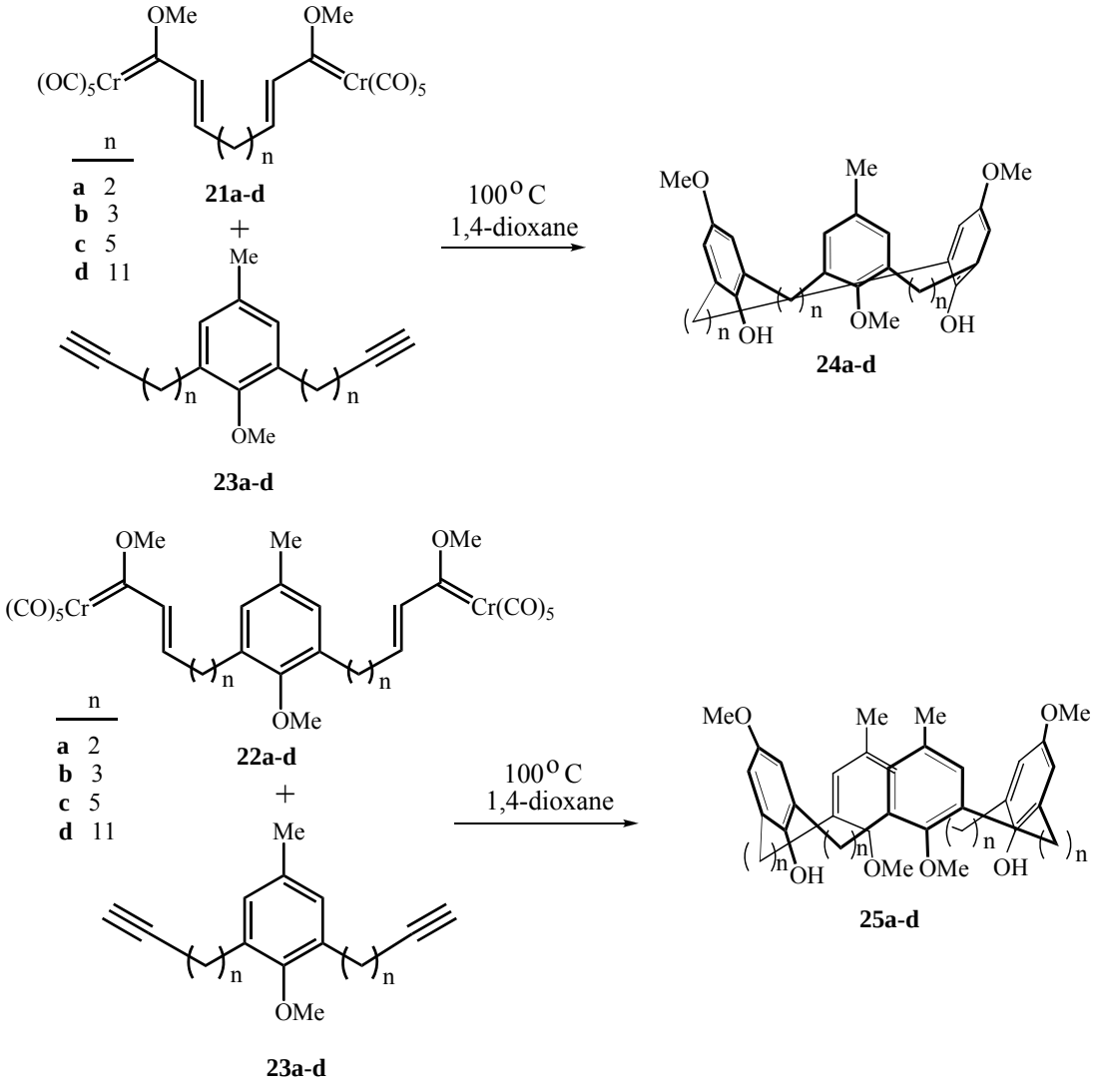


Scheme 3

The syntheses are simple, and the obtained homocalixarenes have roomy cavities, allowing the inclusion of large guest molecules. This fact is promising for their use in supramolecular chemistry.[62] Another example of a homocalixarene is **19**, obtained from diphenylmethane dialdehyde **20** using aluminum powder and sodium hydroxide.[63] Compound **19** has proven useful as a synthon for further reactions.[64] (Scheme 3)

