Kinetic Stabilization of the [1.1]Paracyclophane System: Isolation and X-ray Structural Analysis of a [1.1]Paracyclophane Derivative and Its Interconversion with the Transannular Adduct

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Abstract: Intentionally designed kinetic stabilization of the [1.1]paracyclophane skeleton has been achieved by multiple substitution of the aromatic rings with trimethylsilylmethyl and *N*,*N*-dimethylcarbamoyl groups, which serve to shield the proximate bridgehead carbon atoms sterically from access by other reagents. The bis(Dewar benzene) precursor (**1a**) has been prepared in essentially the same manner as previous derivatives—starting from the photocycloaddition of 1,4-bis(trimethylsilyl)-2-butyne to octahydroindacene-1,5-dione—except for a few critical modifications described in the text. Substituted [1.1]paracyclophane (**2a**), photochemically generated from the precursor, is indefinitely stable at 50 °C and suffers decomposition only by 8% after 2 h at 100 °C in degassed *n*-decane, demonstrating its greatly improved kinetic stability compared to previous [1.1]paracyclophanes. Since **2a** undergoes efficient photochemical transformation into the transannular addition product **3a**, irradiation of **1a** tends to produce a mixture of products consisting mainly of **3a**. Compound **3a**, however, reverts thermally to **2a** in a process of half life 40 min at 55 °C; the activation parameters for this process are $\Delta H^{\neq} = 21.1 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\neq} = -10.5 \pm 2.6$ cal K^{-1} mol^{-1}. Thus, on heating **3a** in benzene and cooling the resultant solution, **2a** is obtained as orange-red crystals. X-ray crystallographic analysis of **2a** reveals benzene rings bent to the highest degree ever reported for a paracyclophane, with their face-to-face arrangement in unusually close proximity. The shortest nonbonding interatomic distance is 2.376 Å; less than the sum of the van der Waals radii by more than 1.0 Å. The generation of related substituted [1.1]paracyclophanes and their kinetic stabilities are also reported.

Keywords: arenes · cycloadditions · cyclophanes · kinetic stabilization · strained molecules

Introduction

A salient feature of the [1.1]paracyclophane structure is the arrangement of two strongly bent benzene rings face-to-face in unusually close proximity. Both the physical and the chemical properties that arise from the enforced transannular interactions between the aromatic rings are of considerable interest. The parent compound and a few initially produced derivatives, however, are persistent only in dilute solution and below −20 °C, largely precluding exploration of their structures and properties.[1] Although the decomposition products are intractable polymeric materials, the known reactivity of highly strained paracyclophanes[2] suggests that their lability most probably arises from the susceptibility of bridgehead carbon atoms towards the addition of diverse reagents, by which means the steric strain inherent in the system is largely relieved. This implies that the [1.1]paracyclophane ring system might be kinetically stabilized by introducing sterically demanding substituents, effectively shielding all four bridgehead sites from access by other reagents. These considerations brought us to the design of kinetically stabilized derivatives and eventually to the successful synthesis, isolation, and X-ray crystallographic analysis of a derivative (**2a**).[3] In this paper we present details of the investigation into the preparation of **2a** and related kinetically stabilized [1.1]paracyclophane derivatives, and on the interconversion of **2a** and the transannular adduct **3a** (Scheme 1).

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Results and Discussion

Design of kinetically stabilized [1.1]paracyclophanes: Substituents conventionally used to protect active sites sterically are bulky and inert. The effective bulkiness remains largely unaffected by conformational changes, as the *tert*-butyl group illustrates. Examination of molecular models suggests that the bridgehead sites of [1.1]paracyclophane would be adequately shielded sterically by the introduction of *tert*-butyl groups

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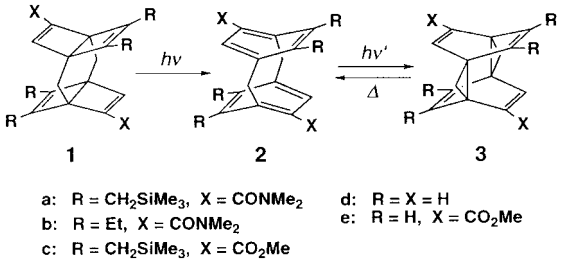
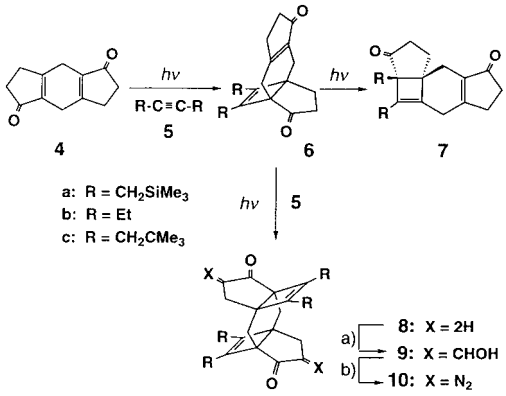


Scheme 1. Generation and isomerization of [1.1]paracyclophanes.

onto the aromatic rings, but also shows that severe steric repulsion between the substituents would result if steric protection of all the bridgehead sites were attempted. The synthetic difficulties accompanying the preparation of the corresponding bis(Dewar benzene) precursor (**1**) would be insurmountable.[4] The effective steric bulkiness of the neopentyl group, on the other hand, is highly dependent on the orientation, in the preferred conformation, of the *tert*-butyl moiety. Molecular modeling, however, suggests that the degree of conformational freedom of neopentyl groups vicinally substituted on the aromatic ring of [1.1]paracyclophane is restricted by mutual and transannular steric interactions in such a manner as to position their bulky moieties near the neighboring bridgehead carbon atoms. In the preferred conformation, this effectively shields these bridgehead carbon atoms from access by other reagents. Importantly, introduction of neopentyl groups appears not to incur excessive steric repulsion in the [1.1]paracyclophane structure and its bis(Dewar benzene) precursor. Steric congestion in both [1.1]paracyclophane and its precursor appeared to be slightly relaxed if the trimethylsilylmethyl group was employed in place of the neopentyl group—without appreciably impairing the steric shielding effect—and so we also chose this as an alternative substituent.

For the construction of 1,4-bridged Dewar benzene skeletons, we have thus far made use of the photo-Wolff ring contraction of α-diazocyclopentanone derivatives to the corresponding cyclobutanecarboxylic acid derivatives.[5] While the resultant alkoxycarbonyl substituent on the aromatic ring of [1.1]paracyclophane appeared not to contribute appreciably to steric protection of the skeleton, the corresponding *N,N*-dimethylcarbamoyl group seemed to exert a substantial stabilizing effect; in the preferred *s-trans* (with respect to the bridgehead carbon atom) conformation, one of the methyl groups is placed over the proximate bridgehead carbon atom. These expectations—based on molecular modeling—were verified experimentally as described later.

Preparation of the bis(Dewar benzene) precursors: The preparation of the substituted bis(Dewar benzene) precursors (**1a–c**) was carried out in essentially the same manner, apart from a few critical modifications, as for the precursors of the previously reported [1.1]paracyclophanes **1d** and **1e**,[1] as outlined in Schemes 2 and 3. Thus, the photocycloaddition of 1,4-bis-(trimethylsilyl)-2-butyne **5a**[6] to **4** proceeded smoothly to afford monoadduct **6a**. Subsequent addition of a second unit of **5a** to **6a** was significantly more difficult than the first, but eventually proceeded in a saturated solution of **5a** in CH_2Cl_2

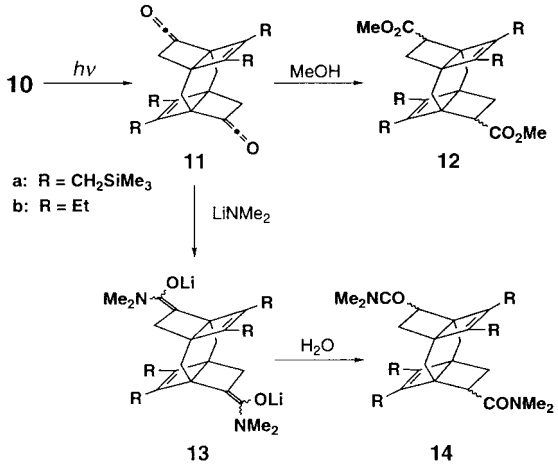


Scheme 2. Photochemical cycloaddition of substituted acetylenes (**5a–5c**) to **4**. a) HCO_2Et, MeONa. b) *p*-$MeC_6H_4SO_2N_3$, Et_3N.

to furnish **8a** in 76% yield after 30% conversion. Extended irradiation only increased the production of an isomer of **6a**, to which the structure **7a** was tentatively assigned.[7] The bis-adduct **8a** is structurally homogeneous; the product of the addition of two molecules of **5a** to the opposite faces of **4**, as was later confirmed by X-ray structural analysis of its derivatives **2a** and **3a**. The same face-selectivity has been observed in the photocycloaddition of acetylene to **4**.[1]

On the other hand, irradiation of **4** in a solution of 2,2,7,7-tetramethyl-4-octyne **5c**[8] in CH_2Cl_2 afforded a mixture of **6c** and **7c** in a ratio of about 5:1 in 69% yield after 56% conversion. The second addition of **5c** to **6c**, however, was too inefficient to be practical, and prolonged irradiation of **6c**, even in a concentrated solution of **5c**, predominantly produced **7c**. Hence, the preparation of **8c** was effectively denied. The carbon–silicon single bond (1.89 Å) is significantly longer than the carbon–carbon single bond (1.54 Å) and this would sterically facilitate the addition of **5a** to **6a**, relative to that of **5c** to **6c**.

The α-diazotization of diketone (**8a**) to afford **10a**, followed by photo-Wolff rearrangement in methanol, furnished **12a** in 84% yield as an almost stereochemically homogeneous product (Scheme 3).[9] Irradiation of **10a** in an aprotic solvent yielded diketene **11a**, from which amide **14a**



Scheme 3. Preparation of diketene **11** and its subsequent reactions.

