# [6+4] Cycloaddition reactions of acceptor thiophene dioxides: the synthesis of substituted azulenes

*A. M. Moiseev, E. S. Balenkova, and V. G. Nenajdenko**

*Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (495) 932 8846. E-mail: nen@acylium.chem.msu.ru*

[6+4] Cycloaddition reactions of functionalized thiophene dioxides with various fulvenes provided the corresponding azulenes. The observed regiochemistry was explained in terms of the HOMO—LUMO orbital coefficients.

**Key words:** [6+4] cycloaddition reactions, azulenes, regioselectivity, acceptor thiophene 1,1-dioxides, fulvenes.

Azulene is an aromatic hydrocarbon consisting of fused seven-membered and five-membered rings.[1] In contrast to structurally isomeric nonpolar naphthalene, the azulene molecule is polar with a dipole moment of 0.796 D (see Ref. 1) and absorbs light in the visible range, which gives rise to a remarkable light blue color of azulene solutions.

In recent years, azulene and its derivatives have received more and more attention as substances with unique properties. Having unusual electronic and optical characteristics, these compounds are used as components for creation of novel materials: chromophores,[2] stable carbocations,[3] and building blocks in supramolecular chemistry.[4] In addition, azulene and its derivatives find applications in medicine and the production of various cosmetics because of their antiinflammatory and antimicrobial properties.[5]

Nevertheless, the synthesis of azulene derivatives still remains of topical interest.[6] The most familiar methods for creation of the aromatic azulene structure involve pyridine and cyclopentadiene derivatives (Ziegler—Hafner synthesis[6a]). The latest achievements in the synthesis of azulene hydrocarbons allowed cinnamic acids,[6b] tropolone,[6c] and cycloheptatriene[6d] to be employed as the starting reagents. However, all these methods are limited since the starting reagents are not easily accessible and a large number of steps are required, which inevitably decreases the overall yields of the target products.

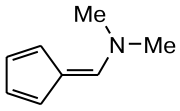
One of the most attractive routes to substituted azulenes involves [6+4] cycloaddition reactions. As a rule, 6-dimethylaminofulvene is used as the six-electron component, while substituted pyrones or thiophene 1,1-dioxides capable of extruding gases ($CO_2$ or $SO_2$) from intermediate bridged adducts[1] serve as four-electron components. A variation of substituents in pyrone or thiophene dioxide affords azulene derivatives substituted in the seven-membered ring, which are inaccessible through other methods. Such reactions have not received wide application since, on the one hand, substituted pyrones and thiophene dioxides are not easily accessible and, on the other hand, they provide low yields.

It should be noted that reactions of thiophene dioxides with fulvenes remain poorly studied so far; functionalized thiophene dioxides have not been involved in this reaction at all. The use of the latter opens up a direct route to azulenes containing substituents in the seven-membered ring, whose synthesis is a challenge.

## Results and Discussion

Earlier,[7] we have developed methods for the synthesis of thiophene 1,1-dioxides **1** with a broad range of substituents, including those containing electron-withdrawing functional groups. We have also demonstrated that such compounds can react with 1,3-dienes, acting as both dienophiles[8a,b] and dienes.[8c] All these transformations leading to complex carbo- and heterocycles make thiophene dioxides useful tools in organic synthesis. Because the starting thiophenes are accessible and can be easily modified in order to prepare various substituted thiophene dioxides, we proposed them for the synthesis of previously inaccessible functionalized azulenes.


**1**




**2a**

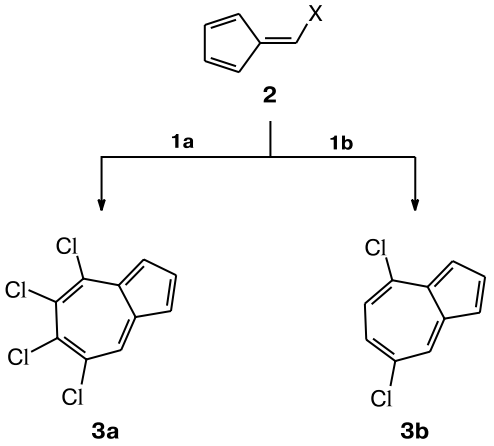
$R^1 = R^2 = R^3 = R^4 = Cl$ (**1a**); $R^1 = R^4 = Cl$, $R^2 = R^3 = H$ (**1b**)

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 137—142, January, 2006.