3.2. All-homocalixarenes

A synthesis of all-homocalixarenes, *i.e.* homocalixarenes having all bridges greater than one carbon atom, involves the reaction of biscarbene complexes **21** or **22** with diyne **23**, affording homocalix[3]arene **24** and homocalix[4]arene **25**, respectively.[65] The syntheses proceed by triple annulation which forms two aromatic rings and one macrocyclic ring. The above procedure enables control over the cavity size and over the symmetry of the whole molecule. (Scheme 4)



Scheme 4

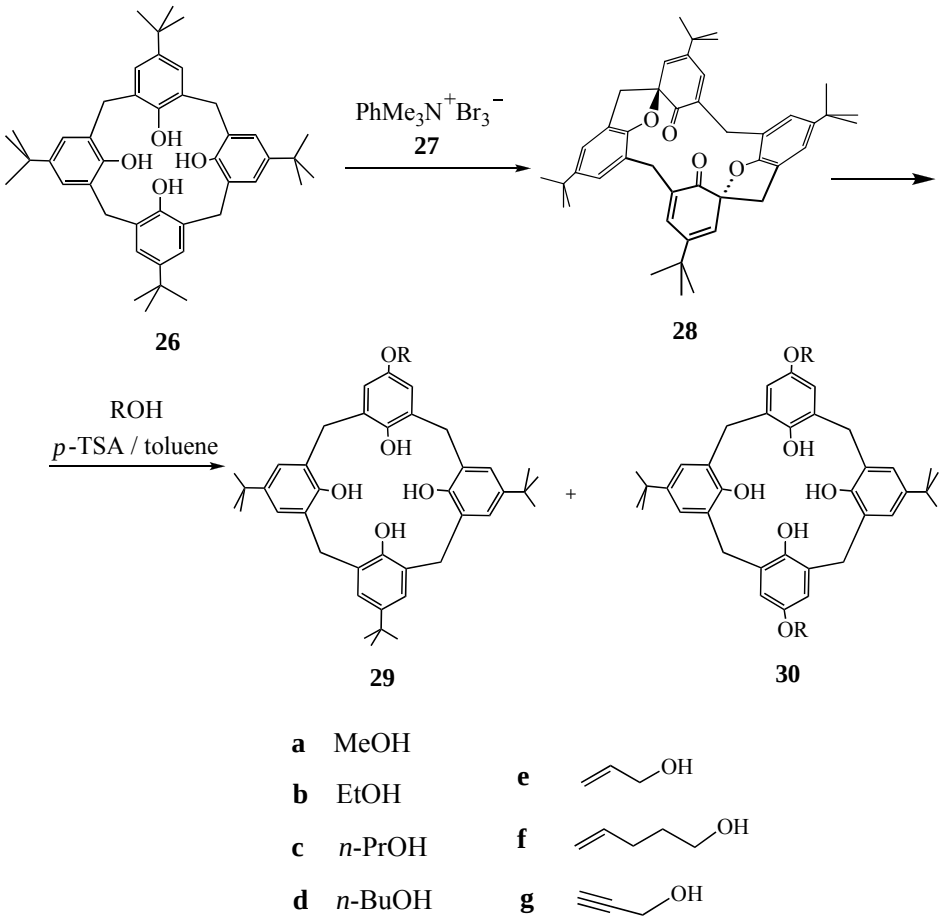
4. Compounds Related to Spirodienonecalixarenes Serving as Synthons

Among reactions of bis(spirodienone)calix[4]arene and related compounds, an important example is the functionalization of the wide rim of a calixarene. Two main approaches are described below: the acid-mediated bis(spirodienone) route, and the silver-mediated *p*-bromodienone route.

