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Synthesis and Intramolecular Pericyclization of 1-Azulenyl Thioketones

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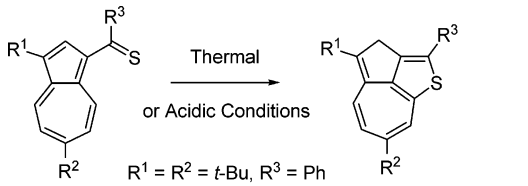

Several azulene-substituted thioketones, 1-thiobenzoylazulene (**1a**) and di(1-azulenyl) thioketone (**2a**) and their derivatives (**1b** and **2b**−**d**) with alkyl substituents on each azulene ring, were prepared and their intramolecular pericyclization reaction was examined. The thioketones with a 3-alkyl substituent on each azulene ring exhibited the presumed pericyclization reaction under thermal and acid-catalyzed conditions, although the cases of the 1-azulenyl thioketones without the 3-alkyl substituents afforded a complex mixture under similar conditions. The intramolecular reaction following the intramolecular hydrogen transfer afforded the products **13b**, **14b**, and **14c**. The products **13b** and **14b** were converted into the corresponding cations $\mathbf{18}^+$ and $\mathbf{19}^+$, which have structural similarity with that of the phenalenyl cation. These cations exhibited the expected two-step reduction waves upon CV, although the ESR analysis revealed that the neutral radical state did not have the presumed high stability.

Introduction

Thiocarbonyl compounds have been extensively studied because of their unique and interesting properties.[1] Stabilized carbothialdehydes are also now accessible and their quite different properties from those of aldehydes are reported.[2] Pericyclization reactions of aromatic thioketones are examined by Cox et al. under photochemical conditions to afford the cyclized products after intermolecular hydrogen transfer.[3]

Azulene ($C_{10}H_8$) has attracted the interest of many research groups due to its unusual properties as well as its beautiful blue color.[4] Cox et al. also have reported the photochemical reaction of 1-thiobenzoylazulene (**1a**), which never produces the cyclized product, but results in the recovery of the starting material under their photochemical reaction conditions.[3] They have concluded that the photochemical pericyclization reaction proceeds through the n,π* singlet state, which distinguishes the photochemical reaction of aromatic thioketones from that of ketones, although the other photophysical and photochemical properties might affect the photochemical reaction. In the case of aromatic

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(1) Duus, F. Thiocarbonyl Compounds. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Jones, D. N., Eds.; Pergamon: Oxford, UK, 1979; Vol. 3, pp 373−487.

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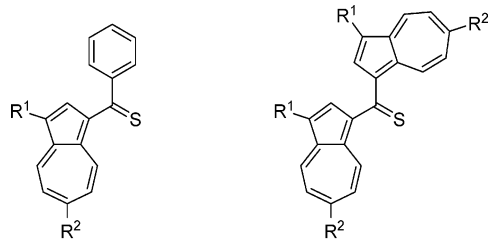
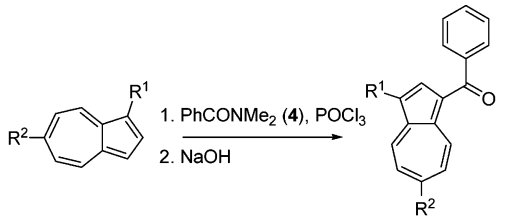
CHART 1



1a: $R^1 = R^2 = H$
1b: $R^1 = R^2 = t$-Bu

2a: $R^1 = R^2 = H$
2b: $R^1 = R^2 = t$-Bu
2c: $R^1 = Me$, $R^2 = H$
2d: $R^1 = H$, $R^2 = t$-Bu

SCHEME 1



3a: $R^1 = R^2 = H$
3b: $R^1 = R^2 = t$-Bu

5a: $R^1 = R^2 = H$
5b: $R^1 = R^2 = t$-Bu

thioketones including the nonalternant azulene skeleton the π,π^* state should be very close to the n,π^* state. Thus, the pericyclization reaction under thermal conditions might be possible in the case of azulene derivatives. However, little is known about the azulene-substituted thioketones except for the attempt for the photochemical pericyclization of 1-thiobenzoylazulene (**1a**). The pericyclization reaction of azulene-substituted thioketones under thermal conditions has never been examined.

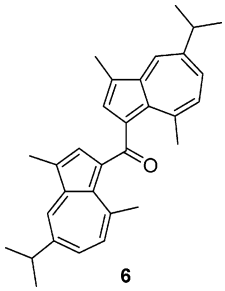
We report herein the efficient preparation of 1-thiobenzoylazulenes (**1a** and **1b**) and di(1-azulenyl) thioketones (**2a**−**d**) by the reaction of the corresponding carbonyl compounds with sulfur-donating reagents (P_2S_5/Et_3N and/or Lawesson's reagent), the pericyclization reaction of the azulene-substituted thioketones under thermal and acid-catalyzed conditions, and the conversion of the cyclized products, 3*H*-azulenothiophene derivatives, into cationic species (Chart 1).

Results and Discussion

Preparation of 1-Azulenyl Ketones. 1-Benzoylazulene (**5a**) was prepared by Vilsmeier−Haack reaction of azulene (**3a**), using *N*,*N*-dimethylbenzamide (**4**) according to the literature.[5] 1-Benzoyl-3,6-di-*tert*-butylazulene (**5b**) was synthesized by the procedure with use of 1,6-di-*tert*-butylazulene (**3b**)[6] (83%). It is noteworthy that the yield of the reaction was significantly increased by the *tert*-butyl substituents on the azulene ring (Scheme 1).

