

Synthesis and photochromic reaction of 1,2-diphenylperfluorocyclopentenes

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ABSTRACT: The synthesis and photochromic reaction of 1,2-diphenylperfluorocyclopentenes are reported. Upon UV irradiation, hexane solutions of 1,2-diphenylperfluorocyclopentenes afforded red solution of dihydrophenanthrenes, which gradually give the initial 1,2-diphenylperfluorocyclopentenes at room temperature thermally or under irradiation with visible light. The activation energies for the thermal isomerization of the dihydrophenanthrenes are estimated. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; diarylethene; activation energy; thermal reaction; stilbene

INTRODUCTION

Photochromism is defined as the reversible transformation of a single chemical species being induced in one or both directions by electromagnetic radiation between two states having a distinguishable absorption change.¹ Photochromic compounds are classified into two categories, thermally reversible and thermally irreversible. Dithienylethenes and fulgides have been reported as thermally irreversible photochromic compounds, whereas most of the other photochromic compounds are thermally reversible.²

Stilbenes are well-known photochromic compounds and the photochromic reaction is both photochemically and thermally reversible.³ In the presence of air, the colored form 4a,4b-dihydrophenanthrene is easily oxidized to form phenanthrene.⁴ On the other hand, 2,2',6,6'-tetra-substituents, e.g. methyl groups, can prevent the following oxidation and the photochromic reaction is reversible even in the presence of air.^{5,6} The use of a cycloalkene instead of a bridge olefin can inhibit *cis-trans* isomerization and the quantum yield for photocyclization to form dihydrophenanthrene can be increased.^{5,6} Recent diarylethene compounds have a cyclopentene ring for bridging two aromatic rings.⁷ The perfluorocyclopentene ring has become popular^{8–11} since the perfluorocyclopentene ring was used in dithienylethenes first time.¹² There are many reports on diarylperfluorocyclopentenes with heteroaromatic rings as both

thermally irreversible and reversible photochromic compounds, but in the case of a benzene ring as an aryl substituent, only one diphenylperfluorocyclopentene (**5**) has been reported.¹³

Recently, we reported the synthesis and photochromic properties of [2.*n*]metacyclophan-1-enes which are composed of two benzene rings with bridges.^{14,15} The lifetime of the colored form is dependent on the chain length (*n*); when *n* is small (*n* = 2), the half-life is 53 days at 273 K, and when *n* = 3, it is 25 min. We are interested in the lifetime of the colored form of the *n* = 0 compound (stilbenes).

In this paper, we describe the synthesis and photochromic properties of 1,2-diphenylperfluorocyclopentenes and the thermal isomerization of the colored form (methyldiphenylperfluorocyclopentenes).

