# [14π]Electrocyclization Followed by Preferential [1,9]Hydrogen Migration in the Thermolysis of 1-Formyl-4-[(2,4,6-cycloheptatrienyl)(phenylsulfinyl)methyl]azulene

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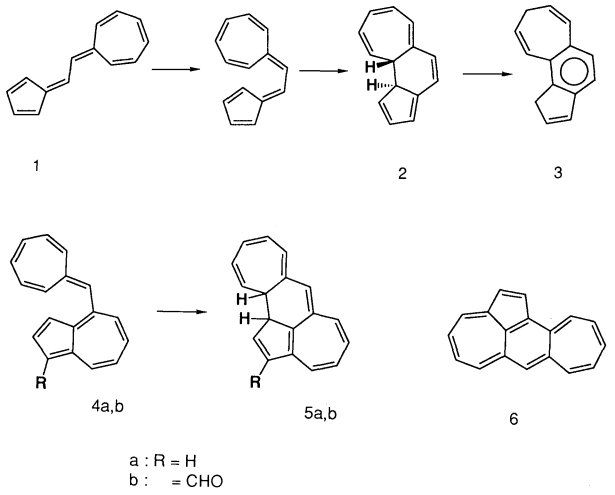
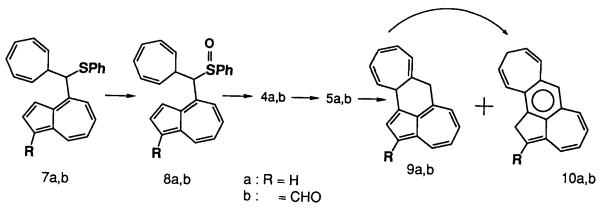
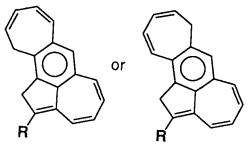
**Synopsis.** 1-Formyl-4-[2,4,6-cycloheptatrienyl)(phenylsulfinyl)methyl] azulene (**8b**) was thermolyzed at 65°C for 100 min to give 7,12a-dihydro-2-formyldicyclohept[*cd,g*]indene (**9b**), which was isomerized to 1,10-dihydro-2-formyldicyclohept[*cd,g*]indene (**10b**), upon heating at the higher temperature.

Electrocyclization has been the useful tool in the syntheses of some polycyclic nonalternant hydrocarbons.[1] The problem of the strategy, however, is that electrocyclization is often followed by fast hydrogen migration to give the isomer which is not necessarily fitted to further dehydrogenation. Hence, it is important to examine structural features to alter the hydrogen migration behavior. A typical example of electrocyclization and concomitant hydrogen migration has been reported for 7-(2,4-cyclopentadien-1-ylideneethylidene)-1,3,5-cycloheptatriene (**1**)[2] which, on thermolysis, was transformed into 1,8-dihydrocyclohept[*e*]indene (**3**) quantitatively even at 20°C. Formation of **3** was rationalized by the [14π]electrocyclization of **1** followed by the facile hydrogen migration. 4-(8-Heptafulvenyl) azulene (**4a**) is regarded as a molecule in which the pentafulvene moiety in **1** constitutes a part of the more stable azulene nucleus. It is, therefore, intriguing to study the cyclization and the hydrogen migration mode of **4a** from the viewpoint of both the reaction mechanism and the utility in the syntheses of the fused nonalternant hydrocarbons. In the previous paper[3] concerning the first successful construction of the conjugated system of dicyclohept[*cd,g*]indene (**6**), we have claimed a reaction sequence consisting of thermal formation of **4a**, the [14π] electrocyclization of **4a**, and the subsequent [1,9] hydrogen migration in **5a** to yield 7,12a-dihydrodicyclohept[*cd,g*]indene (**9a**). Here we disclose our further study associated with the thermolysis of **4b.**

