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

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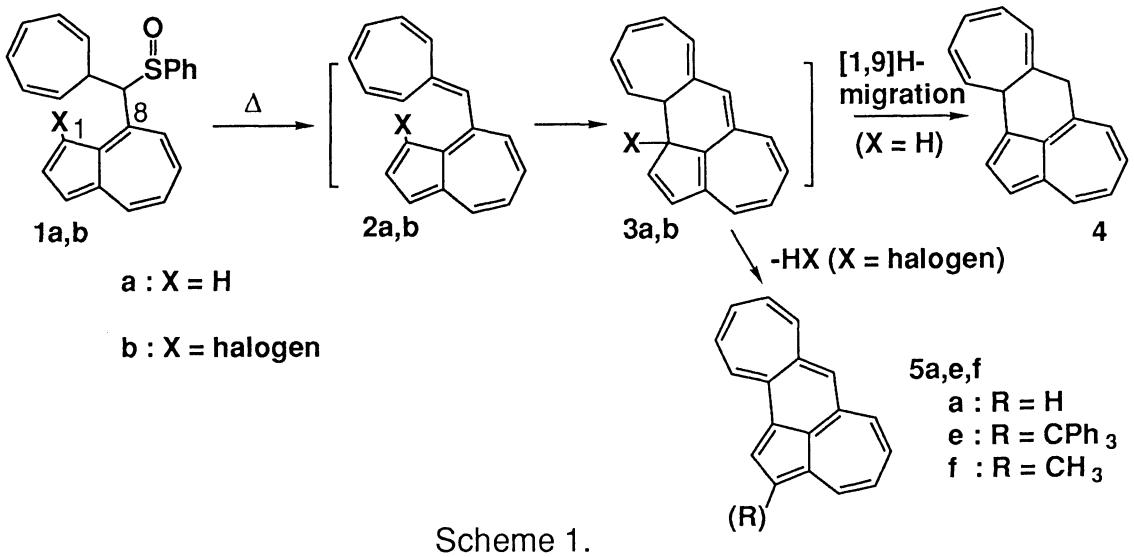
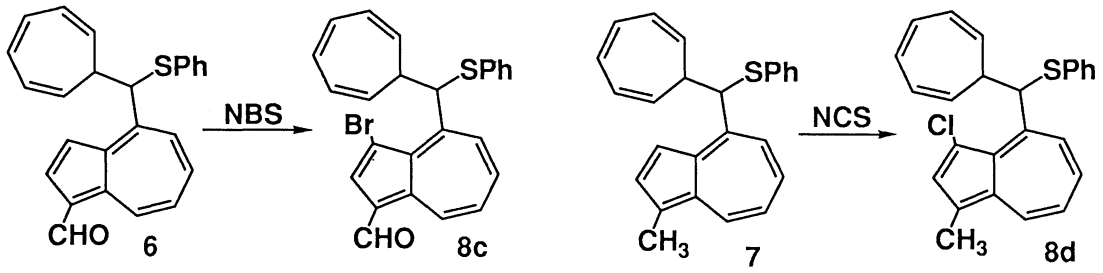
An oxidation product of 3-bromo-1-formyl-4-[(2,4,6-cycloheptatrienyl)-(phenylthio)methyl]azulene with *m*-chloroperbenzoic acid was transformed into 3-bromo-1-formyl-4-(E)-styrylazulene upon standing at 0 °C in a solid state. A similar rearrangement was also observed in the oxidation of 3-chloro-1-methyl-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl]azulene.

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, [14π]electrocyclization, and subsequent preferential [1,9]hydrogen migration.



