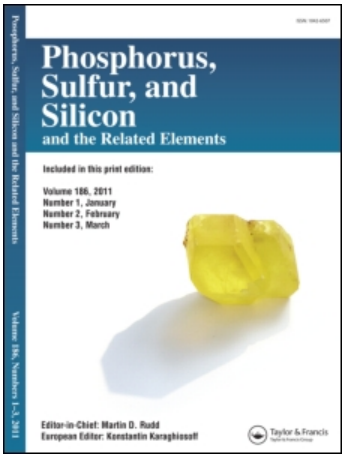

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Synthesis of Highly Reactive Organosulfur Species using Newly Designed Molecular Cavities

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Synthesis of Highly Reactive Organosulfur Species using Newly Designed Molecular Cavities

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Endohedral phases of molecular cavities have great potential for serving as a reaction environment for the internal functionality as well as a complexing site for the guest molecule. The design of novel bowl- and capsule-shaped molecules bearing an endohedral functionality and their application to the stabilization of highly reactive organosulfur species such as sulfenic acid, sulfenyl iodide, and thioformaldehyde are described.

Keywords: Molecular cavity; sulfenic acid; selenenic acid; sulfenyl iodide; thioformaldehyde; simple enol

INTRODUCTION

The design of a reaction environment which can specifically regulate the reactivity of a functional group is a major area of current interest

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and importance. In this paper, we describe the synthesis of the bowl- and capsule-shaped molecules, which are schematically depicted in Figure 1, and their application to the stabilization of highly reactive organosulfur compounds, such as sulfenic acid, sulfenyl iodide, and thioformaldehyde.

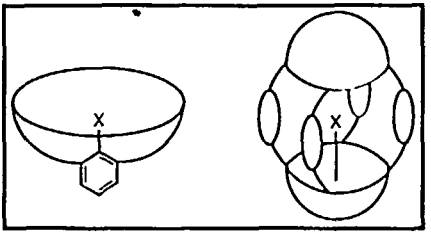


FIGURE 1 Schematic drawings of a *reaction bowl* and a *molecular lantern*.

SYNTHESIS AND APPLICATION OF THE "REACTION BOWLS"

Concept and Molecular Design

If the functional groups X and Y are embedded in the cabity of the two *reaction-bowl*-type molecules as shown in Figure 2, they cannot approach each other because of the steric repulsion of the brims of the bowls, whereas they can react with other reagents because there is relatively large space around them. The functionalities X and Y can be either of the same kind or of different kinds. In order to embody this concept, we have designed three types of leading compounds shown in Figure 3, that is, a bimacrocyclic cyclophane, a bridged calix[6]arene, and a molecular bowl with an all-carbon and acyclic framework. The compounds shown in Figure 3 have been designed so that they have a diameter of 13 or 14 Å.

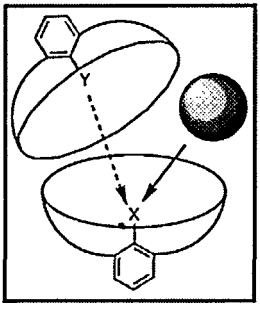


FIGURE 2 Concept of *reaction bowls.*

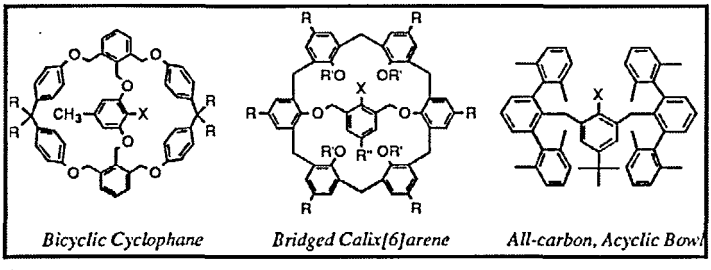


FIGURE 3 *Reaction-bowl*-type molecules.

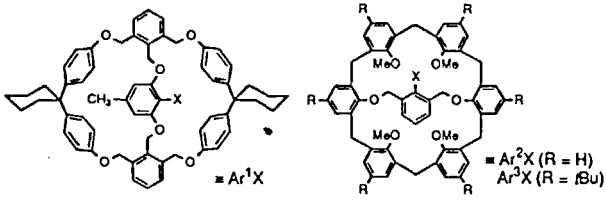
Reaction Bowls Based on a Bimacrocyclic Cyclophane Framework

Synthesis and structure

Bromide **1** (Ar^1Br, Figure 4) was synthesized via initial construction of the central bridge followed by cyclization (Scheme 1).[1] The structure of **1** was established by X-ray crystallographic analysis. Several kinds of functionalities such as aldehyde, thiol, and sulfide were introduced into the cavity via lithiation of bromide **1** followed by quenching with an appropriate electrophile.