Preparation of bis(5-isopropyl-3,8-dimethyl-1-azulenyl) ketone (**6**) has been reported utilizing the reaction of 7-isopropyl-1,4-dimethylazulene (guaiazulene) with oxalyl chloride in dichloromethane in low yield (Chart 2).[7] Similarly, the reaction of azulene with oxalyl chloride affords the presumed di(1-azulenyl) ketone (**8a**) along with di(1-azulenyl) diketone (**9a**).[8] Oxalyl bromide (**7**) is used instead of oxalyl chloride in the reaction of azulenes to afford 1-azulenecarbonyl bromides as the reaction intermediate, which reacts with azulene derivatives to give di(1-azulenyl) ketones including unsymmetrical derivatives.[9] Several di(1-azulenyl) ketone derivatives including the parent ketone **8a** are also obtained from the autoxidation products of azulenes in trace yields.[10] Recently, the ketone **8a** is obtained by the two-step sequence starting from 1-azulenecarboxylic acid via ethyl 1-azuleneglyoxylate.[11]

CHART 2



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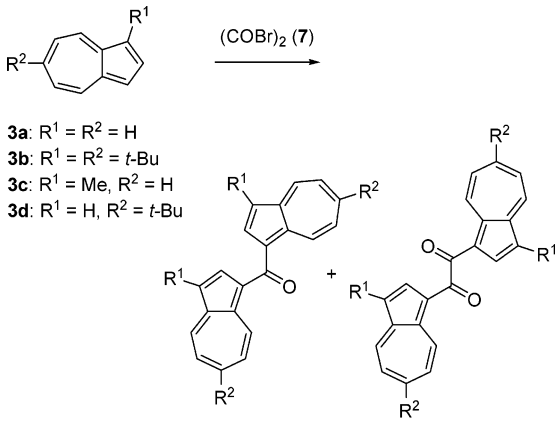
SCHEME 2



3a: $R^1 = R^2 = H$
3b: $R^1 = R^2 = t$-Bu
3c: $R^1 = Me$, $R^2 = H$
3d: $R^1 = H$, $R^2 = t$-Bu

8a: $R^1 = R^2 = H$
8b: $R^1 = R^2 = t$-Bu
8c: $R^1 = Me$, $R^2 = H$
8d: $R^1 = H$, $R^2 = t$-Bu

9a: $R^1 = R^2 = H$
9b: $R^1 = R^2 = t$-Bu
9c: $R^1 = Me$, $R^2 = H$
9d: $R^1 = H$, $R^2 = t$-Bu

We prepared the desired di(1-azulenyl) ketones (**8a**−**d**) by the one-step reaction of azulenes (**3a**−**d**) with **7** in dichloromethane (Scheme 2). The reaction of 4 molar amounts of azulene (**3a**) with **7** in dichloromethane at room temperature

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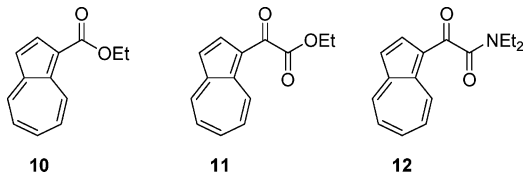
CHART 3



10 **11** **12**

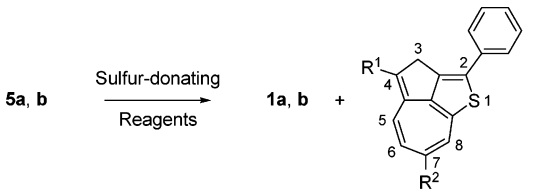
for several hours, following the treatment with ethanol, afforded the desired ketone **8a** (17%) along with diketone **9a** (3%) and ethyl azulene-1-carboxylate (**10**) (3%) (Chart 3).[12] Addition of sodium acetate to the reaction of **3a** with **7** in dichloromethane slightly improved the yields of the desired ketone **8a** (24%) with diketone **9a** (15%). Lowering the reaction temperature did not improve the yield of the desired products. When the reaction was carried out at −78 °C, ethyl (1-azulenyl)glyoxylate (**11**) was obtained as a major product in 76% yield. Changing the base to triethylamine resulted into the formation of *N*,*N*-diethyl-(1-azulenyl)glyoxylamide (**12**) as a major product (34%).

Bis(3,6-di-*tert*-butyl- and 3-methyl-1-azulenyl) ketones (**8b**[13] and **8c**[10b]) were obtained by the similar reaction of **3b** and 1-methylazulene (**3c**)[14] in 71% and 61% yields, respectively, along with a small amount of diketones **9b** (4%) and **9c** (3%). However, similar to the reaction of **3a** with **7**, the yields of ketone **8d** (17%) and diketone **9d** (1%) by the reaction of 6-*tert*-butylazulene (**3d**)[6] with **7** were relatively low. Consequently, the yield of the reaction of **3a**−**d** with **7** is significantly affected by the existence of the 1-alkyl substituent on the azulene ring, similar to the results on the Vilsmeier−Haack reaction with *N*,*N*-dimethylbenzamide (**4**).

Synthesis of 1-Azulenyl Thioketones. Thiocarbonyl compounds are usually synthesized from the corresponding carbonyl compounds by the reaction with sulfur-donating reagents such as H_2S,[15] P_2S_5,[16] and Lawesson's reagent.[17] Indeed, 1-thiobenzoylazulene (**1a**) has been synthesized by the reaction of **5a** with HCl−H_2S in relatively low yield.[3] We applied the reaction of 1-azulenyl ketones with P_2S_5/Et_3N and Lawesson's reagent for the preparation of the corresponding 1-azulenyl thioketones (Schemes 3 and 4). The results are summarized in Table 1. The yield of 1-thiobenzoylazulene (**1a**) was significantly improved by the use of these reagents. When 1-benzoylazulene (**5a**) was treated with P_2S_5 in the presence of triethylamine, **1a** was obtained in 79% yield (entry 1). The reaction of **5a** with Lawesson's reagent also afforded the desired thioketone **1a** in 74% yield (entry 2).

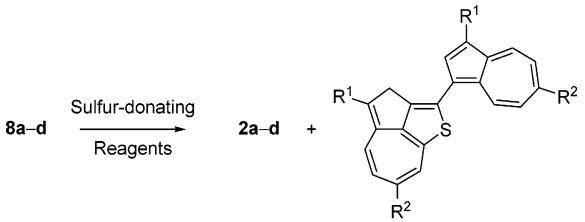
Thioketone **1a** reacted with 2,3-dimethyl-1,3-butadiene (**15**) to afford a [2 + 4] cycloadduct, 2-(1-azulenyl)-2-phenyl-4,5-dimethyldihydrothiopyran (**16**), which indicated the C═S structure in thioketone **1a** (Scheme 5).[1]

SCHEME 3



13a: $R^1 = R^2 = H$
13b: $R^1 = R^2 = t$-Bu

SCHEME 4

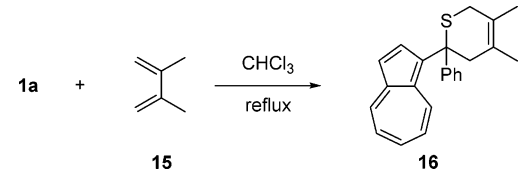


14a: $R^1 = R^2 = H$
14b: $R^1 = R^2 = t$-Bu
14c: R^1 = Me, $R^2 = H$
14d: $R^1 = H$, $R^2 = t$-Bu