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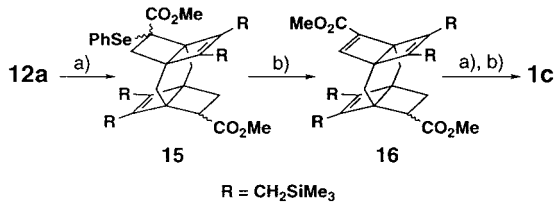
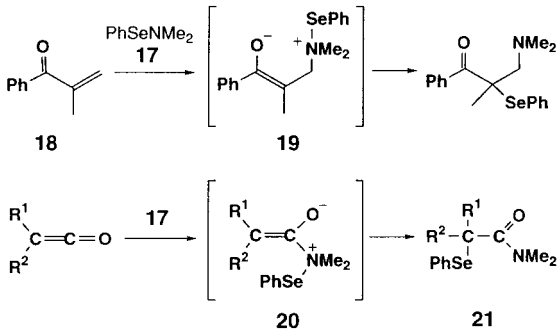
was obtained by the addition of $LiNMe_2$, followed by hydrolysis.[10] Ester **12a** and amide **14a**, however, are already so sterically congested that attempts to α-phenylselenenylate them met with difficulty. Thus, neither treatment of **12a** with lithium diisopropylamide (LDA)/PhSeBr,[11] nor attempts to react PhSeBr with the enolate ion generated from **11a** and NaOMe[12] provided the desired product. Treatment with KH in the presence of $(PhSe)_2$ has been recommended for the selenenylation of sterically hindered esters.[13] Application of this method to **12a** resulted in the formation of **15** in modest yield, and **16** was obtained from this by following the usual oxidation–elimination protocol (Scheme 4).[11] By repetition of the same reaction sequence, **16** was finally converted to **1c** in 20% yield.



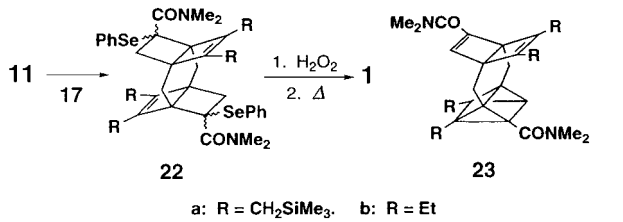
Scheme 4. Synthesis of **1c** from **12a**. a)KH, $(PhSe)_2$. b) 1. H_2O_2; 2. Δ.

The selenenylation of **14a** was all the more difficult and the above methods proved useless. It is known that selenenamide **17** adds to the carbon–carbon double bond of conjugated enone **18** by way of the initial formation of zwitterion **19**, followed by intramolecular migration of the phenylselenyl group (Scheme 5).[14] The central carbon atoms of the ketene



Scheme 5. Hypothetical pathway for the reaction of ketene with selenenamide.

moieties of **11a** are apparently less sterically encumbered than the carbon atoms adjacent to the amide groups of **14a**. If **17** can add to ketene to generate zwitterionic intermediate **20**, α-selenenylated amide **21** may well be produced through subsequent migration of the phenylselenyl group. This hypothesized reaction worked excellently in practice, and treatment of **11a** with **17** furnished **22a**, from which **1a** was obtained following the usual oxidation–elimination procedure (Scheme 6). The less sterically congested amide **1b** was also prepared in the same manner from the twofold adduct of 3-hexyne to **4**.



Scheme 6. Synthesis of **1** from **11** and the structure (**23**) tentatively assigned to a side product in photochemical generation of **2** from **1** (R = CH_2SiMe_3 or Et).

Generation of [1.1]paracyclophanes and their kinetic stabilities: Amide **1a** exhibits in its UV/Vis absorption spectrum a featureless end absorption that extends to 350 nm with a barely discernible shoulder at about 255 nm (ε 6900). Irradiation of **1a** in degassed *n*-decane with a low-pressure mercury lamp led to the formation of species exhibiting a characteristic UV/Vis absorption with λ_{max} at 267, 321, and 376.5 nm, accompanied by a weak, broad band (λ_{max} 464 nm[15]) in the range 400–530 nm (Figure 1). The generated species is

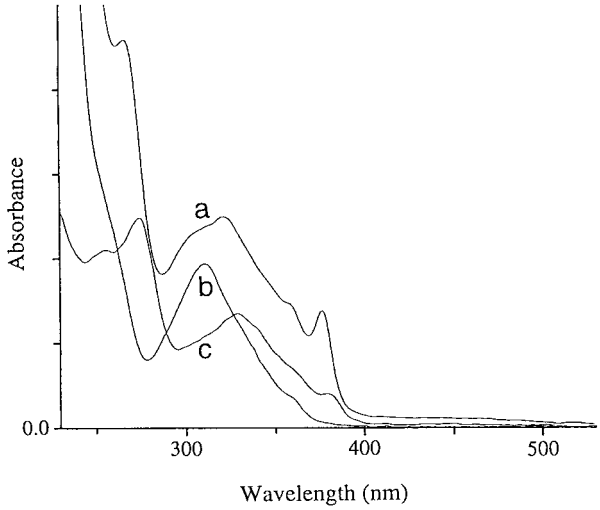


Figure 1. Difference UV/Vis absorption spectra (spectrum after irradiation minus spectrum prior to irradiation) for the photochemical isomerization of **1** to **2** with light of wavelength 254 nm: a) **1a** → **2a** in *n*-decane, λ_{max} = 267, 312 (sh.), 321, 357 (sh.), 376.5 nm ; b) **1b** → **2b** in diethyl ether, λ_{max} = 311, 357 (sh.) nm; c) **1c** → **2c** in *n*-decane, λ_{max} = 275, 330, 379 nm. The scales of absorbance for spectra **a**–**c** differ from each other.

photochemically reactive and rapidly consumed when the resulting mixture is irradiated with filtered light of wavelength > 420 nm. The observed spectral changes are due to the initial transformation of **1a** into **2a**, followed by the secondary transannular addition to give **3a** as confirmed by the isolation of respective products as described later.[16] The second process represents, to our knowledge, the first direct formation of benzene *p*,*p*′-dimer.[17] The intensity of the UV/Vis absorption due to **2a** remains unchanged at 50 °C in darkness and decreases only by 8% after 2 hours at 100 °C, demonstrating the pronounced kinetic stabilization of the [1.1]paracyclophane skeleton by these substituents. It should be recalled that both **2d** and **2e** suffer complete decomposition within four hours at room temperature in degassed dilute

solution. Compound **2a**, however, is only marginally stable in the presence of air. When the seal of an NMR tube containing a degassed C_6D_6 solution of **2a** was broken and the solution shaken for one minute before rerecording the spectrum, the intensities of signals due to **2a** had decreased to about half their previous values.

Compound **1b** also underwent successive phototransformation into **2b** and then into **3b**, as ^{1}H NMR measurements revealed. The UV/Vis absorption due to **2b**, which is blue-shifted by 10–20 nm relative to that of **2a**, slowly decays with a half life of about five days at ambient temperature, indicating that **2b** is more stable than **2d** and **2e**, but significantly inferior to **2a** in kinetic stability. Thus, the ethyl substituents appear significantly less effective for kinetic stabilization of the [1.1]paracyclophane system than do the trimethylsilylmethyl groups.

Irradiation of **1c** with a low-pressure mercury lamp similarly led to the development of UV/Vis absorptions with λ_{max} at 275, 330, and 379 nm, accompanied by a weak, broad band extending over 500 nm. The observed spectrum was slightly red-shifted from that of **2a**, but both spectra were similar in shape, including the characteristic broad bands in the 400–500 nm region. Upon subsequent irradiation with filtered visible light (>420 nm), the developed absorption rapidly decayed, like that observed with **2a**. Accordingly, it was ascribed to **2c**. In darkness, the intensity of the absorption decreased by 25% after 4.5 days at room temperature and by 20% after 80 min at 50 °C, revealing that **2c** is slightly more stable than **2b**, but significantly inferior to **2a** in kinetic stability. This is in accord with predictions based on molecular modeling.

Thermal cycloreversion of 3a to 2a: When a degassed *n*-decane solution containing **3a** was allowed to stand in darkness at room temperature, the characteristic UV/Vis absorption due to **2a** slowly developed, demonstrating the ability of **3a** to revert thermally to **2a**.[18] The corresponding cycloreversion is also observed for **3b** and **3c**. This reactivity of **3** proved to be quite advantageous for the preparation and purification of the air-sensitive **2**, since the latter is difficult to prepare in pure form and reasonable yield directly from **1**. The photochemical isomerization of **1** tends, except at very low degrees of conversion, to produce mainly **3** rather than the primary product **2**, because **2** is very susceptible to photochemical transformation into **3** and, moreover, its high absorptivity extends to a wavelength much longer than that of the precursor **1**. In the photochemical reaction of **1a** in C_6D_6 (irradiation with a high-pressure mercury lamp through Pyrex), for example, **3a** is already the major product after 15% conversion of **1a**. After 80% conversion, **2a**, **3a**, and a third product to which structure **23** was tentatively assigned are formed in yields of 5, 66, and 6%, respectively.[19] Thus, air-stable **3a** is readily obtained as colorless crystals by successive irradiation of a solution of **1a** with a high-pressure mercury lamp and then with a xenon lamp (to convert remaining **2a** into **3a**). The transannular adduct **3a** reverts quantitatively to **2a** when heated in darkness at 37 °C for 23 h in degassed CD_2Cl_2, and is regenerated cleanly upon subsequent irradiation of the resulting solution with visible light (>420 nm) (Figure 2).[20] When a solution of **3a** in degassed benzene was heated at 45 °C for 16 h, concentrated, and then cooled to 5 °C, the resulting **2a** separated from solution in the form of orange-red crystals.