Application to the stabilization of a sulfenic acid

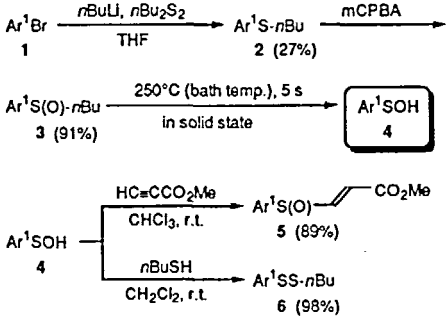
As the first target species to be stabilized in the *reaction bowl*, we have



1: X = Br

7: X = S-*t*Bu, R = H
8: X = Se-*n*Bu, R = *t*Bu

FIGURE 4 Bicyclic cyclophane **1** and calixarenes **7** and **8**.



SCHEME 1

chosen sulfenic acids (RSOH). In spite of their importance, they have been difficult to be synthesized[2,3] and most of the sulfenic acids isolated to date have been stabilized by the electronic effect of neighboring substituents and intramolecular hydrogen bonding, which inevitably perturb the properties of the SOH group. While there have been two alkanesulfenic acids isolated by kinetic stabilization,[3a,4] no stable arenesulfenic acid has been obtainable even with such bulky substituents as a 2,4,6-tri-*tert*-butylphenyl or a 2,4,6-triisopropylphenyl group.[5]

Sulfenic acid **4** was obtained via sulfide **2** and sulfoxide **3** as a crystalline solid (90% based on conversion of **3**, see Scheme 1).[1] Sulfenic acid **4** is stable at room temperature in air for more than several weeks, but **4** readily reacted with methyl propiolate or 1-butanethiol to give the corresponding adduct **5** or **6**, respectively (Scheme 1). These results validate the concept of a *"reaction bowl"* that a functional group in its inside is stabilized, yet capable of undergoing an intermolecular reaction with an appropriate molecule.

Reaction Bowls Based on a Bridged Calix[6]arene Frameworks

Synthesis of tetramethoxy and tetrabenzyloxy compounds

The calix[6]arene macroring can be easily prepared on a large scale unlike other cyclophanes of this size and the bridged calix[6]arenes of type **7** and **8** were synthesized simply by building a bridge with a substituted *m*-xylenyl unit over the distal positions of a parent calix[6]arene.[6,7,8]

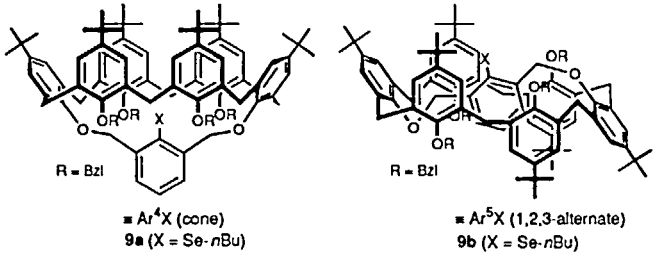


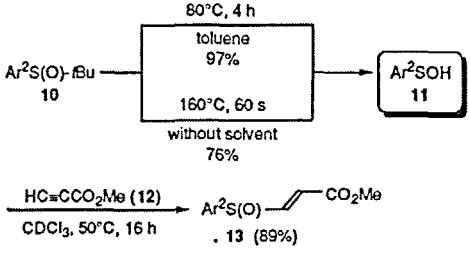
FIGURE 5 Two conformational isomers of a bridged calix[6]arene.

Similarly, tetrabenzylated **9a** and **9b** with a *n*-BuSe group were synthesized (Figure 5). The ^{1}H NMR spectral patterns of **9a** and **9b** at room temperature are completely consistent with their adopting the cone and 1,2,3-alternate conformations, respectively, and the interconversion between them or their conversion to other isomers

was not observed even after heating either of them at 120 °C for 24 h.