4.1.Wide rim-functionalized calixarenes obtained by acid-mediated bis(spirodienone) route

The parent calixarene **26** upon mild oxidation with trimethylphenylammonium tribromide **27** affords bis(spirodienone)calix[4]arene **28**. The subsequent acid-mediated reaction of **28** with alcohols leads to functionalization of a calixarene wide rim, affording mono- and di-alkoxycalix[4]arenes **29** and **30**; this procedure overcomes the need for prior protection of the narrow rim hydroxyl groups. Reactions were performed in the presence of *p*-toluenesulfonic acid (*p*-TSA).[66]

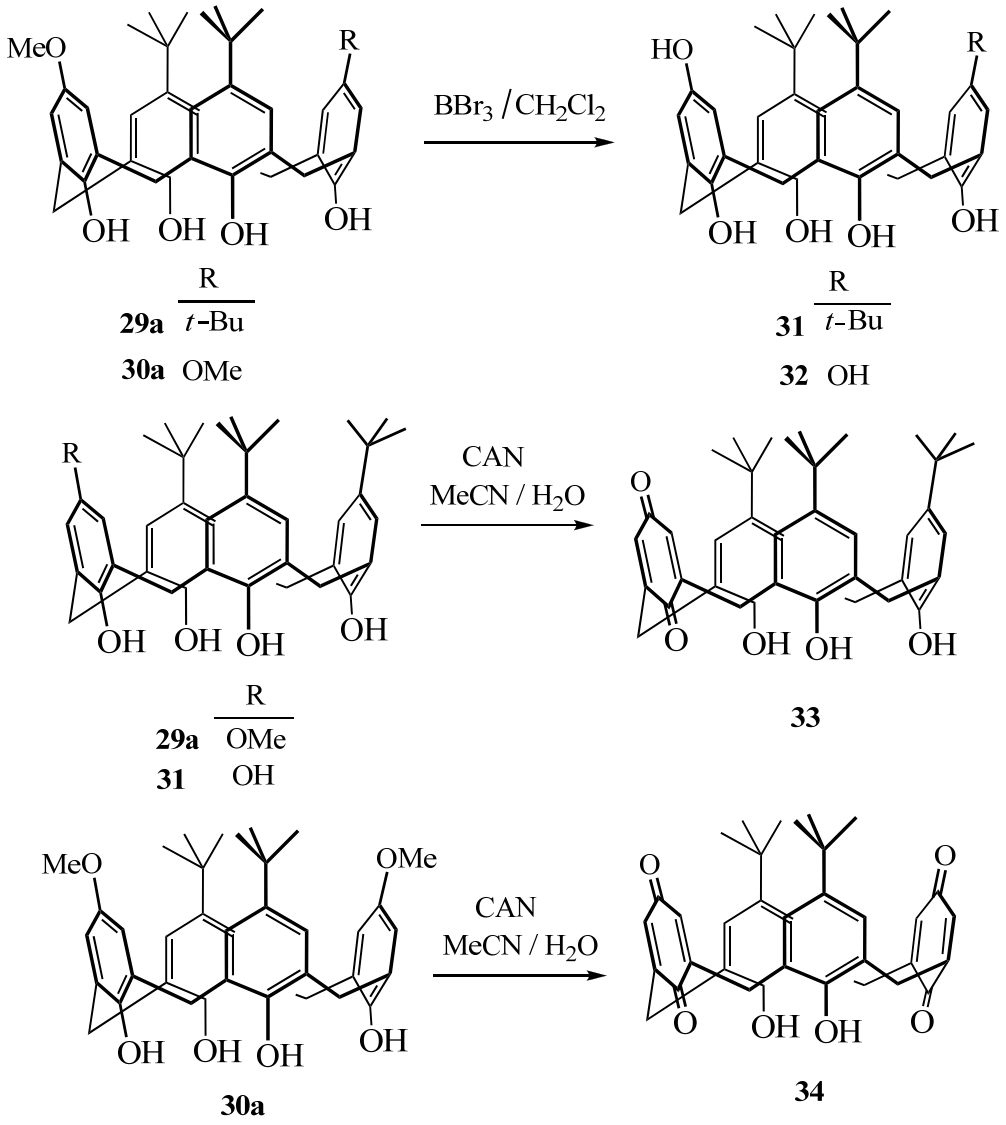
As a trial, alcohols **a**-**g** were used with **28**. Methanol **a** and propargyl alcohol **g** yielded two products, *i.e.* mono- and di-alkoxycalixarenes, whereas other alcohols afford only monoalkoxy-calixarenes. (Scheme 5)