TABLE 1. Syntheses of Azulene-Substituted Thioketones

entry	ketone	R^1	R^2	reagents	yield **1** or **2**	%	yield **13** or **14**	%
1	**5a**	H	H	P_2S_5/Et_3N	**1a**	79	**13a**	0
2	**5a**	H	H	Lawesson's reagent	**1a**	74	**13a**	0
3	**5b**	*t*-Bu	*t*-Bu	P_2S_5/Et_3N	**1b**	65	**13b**	0
4	**5b**	*t*-Bu	*t*-Bu	Lawesson's reagent	**1b**	0	**13b**	89
5	**8a**	H	H	P_2S_5/Et_3N	**2a**	59	**14a**	0
6	**8a**	H	H	Lawesson's reagent	**2a**	56	**14a**	0
7	**8b**	*t*-Bu	*t*-Bu	P_2S_5/Et_3N	**2b**	82	**14b**	0
8	**8b**	*t*-Bu	*t*-Bu	Lawesson's reagent	**2b**	0	**14b**	88
9	**8c**	Me	H	P_2S_5/Et_3N	**2c**	80	**14c**	0
10	**8c**	Me	H	Lawesson's reagent	**2c**	13	**14c**	67
11	**8d**	H	*t*-Bu	P_2S_5/Et_3N	**2d**	61	**14d**	0
12	**8d**	H	*t*-Bu	Lawesson's reagent	**2d**	72	**14d**	0

SCHEME 5



15 **16**

The reaction of **5b** with P_2S_5/Et_3N also afforded the corresponding thioketone, 3,6-di-*tert*-butyl-1-thiobenzoylazulene (**1b**), in good yield (entry 3). In contrast to the reaction with P_2S_5/Et_3N, the reaction of ketone **5b** with Lawesson's reagent, following chromatographic purification on Al_2O_3, afforded 3*H*-azuleno[8,1-*b*,*c*]thiophene **13b** as a sole product (entry 4). Several azulenothiophene derivatives are prepared by the reaction of azulene derivatives with sulfur,[18] intramolecular cyclization reactions,[19] and the reaction of oxaazulanones with enamines.[20] This is the first example of the preparation of the azulenothiophene derivative with 3*H*-azuleno[8,1-*b*,*c*]thiophene skeleton by the pericyclization reaction of the 1-azulenyl

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TABLE 2. Pericyclization Reaction of Azulene-Substituted Thioketones

entry	thio-ketone	R^1	R^2	time	condi-tions[a]	results
1	**1a**	H	H	14 h	acidic	complex mixture
2	**1a**	H	H	5 d	thermal	complex mixture
3	**1b**	*t*-Bu	*t*-Bu	1 h	acidic	**13b** (35%), **5b** (18%)
4	**1b**	*t*-Bu	*t*-Bu	1 d	thermal	**13b** (37%), **5b** (24%)
5	**2a**	H	H	1 h	acidic	complex mixture
6	**2a**	H	H	3 d	thermal	complex mixture
7	**2b**	*t*-Bu	*t*-Bu	20 min	acidic	**14b** (100%)
8	**2b**	*t*-Bu	*t*-Bu	1 d	thermal	**14b** (76%)
9	**2c**	Me	H	1 h	acidic	**14c** (67%)
10	**2c**	Me	H	2 d	thermal	**14c** (35%)
11	**2d**	H	*t*-Bu	2 h	acidic	complex mixture
12	**2d**	H	*t*-Bu	4 d	thermal	complex mixture

[a] Acid-catalyzed cyclization was carried out in $CHCl_3$ with concentrated HCl. Thermal reaction was carried out in refluxing toluene.

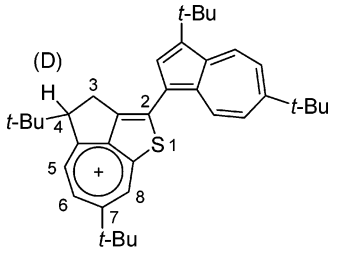
thioketone. The methylene protons of **13b** were observed at 3.45 ppm on the ^{1}H NMR spectrum. The seven-membered-ring protons of **13b** were observed at the olefinic region [δ 6.45 (d, 1H, J = 12.8 Hz, H_5), 5.97 (s, 1H, H_8), 5.66 (d, 1H, J = 12.8 Hz, H_6) ppm]. Therefore, 3*H*-azuleno[8,1-*b*,*c*]thiophene **13b** has the fused-ring structure between heptafulvene and thiophene moieties.

The reaction of di(1-azulenyl) ketones **8a**−**d** with P_2S_5 in the presence of triethylamine afforded the corresponding thioketones **2a**−**d** in 59−82% yields (entries 5, 7, 9, and 11). In contrast to the reaction with P_2S_5/Et_3N, the reaction of **8b** and **8c** with Lawesson's reagent afforded **14b** and **14c**, respectively, as major products along with the presumed thioketones in a small amount in the case of the reaction of **8c** (entries 8 and 10). However, the reaction of **8a** and **8d** with Lawesson's reagent afforded thioketones **2a** and **2d**, exclusively (entries 6 and 12). Thus, 3*H*-azuleno[8,1-*b*,*c*]thiophene derivatives were obtained by the reaction of the 1-azulenyl ketones with the 3-alkyl substituents with Lawesson's reagent (Table 1).

The formation of the 3*H*-azuleno[8,1-*b*,*c*]thiophene derivatives indicates that the expected intramolecular pericyclization of the corresponding thioketones **1** and **2** proceeds under preparatory conditions. The 1,5-hydorogen transfer of the presumed pericyclization products results in the formation of 3*H*-azuleno[8,1-*b*,*c*]thiophene derivatives **13** and **14**. To clarify the formation of the azulenothiophene derivatives, the intramolecular pericyclization of these thioketones under various reaction conditions was examined.