EXPERIMENTAL

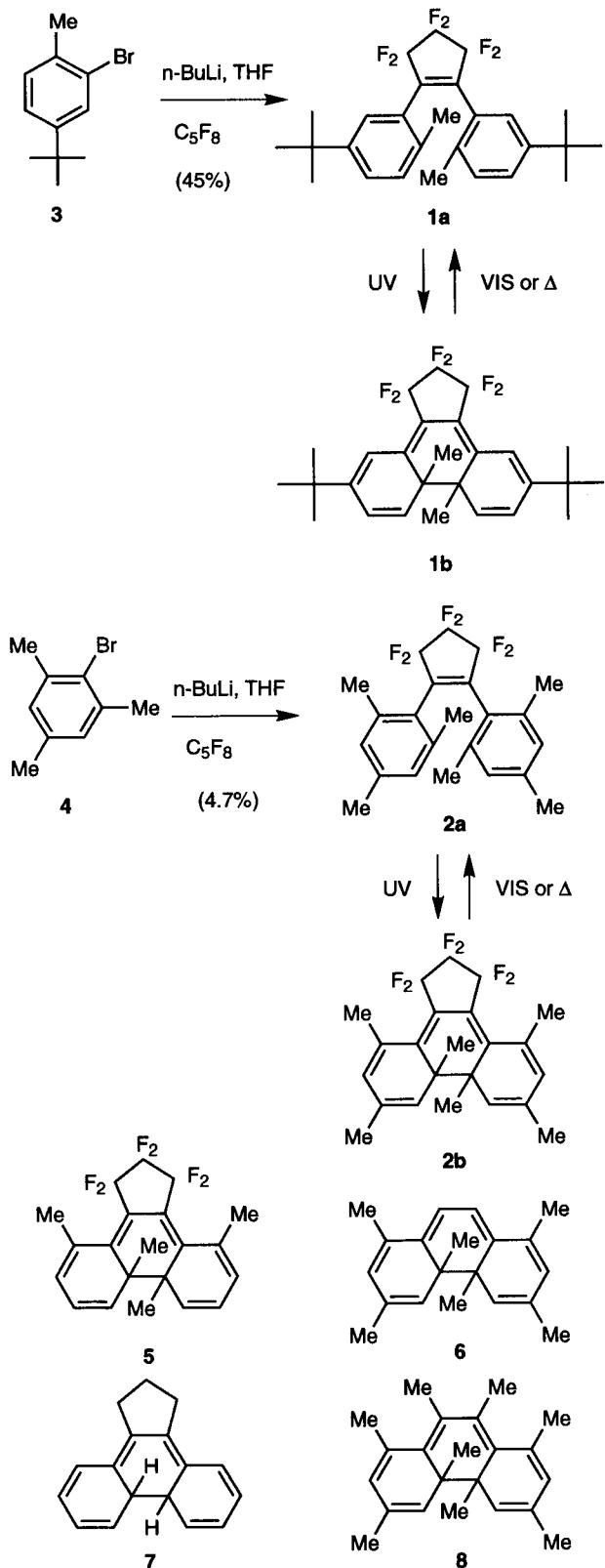
The light source was a 500 W super-high-pressure mercury lamp and monochromatic light was obtained by passing it through a monochromator (Johin Yvon).

Synthesis of 1,2-bis(2-methyl-5-*tert*-butylphenyl)-3,3,4,4,5,5,6,6-hexafluorocyclopentene (1a**).** A solution of 8.7 g of 2-bromo-4-*tert*-butyltoluene (**3**) (40 mmol) in 50 ml of dry THF was added dropwise to 27 ml of 1.6 M *n*-butyllithium in hexane (43.2 mmol) at –74 °C under Ar. The solution was stirred at the same temperature for 1 h and to the mixture 2.8 ml of octafluorocyclopentene was added four times. The mixture was stirred for 2 h at the same temperature and then allowed to stand at room temperature. Water was

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Scheme 1

added to the mixture and the organic phase was separated, washed with brine and dried (MgSO_4). The solvent was evaporated *in vacuo* and the residue was

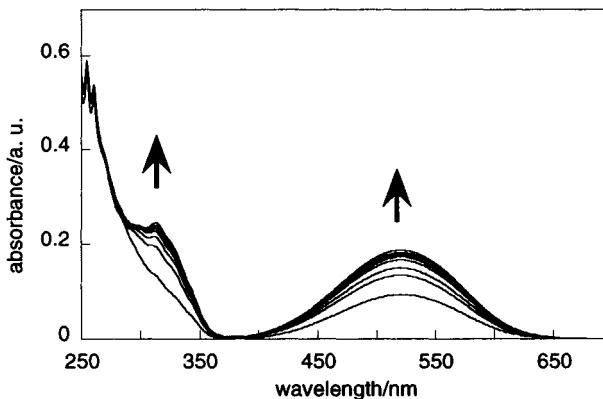


Figure 1. Absorption spectral change of a hexane solution of **1a** ($5.0 \times 10^{-5} \text{ mol dm}^{-3}$) upon irradiation with 254 nm light