Scheme 5

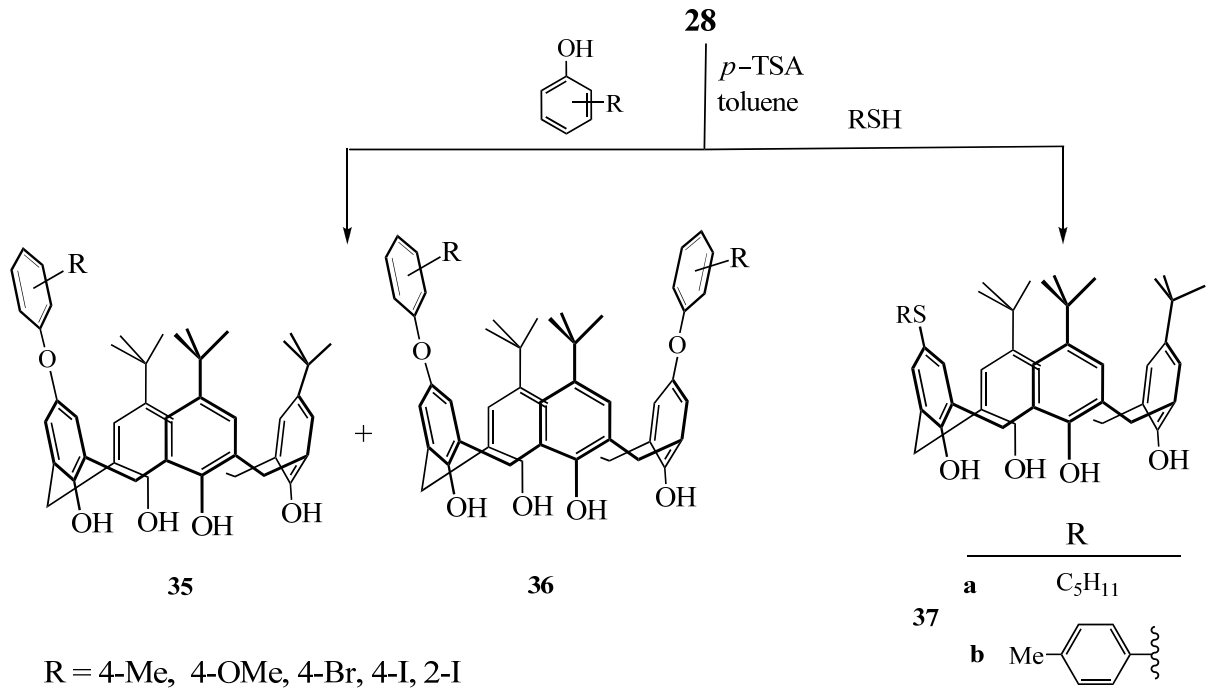
The value of this method should be emphasized, since functionalization of the wide rim of calixarenes is more difficult than that of a narrow rim. It is noteworthy that the above direct substitution of the wide rim of calixarene *via* bis(spirodienone)calixarene **28** proceeds by an efficient and mild procedure. The obtained mono- and di-methoxycalixarenes **29a** and **30a** may serve for the synthesis of calix[4]mono- and diquinones which are difficult to achieve using any other route.[66] For this purpose, **29a** and **30a** were treated with BBr_3. The resulting demethylation yielded **31** and **32** containing one and two 1,4-dihydroxybenzene rings, respectively.