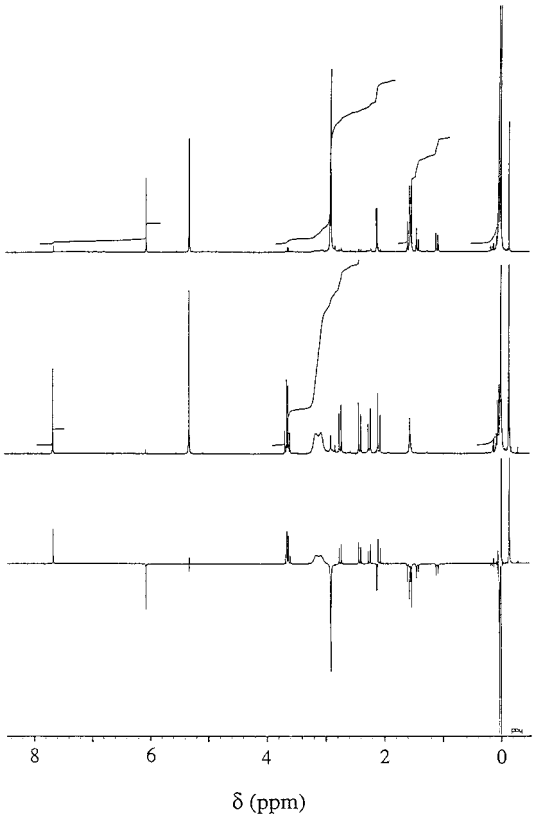


Figure 2. ^{1}H NMR (400 MHz) spectral changes observed in the thermal cycloreversion of **3a** to **2a** in CD_2Cl_2 (signals at δ 1.55 and 5.33 are due to water and residual solvent proton, respectively). Top: Before heating. Weak signals due to **2a**, generated from **3a** during the preparation of the sample, are already observed. Middle: After heating the sample at 37 °C for 23 h. The resulting spectrum is essentially that of **2a**. Bottom: Difference spectrum. Clean, quantitative reverse transformation was observed upon irradiation of the resultant solution with visible light (>420 nm).

Molecular structures of 2a and 3a: The molecular structures of **2a** and **3a** are given in Figures 3 and 4, respectively. Selected bond lengths, nonbonding interatomic distances, and bond and torsion angles are listed in Tables 1 and 2. Both **2a** and **3a** are C_i symmetric in the crystalline state and their polycyclic cores are slightly distorted from ideal D_{2h} symmetry.[21]

The transannular interatomic distance between the opposing bridgehead carbon atoms C(1)–C(4′) of **2a** is 2.376(5) Å, less than the sum of the van der Waals radii (3.5–3.6 Å)[22] by more than 1.0 Å. The corresponding distances between nonbridgehead aromatic carbon atoms C(2)–C(5′) and C(3)–C(6′) are 3.025(5) and 2.996(5) Å, respectively. The enforced electronic transannular interactions in [1.1]paracyclophane and derivatives are reflected in the appearance of characteristic, markedly red-shifted broad bands commonly observed in their UV/Vis absorption spectra. The dihedral angle α between the mean plane of the four non-bridgehead carbon atoms and the plane of adjoining flap is 25.6° on the side bearing the amide group and 24.3° on the other. The

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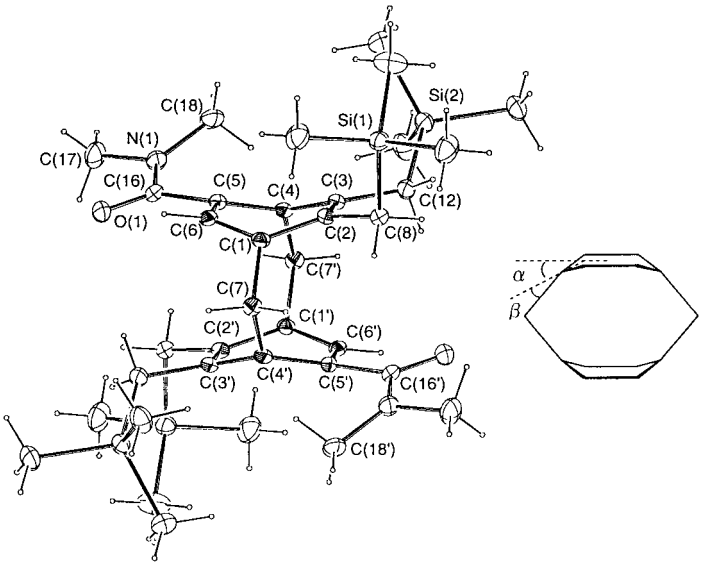


Figure 3. Crystal structure of **2a**.

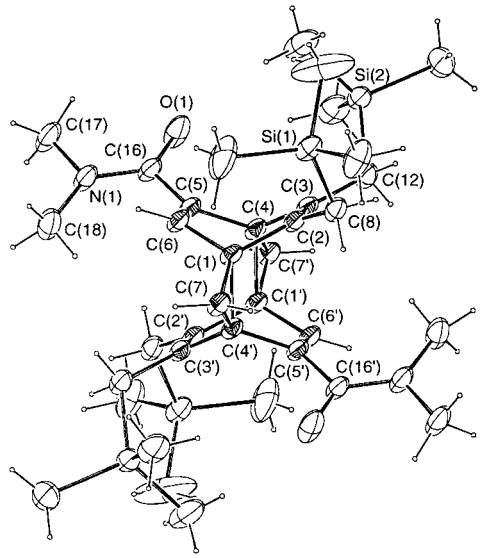


Figure 4. Crystal structure of **3a**.

Table 1. Selected bond lengths [Å], nonbonding interatomic distances [Å], and bond and torsion angles [°] in **2a**.

C(1)–C(2)	1.443(6)	C(2)–C(3)	1.396(6)	C(3)–C(4)	1.422(6)
C(4)–C(5)	1.421(6)	C(5)–C(6)	1.400(6)	C(1)–C(6)	1.386(6)
C(1)–C(7)	1.551(6)	C(4)–C(7′)	1.560(6)	C(1)···C(4′)	2.376(5)
C(2)···C(5′)	3.025(5)	C(3)···C(6′)	2.996(5)	C(1)···C(4)	2.760(5)
C(2)···C(6)	2.392(5)	C(3)···C(5)	2.418(5)	C(8)···C(16′)	3.245(5)
C(1)-C(2)-C(3)	117.6(4)	C(2)-C(3)-C(4)	119.3(4)		
C(3)-C(4)-C(5)	116.5(4)	C(4)-C(5)-C(6)	116.4(4)		
C(5)-C(6)-C(1)	121.6(4)	C(2)-C(1)-C(6)	115.4(4)		
C(2)-C(1)-C(7)	120.9(4)	C(6)-C(1)-C(7)	118.2(4)		
C(1)-C(7)-C(4′)	99.6(3)	C(3)-C(4)-C(7′)	117.9(4)		
C(5)-C(4)-C(7′)	118.0(4)	C(4)-C(5)-C(16)	127.1(4)		
C(6)-C(5)-C(16)	115.1(4)	C(1)-C(2)-C(3)-C(4)	0.4(4)		
C(2)-C(3)-C(4)-C(5)	28.9(4)	C(3)-C(4)-(5)-C(6)	29.5(4)		
C(1)-C(6)-C(5)-C(4)	0.8(4)	C(2)-C(1)-C(6)-C(5)	28.2(4)		
C(3)-C(2)-C(1)-C(6)	28.4(4)	C(2)-C(3)-C(4)-C(7′)	120.2(5)		
C(3)-C(2)-C(1)-C(7)	124.9(5)	C(5)-C(6)-C(1)-C(7)	125.9(5)		
C(6)-C(5)-C(4)-C(7′)	119.6(5)	C(1)-C(2)-C(3)-C(12)	168.3(6)		
C(1)-C(6)-C(5)-C(16)	167.9(5)	C(4)-C(3)-C(2)-C(8)	172.8(6)		
C(6)-C(5)-C(16)-O(1)	14.0(4)	C(6)-C(5)-C(16)-N(1)	163.1(5)		
C(3)-C(2)-C(8)-Si(1)	103.2(5)	C(2)-C(3)-C(12)-Si(2)	140.2(5)		
C(17)-N(1)-C(16)-O(1)	4.6(4)	C(18)-N(1)-C(16)-O(1)	161.3(7)		

degree of out-of-plane bending of the bridging bonds, β, is 26.8° on the side nearer to the amide group and 22.9° on the far side.[23] Thus, the averaged total bending angle ($\alpha+\beta$) is 49.8°: the largest value ever reported for a paracyclophane[24] and only slightly less than the calculated value for [5]paracyclophane.[25, 26] Despite the extreme deformation of the aromatic rings, no systematic bond alternation is discernible in them and their carbon–carbon bond lengths appear rather to be primarily affected by the degrees of steric repulsion between the substituents. The bonds of methylene bridges are lengthened from the normal 1.50–1.52 Å to 1.55–1.56 Å, probably because of the steric repulsion between the aromatic rings. The bond angle C(1)–C(7)–C(4′) is narrowed from 112.5° in diphenylmethane[27] to 99.6°, to accommodate the planarity-preferring benzene rings in the [1.1]paracyclophane structure. These geometric parameters are satisfactorily reproduced by theoretical calculations for the parent **2d** at the RHF/6–31G*, B3LYP/6–31G*, or MP2/6–31G* level,[1b] suggesting that the distortion of the [1.1]paracyclophane core by the substituents is only modest. Besides the bridgehead carbon atoms, the residual aromatic carbon atoms are also pyramidalized and the substituents are consequently bent inward (e.g., torsion angle C(1)–C(6)–C(5)–C(16) is 167.9(6)°) against the transannular steric repulsion between them,[28] so as better to maintain cyclic conjugation[29] in the aromatic rings, as has been observed in [2.2]paracyclophanes[30] and theoretically predicted for strained [n]paracyclophanes.[5c] The amide groups are bent away from the adjacent methylene bridge and the nitrogen atoms are slightly pyramidalized to ease the steric repulsion between the amide groups and the cyclophane core.

In good agreement with the molecular modeling results, the four bridgehead carbon atoms are effectively shielded sterically by the substituents. Thus, the nearly planar amide group adopts the *s-trans* conformation with respect to the adjacent bridgehead carbon atom, placing one of the methyl groups (C(18) and C(18′)) above the bridgehead site. Preferential adoption of a similar conformation in solution is supported by the observation of a positive nuclear Overhauser effect (NOE) between one of the methylene-bridge protons and the *N*-methyl protons. The inferior kinetic stability of ester **2c** compared to that of amide **2a**, as presumed from molecular modeling, is most probably due to the lack of the corresponding methyl group protruding above the neighboring bridgehead site. The trimethylsilyl groups preferentially occupy the space near the proximate bridgehead carbon atom and so sterically hinder access to this by other reagents, thereby minimizing repulsive steric interactions: mutual, transannular, and with the methylene bridges.