subjected to silica gel column chromatography with hexane as eluent. Recrystallization of the first eluent afforded 5.0 g of **1a** (10.7 mmol) in 53% yield. **1a**: colorless prisms, m.p. 86.0–87.0 °C; ^1H NMR (CDCl_3 , 300 MHz, 25 °C), δ 1.25 (s, 18H), 2.07 (s, 6H), 7.02 (d, 2H, J = 8 Hz), 7.19 (d, 2H, J = 2 Hz), 7.20 (dd, 2H, J = 8, 2 Hz); MS, m/z 468 (M^+). Anal. Calcd for $\text{C}_{27}\text{H}_{30}\text{F}_6$: C, 69.22; H, 6.45. Found: C, 69.01; H, 6.43%.

Synthesis of 1,2-bis(2,4,6-trimethylphenyl)-3,4,4,5,5,6,6,6-hexafluorocyclopentene (2). Compound **2** was obtained from **4** in 4.7% yield in a similar manner to that described above. **2a**: colorless prisms, m.p. 116.0–120.0 °C; ^1H NMR (CDCl_3 , 300 MHz, 25 °C) δ 2.15 (s, 18H), 6.80 (s, 4H); MS, m/z 412 (M^+). Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{F}_6$: C, 66.98; H, 5.38. Found: C, 67.23; H, 5.55%.

RESULTS AND DISCUSSION

Diphenylperfluorocyclopentenes **1** and **2** were synthesized from the corresponding bromobenzene derivatives

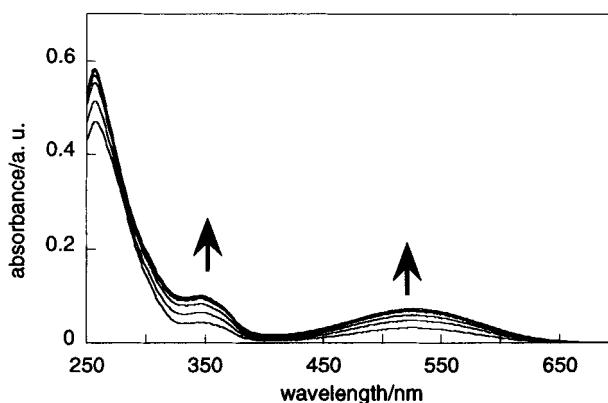
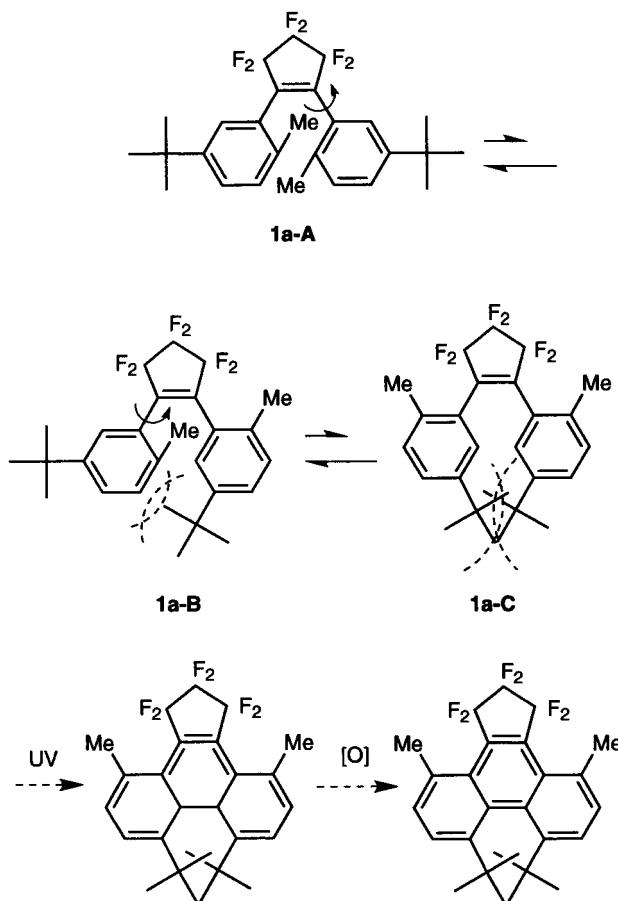