1066-5285/06/5501-0141 

According to the literature data, 6-substituted fulvenes are the most suitable six-electron components for this reaction. It is worth noting that earlier,[1,9] only 6-dimethylaminofulvene **2a** has been used as the "fulvene" component in the majority of studies. Preliminary experiments with a number of substituted thiophene dioxides **1** revealed that their reactions with compound **2a** mostly yield the target azulenes in trace amounts. Only for halogen-containing thiophene 1,1-dioxides **1a,b** were target products **3a** and **3b** isolated in 10 and 8% yields, respectively (Scheme 1). Apparently, the major side reaction in this way is addition of the liberated dimethylamine to the starting thiophene dioxide and, consequently, the formation of an inert compound. In addition, the reaction mixture underwent considerable resinification even at 0 °C.

**Scheme 1**

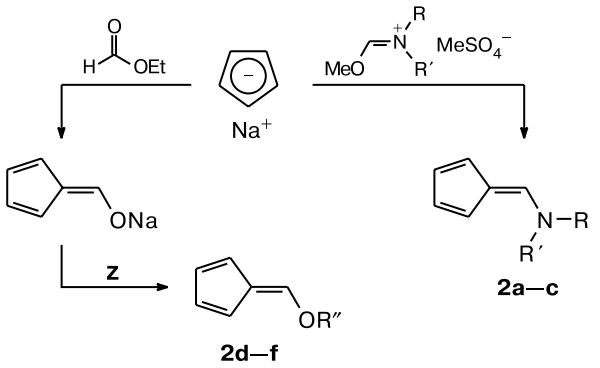



We assumed that the better results can be obtained with 6-substituted fulvene containing a less nucleophilic leaving group than the dimethylamino one. To do this, we synthesized a number of fulvenes **2b—f** (Scheme 2). Fulvenes **2d—f** have been employed earlier[10] in [4+2] cycloaddition reactions.

All the fulvenes obtained contain substituents with different electronic properties and sizes. In the compounds synthesized by us, the nucleophilic properties of the leaving group are decreased by either the steric or electronic factors compared to the previously used 6-dimethylaminofulvene **2a**.

Preliminary experiments were carried out with tetrachloro- (**1a**) and 2,5-dichlorothiophene 1,1-dioxides (**1b**) as model compounds (Table 1). The reactions with 6-substituted fulvenes **2a—f** were carried out in THF while varying the temperature from 0 to 66 °C (boiling point of the solvent). Thus, we found the reaction conditions under which products were detected in all the cases but fulvene **2b**. We were the first to vary the fulvene component and obtain data on the reactivities of various 6-substituted fulvenes. For instance, it was found that this reaction is not unique to fulvene **2a** as the 6-electron component. The yields of the target azulenes from fulvenes **2c** and **2e** were 11—19%; this is a satisfactory result since the yields of the target azulenes in most published studies[1,9] have rarely exceeded 16%.

**Scheme 2**




| **2** | R | R′ | Yield (%) | Reagent **Z** | **2** | R″ | Yield (%) |
|---|---|---|---|---|---|---|---|
| **a** | Me | Me | 77 | $Ac_2O$ | **d** | Ac | 56 |
| **b** | $Pr^i$ | $Pr^i$ | 41 | $Me_2SO_4$ | **e** | Me | 33 |
| **c** | Me | Ph | 54 | $Me_3SiCl$ | **f** | $SiMe_3$ | 95 |