Oxidation of **29a** and **31** with cerium(IV) ammonium nitrate (CAN) affords calix[4]monoquinone **33**, and oxidation of **30a** leads to the formation of calix[4]diquinone **34**. (Scheme 6)



Scheme 6

For similar functionalization of the wide rim of calixarenes *via* a bis(spirodienone) route phenols and thiols were also used. The reaction of **28** with phenols affords mono- and diaryloxycalixarenes **35** and **36**, respectively, whereas in the case of thiols only monosubstituted products **37** were obtained.[67] (Scheme 7)

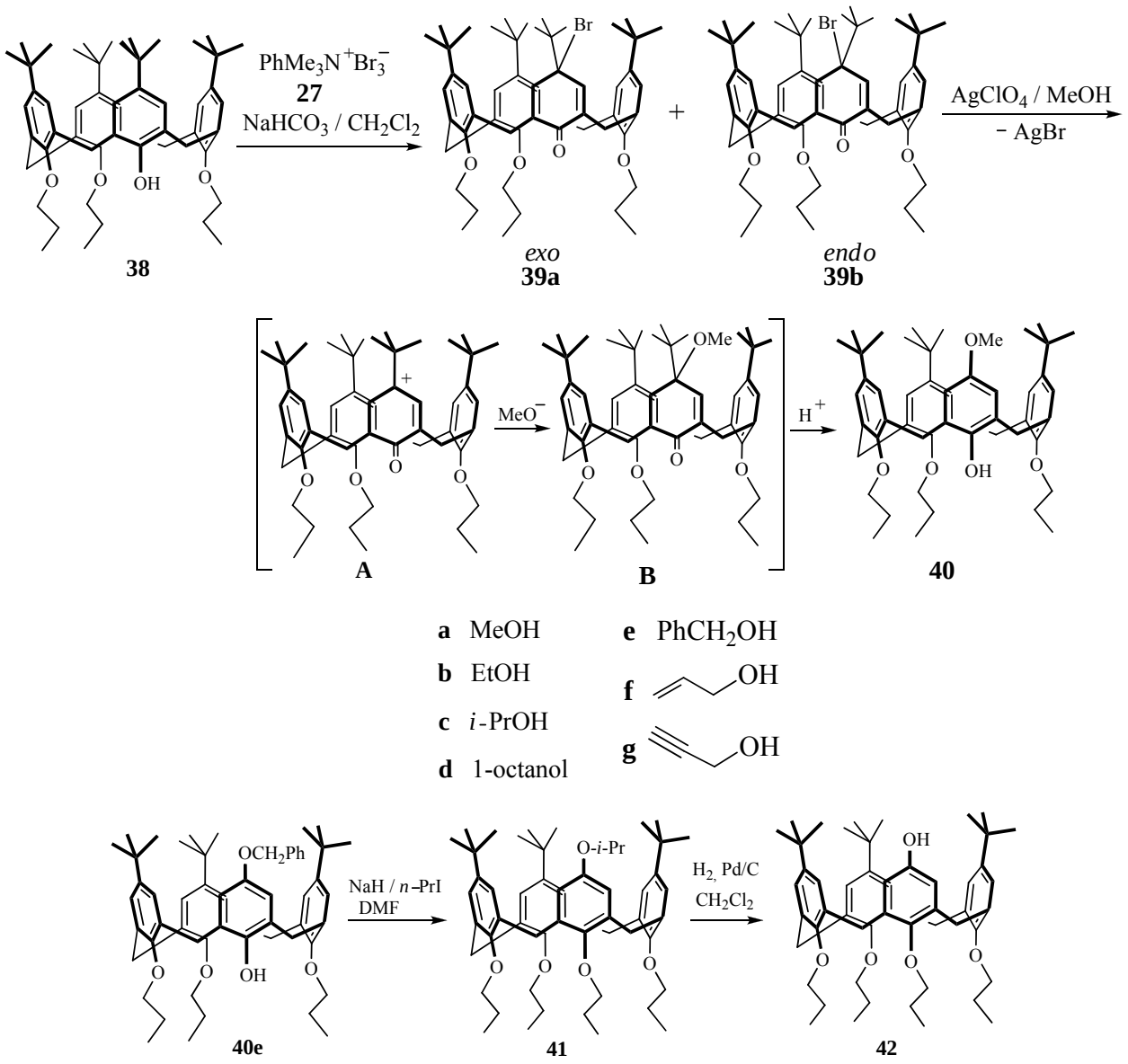


Scheme 7

4.2. Wide-rim functionalized calixarenes obtained by silver-mediated *p*-bromodienone route

A related approach to calixarene wide-rim functionalization, referred to as a *p*-bromodienone route, involves the procedure often used for preparation of spirodienonecalixarenes, *i.e.* the treatment of the appropriate calixarene, *e.g.