Figure 2. Absorption spectral change of a hexane solution of **2a** ($5.0 \times 10^{-5} \text{ mol dm}^{-3}$) upon irradiation with 254 nm light



3 and 4 as shown in Scheme 1. Lithiation of 3 and 4 was carried out in low temperature and addition of octafluorocyclopentene afforded the corresponding diphenylperfluorocyclopentenes. The yield of the hexamethyl derivative 2 was low since the lithiated intermediate had poor reactivity owing to the steric hindrance of the methyl groups of the lithiated intermediate of 4.

The obtained diphenylperfluorocyclopentenes 1 and 2 undergo photochromic reaction. A colorless solution of 1a and 2a in hexane turned red upon irradiation with 254 nm light. Upon UV irradiation new absorption maxima were observed at 312 and 518 nm in the case of 1 (Fig. 1) and at 347 and 527 nm in the case of 2 (Fig. 2). The red color is due to the formation of the closed ring form dihydrophenanthrenes 1b and 2b. The absorbance of 1b at 518 nm was 0.19 ($[1] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$) in the photostationary state at 254 nm (PSS₂₅₄) and that of 2b at 527 nm was 0.072 ($[2] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$) at 293 K, as shown in Figs 1 and 2. The formation of dihydrophenanthrenes 1b and 2b was confirmed by the ¹H NMR spectra. UV-irradiated CDCl_3 solutions of 1 and 2 at 25°C showed new signals: δ 1.08 (s, 18H), 1.60 (s, 6H), 6.06 (d, 2H, $J = 11 \text{ Hz}$), 6.15 (d, 2H, $J = 11 \text{ Hz}$), 6.22 (s, 2H) for 1b and δ 1.74 (s, 6H), 2.02 (s, 6H), 2.15 (s, 6H), 5.86 (s, 4H) for 2b.

The red solution obtained was decolorized by visible

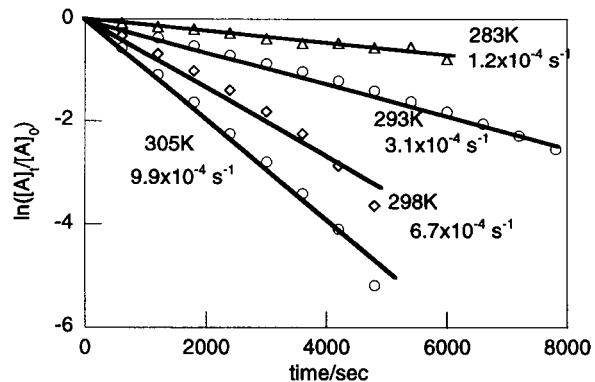


Figure 3. Rate of the decoloration reaction of 1b in hexane measured at 518 nm

irradiation at wavelengths $>460 \text{ nm}$ to give the original spectrum. The red color of the solutions of 1b and 2b gradually disappeared at ambient temperature. Hence the dihydrophenanthrenes 1b and 2b return to the diphenylperfluorocyclopentenes 1a and 2a both photochemically and thermally.

It is well known that stilbenes having hydrogen atoms as inner substituents are easily oxidized by oxygen in air to yield the phenanthrene derivatives followed by photocyclization. In the case of 1 the dihydrophenanthrene formed from the conformation 1a-c could be oxidized to yield the corresponding phenanthrene (Scheme 2). However, 1 is stable even when irradiated with UV light in the presence of air with high fatigue resistance. This effect shows that the photocyclization of 1a proceeds from 1a-A and not 1a-B or 1a-C. The other conformations such as 1a-B and 1a-C could not form because of the steric hindrance between the *tert*-butyl groups and the opposite benzene rings. Therefore, further oxidation from the dihydrophenanthrenes was prevented. This indicates that *tert*-butyl groups at 5,5'-positions are useful for avoiding the further irreversible oxidation step.