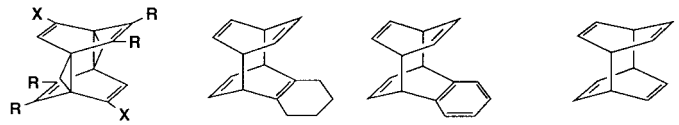
Table 2. Selected bond lengths [Å], nonbonding interatomic distances [Å], and bond and torsion angles [°] in **3a**.

C(1)–C(2)	1.508(2)	C(2)–C(3)	1.350(2)	C(3)–C(4)	1.516(2)
C(4)–C(5)	1.505(2)	C(5)–C(6)	1.345(2)	C(1)–C(6)	1.493(2)
C(1)–C(4′)	1.601(2)	C(1)–C(7)	1.499(2)	C(4)–C(7′)	1.494(2)
C(2)···C(5′)	2.789(2)	C(3)···C(6′)	2.808(2)	C(1)···C(4)	2.519(2)
C(2)···C(6)	2.991(2)	C(3)···C(5)	2.512(2)	C(8)···C(16′)	3.861(2)
C(1)-C(2)-C(3)	112.8(2)	C(2)-C(3)-C(4)	112.7(2)		
C(3)-C(4)-C(5)	112.5(1)	C(4)-C(5)-C(6)	112.3(2)		
C(5)-C(6)-C(1)	113.8(2)	C(2)-C(1)-C(6)	112.2(1)		
C(1)-C(4′)-C(7)	57.8(1)	C(1)-C(7)-C(4′)	64.7(1)		
C(4′)-C(1)-C(7)	57.5(1)	C(4)-C(5)-C(16)	119.8(1)		
C(6)-C(5)-C(16)	127.5(2)	C(1)-C(2)-C(3)-C(4)	0.5(1)		
C(2)-C(3)-C(4)-C(5)	51.0(2)	C(3)-C(4)-C(5)-C(6)	49.9(2)		
C(1)-C(6)-C(5)-C(4)	1.4(1)	C(2)-C(1)-C(6)-C(5)	52.0(2)		
C(3)-C(2)-C(1)-C(6)	50.6(2)	C(1)-C(2)-C(3)-C(12)	177.7(2)		
C(1)-C(6)-C(5)-C(16)	174.4(2)	C(4)-C(3)-C(2)-C(8)	176.8(2)		
C(6)-C(5)-C(16)-O(1)	136.9(2)	C(6)-C(5)-C(16)-N(1)	43.1(2)		
C(3)-C(2)-C(8)-Si(1)	111.5(2)	C(2)-C(3)-C(12)-Si(2)	120.4(2)		
C(17)-N(1)-C(16)-O(1)	3.7(2)	C(18)-N(1)-C(16)-O(1)	175.7(3)		

The most prominent feature in the structure of **3a** is the unusual lengthening of the inner cyclopropane bonds to 1.601(2) Å. They are longer by 0.10–0.11 Å than the peripheral cyclopropane bonds, while the latter appear slightly shortened from a bond length of 1.51 Å for cyclopropane.[31] Compound **3a** possesses the structure of benzene *p*,*p*′-dimer bridged by methylenes. Similar lengthening of bonds has been observed for related dibenzene structures[32] and, to explain the anomalous bond lengthening, π-σ-π through-bond coupling[33] has previously been invoked.[32, 34, 35] Siegel and coworkers recently questioned this explanation and asserted that steric/electrostatic repulsion is the dominant cause of bond elongation.[36] Nonbonding interatomic distances between the proximate unsaturated carbon atoms C(2)···C(5′) and C(3)···C(6′) are only 2.789 and 2.808 Å, respectively, and thus significantly shorter than the sum of the van der Waals radii. It is interesting to note in this context that the length of the inner cyclopropane bond of **3a** is reproduced satisfactorily by the theoretical calculations for the parent **3d** at both the B3LYP/6–31G* (1.607 Å) and MP2/6–31G* (1.597 Å) levels,[37, 38] but only poorly at the RHF/6–31G* level (1.564 Å) and by the semiempirical AM1 (1.563 Å) and PM3 (1.548 Å) methods.[39]

The molecular shapes of **2a** and **3a** appear similar, the conformations adopted by the trimethylsilylmethyl groups included, except that the carbamoyl group adopts an *s-cis* conformation in **3a**, compared to an *s-trans* conformation in **2a**. NOE experiments on **3a** unambiguously demonstrated that the carbamoyl groups preferentially adopt the *s-cis* conformation in solution as well; a positive NOE was observed between the *N*-methyl and the olefinic protons, while the effect was not discerned between the *N*-methyl and the cyclopropane protons. The aromatic rings of **2a** are significantly flattened relative to the cyclohexadiene rings of **3a**, due to the alteration in hybridization of the bridgehead carbon atoms and—possibly—to maintain the aromatic cyclic conjugation of the π bonds. The carbamoyl groups of **2a** consequently seem to prefer the *s-trans* conformation in which transannular steric repulsion between the *N*-methyl groups and the substituents on the opposite ring is substantially eased compared to that in the *s-cis* conformation.

Kinetics of thermal cycloreversion of 3 to 2: The rates of thermal cycloreversion of **3a** to **2a** were measured at 30, 40, 48, and 55 °C in degassed hexane by monitoring the development of UV/Vis absorption due to the latter compounds. The reaction follows first-order kinetics and activation parameters for the process are $\Delta G^{\ddagger} = 24.4$ kcal mol^{-1} at 40 °C, $\Delta H^{\ddagger} = 21.1 \pm 0.8$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -10.5 \pm 2.6$ cal K^{-1} mol^{-1} (Scheme 7). The half lives of **3a** in hexane at 55 and 30 °C are 40 and 625 min, respectively. Activation parameters for the cycloreversion of related *p*,*p*′-dibenzene derivatives **24**[40] and **25**[41] are also listed in Scheme 7 for comparison.



R = CH_2SiMe_3, X = $CONMe_2$

$\Delta H^{\ddagger}$	21.1 ± 0.8	22.4 ± 1.2	22.8 ± 0.4 kcal mol^{-1}
$\Delta S^{\ddagger}$	-10.5 ± 2.6	0.9 ± 3.9	-1.4 ± 1.3 cal K^{-1}mol^{-1}

Scheme 7. Activation parameters for the cleavage of dibenzene derivatives.

Calculated relative energies of **3d** to **2d** and of the unknown parent *p*,*p*′-dibenzene (**26**) to two molecules of benzene are listed in Table 3.[43] The heat of reaction for the isomerization of **3a** to **2a** is −22.0 kcal mol^{-1} by the PM3 method, compared to −18.9 kcal mol^{-1} for the parent system, which indicates that the isomerization energy remains largely unaffected by the substituents. Despite the large difference in heats of reaction, the magnitude of the activation barrier for **3a** is comparable to those for **24** and **25**. The cleavage of benzene *p*,*p*′-dimer is a highly exothermic process and may proceed by way of an early transition state in conformity to the Hammond postulate,[44] while the transition state for the transformation of **3** into **2** is perhaps relatively later and the bond cleavage may be more advanced because of the lesser

Table 3. Calculated relative energies [kcal mol^{-1}] of **3d** to **2d** and of benzene *p*,*p*′-dimer (**26**) to two molecules of benzene.

	MNDO	AM1	PM3	RHF/6–31G*	B3LYP/6–31G*
3d	9.7	28.4	18.9	8.7	26.2
26	45.3[a]	38.1	36.9	81.4[b]	78.4

[a] From ref. [34b]. [b] 81.8 kcal mol^{-1} at the RHF/6–31G*//RHF/3–21G level, see ref. [42]

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exothermicity. The bonds to be ruptured in the latter reaction are, however, relatively weak, strained cyclopropane bonds and, accordingly, the magnitudes of the activation barriers for the two processes—the isomerization of **3a** to **2a** and the fission of **24** and **25**—may become comparable.

Interestingly, **3c** undergoes cycloreversion to **2c** 20–25 times faster than **3a** at ambient temperature, while the rate for **3b** is comparable to that for **3a**. These observations suggest that the rate of cycloreversion is also subject to substituent electronic effects.[45]

Conclusion

The parent [1.1]paracyclophane (**2d**) is a highly strained, thermally labile species. These results demonstrate that compounds possessing the [1.1]paracyclophane skeleton can be isolated and handled at ambient temperature, provided that the reactivity toward intermolecular reactions at the bridgehead sites is adequately suppressed by substituents. X-ray structure analysis of a kinetically stabilized derivative has revealed the face-to-face arrangement of strongly bent aromatic rings, with the transannular distance less than the sum of the van der Waals radii by more than 1.0 Å, suggesting strong electronic interactions between the rings. [1.1]Paracyclophane (**2**) undergoes photochemical transformation into the transannular addition product (**3**), accompanied by pronounced changes in the electronic absorption spectrum. Compound **3** readily reverts thermally into compound **2**. Yet the attendant changes in the shape of molecule are relatively small. This interconversion may constitute an interesting photo-/thermochromic system.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on JEOL EX-400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) spectrometers in $CDCl_3$ unless otherwise indicated. IR spectra were taken on a Hitachi Model 215 grating spectrometer. Mass spectra were recorded on JEOL JMS-DX 500 (EI) and JMS-01SG-2 (FD) spectrometers. UV/Vis spectra were recorded on a Hitachi U-4000 spectrophotometer. Column and thin-layer chromatography (TLC) were performed on silica gel 60 (Merck) of particle size 63–200 and 5–20 μm, respectively. HPLC was carried out on LiChrosorb Si60 (Merck, 7 μm). Elemental analyses were performed at the Center for Instrumental Analysis of Hokkaido University. The reactions were carried out in dried glassware under argon atmosphere. Halos (Eiko-sha, Japan) 500-W high-pressure and 120-W low-pressure mercury lamps were employed as light sources for photochemistry. A 500-W high-pressure mercury lamp fitted with a Corning 0-52 glass filter was used as a >335 nm light source and a 500-W xenon lamp fitted with a Corning 3-73 glass filter as a >420 nm light source. 1,2,3,4,5,6,7,8-Octahydroindacene-1,5-dione,[1b] 1,4-bis(trimethylsilyl)-2-butyne,[6] 2,2,7,7-tetramethyl-4-octyne,[8] and *N*,*N*-dimethylphenylselenenamide[14] were prepared following known procedures. Other reagents and solvents were obtained from commercial sources and purified prior to use.