* **38** with trimethylphenylammonium tribromide **27** in the presence of a base. This reaction yields a mixture of the *exo* and *endo* stereoisomers of *p*-bromodienonecalixarenes **39a** and **39b**. The *exo* isomer **39a** reacts with a methanolic solution of $AgClO_4$ to give *p*-methoxycalixarene **40**. It was observed that this reaction leading to **40** proceeds also when using the mixture of stereoisomers **39a** and **39b** without the isolation step.[68] The procedure involves the silver-mediated formation of aryloxenium cation **A**,[69] which, upon reaction with methanol forms intermediate **B**, undergoing rearomatization into **40**. In this functionalization of the wide rim, the alcohols **a-g** were used.

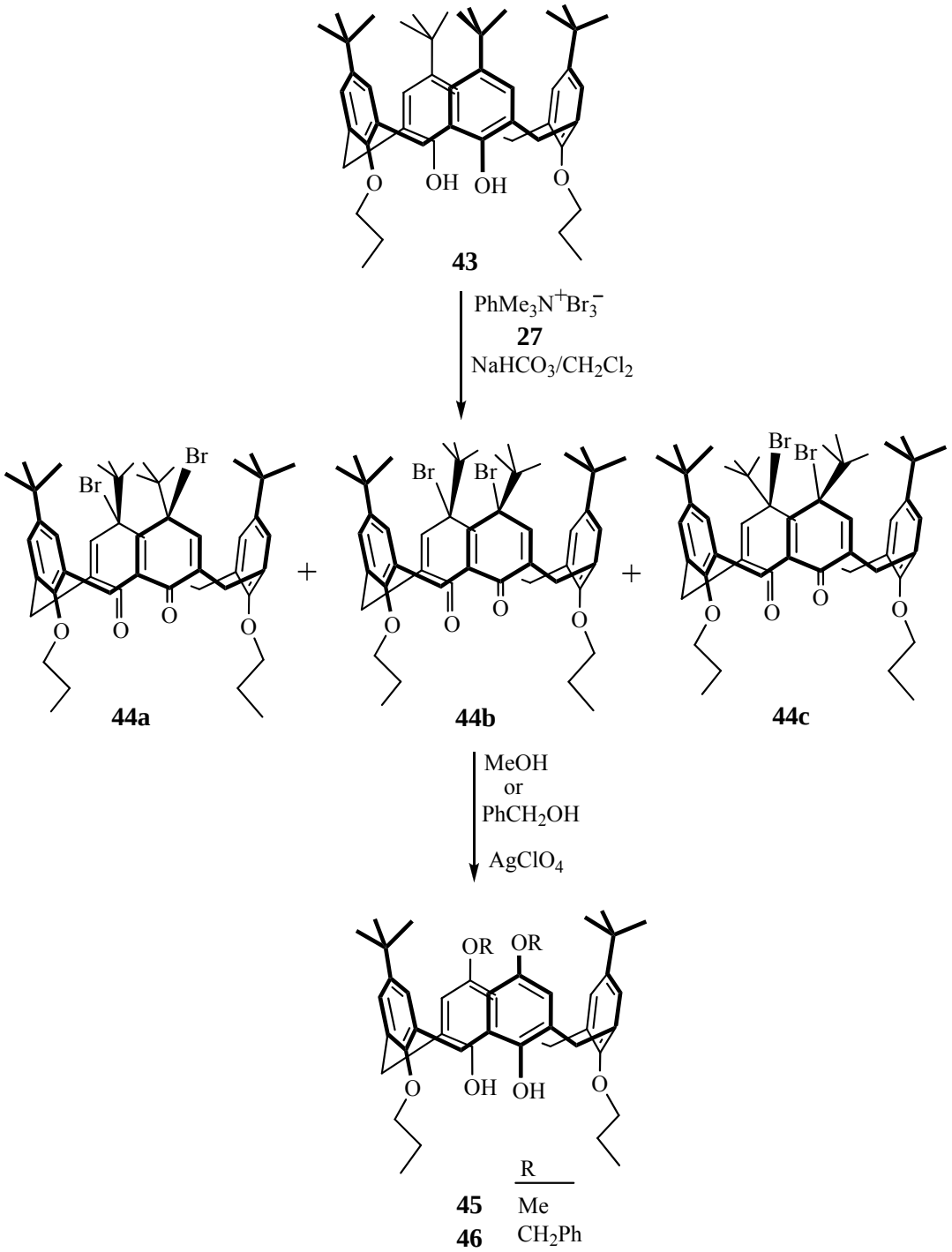
It is noteworthy that the obtained products may undergo modification of the introduced nucleophile, *e.g.* **40e** was propylated to give **41** which upon hydrogenolysis afforded calixarene **42** containing a single hydroxyl group on the wide rim, which is difficult to achieve by any other approach.[70] (Scheme 8)