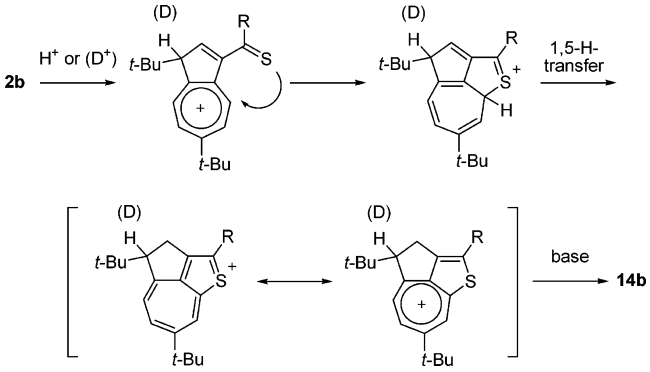
Acid-Catalyzed Isomerization. We found that several thioketones were transformed into the corresponding 3*H*-azuleno[8,1-*b*,*c*]thiophene derivatives under acidic conditions (Table 2). The treatment of thioketone **1b** with concentrated hydrochloric acid in chloroform at room temperature afforded **13b** in 35% yield along with **5b** in 18% yield, which should be attributed to the acid-catalyzed hydrolysis of the thioketone **1b** (entry 3). However, the reaction of **1a** afforded a complex mixture instead of the 3*H*-azuleno[8,1-*b*,*c*]thiophene derivative **13a** under similar acidic conditions (entry 1). In the cases of

CHART 4



17$^+$

SCHEME 6. Proposed Reaction Mechanism for the Acid-Catalyzed Pericyclization of 1-Azulenyl Thioketones



di(1-azulenyl) thioketones, two thioketones **2b** and **2c** exhibited the presumed pericyclization to afford **14b** and **14c** by a similar acid-catalyzed reaction (entries 7 and 9). However, thioketones **2a** and **2d** did not afford the corresponding thiophene derivatives **14a** and **14d** under similar acidic conditions (entries 5 and 11). Thus, the presence of alkyl substituent at the 3-position on each azulene ring is important to the success of the pericyclization reaction under acid-catalyzed conditions, as similar to the observation of the reaction with Lawesson's reagent. The 1-azulenyl thioketones without the 3-alkyl substituents afforded a complex mixture instead of the corresponding 3*H*-azuleno-[8,1-*b*,*c*]thiophene derivatives by the acid-catalyzed reaction (Table 2).

^{1}H and ^{13}C NMR spectra were measured by using the deep blue solution prepared by the addition of concentrated hydrochloric acid to a solution of thioketone **2b** in $CDCl_3$. The NMR spectra, which are represented in the Supporting Information, revealed the formation of cationic species **17**$^+$ as an intermediate (Chart 4). ^{1}H NMR chemical shifts of H_5, H_6, and H_8 signals in **17**$^+$ are apparently observed at downfield locations compared with those of **14b**, which exhibit the tropylium ion structure of the intermediate. Neutralization of the deep blue solution with an aqueous sodium hydrogencarbonate solution afforded **14b**.

To demonstrate the hydrogen transfer during the formation of the 3*H*-azuleno[8,1-*b*,*c*]thiophene derivatives, ^{1}H NMR measurement was examined utilizing DCl instead of HCl in $CDCl_3$, which led to the incorporation of only one deuteron at the 4-position in the cationic intermediate **17**$^+$, essentially quantitatively. Thus, a plausible reaction path could be drawn as represented in Scheme 6. Pericyclization should be accelerated by the protonation at the 3-position on the azulene ring. Along the reaction path a hydrogen atom must be transferred. This could be, in principle, a concerted 1,5-hydrogen transfer or a two-step intermolecular process. We could conclude that the isomerization involves the 1,5-hydrogen transfer process

(19) See e.g.: (a) Matsui, K.; Nozoe, T. *Chem. Ind.* **1960**, 1302−1303. (b) Replogle, L. L.; Katsumoto, K.; Ammon, H. L. *J. Am. Chem. Soc.* **1968**, *90*, 1086−1087. (c) Ammon, H. L.; Replogle, L. L.; Watts, P. H., Jr.; Katsumoto, K.; Stewart, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2196−2202. (d) Yamane, K.; Fujimori, K.; Takeuchi, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2537−2538.

(20) Fujimori, K.; Fujita, T.; Yamane, K.; Takase, K. *Chem. Lett.* **1983**, 1721−1724.

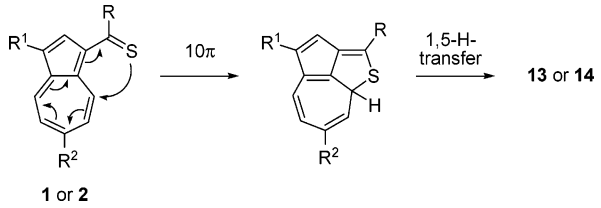
under acidic conditions because no deuterium exchange was observed at the 3-position on the cationic species **17**$^+$ when DCl was used.

Thermal Isomerization. The pericyclization reaction of these thioketones was also examined under thermal conditions. The thioketones, which gave the 3*H*-azuleno[8,1-*b*,*c*]thiophene derivatives under acid-catalyzed reaction, also afforded the pericyclized products under thermal conditions. However, the thioketones, which gave a complex mixture under acidic conditions, also did not give the pericyclized products (Table 2). When a solution of thioketone **1b** in toluene was refluxed for 1 day under an Ar atmosphere, the thiophene derivative **13b** was obtained in 37% yield along with **5b** in 24% yield (entry 4). The formation of **5b** under thermal conditions should be ascribed to the hydrolysis of **1b** during the prolonged heating in toluene. Similar to the acid-catalyzed reaction, thioketone **1a** afforded a complex mixture instead of **13a** under thermal conditions (entry 2). Thioketones **2b** and **2c** were also transformed into the thiophene derivatives **14b** and **14c** under thermal conditions (entries 8 and 10). As expected, thioketones **2a** and **2d** produced a complex mixture under thermal conditions (entries 6 and 12). Therefore, under both thermal and acid-catalyzed conditions the presence of an alkyl substituent at the 3-position on each azulene ring is important in the formation of 3*H*-azuleno[8,1-*b*,*c*]thiophene derivatives.

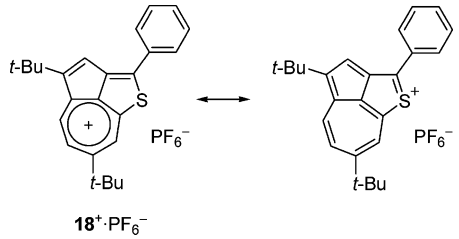
The question arises as to why the pericyclization products are not obained without 3-alkyl substituents. The azulene system has high reactivity at 1,3-positions toward the electrophilic reagents.[4] It is well-known that the azulene derivatives react with carbonyl compounds to give condensed products such as di(1-azulenyl)methane derivatives under acidic conditions.[6,21] 3*H*-Azuleno[8,1-*b*,*c*]thiophenes **13b**, **14b**, and **14c** have a fused-ring structure between heptafulvene and thiophene moieties. The heptafulvene is well-known as a highly reactive compound.[22] In consideration of the results on the synthesis with Lawesson's reagent, the thioketones without 3-alkyl substituents are less reactive toward the intramolecular pericyclization reaction, compared with those with 3-alkyl substituents. Thus, the explanation should be attributed to the smaller reactivity toward the pericyclization reaction, which might accelerate the side reaction to give a complex mixture due to the high reactivity of the 3-position of the starting azulenyl thioketones or the instability of the final thiophene derivatives under pericyclization conditions.