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1-Formyl-4-[(2,4,6-cycloheptatrienyl)(phenylsulfinyl) methyl] azulene (**8b**) was obtained as a mixture of diastereomers by oxidation of 1-formyl-4-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl] azulene (**7b**)[3] with *m*-chloroperbenzoic acid. The mixture (**8b**) underwent facile thermal elimination of sulfenic acid in deaerated benzene at 65°C to yield dark violet crystals (**9b**) in 64% yield together with a trace amount of dark brown crystals (**10b**). Upon thermolysis of **8b** at 130—140°C, the compound (**10b**) was predominantly produced in 52% yield. $^1$H NMR and electronic spectra of **9b** unambiguously confirmed the structure of 1-formyl derivative of **9a**. The identity of the structure (**10b**) was established by the spectral data. In $^1$H NMR spectrum of **10b**, signals due to four hydrogens appear at $\delta$=6.53, 6.06, 6.21, and 7.24 and are assigned to hydrogens arranged in series on the seven-membered ring on the basis of the respective vicinal coupling constants. The chemical shifts of these hydrogens, however, are no longer in the aromatic region except for that of the signal at $\delta$=7.24. Hence, the compound (**10b**) does not possess the azulene nucleus as the partial structure. A triplet at $\delta$=2.56 due to methylene hydrogens is interrelated with four olefinic hydrogens by their respective vicinal coupling constants, indicating that the cycloheptatrienyl ring is condensed at its 4- and 5-positions. Two singlet signals at $\delta$=3.72 and 7.05 are reasonably assigned to 1-H and 7-H, respectively.

Though treatment of **8a** or **9a** at the elevated temperatures gave the intractable polymeric materials, it was found that the solution of **9b** in toluene was refluxed overnight to give **10b**, contaminated with the position isomer (**11**) with respect to the double bond in the cycloheptatrienyl ring in 61% yield. The thermal

reaction of **8b** to **9b** is likewise rationalized by a reaction sequence shown in Scheme 3. The marked feature of the thermolysis of **8b**, therefore, is that the kinetically controlled product (**9b**) is obtained in a synthetically good yield with competitive formation of the thermodynamically more stable isomer (**10b**). The dipolar structure of the respective azulene nuclei in **8a** and **8b**, which is expected to accelerate elimination of sulfenic acid,[4] and the aromatic stabilization due to the azulene nuclei in the primary products (**9a** and **9b**), which is not present in the thermolysis product of **1**, are considered to make the isolation of the thermodynamically less stable products (**9a** and **9b**) possible. Furthermore, these two factors are also responsible for our first synthesis of the derivative of **6**, since the parent compound (**10a**), which is devoid of any electron-withdrawing group at C-8 of the heptafulvene chromophore, was too unstable to be synthesized under our reaction conditions.

## Experimental

**1-Formyl-4-[2,4,6-cycloheptatrienyl)(phenylsufinyl)methyl] azulene (8b):** 1-Formyl-4-[(2,4,6-cycloheptatrienyl) (phenylthio)methyl]azulene (**7**) (1.06 g, 2.88 mmol) in dichloromethane (20.0 ml) was oxidized with *m*-chloroperbenzoic acid (80%) (870 mg, 4.03 mmol) in dichloromethane (10.0 ml) at −78 °C. After 20 minutes, the mixture was treated with aqueous sodium thiosulfate and extracted with dichloromethane. The extract was successively washed with water and brine, and dried over magnesium sulfate. After filtration, the solvent was removed and the residue was chromatographed over deactivated silica gel (20% $H_2O$) with a mixture of hexane and ether (1 : 2 v/v). The eluate was concentrated to some extent and allowed to stand in a refrigerator. Violet plates were obtained in 71.5% yield. The signal pattern of $^1$H NMR spectrum of **8b** essentially resembles that of **7**.[3]

