

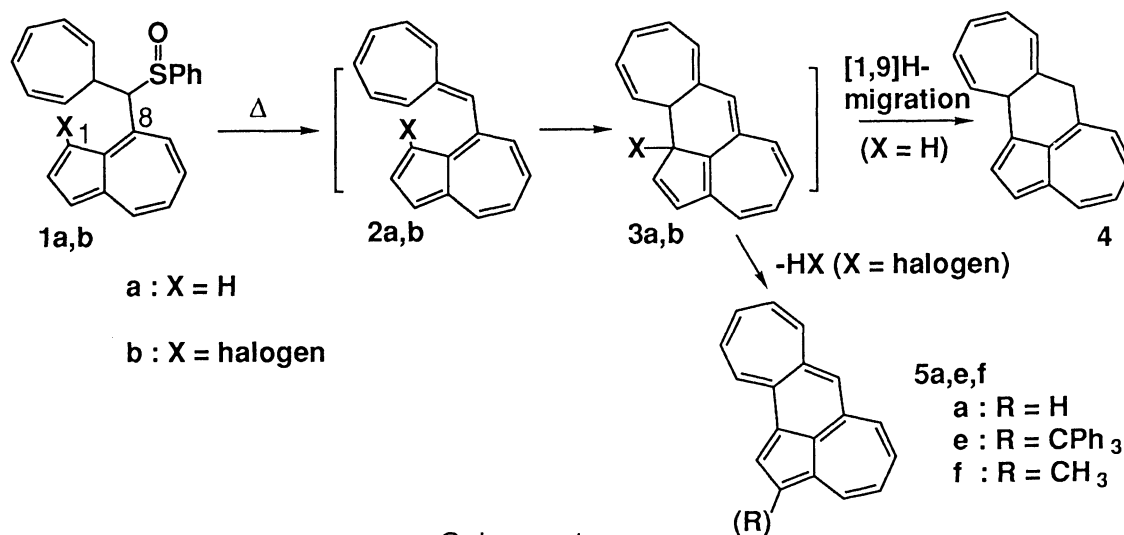
A Novel Rearrangement in the Sterically Congested (2,4,6-Cycloheptatrienyl)(phenylsulfinyl)methyl Group

Yoshikazu SUGIHARA,* Jun-ichi KANEMARU, Junji SAITO, and Ichiro MURATA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

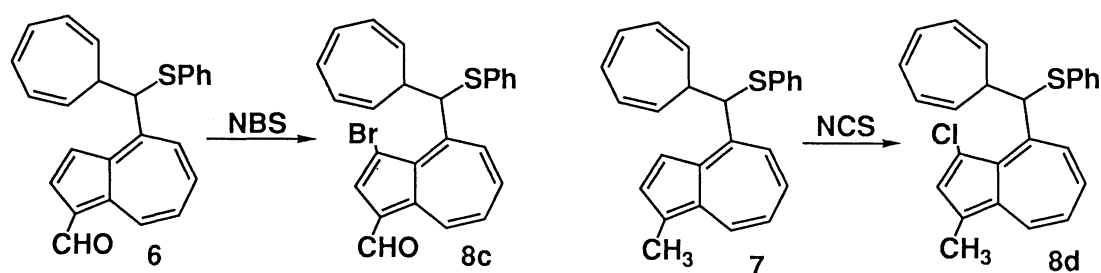
An oxidation product of 3-bromo-1-formyl-4-[(2,4,6-cycloheptatrienyl)-(phenylthio)methyl]azulene with *m*-chloroperbenzoic acid was transformed into 3-bromo-1-formyl-4-(*E*)-styrylazulene upon standing at 0 °C in a solid state. A similar rearrangement was also observed in the oxidation of 3-chloro-1-methyl-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl]azulene.