Application to the synthesis of a stable sulfenic acid

Thermolysis of *tert*-butyl sulfoxide **10** was carried out in solution or in the solid state and in either case sulfenic acid **11** was obtained as stable colorless crystals in good yields (Scheme 2).[6] The structure of **11** was established by X-ray crystallographic analysis (Figure 6). It was found that its conformation is the (u,u,d,d,d,u) 1,2,3-alternate.



SCHEME 2

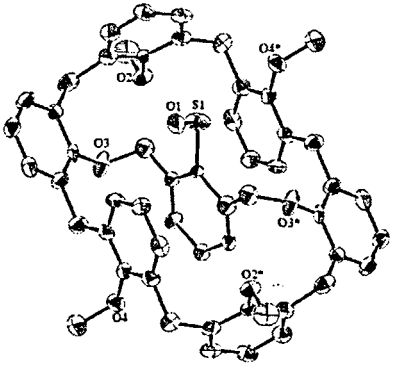


FIGURE 6 ORTEP drawing of **11** (30% probability).

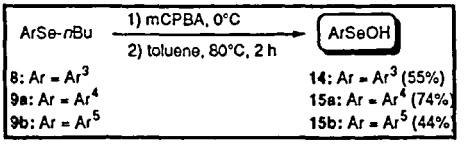
The reaction of **11** with methyl propiolate (**12**) in $CDCl_3$ at

50°C afforded sulfoxide **13** (86%) although it took 16 h to be completed (Scheme 2). Considering the facts that **12** is known as an efficient trapping reagent of sulfenic acids,[2] and that the reaction of sulfenic acid **4** bearing the bimacrocyclic cyclophane framework with **12** went to completion within 12 h at room temperature,[1] this slow reaction rate suggests that the SOH group of **11** is strongly shielded by the calix[6]arene macroring.

Application to the synthesis of a stable selenenic acid

Selenenic acids (RSeOH) play a central role in the oxidation and reduction processes of organoselenium compounds, for example, in the selenoxide syn elimination, the reduction of seleninic acids, and the oxidation of selenols and diselenides.[9] They are also of great interest from a biological point of view as illustrated by a number of reports which postulate the intermediacy of a selenenic acid in the catalytic cycle of glutathione peroxidase (GPX)[10] and its synthetic model compounds.[11] However, despite their importance, much of our knowledge on their chemistry has been derived in quite an indirect and speculative fashion because of their great instability; they are known to undergo a rapid disproportionation to form the corresponding diselenides (RSeSeR) and seleninic acids ($RSeO_2H$). Several areneselenenic acids stabilized by coordination to ortho nitro,[12] carbonyl,[13] or amino groups[11c] have been reported to be observable, but only in solution. It has been reported that even the employment of a 2,4,6-tri-*tert*-butylphenyl group, one of the most effective steric protection groups, cannot prevent the disproportionation of a selenenic acid.[14] Thus, no selenenic acid has been isolated in pure form so far and the development of a new methodology to stabilize this important but elusive species has long been awaited.

Selenenic acids **14**, **15a**, and **15b**, synthesized by thermolysis of the corresponding selenoxides (Scheme 3), showed high stability both in crystalline state and in solution. Even after heating at 120°C for 5 h in $CDCl_2CDCl_2$, **14** and **15b** underwent only slight decomposition, and no decomposition was observed for **15a**. Considering the reported fact that even 2,4,6-tri-*tert*-butylbenzeneselenenic acid disproportionates completely within 2 h in 4% D_2O/CD_3CN at 25°C,[14] such high stability of these selenenic acids is remarkable.



SCHEME 3

Reaction Bowl Based on An All-carbon and Acyclic Framework

Synthesis of the bromide

Although the construction of the bimacrocyclic cyclophane framework or the bridged calix[6]arene framework stated above is relatively easy for macrocycles of this size, it still requires a multistep synthesis. Furthermore, the presence of the oxygen atoms in their frameworks gives rise to side reactions with some reagents such as alkyllithiums, and the interaction between the oxygen atoms and the endohedral functionality is sometimes undesirable especially when these frameworks are applied to the kinetic stabilization of reactive species. The development of a *reaction bowl* with higher accessibility and a more inert framework would lead to the wider application of this type of reaction environment. We have designed a novel bowl-shaped substituent, 4-*tert*-butyl-2,6-bis[(2,2",6,6"-tetramethyl-*m*-terphenyl-2'-yl)methyl]phenyl group (denoted as Bmt hereafter), with an all-carbon and acyclic framework (Figure 7).