To obtain the theoretical aspect of 1-azulenyl thioketones, the molecular orbital calculation of 1-azulenecarbothialdehyde was performed by the B3LYP/6-31G** density functional calculations (see the Supporting Information).[23] The HOMO includes the n orbital of the sulfur atom. On the other hand, the HOMO-1, which is located at a similar energy level as that of HOMO, and the LUMO are delocalized over the π system including that of the sulfur atom. The examination of the HOMOs and the LUMO suggests the possibility for the thermal intramolecular pericyclization between the sulfur atom and the 8-position of the azulene ring by the 10π cyclization mode instead of the photochemical reaction (Scheme 7). The thermal pericyclization reaction of **2b** was also examined in the presence of galvinoxyl as a radical scavenger, but the pericyclization reaction was not affected by the radical scavenger. The reaction of **2b** in refluxing toluene afforded the corresponding cyclization product **14b** in 85% yield, even in the presence of the radical scavenger.

SCHEME 7. Proposed Reaction Mechanism for the Pericyclization of 1-Azulenyl Thioketones under Thermal Conditions



SCHEME 8



To estimate the formation of the thiophene derivatives **13b**, **14b**, and **14c** as the pericyclized products, we have also performed the B3LYP/6-31G** density functional calculations[24] of the nine possible azuleno[8,1-*b*,*c*]thiophene structures without other substituents, although the reaction has not been proved to proceed under thermodynamic control (see the Supporting Information). Consideration of the relative stabilities of the structural isomers based on the calculated total energy demonstrates that the 3*H*-azuleno[8,1-*b*,*c*]thiophene structure is one of the highly stable regioisomers among all possible structural isomers. However, the presumed initial cyclization products illustrated in Schemes 6 and 7 exhibited relatively high total energies, which might be the reason for the formation of the thiophene derivatives **13b**, **14b**, and **14c** as the isolable products.

Preparation of Cationic Species. The pericyclized products **13b** and **14b** produced a stabilized cationic species **18**$^+$ and **19**$^+$ by hydride abstraction reaction. The reaction of **13b** with DDQ in dichloromethane at room temperature, followed by an addition of a 60% aqueous HPF_6 solution, yielded cation **18**$^+$ (96%) as a hexafluorophosphate (Scheme 8).[6,13,25] The salt **19**$^+$·PF_6^- was obtained by a similar reaction of **14b** with DDQ in 67% yield (Scheme 9). These new salts **18**$^+$·PF_6^- and **19**$^+$·PF_6^- are stable, deep-colored crystals, and are storable in

(21) See e.g.: Franke, H.; Mühlstädt, M. *J. Prakt. Chem.* **1967**, *35*, 262−270.

(22) (a) Doering, W. v. E.; Wiley, D. W. *Tetrahedron* **1960**, *11*, 183−198. (b) Zimmerman, H. E.; Sousa, L. R. *J. Am. Chem. Soc.* **1972**, *94*, 834−842. (c) Neuenschwander, M.; Schenk, W. K. *Chimia* **1972**, *26*, 194−197.

(23) The molecular orbital calculations were done with a Gaussian revision E.2 program package, which was installed in an UNIX workstation under a molecular design support system in IMRAM. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian*, revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(24) The B3LYP/6-31G** density functional calculations were performed by Spartan'04, Wavefunction, Inc.: Irvine, CA.

(25) Ito, S.; Kikuchi, S.; Morita, N.; Asao, T. *J. Org. Chem.* **1999**, *64*, 5815−5821.

SCHEME 9

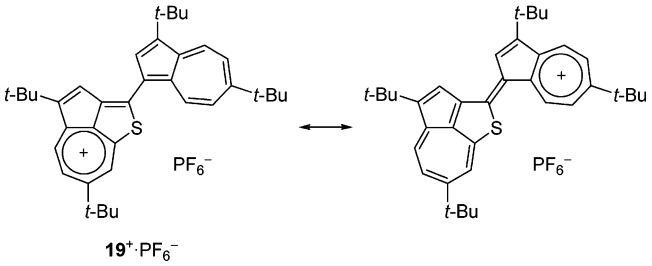


TABLE 3. Redox Potentials[a] of Compounds 18^+ and 19^+

sample	E_1^{red}	E_2^{red}	E_3^{red}	E_1^{ox}	E_2^{ox}
18^+	(−0.49)	(−1.50)		(+1.73)	
19^+	−0.70	−1.58	(−1.97)	+0.94	(+1.43)

[a] The redox potentials were measured by CV (0.1 M Et_4NClO_4 in acetonitrile, Pt electrode, scan rate 100 mV s^{-1}, and $Fc/Fc^+ = +0.07$ V). In the case of irreversible waves, which are shown in parentheses, E_{ox} and E_{red} were calculated as E_{pa} (anodic peak potential) − 0.03 V and E_{pc} (cathodic peak potential) + 0.03 V, respectively.

the crystalline state. These cations 18^+ and 19^+ were fully characterized by the spectral data as shown in the Supporting Information. The UV−vis spectra of 18^+ and 19^+ in acetonitrile are represented in Figure 1. These cations showed characteristic absorption in the visible region [18^+, 546 nm (log ϵ 3.43); 19^+, 639 nm (log ϵ 4.56)]. The strong absorption of 19^+ in the visible region could be explained by the CT transition from the substituted 3,6-di-*tert*-butyl-1-azulenyl group, as described by the resonance structure in Scheme 9.

Redox Behavior. These cations 18^+ and 19^+ possess a structural similarity with the phenalenyl systems[26] in the point of the peripheral 12π electrons, counting the sulfur atom as two electrons like thiophene derivatives, with one central sp^2 carbon atom, although these cations are not symmetrically as distinct from the phenalenyl systems. To clarify the electrochemical property, the redox behavior of 18^+ and 19^+ was examined by cyclic voltammetry (CV). Measurements were made by using a standard three electrode configuration. Tetraethylammonium perchlorate (0.1 M) in acetonitrile was used as a supporting electrolyte with platinum wire auxiliary and working electrodes. All measurements were carried out under an argon atmosphere and potentials were related to the reference electrode formed by $Ag/AgNO_3$ and using as internal reference Fc/Fc^+ that discharges at +0.07 V.