In the previous paper we reported the first successful construction of a dicyclohept[*cd,g*]indene system (**5e**).¹⁾ As noted,^{1,2)} the success appreciably relied upon establishment of the way to obtain the pertinent intermediate (**4**), which could be subjected to the dehydrogenation in the final synthetic step. Formation of **4** was rationalized by a reaction sequence in Scheme 1, which consists of thermal elimination of sulfenic acid, [14 π]electrocyclization, and subsequent preferential [1,9]hydrogen migration.



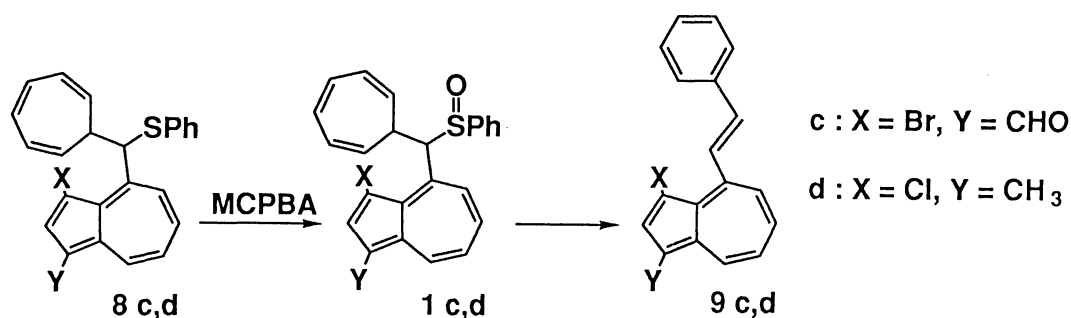
Scheme 1.

Hence, if a sulfoxide (**1b**) suffers from an similar reaction sequence to yield **3b**, it is expected that hydrogen halide is eliminated from **3b** to give the parent compound (**5a**).³⁾ During examinations on these lines, however, we found a novel skeletal rearrangement in the sterically congested (2,4,6-cycloheptatrienyl)(phenylsulfinyl)methyl group, which is considered to be promoted by a neighboring halogen atom. Here we show the rearrangement together with possibility of the way from **1b** to **5a** in Scheme 1.



Scheme 2.

Since selective introduction of substituents to both 1 and 8 positions of an azulene nucleus requires many synthetic steps, derivatives bearing an extra substituent at an alternative peri site on the five membered ring were examined (Scheme 2). Reaction of 1-formyl-4-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl]azulene (**6**)⁴⁾ with 2.3 equiv. of *N*-bromosuccinimide in ether yielded a violet oil (**8c**) in 62% yield.⁵⁾ The ¹H NMR spectrum of **8c** is essentially similar to that of **6** except for signals due to two protons. Of the signals attributable to these protons, one singlet at δ 8.14 is reasonably assigned to a proton attached to a β carbon of the formyl group, indicating that the bromine atom was introduced at a 3-position. The other proton attached to the carbon atom bearing phenylthio group resonated at δ 7.02 which is substantially lower field by 1.74 ppm than that of the corresponding signal of **6**. It seems reasonable to explain the downfield shift by both, effects of anisotropy, and steric compression caused by close proximity of the bromine atom to the proton.⁶⁾ In order to examine the proximity effect of a halogen atom, an chlorine atom seemed to be the next good choice. Due to the electron withdrawing character of a formyl group in **6**, however, effective introduction of a chlorine atom to **6** resulted in failure.⁷⁾ Hence, a chlorine atom was introduced to **7**⁸⁾ with *N*-chlorosuccinimide in a refluxing mixture of ether and benzene (1:1 v/v). As expected, the corresponding proton of **8d** resonated at δ 6.86, which is an intermediate position between those of **6** (or **7**) and **8c**.



Scheme 3.