Bromide **18** was readily synthesized by cross coupling reaction between *m*-terphenyl unit **16** and tribromide **17** (Scheme 4).[15] X-ray crystallographic analysis revealed that **18** has a bowl-shaped structure although it is an acyclic molecule.

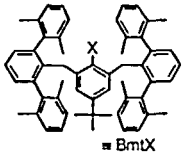
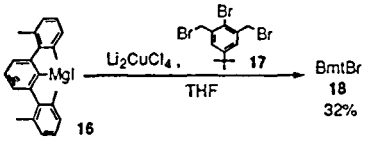


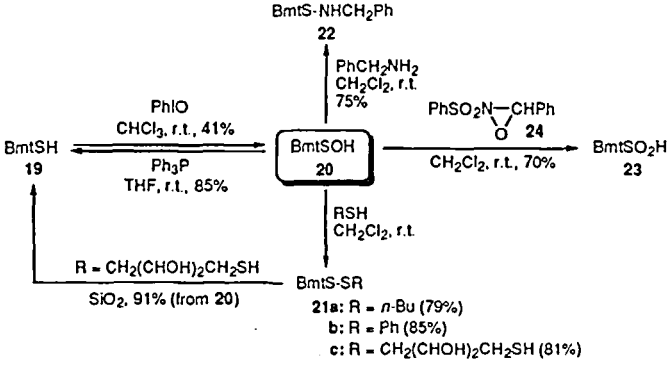
FIGURE 7 All carbon, acyclic *reaction bowl.*



SCHEME 4

Synthesis of a sulfenic acid by direct oxidation of a thiol

The reaction of thiol **19** with iodosobenzene, a mild oxidant which usually converts thiols to disulfides, afforded sulfenic acid **20**, which was isolated by silica gel chromatography as stable crystals (Scheme 5).[16] X-ray crystallographic analysis has established the structure of **20**, where two rigid *m*-terphenyl units surround the SOH group like a brim of a bowl (Figure 8). This represents the first example of direct oxidation of a thiol to a sulfenic acid.



SCHEME 5

The reactions of sulfenic acid **20** with 1-butanethiol and thiophenol afforded the corresponding unsymmetrical disulfides **21a**

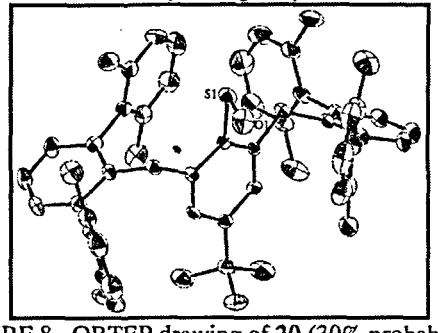


FIGURE 8 ORTEP drawing of **20** (30% probability).

and **21b**, respectively (Scheme 5). Dithiothreitol reduced **20** to thiol **19** via the intermediary disulfide **21c**. Treatment of **20** with benzylamine afforded sulfenamide **22**. These reactions of **20** with nucleophiles demonstrate that a sulfenic acid exhibits the electrophilic reactivity even under basic conditions. Sulfenic acids can be regarded as sulfur analogs of hydroperoxides and trivalent phosphorus reagents have been suggested to reduce a transient sulfenic acid. The reduction of **20** with triphenylphosphine gave thiol **19** in a good yield. Sulfenic acid **20** was oxidized to sulfinic acid **23** by oxaziridine **24**.

Redox reactions of a stable selenenic acid

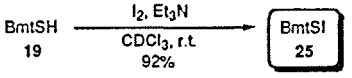
Oxidation of selenol BmtSeH bearing a Bmt group with hydrogen peroxide or iodosobenzene afforded selenenic acid BmtSeOH as a major product along with the corresponding diselenide and seleninic acid.[17] The use of the stable selenenic acid enabled us to experimentally demonstrate all the postulated reactions in the catalytic cycle of glutathione peroxidase.