Scheme 8

In a similar way, calixarenes containing two distal *p*-bromodienone moieties were formed. For this purpose, dipropoxycalixarene **43** was treated with **27** to give a mixture of stereoisomers **44a**,**b**,**c**. The reaction of this mixture with methanol or benzyl alcohol in the presence of $AgClO_4$ affords corresponding calixarenes **45** or **46** containing two rings substituted at the wide rim by methoxy- or benzyloxy groups, respectively. (Scheme 9)

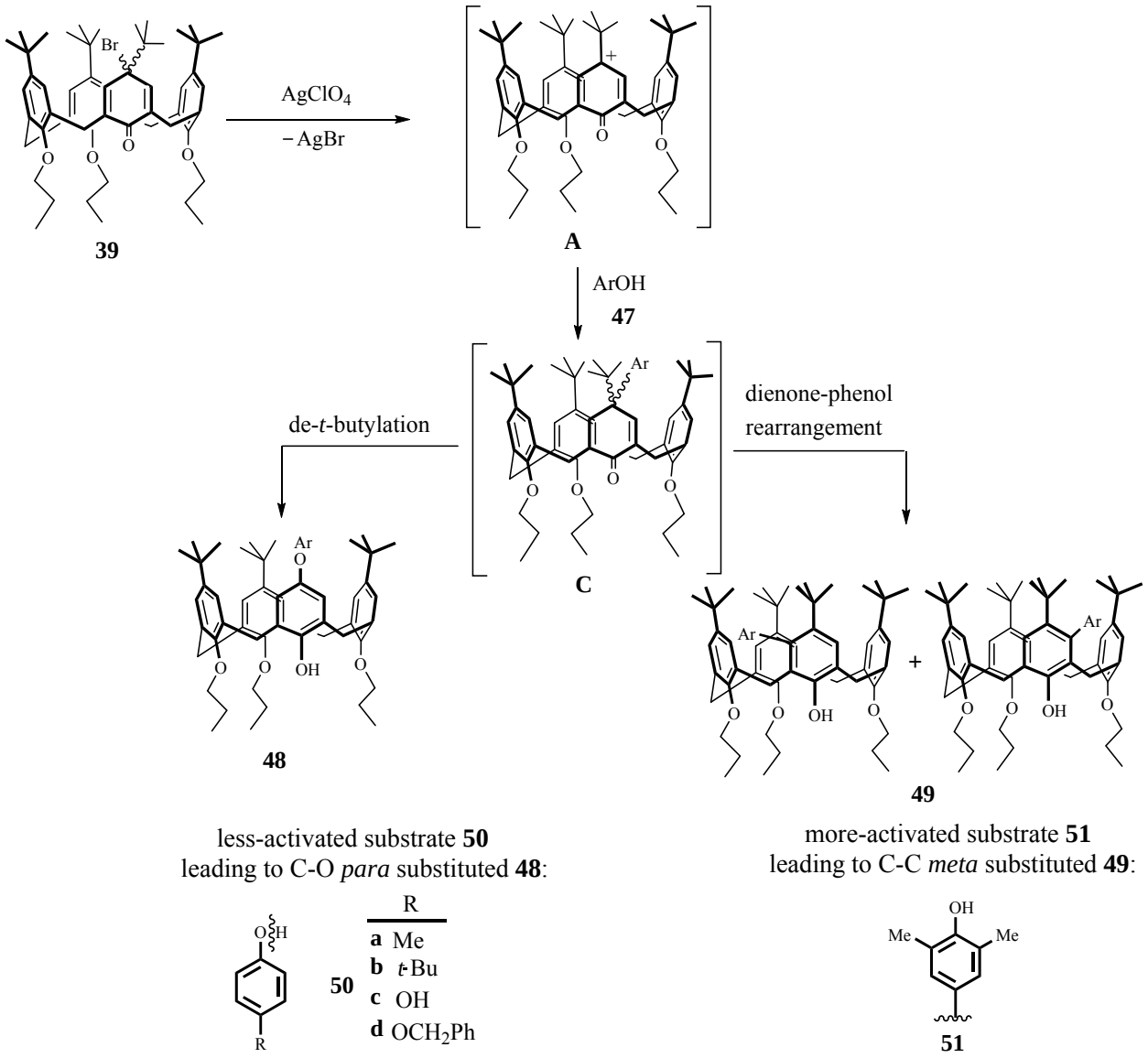
One should note that the above procedure, *i.e.* the *p*-bromodienone route, is a convenient method for wide rim functionalization of calixarenes using the easily accessible *p*-bromodienonecalixarenes.[68]