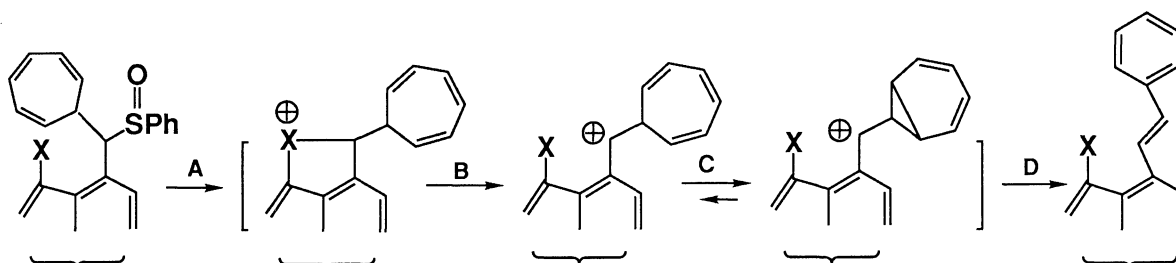
Reaction of **8c** with *m*-chloroperbenzoic acid in dichloromethane at -78°C was monitored by means of silica gel thin layer chromatography (TLC). After 2 h, the original spot ($R_f = 0.7$, CH_2Cl_2) of **8c** was completely replaced by two purple spots at R_f 0.1 (**1c α** : major) and 0.2 (**1c β** : minor). The behavior on TLC indicates that **8c** was oxidized to diastereomers of the sulfoxide. Usual aqueous work-up and subsequent chromatography over silica gel gave the more polar product (**1c α**) as a violet solid. Interestingly, the violet solid (**1c α**) turned dark green upon standing at 0°C overnight. Column chromatography of the dark green solid over

silica gel afforded dark green needles (**9c**) (mp 137 - 139 °C) in 33% yield.¹⁰⁾ The structure of **9c** was established to be 3-bromo-1-formyl-4-(E)-styrylazulene on the basis of spectral data. Thus, the UV/VIS spectrum revealed a broad absorption ranging from 450 to 780 nm characteristic of the azulene chromophore. Double resonance experiments confirmed assignment of the ¹H NMR signals at δ 9.62, 7.50, and 7.78 (2H) to protons arranged in series on the seven membered azulene nucleus. By their respective vicinal coupling constants, signals at δ 7.35, 7.44 (2H), and 7.65 (2H) are interrelated and reasonably assigned to protons attached to a phenyl group. With respect to geometry of the olefinic part, the large vicinal coupling constant ($J = 16.0$ Hz) unambiguously indicates the (E)-configuration.

The sulfoxide (**1d**) could be quantitatively obtained by the oxidation as an blue solid, which was quite stable at 0 °C. Upon standing at room temperature, however, the solid turned greenish blue, indicating that **1d** underwent the same rearrangement. Actually, separation of the mixture yielded **9d**¹⁰⁾ as dark green needles (mp 79.5 - 81.1 °C) in 20% yield. Since the sulfoxide (**1a**) is quite stable below the temperature (54 - 65 °C) required for thermal elimination of sulfenic acid, relative stability of the sulfoxides (**1c,d**) in a solid state is evidently consistent with an increasing steric bulk of the neighboring halogen atoms.

In benzene solutions **1c** and **1d** showed different behavior. While the sulfoxide (**1c**) was slowly converted into **9c** at room temperature, **1d** suffered from gradual decomposition without any formation of **9d**. To our surprise, thermolysis of **1d** at 50 °C in a mixture of benzene and pyridine (20 : 1 v/v) afforded a new product (**10**) together with an unidentified compound. Though the new product (**10**) could not be purified, analysis of ¹H NMR spectrum indicated the structure to be 2-methyldicyclohept[*cd,g*]indene (**5f**),¹¹⁾ revealing that the aforementioned, desired reaction sequence took place. To summarize, it was shown that, while the reaction sequence from **1b** to **5a** in Scheme 1 is a possible route to synthesize dicyclohept[*cd,g*]indene (**5a**), the sterically congested sulfoxide (**1b**) like **1c** and **1d** has a potential problem to undergo an anomalous rearrangement, especially, in a solid state.