The rates for the thermal decolorization reaction of 1b and 2b in hexane at various temperatures are shown in Figs 3 and 4. The experiments were carried out by use of

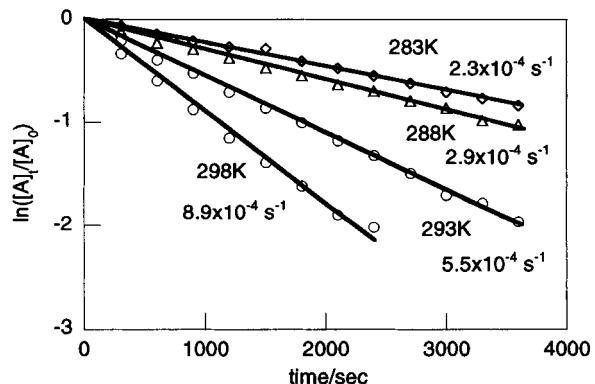


Figure 4. Rate of the decoloration reaction of 2b in hexane measured at 527 nm

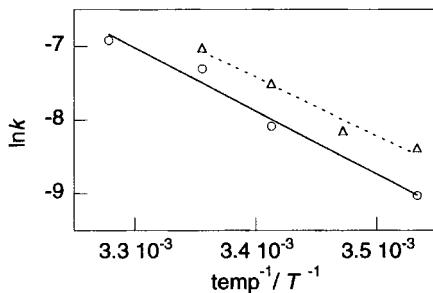


Figure 5. Arrhenius plots for thermal decoloration reaction of **1b** (○) and **2b** (△)

a water-bath in the dark. With the absorbance decrease of **1b** or **2b** at their λ_{max} (518 or 527 nm) at time t (A_t) and the photoinduced initial absorbance (A_0), first-order decay of A_t/A_0 was observed for both **1b** and **2b**.

Figure 5 shows Arrhenius plots for the decoloration reactions of **1b** and **2b**. From these plots, the activation energies for thermal isomerization of **1b** and **2b** to form **1a** and **2a** are estimated as 17.1 and 15.7 kcal mol⁻¹ (1 kcal = 4.184 kJ), respectively, and the pre-exponential factors are 1.8×10^9 and 2.9×10^8 s⁻¹, respectively. At 273 K, the rates of decoloration of **1b** and **2b** are 4.1×10^{-5} and 7.6×10^{-5} s⁻¹ and their half-lives at 298 K are 17 and 13 min, respectively. The half-lives of the similar stilbene derivatives are given in Table 1.

The activation energies for the thermal ring-opening reactions of the dihydrophenanthrenes with cyclopentene ring (**1b**, **2b**, **5** and **7**) are in the range 15–17 kcal mol⁻¹ and the half-lives are 13–23 min at 298 K. On the other hand, those of the dihydrophenanthrenes in the absence of cyclopentene (**6** and **8**) vary widely. The structures of both isomers and the geometry change in the ring-opening reaction of the dihydrophenanthrenes with the cyclopentene ring are similar, hence the activation energies and half-lives of these derivatives are also similar.

CONCLUSIONS

Two types of diphenylperfluorocyclopentene derivatives were synthesized and both of them undergo photochromic reactions to give the corresponding dihydrophenan-

Table 1. Activation energy (E_a) and half-life for the thermal ring-opening reaction of dihydrophenanthrenes

Compound	E_a (kcal mol ⁻¹)	Half-life (min) at 298 K
1b	17.1	17
2b	15.7	13
5 ¹³	—	15
6 ⁵	22.5	1980
7 ⁵	15.5	23
8 ¹⁶	—	1.5 (303 K)

threnes upon UV irradiation. Dihydrophenanthrenes return to the initial compound both photochemically and thermally. The activation energies for thermal isomerization reaction were estimated as 15–17 kcal mol⁻¹.

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