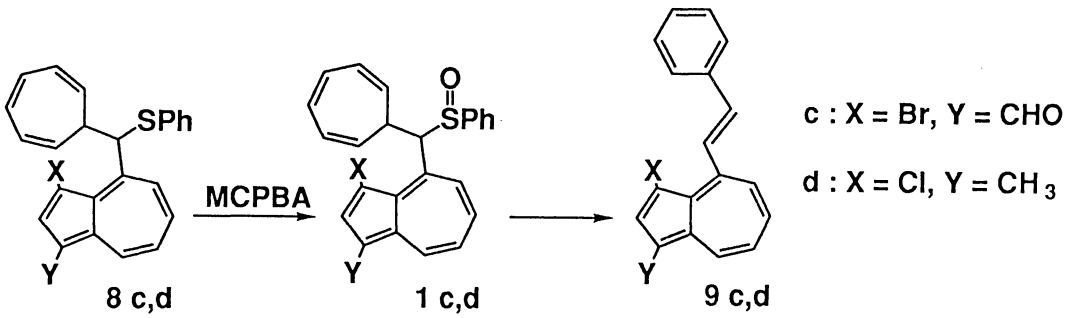
Scheme 1.

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-cyclohepta-trienyl)(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 positons 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 ^{1}H 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.

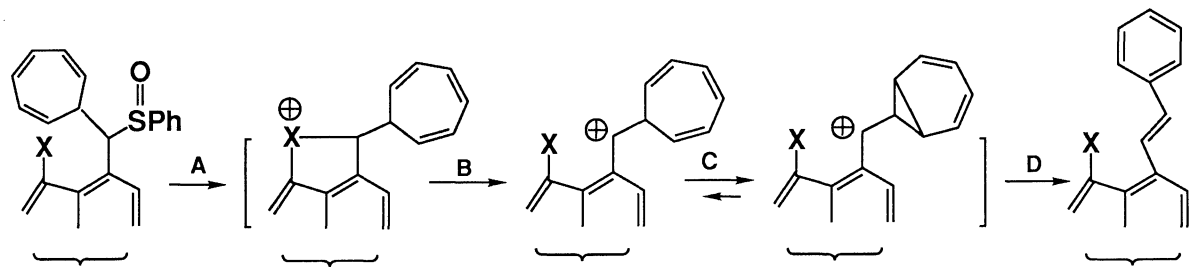
Reaction of **8c** with *m*-chloroperbenzoic acid in dichloromethane at -78 °C was monitored by means of silica gel thin layer chromatography (TLC). After 2 h, the original spot (R_f = 0.7, CH_2Cl_2) of **8c** was completely replaced by two purple spots at R_f 0.1 (**1c**$_\alpha$: major) and 0.2 (**1c**$_\beta$: 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**$_\alpha$) as a violet solid. Interestingly, the violet solid (**1c**$_\alpha$) 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 ^{1}H 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) unambigously 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 ^{1}H 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

1) Y. Sugihara, J. Saito, and I. Murata, *Angew. Chem., Int. Ed. Engl.*, **30**, 1174 (1991).

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-$POCl_3$) of 4-[(2,4,6-cycloheptatrienyl)(phenylthio)methyl]azulene[1] 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-methylazulene[9] 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 $C_{19}H_{13}OBr$: C, 67.67; H, 3.89; Br, 23.70; ^1H NMR ($CDCl_3$) 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 (CCl_4) 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 $C_{19}H_{15}Cl$: M, 278.0859; ^1H NMR ($CDCl_3$) 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 ($CDCl_3$) 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).

12) E. Vogel, *Pure. Appl. Chem.*, **20**, 237 (1969); T. Toda, *Yuki Gosei Kagaku Kyokai Shi*, **30**, 412 (1972); M. B. Rubin, *J. Am. Chem. Soc.*, **103**, 7791 (1981); K. Takeuchi, *Yuki Gosei Kagaku Kyokai Shi*, **43**, 40 (1985).

13) "Steric Effects in Organic Chemistry," ed by M. S. Newman, John Wiley & Sons, New York(1956); E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York(1962); J. March, "Advanced Organic Chemistry," 3rd ed, Wiley-Interscience, New York(1985), p. 163.

14) T. Tezuka and T. Otsuka, *Chem. Lett.*, **1989**, 1051; T. Tezuka, H. Kasuga, Y. Isahaya, and T. Nozoe, *ibid.*, **1990**, 255.

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