Scheme 9

The *p*-bromodienone route serves also for substitution of *para*- and *meta*- positions of calixarene rings by aromatic moieties. The aromatics used in this process should be sufficiently activated. It was observed that less reactive substrates yield mainly C-O *para*-substituted products, while more activated substrates mainly afford the inherently chiral C-C *meta*-substituted compounds. As an example, the mixture of *exo*/*endo* stereoisomers of **39**, obtained as

above, reacted with $AgClO_4$ and nucleophile ArOH **47** in 1,2-dimethoxyethane in the presence of Na_2CO_3 to give calixarene **48** and calixarenes **49** as a racemic mixture.[71] (Scheme 10)



Scheme 10

The mechanism proposed for the synthesis involves the silver-mediated initial formation of the aryloxenium cation **A**, which upon reaction with the nucleophile forms the intermediate **C.** Intermediate **C** reacts by two routes: the de-*t*-butylation and the dienone-phenol rearrangement. The de-*t*-butylation of **C** yields the rearomatized *para*-substituted calixarene **48**. The dienone-phenol rearrangement of **C** however, (involving the 1,2-migration of the nucleophilic moiety), affords the *meta*-substituted calixarene **49**. Compound **49** is inherently chiral and is obtained as a racemic mixture. (Scheme 10).

For investigation two compounds were chosen as nucleophiles, namely, as less activated substrates substituted phenols **50a-d**, and as a more activated substrate 2,6-dimethylphenol **51**. As expected, the less activated substrates **50a**–**d** afforded only *para*-substituted products, while the more activated **51** yielded only *meta*-substituted products as a racemic mixture.

The above reactions lead to deep calixarenes, and the use of highly activated aromatic substrates enables formation of inherently chiral calixarenes which are promising in enantio-discrimination.[71]

5. Conclusions

In view of the rapid progress in calixarene chemistry,[72-74] as well as in that of cyclodextrins[75-77] and cucurbiturils,[78-80] promising for various applications, it seemed of interest to add the above described examples of calixarenes with modified *meso* bridges and the procedures leading to the synthesis of wide rim functionalized calixarenes; one may hope that they will to some extent enlarge knowledge in the calixarene area.

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