Redox potentials (in volts vs $Ag/AgNO_3$) of 18^+ and 19^+ are summarized in Table 3. The redox waves of 18^+ and 19^+ are shown in the Supporting Information. The reduction of 18^+ exhibited a quasireversible two-step wave. The E_1^{red} wave might be attributable to the one-electron injection to the cation forming a neutral radical. The second reduction wave is considered as the generation of an anionic species (Scheme 10).

Cation 19^+ exhibited the three-step reduction, which was characterized as two reversible processes at −0.70 and −1.58 V following an irreversible process at −1.97 V. The three-step reduction may be considered as the formation of a neutral radical and an anionic species in addition to the redox reaction of the

(26) (a) Goto, K.; Kubo, T.; Yamamoto, K.; Nakasuji, K.; Sato, K.; Shiomi, D.; Takui, T.; Kubota, M.; Kobayashi, T.; Yakushi, K.; Ouyang, J. *J. Am. Chem. Soc.* **1999**, *121*, 1619−1620. (b) Kubo, T.; Yamamoto, K.; Nakasuji, K.; Takui, T.; Murata, I. *Bull. Chem. Soc. Jpn.* **1999**, *74*, 1999−2009. (c) Nakasuji, K.; Kubo, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1791−1804.

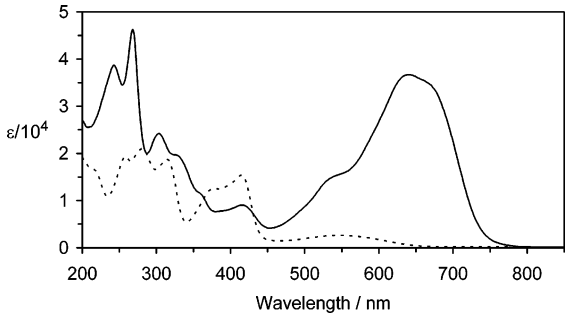
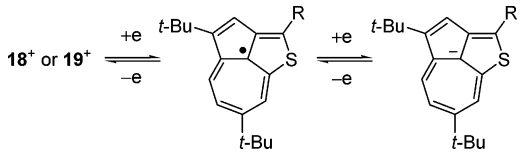


FIGURE 1. UV−vis spectra of $18^+ \cdot PF_6^-$ (broken line) and $19^+ \cdot PF_6^-$ (solid line) in acetonitrile.

SCHEME 10



substituted 1-azulenyl group. The potential shift of the first reduction wave of 19^+ can be explained by the stabilization of the cationic state owing to the substituted 1-azulenyl group. In the case of reduction of the tri(1-azulenyl)methyl cation, the second reduction wave is irreversible in all cases owing to the destabilization of the anionic species arising from the destabilization by the electron-donating 1-azulenyl substituents.[6] The reversibility upon CV of the second reduction wave of 19^+ might be attributed to the structural similarity with the phenalenyl systems, which would stabilize the corresponding neutral radical and the anionic species.

The oxidation of 18^+ exhibited an irreversible wave at +1.73 V. In contrast to the one-step oxidation of 18^+, cation 19^+ exhibited a two-step oxidation wave. The reversible E_1^{ox} wave of 19^+ should be ascribed to the electron removal from the 1-azulenyl group forming a dicationic species.

Electrochromic Analysis. To obtain the aspect for the reduced species, the electrochemical reduction of 19^+ was conducted by visible spectral monitoring and ESR measurements. The visible spectral changes of 19^+ are summarized in the Supporting Information. The absorption bands of 19^+ in the visible region gradually disappeared along with increasing the new absorption maxima at 448 nm during the electrochemical reduction. The color of the solution gradually changed from deep blue to yellow during the electrochemical reduction. The yellow solution turned reddish brown on further reduction. The two-step color changes might correspond to the formation of a neutral and an anionic species. The reverse oxidation of the intermediary yellow solution did not regenerate the spectrum of 19^+ completely (regeneration 37%), even though good reversibility was observed upon CV. Low reversibility for the reduction of 19^+ suggests that the neutral and anionic species produced by the electrochemical reduction are unstable under the conditions of the spectral measurements.

ESR Measurements. The ESR measurements were also examined by using the cation 19^+ under electrochemical reduction conditions with use of a degassed dimethylformamide solution prepared under a vacuum line containing tetrapropylammonium perchlorate as a supporting electrolyte at room temperature. The spectra are summarized in the Supporting Information. The deep blue solution of 19^+ did not indicate any

ESR signals before the electrochemical reduction. The yellow solution obtained by the electrochemical reduction of $\mathbf{19}^+$ was also ESR silent. This fact indicates that the yellow originates from the closed shell species, probably due to the rapid coupling of the unstable neutral radical to form ESR silent species during the electrochemical reduction.

The ESR spectrum split into multiple lines due to hyperfine interactions was obtained from the reddish brown solution produced by further reduction of the yellow solution obtained by the reduction of $\mathbf{19}^+$. The reddish brown solution should correspond to the two-electron reduction product of $\mathbf{19}^+$. The simulation with a *g*-value of 2.00235 and proton hyperfine coupling (hfc) constants of 0.625 (2H), 0.360 (1H), and 0.170 mT (2H) well-reproduced the observed spectrum. The hfc constants for the radical species are very similar to those of the anion radical of azulene derivatives.[27] Therefore, the observed ESR spectrum could be explained by the hyperfine interactions with 4,8-protons, 2-proton, and 5,7-protons, respectively, on the anion radical of the 3,6-di-*tert*-butyl-1-azulenyl group. Therefore, by combined electrochromic and ESR analyses it was determined that the neutral radical species produced by the one-electron reduction of $\mathbf{19}^+$ is the reactive species that turned into the ESR-silent yellow ones. The second electron injection, in this case, could be caused by the redox reaction of the substituted 3,6-di-*tert*-butyl-1-azulenyl group to the azulenothiophene moiety in contrast to the expectation. We also tried the reaction of **14b** with potassium *tert*-butoxide in dry THF-d_8 to obtain the anionic species chemically, but the reaction did not afford any evidence for the formation of the anionic species as suggested by the results on the electrochromic and ESR measurements.