The rearrangement mechanism postulated by us is as follows (Scheme 4). In the first step(A) a neighboring halogen enhances detachment of a phenylsulfinyl group to form a bridging bond, though the group is normally inactive as a leaving group. Cleavage of the bond leads to make an α carbon of a cycloheptatrienyl ring bear a positive charge (B). The charge causes tautomerism of the cycloheptatrienyl ring in favor of a norcaradiene form (C).¹²⁾ Finally deprotonation and concomitant bond cleavage of a three membered ring give the product (D).



Scheme 4.

Steric effects have been recognized as important factors in characterizing both the chemical and physical behavior of molecules.¹³⁾ Further, some reactions have recently been interpreted in terms of the steric

compression effect, and its utility in understanding anomalous reactions has been emphasized.¹⁴⁾ We think that the rearrangement described here should be noted as a novel class which has been unfamiliar to date.

References

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- 2) Y. Sugihara, J. Saito, and I. Murata, *Bull. Chem. Soc. Jpn.*, in press.
- 3) Related study : I. Murata, K. Yamamoto, and M. Tamura, *Chem. Lett.*, **1974**, 307.
- 4) Compound **6** was synthesized by usual formylation (DMF-POCl₃)-of 4-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl]azulene¹⁾ in 91% yield.
- 5) All the new compounds were fully characterized by spectral data.
- 6) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Braunschweig(1969),p. 72.
- 7) A very small amount of 3-chloro-1-formyl-4-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl]-azulene could be obtained. The corresponding hydrogen of this compounds resonated at δ 6.86.
- 8) 1-Methyl-4-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl]azulene (**7**) was prepared from 1-methylazulene⁹⁾ in a similar manner as that of 4-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl]azulene.¹⁾ The doublet at δ 5.34 was assigned to the corresponding hydrogen of **7**.
- 9) K. Hafner and C. Bernhard, *Justus Liebigs Ann. Chem.*, **625**, 108 (1959).
- 10) Selected spectral data of **9c** and **9d**. **9c**: Found : C, 68.00; H, 3.98; Br, 23.56. Calcd for C₁₉H₁₃OBr: C, 67.67; H, 3.89; Br, 23.70; ¹H NMR (CDCl₃) δ = 7.09 (1H, d, *J* 16.0 Hz), 7.34 - 7.52 (4H, m), 7.64 - 7.67 (2H, m), 7.76 - 7.79 (2H, m), 8.19 (1H, s), 8.64 (1H, d, *J* 16.0 Hz), 9.62 (1H, d, *J* 9.5 Hz), and 10.26 (1H, s); IR (CCl₄) 1660 cm⁻¹; UV (benzene) 313 (log ϵ , 4.31), 366 sh (4.08), and 580 sh (2.82) nm. **9d**: Found : m/z 278.0836. Calcd for C₁₉H₁₅Cl: M, 278.0859; ¹H NMR (CDCl₃) δ = 2.61 (3H, s), 6.95 (1H, dd, *J* 9.7 and 9.4 Hz) 7.05 (1H, d *J* 16.1 Hz), 7.25 (1H, d, *J* 10.4 Hz), 7.29 - 7.34 (1H, m), 7.38 - 7.43 (2H, m), 7.46 (1H, t, *J* 10.4 and 9.1 Hz), 7.51 (1H, s), 7.61-7.63 (2H, m), 8.10 (1H, d, *J* 9.4 Hz), and 8.62 (1H, d, *J* 16.1 Hz).
- 11) ¹H NMR (CDCl₃) of **5f** : δ = 2.22 (3H, s), 4.98 (1H, s), 5.30 (1H, d, *J* 10.6 Hz), 5.31 (1H, dd, *J* 9.7 and 9.3 Hz), 5.55 (1H, dd, *J* 10.1 and 8.3 Hz), 5.70 (1H, dd, *J* 11.4 and 8.3 Hz), 5.77 (1H, d, *J* 11.4 Hz), 5.86 (1H, dd, *J* 10.1 and 9.9 Hz), 5.88 (1H, dd, *J* 10.6 and 9.3 Hz), 6.46 (1H, d, *J* 9.9 Hz), 6.55 (1H, d, *J* 9.7 Hz), and 7.05 (1H, s).
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