Photocycloaddition of 5a to 4: *Preparation of 6a:* A solution of **4** (450 mg, 2.39 mmol) and **5a** (4.95 g, 23.9 mmol) in CH_2Cl_2 (120 mL) with added $NaHCO_3$ (60 mg) was placed in a Pyrex vessel, cooled to $-50\,^\circ$C, and irradiated with a 500-W high-pressure mercury lamp. The reaction was monitored by GLC and irradiation was continued until the amount of **6a** ceased to increase (3 h). The mixture was warmed to room temperature, filtered, and concentrated in vacuo. The unreacted **5a** was recovered from the residue by distillation (80 °C, 20 mmHg). The resultant mixture was diluted with diethyl ether to facilitate the precipitation of unreacted **4** (200 mg, 44 %) and filtered. After removal of the solvent, the residue was subjected to chromatography on silica gel eluted with diethyl ether–hexane (1:3) to produce **6a** (478 mg, 52 %) as a colorless solid, together with a small amount of **8a** (<8 mg). Crystallization from hexane afforded pure **6a**. M.p.: 92–94 °C; ^{1}H NMR: $\delta = 0.01$ (s, 9H), 0.05 (s, 9H), 1.32 (d, $J =$ 14.7 Hz, 1H), 1.36 (d, $J = 14.7$ Hz, 1H), 1.40 (d, $J = 14.7$ Hz, 1H), 1.49 (d, $J = 14.7$ Hz, 1H), 1.56 (ddd, $J = 13.2$, 12.2, 8.3 Hz, 1H), 1.95 (br d, $J =$ 16.6 Hz, 1H), 2.14 (ddd, $J = 13.2$, 9.3, 1.0 Hz, 1H), 2.22 (ddd, $J = 17.6$, 8.3, 1.0 Hz, 1H), 2.45 (br d, $J = 18.1$ Hz, 1H), 2.46 (br s, 2H), 2.50 (br s, 2H), 2.56 (br d, $J = 18.1$ Hz, 1H), 2.71 (br d, $J = 16.6$ Hz, 1H), 2.91 (ddd, $J = 17.6$, 12.2, 9.3 Hz, 1H); ^{13}C NMR: $\delta = -0.37$, -0.11, 15.91, 16.53, 27.01, 27.23, 27.89, 30.03, 35.44, 36.14, 51.10, 59.35, 137.00, 137.22, 143.07, 172.20, 207.95, 218.54; IR (KBr): 1720, 1690, 1644 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 305.5 (530, sh), 315 (570), 327.5 nm (410 mol^{-1} dm^{-3} cm^{-1}, sh); MS (EI): *m/z* (%): 386 (49) $[M]^+$, 371 (25), 358 (13), 313 (24), 285 (13), 261 (20), 73 (100); HR-MS (EI): found 386.2070 $[M]^+$; $C_{22}H_{34}O_2Si_2$ calcd 386.2097.

Preparation of 8a: A solution of **6a** (368 mg, 0.95 mmol) and **5a** (7.3 g, 37 mmol) in CH_2Cl_2 (10 mL) with added $NaHCO_3$ (40 mg) was placed in a Pyrex vessel, cooled to $-50\,^\circ$C, and irradiated with a 500-W high-pressure mercury lamp. The reaction was monitored by GLC and irradiation was discontinued when the formation of **8a** slowed down and the proportion of side products to **8a** began to increase. The GLC yield of **8a** was 23 % (76 % based on **6a** consumed). After removal of the solvent, the unreacted **5a** was recovered by distillation (80 °C, 20 mmHg) and the residue was chromatographed on silica gel. Elution with diethyl ether–hexane (1:19–1:3) afforded a mixture containing **8a** and, then, unreacted **6a** (254 mg, 71 %). The crude **8a** was again subjected to chromatography on silica gel eluted with benzene-hexane (35:65) to produce **8a**, which was further purified by crystallization from hexane. M.p.: 119–121 °C; ^{1}H NMR: $\delta = 0.01$ (s, 9H), 0.09 (s, 9H), 1.33 (d, $J = 14.7$ Hz, 2H), 1.35 (d, $J = 14.7$ Hz, 2H), 1.44 (d, $J =$ 14.7 Hz, 2H), 1.45 (d, $J = 14.7$ Hz, 2H), 1.55 (ddd, $J = 13.2$, 10.8, 8.8 Hz, 2H), 1.67 (d, $J = 14.2$ Hz, 2H), 1.93 (ddd, $J = 13.2$, 9.8, 1.5 Hz, 2H), 2.03 (d, $J = 14.2$ Hz, 2H), 2.12 (ddd, $J = 17.6$, 8.8, 1.5 Hz, 2H), 2.79 (ddd, $J = 17.6$, 10.8, 9.8 Hz, 2H); ^{13}C NMR: $\delta = -0.29$, 0.15, 16.97, 17.12, 26.81, 30.74, 36.34, 50.22, 59.00, 139.70, 145.41, 218.10; IR (KBr): 1722, 1650 cm^{-1}; MS (EI): *m/z* (%): 584 (43) $[M]^+$, 556 (11), 460 (29), 459 (69), 386 (13), 358 (11), 73 (100); HR-MS (EI): found 584.3367 $[M]^+$; $C_{32}H_{56}O_2Si_4$ calcd 584.3358.

Preparation of bis(diazoketone) (10a): Ethyl formate (115 mg, 1.55 mmol) and MeONa (75 mg, 1.4 mmol) were added to a solution of **8a** (81 mg, 0.14 mmol) in benzene (2.0 mL) under argon, and the mixture was stirred for 16 h at room temperature, after which the reaction was quenched with water. Solid NH_4Cl was added to neutralize the mixture, from which the product was extracted with diethyl ether (3 ×). The ethereal extracts were combined, washed with water, dried with $MgSO_4$, and concentrated in vacuo to afford **9a** as a pale yellow, viscous oil. This crude **9a** was dissolved in CH_2Cl_2 (3.0 mL) and treated with *p*-toluenesulfonyl azide (TsN_3; 109 mg, 0.55 mmol) and Et_3N (112 mg, 1.11 mmol). After 18 h at room temperature, the consumption of **9a** was confirmed by TLC and the reaction was quenched with 5 % aqueous KOH. The aqueous layer was separated from the CH_2Cl_2 layer and extracted with diethyl ether (3 ×). The ethereal extracts were combined with the CH_2Cl_2 fraction, washed with water and brine, dried with $MgSO_4$, concentrated in vacuo, and subjected to chromatography on silica gel. Elution with diethyl ether–hexane (3:97) afforded unreacted TsN_3. Further elution with diethyl ether–hexane (4:96) delivered **10a** (52 mg, 59 % from **8a**) as yellow crystals. ^{1}H NMR: $\delta = 0.02$ (s, 18H), 0.09 (s, 18H), 1.40 (d, $J = 14.7$ Hz, 2H), 1.43 (d, $J = 14.7$ Hz, 2H), 1.48 (d, $J = 14.7$ Hz, 2H), 1.50 (d, $J = 14.7$ Hz, 2H), 1.78 (d, $J = 14.2$ Hz, 2H), 2.09 (br d, $J = 14.2$ Hz, 2H), 2.62 (d, $J =$ 13.7 Hz, 2H), 2.93 (d, $J = 13.7$ Hz, 2H); ^{13}C NMR: $\delta = -0.40$, 0.06, 16.73, 16.95, 30.09, 31.73, 46.64, 58.10, 60.74, 140.89, 143.93, 199.41; IR (KBr): 2084, 1648 cm^{-1}; MS (FD): *m/z* (%): 638 (30) $[M+2H]^+$, 637 (55) $[M+H]^+$, 636 (100) $[M]^+$; HR-MS (FD): found 636.3185 $[M]^+$; $C_{32}H_{52}N_4O_2Si_4$ calcd 636.3168.

Photochemical conversion of 10a into 12a: A solution of **10a** (66 mg, 0.10 mmol) and Et_3N (one drop) in MeOH (25 mL) was placed in a Pyrex test tube and irradiated with a 500-W high-pressure mercury lamp at 12 °C until the consumption of **10a** was confirmed by TLC. After removal of the solvent, the residue was subjected to chromatography on silica gel eluted with diethyl ether–hexane (3:93) to deliver **12a** (56 mg, 84 %) as essentially a single stereoisomer, which was crystallized from hexane. ^{1}H NMR: $\delta = 0.06$ (s, 18H), 0.12 (s, 18H), 1.16 (d, $J = 15.1$ Hz, 2H), 1.45 (d,

$J = 14.2$ Hz, 2H), 1.47 (d, $J = 15.1$ Hz, 2H), 1.57 (d, $J = 14.2$ Hz, 2H), 1.82 (d, $J = 14.2$ Hz, 2H), 1.86 (dd, $J = 12.2$, 9.8 Hz, 2H), 1.87 (d, $J = 14.2$ Hz, 2H), 2.20 (dd, $J = 12.2$, 6.4 Hz, 2H), 2.86 (dd, $J = 9.8$, 6.4 Hz, 2H), 3.62 (s, 6H); ^{13}C NMR: $\delta = -0.42$, 0.04, 16.31, 18.09, 32.06 (2 C), 42.16, 42.56, 49.62, 50.90, 137.76, 144.46, 174.45; IR (KBr): 1738, 1644 cm^{-1}; MS (EI): *m/z* (%): 644 (54) $[M]^+$, 73 (100); HR-MS (EI): found 644.3565 $[M]^+$; $C_{34}H_{60}O_4Si_4$ calcd 644.3569.