Conclusion

1-Azulenyl thioketones **1a**, **1b**, and **2a**−**d** were synthesized efficiently by the reaction of **5** and **8** with P_2S_5 in the presence of triethylamine. The reactions of **5b**, **8b**, and **8c** with Lawesson's reagent afforded **13b**, **14b**, and **14c** as major products. Thermal and acid-catalyzed intramolecular pericyclization reactions of the 1-azulenyl thioketones, which have 3-alkyl groups on each azulene ring, resulted in the formation of 3*H*-azuleno-[8,1-*b*,*c*]thiophene derivatives **13b**, **14b**, and **14c** via 1,5-hydrogen transfer from the initial cycloadducts. Cationic intermediate $\mathbf{17}^+$ under acidic conditions was detected by NMR spectroscopy. Thiophene derivatives **13b** and **14b** produced the stable cations $\mathbf{18}^+$ and $\mathbf{19}^+$, which could possess a structural similarity with phenalenyl systems, by the reaction with DDQ. However, the electrochromic and ESR analyses revealed that the electrochemical reduction of $\mathbf{18}^+$ and $\mathbf{19}^+$ did not produce the stabilized neutral radical with highly amphoteric redox properties in contrast to the expectation.

Experimental Section

General. For general and electrochemical measurement details, see the Supporting Information. The peak assignment of ^{1}H and ^{13}C NMR spectra reported was accomplished by decoupling, NOE, CH COSY, COLOC, HMQC, and/or HMBC experiments.

General Procedure for the Synthesis of Di(1-azulenyl) ketones (8a−d). Oxalyl bromide (**7**) was added to a solution of azulenes **3a**−**d** in CH_2Cl_2. The resulting mixture was stirred for 1 h to 2 days. After an addition of ethanol to the reaction mixture, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The products were isolated by column chromatography on silica gel with ethyl acetate/CH_2Cl_2 and GPC (gel permeation chromatography) with $CHCl_3$ to afford di(1-azulenyl) ketones **8a**−**d** and di(1-azulenyl) diketones **9a**−**d**.

Di(1-azulenyl) Ketone (8a). The general procedure was followed by using azulene (**3a**) (263 mg, 2.05 mmol) and **7** (108 mg, 0.500 mmol) in CH_2Cl_2 (10 mL) at room temperature for 4 h. Chromatographic purification on silica gel with ethyl acetate/CH_2Cl_2 and GPC with $CHCl_3$ afforded **8a** (24 mg, 17%), di(1-azulenyl) diketone (**9a**) (4 mg, 3%), and ethyl azulene-1-carboxylate (**10**) (3 mg, 3%). The reaction of **3a** (265 mg, 2.07 mmol) with **7** (108 mg, 0.500 mmol) in the presence of sodium acetate (87 mg, 1.1 mmol) in CH_2Cl_2 (10 mL) at room temperature for 4 h afforded **8a** (34 mg, 24%) and **9a** (24 mg, 15%).

8a:[10d,11] purple needles; mp 132.8−134.7 °C [lit.[11] mp 129−131 °C]; MS (70 eV) *m*/*z* 282 (M^+, 100%), 281 (75), 254 ($M^+ - CO$, 20), 253 (40), 252 (48), 127 ($M^+ - COC_{10}H_7$, 50), 126 (22); IR (KBr disk) ν_{max} 1586, 1489, 1460, 1429, 1416, 1393, 812, 766 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 230 sh (4.58), 286 (4.63), 318 (4.56), 405 (4.45), 505 sh (2.98), 541 (3.05), 584 sh (2.91), 644 sh (2.33); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, 2H, J = 9.8 Hz, H_8), 8.50 (d, 2H, J = 9.8 Hz, H_4), 8.21 (d, 2H, J = 4.0 Hz, H_2), 7.80 (dd, 2H, J = 9.9, 9.8 Hz, H_6), 7.54 (dd, 2H, J = 9.9, 9.8 Hz, H_7), 7.43 (dd, 2H, J = 9.8, 9.8 Hz, H_5), 7.34 (d, 2H, J = 4.0 Hz, H_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2 (C═O), 144.4 (C_{3a}), 141.7 (C_2), 140.7 (C_{8a}), 139.2 (C_6), 138.6 (C_8), 138.3 (C_4), 128.6 (C_1), 127.8 (C_7), 126.5 (C_5), 117.4 (C_3). Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.27; H, 5.23.

9a: red crystals; mp 257.0−258.5 °C; MS (70 eV) *m*/*z* 310 (M^+, 7%), 155 ($M^+ - COC_{10}H_7$, 100); IR (KBr disk) ν_{max} 1615 (C═O), 1495, 1408, 1393, 644 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 235 sh (4.55), 269 (4.25), 300 sh (4.59), 317 (4.70), 383 sh (4.36), 403 (4.53), 493 sh (3.14), 520 (3.17), 561 sh (3.02), 616 sh (2.42); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (d, 2H, J = 9.9 Hz, H_8), 8.52 (d, 2H, J = 9.7 Hz, H_4), 8.27 (d, 2H, J = 4.2 Hz, H_2), 7.91 (dd, 2H, J = 9.8, 9.8 Hz, H_6), 7.75 (dd, 2H, J = 9.9, 9.8 Hz, H_7), 7.59 (dd, 2H, J = 9.8, 9.7 Hz, H_5), 7.27 (d, 2H, J = 4.2 Hz, H_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7 (C═O), 146.6 (C_{3a}), 143.0 (C_2), 142.1 (C_{8a}), 139.8 (C_6), 139.6 (C_8), 138.7 (C_4), 130.3 (C_7), 128.7 (C_5), 121.6 (C_1), 119.0 (C_3). Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.06; H, 4.75.

General Procedure for the Thionation Reaction with P_2S_5/Et_3N. To a solution of azulene-substituted ketones **5a**, **5b**, and **8a**−**d** in $CHCl_3$ was added P_2S_5 and triethylamine. After the resulting mixture was stirred for 2−14 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The products were isolated by column chromatography on silica gel or Al_2O_3 with CH_2Cl_2/hexane to afford the corresponding thioketones **1a**, **1b**, and **2a**−**d**.

General Procedure for the Thionation Reaction with Lawesson's Reagent. To a solution of azulene-substituted ketones **5a**, **5b**, and **8a**−**d** in toluene and/or benzene was added Lawesson's reagent. After the resulting mixture was stirred for 1.5−20 h, the reaction mixture was poured into a $NaHCO_3$ solution and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The products were isolated by column chromatography on silica gel or Al_2O_3 with CH_2Cl_2/hexane to afford the thioketones **1a**, **2a**, **2c**, and **2d** and/or the thiophene derivatives **13b**, **14b**, and **14c**.