Stabilization of a sulfenyl iodide

Sulfenyl iodides (RSI) have been suggested to play decisive roles as reaction intermediates in iodination reaction in the human thyroid gland as well as in iodine-oxidation of thiols. However, information about them is very scant because of their instability resulting from their ready disproportionation reaction ($2RSI \rightarrow RSSR + I_2$), ΔH of which is –4.30 kcal mol^{-1}.[18] In the solid state they are much less stable partly because of the large sublimation energy of solid I_2 (14.9 kcal mol^{-1}). The only structure analysis of a sulfenyl iodide was carried out for Ph_3CSI at –118°C,[19] which is stable in the solid state at –78°C and in solution in the dark.[20] Several aromatic acylsulfenyl iodides have been isolated and shown to be stable at room temperature for several hours, but they decompose below 50°C.[21] On the other hand, the reported value of the S–I bond dissociation energy is not so small (49.4±2 kcal mol^{-1} for HS–I),[22] suggesting that this species will be stable if the disproportionation process can be suppressed.

Oxidation of thiol **19** with an equimolar amount of I_2 in the presence of triethylamine afforded sulfenyl iodide **25** as dark brown crystals (Scheme 6).[23] The iodide **25** was very stable, no decomposition being observed after heating at 80°C for 12 h in toluene. The structure of **25** was established by X-ray analysis (Figure 9). Oxidation of thiol **19** with 0.5 equimolar amount of I_2 in the presence of triethylamine afforded a 1:1 mixture of **19** and **25**, no disulfide formation being detected even after 24 h at room temperature. Whereas sulfenyl iodide **25** is unreactive to thiol **19** bearing the same substituent, **25** can readily react with a small thiol. Upon addition of 1-butanethiol to the above-mentioned mixture of **19** and **25**, **25** was immediately converted to the unsymmetrical disulfide

BmtSS-*n*-Bu. These results illustrate that the Bmt system successfully embodies the concept depicted in Figure 2.



SCHEME 6

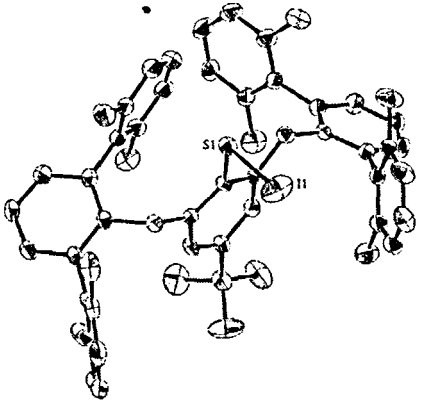


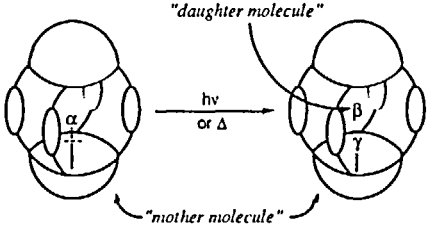
FIGURE 9 ORTEP drawing of **25** (30% probability).

CONSTRUCTION AND APPLICATION OF THE "MOLECULAR LANTERN"

Concept

In the chemistry of capsule-shaped macromolecules, increasing attention has recently been paid to the application of the endohedral space of the capsules as a reaction environment for the guest molecule.[24] Various types of reactions of a guest molecule incorporated in the capsule have been reported and among them there is the generation of long-lived cyclobutadiene[25a] and benzyne[25b] inside a hemicarcerand, which is highly reactive under normal

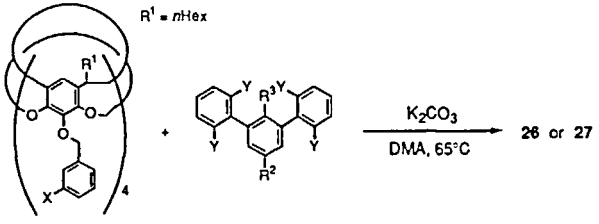
conditions. However, those container molecules are at a disadvantage with respect to functionalization of the endohedral surface because it is difficult to fix an inwardly-directed functional group in their interior. We have designed a *"molecular lantern"* (Figure 1) in order to study the chemistry of the inner phase of a molecular capsule as a reaction environment for the endohedral functionality. This type of *molecular lantern* is interesting not only for the stabilization of highly reactive speices but also as a new type of complex which should be referred to as a *"mother molecule"–"daughter molecule"* complex (Scheme 7).