Conversion of 12a into 16: Potassium hydride (30 mg, 0.75 mmol) and THF (0.8 mL) were placed in a flame-dried flask and a solution of **12a** (41 mg, 65 μmol) and tetracosane (5 mg) as an internal standard in THF (1.0 mL) was added at 0 °C. The mixture was warmed up to room temperature and treated with Ph_2Se_2 (261 mg, 0.84 mmol) in THF (1.0 mL). The reaction was monitored by TLC and GLC, and three additional portions of KH (3 mg each) were added after 5, 21, and 28 h. After 30 h at room temperature, the resulting suspension was diluted with diethyl ether and the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was separated from the organic layer and extracted with diethyl ether (3 ×). The ethereal extracts were combined with the organic fraction, washed successively with water (2 ×), 5% aqueous $NaHCO_3$, water, and brine, dried with $MgSO_4$, concentrated in vacuo, and subjected to chromatography on silica gel. After removal of the unreacted Ph_2Se_2 by elution with hexane, the column was eluted with diethyl ether–hexane (15:85) to deliver 37 mg of a mixture, which was subjected to preparative TLC to afford **15** (16 mg, 32%) as colorless crystals, together with unreacted **12a** (11 mg, 27% recovery). ^{1}H NMR: $\delta = 0.07$ (s, 9H), 0.08 (s, 9H), 0.11 (s, 9H), 0.12 (s, 9H), 1.12 (d, $J = 14.7$ Hz, 1H), 1.35 (d, $J = 15.6$ Hz, 1H), 1.41 (d, $J = 15.6$ Hz, 1H), 1.47 (d, $J = 14.2$ Hz, 1H), 1.52 (d, $J = 14.2$ Hz, 1H), 1.54 (d, $J = 13.7$ Hz, 1H), 1.55 (d, $J = 14.7$ Hz, 1H), 1.67 (d, $J = 14.2$ Hz, 1H), 1.68 (d, $J = 13.7$ Hz, 1H), 1.89 (dd, $J = 12.2$, 9.8 Hz, 1H), 2.02 (d, $J = 13.2$ Hz, 1H), 2.04 (d, $J = 14.2$ Hz, 1H), 2.15 (d, $J = 14.2$ Hz, 1H), 2.17 (dd, $J = 12.2$, 5.9 Hz, 1H), 2.24 (d, $J = 14.2$ Hz, 1H), 2.79 (d, $J = 13.2$ Hz, 1H), 2.83 (dd, $J = 9.8$, 5.9 Hz, 1H), 3.58 (s, 3H), 3.62 (s, 3H), 7.24–7.33 (m, 3H), 7.44–7.47 (m, 2H).

Aqueous H_2O_2 (30%, 2 mL) was added to a solution of **15** (16 mg, 20 μmol) and pyridine (80 μL) in CH_2Cl_2 (10 mL) at 0 °C. After stirring for 5 h at room temperature, the resulting mixture was diluted with CH_2Cl_2 (10 mL), washed successively with water, 5% aqueous $NaHCO_3$, and water, dried with $MgSO_4$, and filtered. Pyridine (1.0 mL) was added to the filtrate and the solution was refluxed for 5 h. The mixture was washed successively with water, 5% aqueous $NaHCO_3$, and water, dried with $MgSO_4$, concentrated in vacuo, and subjected to preparative TLC with benzene–hexane elution (1:1) to afford **16** (8 mg, 62%). ^{1}H NMR: $\delta = 0.010$ (s, 9H), 0.012 (s, 9H), 0.05 (s, 9H), 0.08 (s, 9H), 1.07 (d, $J = 14.7$ Hz, 1H), 1.31 (d, $J = 14.2$ Hz, 1H), 1.42 (d, $J = 14.2$ Hz, 1H), 1.46 (d, $J = 14.7$ Hz, 1H), 1.50 (d, $J = 14.2$ Hz, 1H), 1.53 (d, $J = 14.2$ Hz, 1H), 1.64 (d, $J = 14.2$ Hz, 1H), 1.69 (d, $J = 14.2$ Hz, 1H), 1.81 (d, $J = 14.7$ Hz, 1H), 1.88 (dd, $J = 12.2$, 9.8 Hz, 1H), 1.92 (d, $J = 14.1$ Hz, 1H), 2.11 (d, $J = 14.1$ Hz, 1H), 2.12 (dd, $J = 12.2$, 5.9 Hz, 1H), 2.19 (d, $J = 14.7$ Hz, 1H), 2.93 (dd, $J = 9.8$, 5.9 Hz, 1H), 3.61 (s, 3H), 3.69 (s, 3H), 7.26 (s, 1H); ^{13}C NMR: $\delta = -0.53$ (2 $SiMe_3$), −0.35, −0.29, 16.35, 16.97, 17.34, 17.52, 27.01, 28.07, 29.83, 40.64, 42.74, 50.22, 50.86, 50.97, 52.18, 54.17, 138.11, 141.82, 144.00, 145.45, 148.79, 156.51, 164.01, 174.65.

Preparation of 1c from 16: A solution of **16** (6 mg, 9 μmol) in THF (0.5 mL), with tetracosane (3 mg) as an internal standard, was added at 0 °C to KH (30 mg, 0.75 mmol) and THF (0.5 mL) in a flame-dried flask. The mixture was warmed up to room temperature and treated with Ph_2Se_2 (234 mg, 0.75 mmol) in THF (0.5 mL). Compound **16** remained unchanged at room temperature, and so the mixture was heated at 50 °C. After 3 h at 50 °C, the resulting mixture was diluted with ether and the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was separated from the organic layer and extracted with diethyl ether (3 ×). The ethereal extracts were combined with the organic fraction, washed successively with water (2 ×), 5% aqueous $NaHCO_3$, water, and brine, dried with $MgSO_4$, concentrated in vacuo, and subjected to chromatography on silica gel. After removal of the unreacted Ph_2Se_2 by elution with hexane, the column was eluted with diethyl ether–hexane (1:1) to deliver the phenylselenenylated product. The crude product was purified by preparative TLC elution with benzene–hexane (1:1) and subjected to oxidation–elimination of the phenylselenenyl group as described for **15**. Compound **1c** was isolated from the reaction mixture by HPLC elution with ether–hexane (3:97): ^{1}H NMR: $\delta = -0.01$ (s, 36H), 1.1–1.5 (m, 8H), 2.1–2.5 (2 d, $J = 15$ Hz, 4H), 3.69 (s, 6H), 7.26 (s, 2H); FD-MS: *m/z* (%): 641 (54) $[M+H]^+$, 640 (100) $[M]^+$.

Preparation of 1a from 10a: A solution of **10a** (74 mg, 0.12 mmol) in THF (15 mL) was placed in a Pyrex test tube and irradiated with a 500-W high-pressure mercury lamp at −60 °C. The disappearance of the acyldiazo functionality (2072, 1666 cm^{-1}) and the formation of ketene (2096 cm^{-1}) were confirmed by IR after 1.5 h. The mixture was cooled to −78 °C, treated with freshly prepared $PhSeNMe_2$ (0.12 mL), stirred for 1 h at −78 °C, and allowed to warm slowly to 10 °C before the reaction was quenched with water. The aqueous layer was separated from the organic layer and extracted with diethyl ether (2 ×). The ethereal extracts were combined with the organic fraction, washed with water and brine, dried with $MgSO_4$, concentrated in vacuo, and chromatographed on silica gel. The column was eluted with hexane to remove unreacted Ph_2Se_2, and then with diethyl ether–hexane (1:1) to deliver a mixture of phenylselenenylated products. This was subjected to the oxidation–elimination procedure described for **15**. The crude product was purified by preparative TLC and then by HPLC eluted with diethyl ether–hexane (2:3) to produce **1a** (15 mg, 20%) as a colorless oil. ^{1}H NMR (C_6D_6): $\delta = 0.14$ (s, 18H), 0.24 (s, 18H), 1.55 (d, $J = 14.2$ Hz, 2H), 1.61 (d, $J = 14.2$ Hz, 2H), 1.71 (dd, $J = 14.2$, 1.5 Hz, 2H), 1.85 (dd, $J = 14.2$, 1.5 Hz, 2H), 2.68 (d, $J = 14.2$ Hz, 2H), 2.70 (br s, 6H), 2.76 (br s, 6H), 3.05 (d, $J = 14.2$ Hz, 2H), 6.71 (s, 2H); ^{13}C NMR (CD_2Cl_2): $\delta = -0.78$, −0.71, 16.74, 16.85, 35.19, 37.81, 51.91, 56.57, 143.97, 144.67, 149.20, 150.41, 164.51; IR (neat): 1628, 1578 cm^{-1}; UV/Vis (*n*-hexane): λ_{max} (ε) = 255 nm (6900 mol^{-1} dm^{-3} cm^{-1}); MS (EI): *m/z* (%): 666 (50) $[M]^+$, 651 (41), 594 (48), 576 (43), 522 (44), 309 (72), 307 (40), 73 (100); HR-MS (EI): found 666.3924 $[M]^+$; $C_{36}H_{62}N_2O_2Si_4$ calcd 666.3889.