**7,12a-Dihydro-2-formyldicyclohept[*cd,g*]indene (9b):** 1-Formyl-4-[(2,4,6-cycloheptatrienyl)(phenylsulfinyl)methyl]azulene (**8b**) (314.5 mg, 0.815 mmol) was dissolved in deaerated benzene (15 ml) and thermolyzed at 65 °C for 100 min. After removal of the solvent, the residue was chromatographed over deactivated silica gel (10% $H_2O$) with benzene to give a dark violet solid (**9b**) together with a small amount of **10b**. The dark violet solid (**9b**) was recrystallized from a mixture of hexane and benzene (2 : 3 v/v). Yield 64%, dark violet needles, mp 147 °C (decomp). Found: C,88.02; H,5.44 . Calcd for $C_{19}H_{14}O$: C,88.34; H,5.46%; MS *m/z*, 258 ($M^+$); UV (benzene) 378, 469sh, 539, and 576sh nm; IR($CCl_4$) 1655 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=3.05 (1H, d, *J*=5.9 Hz, 12a-H) 4.15 (1H, d, *J*=21.9 Hz, 7$\alpha$-H), 4.33 (1H, d, *J*=21.9 Hz, 7$\beta$-H), 5.36 (1H, dd,*J*=8.9 and 5.9 Hz, 12-H), 6.32 (1H, m, 11-H), 6.41 (1H, br. s, 8-H), 6.76 (2H, m, 9- and 10-H), 7.35 (1H, d, *J*=9.9 Hz, 6-H), 7.49 (1H, dd, *J*=9.9 and 9.6 Hz, 4-H), 7.77 (1H, t, *J*=9.9 Hz, 5-H), 8.22 (1H, s, 1-H), 9.49 (1H, dd, *J*=9.6 and 1.0 Hz, 3-H), and 10.42 (1H, s, formyl).

**1,10-Dihydro-2-formyldicyclohept[*cd,g*]indene (10b):** 1-Formyl-4-[(2,4,6-cycloheptatrienyl)(phenylsulfinyl)methyl]azulene (**8b**) (308.9 mg, 0.804 mmol) was thermolyzed with potassium carbonate (165.8 mg, 1.66 mmol) in xylene (20 ml) at 135—140 °C for 3 min. After removal of the solvent in vacuo, the residue was chromatographed over deactivated silica gel (20% $H_2O$) with benzene to yield an orange solid (**10b**) together with **9b** (12.5%). The orange solid was recrystallized from a mixture of hexane and benzene (2 : 3 v/v) to afford dark brown needles (**10b**). Yield 52%, mp 166—167.5 °C. Found: C, 88.02; H, 5.42%. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46%; MS *m/z*, 258 ($M^+$); UV (benzene) 331sh, 341, 389, 408, 465sh, 503sh, and 544sh nm; IR (KBr) 1620 and 1540 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=2.56 (2H, t, *J*=6.6 Hz, 10-H), 3.72 (2H, s, 1$\alpha$- and 1$\beta$-H), 5.94 (1H, dt, *J*=10.3, 6.6, and 6.6 Hz, 9- or 11-H), 6.01 (1H, dt, *J*=10.4, 6.6, and 6.6 Hz, 11- or 9-H), 6.06 (1H, dd, *J*=11.7 and 8.2 Hz, 5-H), 6.21 (1H, ddd, *J*=11.9, 8.2, and 1.0 Hz, 4-H), 6.51 (1H, d, *J*=10.4 Hz, 12- or 8-H), 6.53 (1H, d, *J*=11.7 Hz, 6-H), 6.59 (1H, d, *J*=10.3 Hz, 8- or 12-H), 7.05 (1H, s, 7-H), 7.24 (1H, d, *J*=11.9 Hz, 3-H), and 10.10 (1H, s, formyl).

**Thermal Conversion of 7,12a-Dihydro-2-formyldicyclohept[*cd,g*]indene (9b) to 1,10-Dihydro-2-formyldicyclohept[*cd,g*]indene(10b):** 7,12a-Dihydro-2-formyldicyclohept[*cd,g*]indene (**9b**) (177.3 mg, 0.687 mmol) in toluene (10 ml) was heated under reflux. After reflux overnight, disappearace of **9b** was confirmed by means of thin-layer chromatography. The mixture was concentrated and chromatographed over deactivated silica gel (20% $H_2O$) with benzene to give a mixture of **10b** and **11** (7 : 2) in 61% yield. Compound (**11**): $^1$H NMR ($CDCl_3$) $\delta$=3.06 (2H, d, *J*=6.5 Hz, methylene of a cycloheptatrienyl ring), 3.72 (2H, s, 1$\alpha$- and 1$\beta$-H), 5.69—6.31 (4H, m, vinyl), 6.41—6.69 (3H, m, vinyl), 6.91 (1H, br. s, 7-H), 7.21 (1H, d, *J*=12.4 Hz, 3-H), and 10.06 (1H, s, formyl).

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