Earlier,[8c] we have discovered that reactions of various thiophene dioxides with cyclopentadiene are regioselective. To explain the observed regioselectivity, we calculated the LUMO orbital coefficients for a number of thiophene dioxides by the *ab initio* riMP2(full) method with the B11 basis set (see Ref. 8c). The orbital coefficients for fulvenes have been earlier[11] calculated by the

**Table 1.** Variation of the fulvene component **2a—f** in reactions with the model thiophene 1,1-dioxides **1a** and **1b**

| Fulvene **2** | Yield of product **3** (%) | |
|---|---|---|
| | **3a** | **3b** |
| **a** | 10 | 8 |
| **b** | — | — |
| **c** | 9 | 14 |
| **d** | Traces | Traces |
| **e** | 11 | 19 |
| **f** | Traces | 1 |

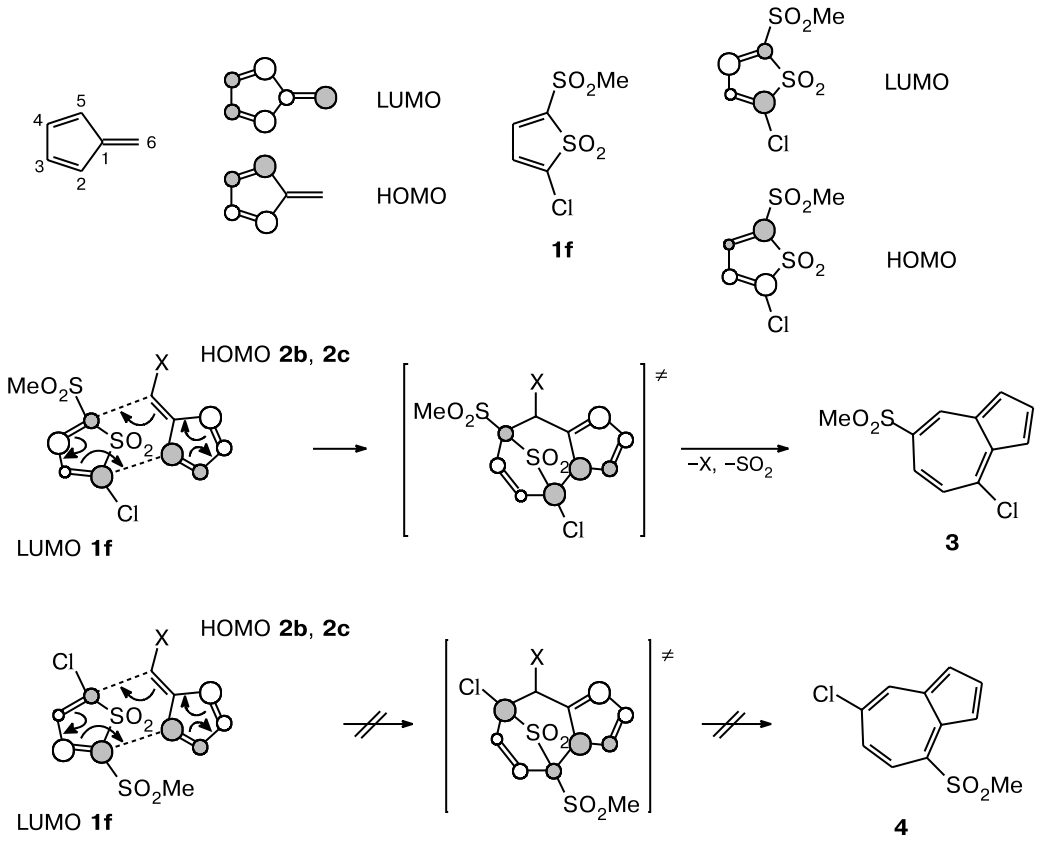



**Fig. 1.** Orbital couplings in the reaction of fulvene with thiophene dioxide **1f**.

semiempirical CNDO/2 method (complete neglect of differential overlap). It was shown that [6+4] cycloaddition reactions are controlled by the HOMO of fulvene and the LUMO of thiophene dioxide (Fig. 1). In addition, the absolute values of the LUMO coefficients at the atoms 2 and 3 in 6-substituted fulvenes are virtually equal (for dimethylfulvene, 0.35 and 0.33, respectively), which can give rise to both regioisomeric [6+4] and [4+2] cycloadducts.[11b]