Photocycloaddition of 5c to 4: A solution of **4** (50 mg, 0.27 mmol) and **5c** (442 mg, 2.7 mmol) in CH_2Cl_2 (15 mL) was placed, together with $NaHCO_3$ (20 mg), in a Pyrex test tube and irradiated using a 500-W high-pressure mercury lamp through a K_2CrO_4 filter solution for 8 h at 0 °C. After removal of the solvent, the unreacted **5c** was recovered by distillation and the residue was triturated with diethyl ether to extract products; 22 mg of diethyl ether-insoluble **4** (44%) was recovered. The ethereal extract was concentrated and chromatographed on silica gel. Elution with diethyl ether-hexane (2:3) delivered a mixture of **6c** and **7c** (36 mg, 38%), from which **6c** (17 mg, 18%) and **7c** (4 mg, 4%) were isolated by preparative TLC. Compound **6c**: ^{1}H NMR: $\delta = 0.89$ (s, 9H), 0.96 (s, 9H), 1.54 (dt, $J = 13.2$, 7.8 Hz, 1H), 1.79 (d, $J = 14.2$ Hz, 1H), 1.97 (d, $J = 14.2$ Hz, 2H), 2.02 (d, $J = 14.2$ Hz, 1H), 2.07 (br d, $J = 16.1$ Hz, 1H), 2.21 (dd, $J = 17.1$, 8.3 Hz, 1H), 2.26 (dd, $J = 13.2$, 8.8 Hz, 1H), 2.44–2.62 (m, 6H), 2.75 (br d, $J = 16.1$ Hz, 1H), 2.95 (ddd, $J = 17.1$, 13.2, 8.8 Hz, 1H); ^{13}C NMR: $\delta = 27.71$, 27.96, 28.18, 29.92, 30.49 (3 C), 30.84 (3 C), 31.35, 31.55, 35.55, 36.41, 40.00, 40.71, 52.36, 59.77, 137.56, 144.75, 150.11, 173.30, 207.53, 218.23; FD-MS: *m/z* (%): 355 (31) $[M+H]^+$, 354 (100) $[M]^+$. Compound **7c**: ^{1}H NMR: $\delta = 0.90$ (s, 9H), 0.91 (s, 9H), 1.34 (d, $J = 15.1$ Hz, 1H), 1.61 (ddd, $J = 13.2$, 11.2, 9.8 Hz, 1H), 1.85 (d, $J = 15.1$ Hz, 1H), 1.86 (br dd, $J = 13.2$, 9.8 Hz, 1H), 1.89 (d, $J = 15.1$ Hz, 1H), 2.07 (d, $J = 15.1$ Hz, 1H), 2.30 (br dd, $J = 19.0$, 9.8 Hz, 1H), 2.39 (br d, $J = 16.6$ Hz, 1H), 2.46–2.64 (m, 5H), 2.70 (ddd, $J = 19.0$, 11.2, 9.8 Hz, 1H), 3.00 (br d, $J = 21.5$ Hz, 1H), 3.09 (br d, $J = 21.5$ Hz, 1H); ^{13}C NMR: $\delta = 26.04$, 28.95, 29.43, 29.55, 29.90, 30.34 (3 C), 31.00, 32.13 (3 C), 34.84, 35.19, 39.32, 40.16, 49.21, 64.94, 138.62, 142.21, 142.76, 169.24, 208.30, 216.44.

Irradiation of **6c** with filtered light (>310 nm) did not furnish **8c** in significant yield either in a 2 M solution of **5c** in CH_2Cl_2 in the presence or absence of xanthone as a triplet sensitizer, or in a 1 M solution of **5c** in acetone. Under these conditions, **6c** predominantly underwent isomerization to **7c**.

Photocycloaddition of 3-hexyne (5b) to 4: A solution of **4** (446 mg, 2.37 mmol) and 3-hexyne (3.6 g, 43.8 mmol) in CH_2Cl_2 (80 mL) and $NaHCO_3$ (250 mg) were placed in a Pyrex vessel, cooled to −50 °C, and irradiated with a 500-W high-pressure mercury lamp. The reaction was monitored by GLC and the irradiation was discontinued when the amount of **6b** ceased to increase. The mixture was filtered and concentrated by distillation to recover the unreacted **5b** together with the solvent. The resulting mixture was diluted with ether to facilitate the precipitation of deithyl ether-insoluble **4** (58 mg, 13%) and filtered. After removal of the solvent, the residue was subjected to chromatography on silica gel eluted with diethyl ether-hexane (1:19) to produce **8b** (146 mg, 17%). Further elution with diethyl diethyl ether-hexane (35:65) delivered **6b** (400 mg, 63%).

A solution of **6b** (129 mg, 0.48 mmol) and 3-hexyne (2.2 g, 26.2 mmol) in CH_2Cl_2 (5 mL) with $NaHCO_3$ (20 mg) were placed in a Pyrex test tube,

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cooled to −40 °C, and irradiated with a 500-W high-pressure mercury lamp. The resultant photolysate was worked up as described above to afford **8b** (37 mg, 22 %), together with unreacted **6b** (80 mg, 62 %). Compound **6b**: ^{1}H NMR: $\delta = 0.94$ (t, $J = 7.7$ Hz, 3H), 1.04 (t, $J = 7.7$ Hz, 3H), 1.60 (m, 1H), 1.8–2.4 (m, 8H), 2.49 (br s, 5H), 2.80 (d, $J = 15.6$ Hz, 1H), 2.98 (ddd, $J =$ 17.6, 11.2, 9.3 Hz, 1H). Compound **8b**: ^{1}H NMR: $\delta = 0.95$ (t, $J = 7.8$ Hz, 6H), 1.06 (t, $J = 7.8$ Hz, 6H), 1.52 (ddd, $J = 13.2$, 11.2, 8.8 Hz, 2H), 1.79 (d, $J = 14.2$ Hz, 2H), 1.97 (ddd, $J = 13.2$, 9.3, 1.5 Hz, 2H), 1.94–2.10 (m, 8H), 2.12 (ddd, $J = 17.6$, 8.8, 1.5 Hz, 2H), 2.15 (d, $J = 14.2$ Hz, 2H), 2.82 (ddd, $J =$ 17.6, 11.2, 9.3 Hz, 2H); ^{13}C NMR: $\delta = 11.91$, 12.53, 19.67, 20.25, 26.85, 30.62, 35.84, 50.12, 58.62, 144.78, 149.62, 218.58; IR (neat); 1724 cm^{-1}; MS (EI): *m/z* (%): 352 (100) $[M]^+$, 324 (44), 323 (36), 296 (30), 295 (57), 281 (21), 271 (46), 267 (43); HR-MS (EI): found 352.2379 $[M]^+$; $C_{32}H_{24}O_2$ calcd 352.2402.

Conversion of 8b into 10b: Ethyl formate (381 mg, 5.14 mmol) and MeONa (253 mg, 4.68 mmol) were added to a solution of **8b** (165 mg, 0.47 mmol) in benzene (8.0 mL) under argon and the mixture was stirred for 20 h at room temperature. The reaction was quenched with water. The aqueous layer was separated from the organic layer and washed with diethyl ether (2 ×). The washings were combined and extracted with water (3 ×). The aqueous extracts were combined with the aqueous fraction, acidified (pH 5) with dilute HCl, and extracted with diethyl ether (3 ×). The ethereal extracts were combined, washed with water, dried with $MgSO_4$, and concentrated in vacuo to afford **9b**. The crude **9b** was dissolved in CH_2Cl_2 (10 mL) and treated with TsN_3 (369 mg, 1.87 mmol) and Et_3N (379 mg, 3.74 mmol). After 24 h at room temperature, the reaction was quenched with 5 % aqueous KOH. The aqueous layer was separated from the CH_2Cl_2 layer and extracted with diethyl ether (2 ×). The ethereal extracts were combined with the CH_2Cl_2 fraction, washed with water, 5 % aqueous $NaHCO_3$, and brine, dried with $MgSO_4$, concentrated in vacuo, and subjected to chromatography on silica gel. Elution with diethyl ether–hexane (3:97) afforded the unreacted TsN_3. Further elution with diethyl ether–hexane (1:4) delivered **10b** (88 mg, 47 % from **8b**). ^{1}H NMR: $\delta = 1.01$ (t, $J = 7.5$ Hz, 6H), 1.06 (t, $J = 7.5$ Hz, 6H), 1.90 (d, $J = 14.3$ Hz, 2H), 2.11 (br q, $J = 7.5$ Hz, 8H), 2.23 (d, $J =$ 14.3 Hz, 2H), 2.56 (d, $J = 13.6$ Hz, 2H), 2.99 (d, $J = 13.6$ Hz, 2H).

Preparation of 1b from 10b: The procedure was identical to that described for **1a**, using the diazoketone **10b** (68 mg, 0.17 mmol) and $PhSeNMe_2$ (0.10 mL) in THF (18 mL). The crude product was purified by preparative TLC and then by HPLC to afford **1b** (6 mg, 8 %). ^{1}H NMR: $\delta = 0.86$ (t, $J =$ 7.3 Hz, 6H), 1.00 (t, $J = 7.3$ Hz, 6H), 1.86 (m, 2H), 2.04–2.16 (m, 6H), 2.31 (d, $J = 14.2$ Hz, 2H), 2.41 (d, $J = 14.2$ Hz, 2H), 2.90 (br s, 6H), 3.06 (br s, 6H), 6.66 (s, 2H); FD-MS: *m/z* (%): 435 (31) $[M+H]^+$, 434 (100) $[M]^+$.

Isolation of 3a and 23a: A solution of **1a** (22 mg, 33 μmol) in CD_2Cl_2 (0.6 mL) was placed in a Pyrex NMR tube. This was sealed under vacuum after three freeze-pump-thaw cycles and irradiated with a high-pressure mercury lamp at −20 °C. Irradiation was discontinued when the content of **3a** ceased to increase (83 % conversion). After removal of the solvent, the residue was subjected to HPLC elution with diethyl ether–hexane (3:7) to furnish **3a** (8 mg, 36 %) as colorless crystals and a colorless oil (1 mg, 5 %) to which the structure **23a** was tentatively assigned. Compound **3a**: ^{1}H NMR (CD_2Cl_2): $\delta = 0.00$ (s, 18H), 0.03 (s, 18H), 1.09 (dd, $J = 14.7$, 1.5 Hz, 2H), 1.43 (dd, $J = 14.7$, 1.5 Hz, 2H), 1.54 (d, $J = 6.8$ Hz, 2H), 1.55 (d, $J = 14.7$ Hz, 2H), 1.58 (d, $J = 14.7$ Hz, 2H), 2.12 (d, $J = 6.8$ Hz, 2H), 2.91 (s, 12H), 6.07 (s, 2H); IR (KBr): 1630, 1248, 844 cm^{-1}; FD-MS: *m/z*(%): 668 (38) $[M+2H]^+$, 667 (44), 666 (100) $[M]^+$; HR-MS (FD): found 666.3929 $[M]^+$; $C_{36}H_{62}N_2O_2Si_4$ calcd 666.3889. Compound **23a**: ^{1}H NMR: $\delta = -0.01$ (s, 9H), 0.02 (s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.75 (d, $J = 15.1$ Hz, 1H), 0.90 (d, $J = 15.1$ Hz, 1H), 0.92 (d, $J = 15.1$ Hz, 1H), 1.07 (d, $J = 15.1$ Hz, 1H), 1.16 (d, $J = 12.7$ Hz, 1H), 1.20 (d, $J = 12.7$ Hz, 1H), 1.25–1.30 (m, 3H), 1.48 (d, $J = 14.1$ Hz, 1H), 2.09 (d, $J = 12.7$ Hz, 1H), 2.22 (d, $J =$ 12.7 Hz, 1H), 2.87 (s, 3H), 2.97 (br s, 3H), 3.06 (s, 3H), 3.10 (s, 1H), 3.16 (br s, 3H), 6.38 (s, 1H); FD-MS: *m/z* (%): 667 (62) $[M+H]^+$, 666 (100) $[M]^+$.