SCHEME 7

Synthesis

In order to introduce an endohedral functionality so that it points inward, we have designed *molecular lanterns* **26** and **27** bearing a *m*-terphenyl unit as the bottom moiety (Figure 10).[26,27] Compounds **26** and **27** were synthesized by the coupling reaction of the capping



28: X = OH
29: X = CH_2Br

30: Y = CH_2Br
31: Y = OH

SCHEME 8

Application to the Stabilization of Reactive Species

As an application of this *molecular lantern*, we have investigated the photochemical reaction of a methylthioacetyl-substituted compound, which is known to generate two highly reactive species, a "simple enol" and thioformaldehyde.[27] Whereas simple enols bearing more than two bulky aryl groups are sometimes isolable,[28] there has been no example of the isolation of a mono-substituted compound of this class. Furthermore, all the stable simple enols isolated so far have two substituents in the β-position of the hydroxyl group. Thioformaldehyde has been known as a very unstable compound.[29] The reaction of a β–ketosulfide **27a** is expected to afford a β-unsubstituted simple enol **27b** and thioformaldehyde **32** stabilized by the surrounding capsule cage.

Irradiation of **27a** in toluene-d_8 in the presence of Danishefsky's diene **33** gave simple enol **27b** together with enone **35**, which was formed by the hydrolysis of **34**, the Diels-Alder adduct of **32** with **33** (Scheme 9).[27] This is the first isolation of a monosubstituted simple enol as well as of a β–unsubstituted simple enol. Simple enol **27b** is stable in $CDCl_3$ at room temperature for more than 4 days. In the presence of excess amount of trifluoroacetic acid, **27b** ketonized to the acetyl derivative **27c** although the reaction was so slow that it

unit **28** or **29** with *m*-terphenyl unit **30** or **31**, respectively (Scheme 8). Depending on the steric demand of the substituent R^2, either of two conformational isomers (concave (C) and convex (V) ones) were obtained. Compound **27a** (R^2 = $COCH_2SMe$, R^3 = H) bearing a methylthioacetyl substituent was found to exists as a V-isomer in toluene-d_8, where the substituent is accommodated in the endohedral space.

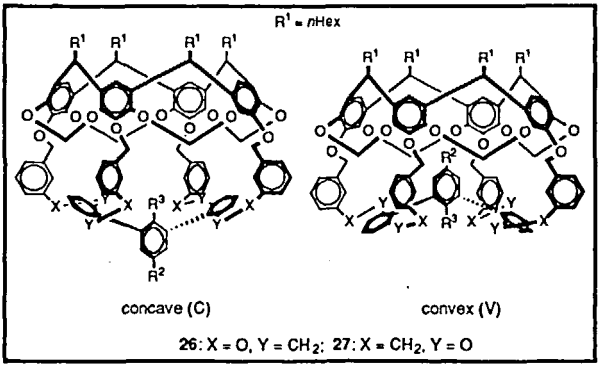
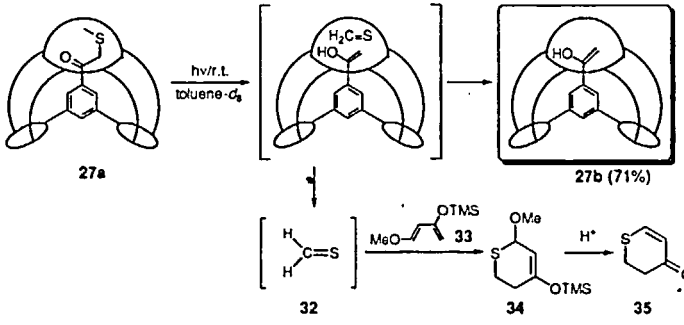
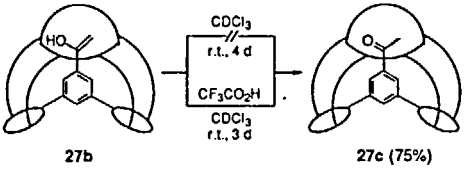


FIGURE 10 Two conformational isomers of *molecular lanterns* **26** and **27**.

took 3 days to be completed at room temperature (Scheme 10).



SCHEME 9



SCHEME 10

In order to estimate the lifetime of the endohedral thioformaldehyde, photolysis without the trapping reagent was carried out. When Danishefsky's diene **33** was added 7 s after the irradiation was stopped, a trace amount of enone **35** was detected by GCMS, indicating that the endohedral thioformaldehyde survived as long as 7 s even in solution at room temperature. The high stability of the endohedral thioformaldehyde ("daughter molecule") is considered to be attributable to the steric protection by the capsule cage of the "mother molecule".

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The author wishes to thank all the coworkers, Drs. Kei Goto, Soichiro

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