1-Thiobenzoylazulene (1a).[3] The general procedure was followed by using 1-benzoylazulene (**5a**) (2.37 g, 10.2 mmol), P_2S_5 (6.10 g, 27.4 mmol), and triethylamine (2.5 mL) in $CHCl_3$ (100 mL) at 0 °C for 3 h. Chromatographic purification on silica gel with CH_2Cl_2 afforded **1a**[3] (1.99 g, 79%). The reaction of **5a** (152 mg, 0.654 mmol) with Lawesson's reagent (226 mg, 0.658 mmol)

(27) (a) Bernal, I.; Rieger, P. H.; Frankel, G. K. *J. Chem. Phys.* **1962**, *37*, 1489−1495. (b) Bachmann, R.; Burda, C.; Gerson, F.; Scholz, M.; Hansen, H.-J. *Helv. Chim. Acta* **1994**, *77*, 1458−1465.

in toluene (10 mL) and benzene (5 mL) at room temperature for 20 h and chromatographic purification on silica gel with CH_2Cl_2 also afforded **1a**[3] (121 mg, 74%). Green crystals; mp 73.8−75.0 °C [lit.[3] mp 68 °C]; MS (70 eV) *m*/*z* 248 (M^+, 56%), 247 ($M^+ - H$, 100); IR (KBr disk) ν_{max} 1452, 1388, 1276, 1214, 1060, 786, 746, 690 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (nm) (log ϵ) 230 (4.50), 290 (4.41), 328 (4.17), 355 sh (4.03), 457 (4.26), 543 sh (3.16), 595 sh (3.03); ^1H NMR (500 MHz, $CDCl_3$) δ 9.61 (d, 1H, J = 9.8 Hz, H_8), 8.46 (d, 1H, J = 9.5 Hz, H_4), 8.03 (d, 1H, J = 4.3 Hz, H_2), 7.81 (dd, 1H, J = 9.8, 9.8 Hz, H_6), 7.63 (dd, 2H, J = 8.2, 1.2 Hz, $H_{2',6'}$), 7.60 (dd, 1H, J = 9.8, 9.8 Hz, H_7), 7.55 (dd, 1H, J = 9.8, 9.5 Hz, H_5), 7.49 (tt, 1H, J = 7.4, 1.2 Hz, $H_{4'}$), 7.38 (t, 2H, J = 8.2 Hz, $H_{3',5'}$), 7.23 (d, 1H, J = 4.3 Hz, H_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 225.6 (C═S), 150.9 ($C_{1'}$), 148.1 (C_{3a}), 142.1 (C_2), 141.5 (C_{8a}), 140.4 (C_6), 139.9 (C_8), 138.9 (C_4), 138.0 (C_1), 130.8 (C_7), 130.3 ($C_{4'}$), 129.3 ($C_{2',6'}$), 128.5 (C_5), 127.7 ($C_{3',5'}$), 118.6 (C_3). HRMS calcd for $C_{17}H_{12}S$ 248.0660, found 248.0665. Anal. Calcd for $C_{17}H_{12}S$: C, 82.22; H, 4.87; S, 12.91. Found: C, 82.52; H, 5.01; S, 12.59.

Typical Example for the Acid-Catalyzed Isomerization into Thiophene Derivatives. To a solution of **2b** (93 mg, 0.18 mmol) in $CHCl_3$ (20 mL) was added hydrochloric acid (0.3 mL) at room temperature. After the resulting mixture was stirred at the same temperature for 20 min, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on Al_2O_3 with 40% CH_2Cl_2/hexane to afford **14b** (93 mg, 100%). The deep blue solution obtained by the addition of hydrochloric acid to a solution of **2b** in $CDCl_3$ afforded the following NMR signals assigned to $\mathbf{17}^+$. ^1H NMR (600 MHz, $CDCl_3$) δ 9.58 (s, 1H, H_8), 9.10 (d, 1H, J = 10.5 Hz, $H_{8'}$), 8.81 (d, 1H, J = 10.8 Hz, $H_{4'}$), 8.37 (d, 1H, J = 10.2 Hz, H_6), 8.22 (d, 1H, J = 10.2 Hz, H_5), 8.07 (s, 1H, $H_{2'}$), 7.94 (dd, 1H, J = 10.5, 1.3 Hz, $H_{7'}$), 7.74 (dd, 1H, J = 10.8, 1.3 Hz, $H_{5'}$), 4.21 (dd, 1H, J = 7.8, 1.9 Hz, H_4), 3.69 (dd, 1H, J = 16.9, 7.8 Hz, H_3), 3.37 (dd, 1H, J = 16.9, 1.9 Hz, H_3), 1.64 (s, 9H, 3′-*t*-Bu), 1.60 (s, 9H, 7-*t*-Bu), 1.52 (s, 9H, 6′-*t*-Bu), 1.09 (s, 9H, 4-*t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8 ($C_{6'}$), 163.8 (C_{8b}), 162.2 (C_{4a}), 160.2 (C_7), 151.5 (C_{8a}), 150.9 (C_2), 143.2 (C_{2b}), 142.4 ($C_{3'}$), 142.1 (C_8), 141.2 (C_6 and $C_{3'a}$), 139.8 ($C_{8'a}$), 137.1 ($C_{4'}$), 136.6 (C_5), 135.7 ($C_{8'}$), 135.0 ($C_{2'}$), 127.8 ($C_{7'}$), 126.0 ($C_{5'}$), 119.2 ($C_{1'}$), 63.0 (C_4), 40.0 (s, 7-*t*-Bu), 39.0 (s, 6′-*t*-Bu), 36.8 (s, 4-*t*-Bu), 33.1 (s, 3′-*t*-Bu), 32.2 (C_3), 31.6 (q, 7-*t*-Bu and 6′-*t*-Bu), 31.4 (q, 3′-*t*-Bu), 27.4 (q, 4-*t*-Bu).

Typical Example for the Thermal Isomerization into the Thiophene Derivatives. A solution of **2b** (90 mg, 0.17 mmol) in toluene (60 mL) was refluxed for 24 h. After removing the solvent, the residue was purified by column chromatography on Al_2O_3 with 40% CH_2Cl_2/hexane to afford **14b** (68 mg, 76%).

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Supporting Information Available: General and experimental details, cyclic voltammograms of $\mathbf{18}^+\cdot PF_6^-$ and $\mathbf{19}^+\cdot PF_6^-$, spectroelectrograms of $\mathbf{19}^+\cdot PF_6^-$, ESR measurements of $\mathbf{19}^+\cdot PF_6^-$, B3LYP/6-31G** density functional calculation of 1-azulenecarbothialdehyde, relative stability of azuleno[8,1-*b*,*c*]thiophene derivatives, and copies of ^1H and ^{13}C NMR spectra of the reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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