Interconversion between 2a and 3a—^{1}H NMR measurement: Compound **3a** (7 mg, 10 μmol) and CD_2Cl_2 (0.5 mL) were placed in an NMR tube. This was sealed under vacuum after three freeze-pump-thaw cycles. The mixture was heated briefly to dissolve **3a** and then irradiated with filtered light of wavelength >420 nm at −10 °C to convert **2a**, formed during the heating, into **3a**. The ^{1}H NMR spectrum indicated that the mixture was essentially free of **2a** (**2a** : **3a** = < 5 : > 95). The thermal isomerization of **3a** to **2a** was conducted at 40 °C in darkness and monitored by ^{1}H NMR spectroscopy. After 5, 8, and 23 h, 61, 78, and 93 %, respectively, of **3a** had been cleanly converted to **2a**. Upon irradiation of the resultant mixture with the filtered light, the generated **2a** quantitatively reverted to **3a**. The cycle could be repeated once again without formation of any detectable side product.

Preparation of 2a for X-ray crystallography: Compound **3a** (4 mg, 6 μmol) and benzene (3 mL) were placed in a glass tube with side tube. This was sealed under vacuum after three freeze-pump-thaw cycles. The mixture was heated for 16 h at 45 °C, cooled to room temperature, concentrated to about one tenth of its original volume by evaporating the benzene into the side tube, which was cooled below 0 °C, and allowed to stand in a refrigerator at 6 °C. The produced **2a** separated as orange-red crystals from the solution in a nearly quantitative yield. ^{1}H NMR (CD_2Cl_2): $\delta = -0.14$ (s, 18H), 0.00 (s, 18H), 2.08 (d, $J = 15.1$ Hz, 2H), 2.25 (d, $J = 15.1$ Hz, 2H), 2.41 (d, $J = 15.1$ Hz, 2H), 2.74 (d, $J = 15.1$ Hz, 2H), 3.07 (br s, 6H), 3.16 (br s, 6H), 3.61 (d, $J = 12.7$ Hz, 2H), 3.67 (d, $J = 12.7$ Hz, 2H), 7.67 (s, 2H); FD-MS: *m/z* (%): 668 (33) $[M+2H]^+$, 667 (51) $[M+H]^+$, 666 (100) $[M]^+$; HR-MS (FD): found 666.3915 $[M]^+$; $C_{36}H_{62}N_2O_2Si_4$ calcd 666.3889.

Preparation of 3b: A solution of **1b** (9 mg, 21 μmol) in C_6D_6 (0.5 mL) was placed in a Pyrex NMR tube. This was sealed under vacuum after three freeze-pump-thaw cycles and irradiated with a high-pressure mercury lamp at below 10 °C. The reaction was monitored by ^{1}H NMR spectroscopy and discontinued when the content of **3b** ceased to increase (79 % conversion). Besides **3b** (43 %), a minor product to which structure **23b** was tentatively assigned was formed in 9 % yield. The yield of **2b** was only a trace, however. After removal of the solvent, the residue was subjected to HPLC eluted with diethyl ether to deliver an approximate 1:2 mixture of **1b** and **3b** (6 mg). Compound **3b**: ^{1}H NMR (CD_2Cl_2): $\delta = 0.87$ (t, $J = 7.3$ Hz, 6H), 0.98 (t, $J = 7.3$ Hz, 6H), 1.62 (d, $J = 7.2$ Hz, 2H), 1.76 (dqq, $J = 14.2$, 7.3, 1.0 Hz, 2H), 1.90 (d, $J = 7.2$ Hz, 2H), 2.00–2.26 (m, 6H), 2.86 (s, 2H), 5.97 (s, 2H).

Thermal generation of 2b from 3b: A solution of **1b** (9 mg, 21 μmol) in CD_2Cl_2 (0.5 mL) was placed in a Pyrex NMR tube. This was sealed under vacuum after three freeze-pump-thaw cycles and irradiated with a high pressure mercury lamp at −20 °C until **1b** had largely been consumed (91 % conversion). The yields of **2b**, **3b**, and **23b** were 1 %, 48 %, and 9 %, respectively, after correction for the conversion of **1b**. When the mixture was heated in darkness for 40 min at 35 °C and then for 50 min at 40 °C, 16 % of **3b** was converted into **2b** in a yield of 93 %, while **1b** and **23b** remained unchanged. When the resulting mixture was allowed to stand in darkness for 18 h at room temperature, an additional 21 % of **3b** had been consumed, but the yield of **2b** had dropped to 50 %, because of its thermal instability. Compound **2b**: ^{1}H NMR (CD_2Cl_2): $\delta = 0.81$ (t, $J = 7.3$ Hz, 6H), 1.10 (t, $J = 7.3$ Hz, 6H), 2.5–3.2 (m, 8H), 3.06 (br s, 12H), 3.63 (d, $J =$ 12.2 Hz, 2H), 3.72 (d, $J = 12.2$ Hz, 2H), 7.49 (s, 2H).

Measurement of difference UV/Vis spectra in photolysis of 1a–c: A solution of **1** in *n*-decane (0.1–0.5 mM) was placed in a quartz cuvet, and this was sealed under vacuum after four freeze-pump-thaw cycles. The cuvet was placed in a quartz Dewar vessel containing methanol and irradiated with a low-pressure mercury lamp at −20 °C to effect the isomerization of **1** into **2**. The resulting mixture was subsequently irradiated with filtered light of wavelength >420 nm to complete the rearrangement of generated **2** into **3**. The difference spectrum (that after irradiation minus that prior to irradiation) for the secondary irradiation was almost an exact mirror image of that of the initial photolysis, at least in the region of wavelength >290 nm, where the spectra were not complicated by absorptions due to **1** and **3**. The observed spectral changes were ascribed to the initial generation of **2** from **1** and the secondary photochemical transformation of the former into **3**.

Kinetic measurements: A solution of **3a** in *n*-hexane (ca. 3 mM) was placed in a quartz cuvet. This was sealed under vacuum after three freeze-pump-thaw cycles and irradiated briefly with filtered light of wavelength >420 nm to convert **2a**, formed from **3a** during the degassing, into **3a**. The solution was heated in darkness in a thermostatically-controlled bath at the specified temperatures, and the generation of **2a** was followed by measurement of absorbance at 321 and 376.5 nm. Plots of absorbance against reaction time fit best to first-order kinetics, and the rate constants were calculated by the method of least squares, using experimental points to as much as 75 % completion.

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[19] The actual yield of **23** seems to be significantly higher than 6%. Compound **23** underwent secondary decomposition under the irradiation conditions; this might proceed via initial transformation into a highly labile [4]paracyclophane derivative.[5b, 5c]

[20] Molar absorptivity of **2a** at λ_{max} in CH_2Cl_2 was calculated by assuming quantitative thermal reversion of **3a** into **2a**: λ_{max} (log ε) 266 (4.26), 324 (3.98), 361 (sh. 3.56), 378 (3.46), and 461 nm (2.43).

[21] Crystal data for **2a**·benzene solvate: $C_{36}H_{62}N_2O_2Si_4 \cdot C_6H_6$, M_r = 745.36, $0.40 \times 0.40 \times 0.10$ mm^3, triclinic $P\bar{1}$, a = 9.564(3), b = 10.156(5), c = 12.299(5) Å, α = 98.86(4), β = 108.85(3), γ = 98.51(4)°, V = 1092(1) Å^3, ρ_{calcd} (Z = 1) = 1.134 g cm^{-3}. A total of 3640 unique data ($2\theta_{max} = 52°$) were measured at T = 203 K with $\omega-2\theta$ scan mode ($Mo_{K\alpha}$ radiation, λ = 0.71073 Å). No absorption correction was applied (μ = 1.097 cm^{-1}). Structure was solved by direct methods (Crystan). Hydrogen atoms were located at the calculated positions. Refinement by full-matrix, least-squares method on F gave the final R value of 0.078 (wR = 0.112) for 3022 reflections with $I > 3\sigma(I)$ and 260 parameters. Residual electron density is 0.37 e Å^{-3}. Crystal data for **3a**: $C_{36}H_{62}N_2O_2Si_4$, M_r = 667.24, $0.40 \times 0.40 \times 0.25$ mm^3, monoclinic $P2_1/n$, a = 17.239(5), b = 10.365(3), c = 11.275(4) Å, β = 95.30(3)°, V = 2006(1) Å^3, ρ_{calcd} (Z = 2) = 1.105 g cm^{-3}. A total of 4358 unique data ($2\theta_{max} = 52°$) were measured at T = 233 K with $\omega-2\theta$ scan mode ($Mo_{K\alpha}$ radiation, λ = 0.71073 Å). No absorption correction was applied (μ = 1.734 cm^{-1}). Structure was solved by the direct method (Crystan). All the hydrogen atoms were located in the D map and refined with isotropic temperature factors. Refinement by full-matrix, least-squares method on F gave the final R value of 0.038 (wR = 0.054) for 3933 reflections with $I > 3\sigma(I)$ and 323 parameters. Residual electron density is 0.71 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-100696 (**2a**) and CCDC-133982 (**3a**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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