Since some of the thiophene dioxides studied contain several different substituents, their [6+4] cycloaddition reactions can yield two regioisomeric products: azulenes **3** and **4**. A task of this work was to investigate the effects of the electronic and steric factors on the regioselectivity of azulene formation. For instance, reaction products from compounds **1f** and **2b** contained two regioisomers, which is associated with the presence of two different groups in the starting thiophene dioxide **1f**.

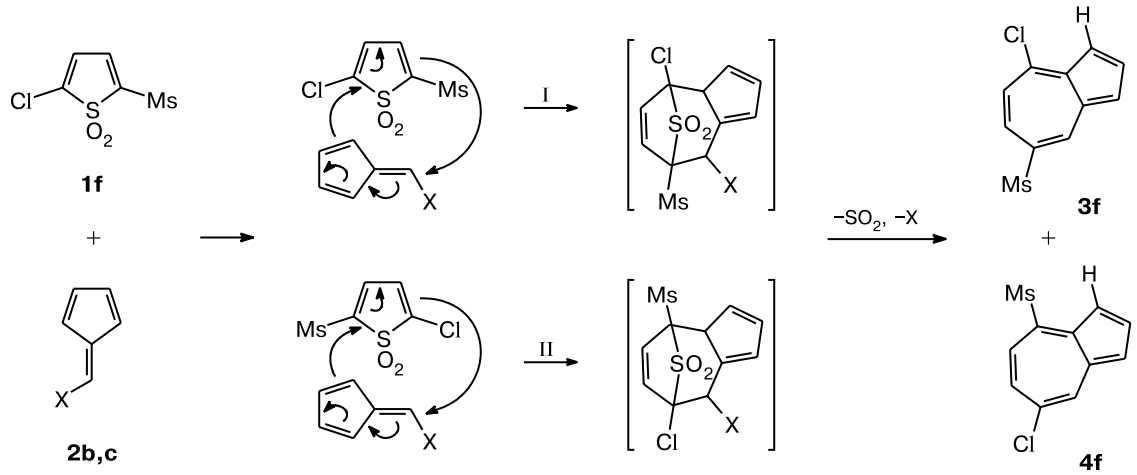
The higher LUMO orbital coefficient on the chlorine-bearing C atom of thiophene dioxide **1f** (see Fig. 1) causes its attack on the fulvene atom with the higher HOMO orbital coefficient. This gives rise to a transition state with a particular orientation and finally (and predominantly) to isomer **3** with the corresponding arrangement of the substituents.

The same mechanism is true for other unsymmetrical thiophene dioxides. This suggests that the regioselectivity of this reaction is controlled by orbital interactions.

The low reactivity of compound **2b** in the reactions with thiophene dioxides can be explained by steric inaccessibility of a reactive site of this fulvene. It is known that [6+4] cycloaddition reactions are very sensitive to steric factors;[1,11] this is illustrated with the reaction of fulvene **2b** with 2-chloro-5-methylsulfonylthiophene 1,1-dioxide **1f** (Scheme 3).

Pathway I is preferred from the viewpoint of electronic factors, while pathway II involves less steric hindrances: in this case, the diisopropyl group is oriented toward the less bulky Cl atom. As the result, the reaction between compounds **1f** and **2b** gave a 1 : 5 mixture of regioisomeric azulenes **3f** and **4f**, the major product being "sterically preferred" regioisomer **4f**. The regioisomeric ratio **3f**/**4f** was determined from the integral intensity ratio of signals for the protons of the five-membered ring (see Scheme 3) at δ 8.44 (for product **3f** with the neighboring Cl atom) and 9.35 (for product **4f** with the neighboring $MeSO_2$ group) in the $^1H$ NMR spectrum. Thus, the reaction with fulvene **2b** containing the bulky $N(Pr^i)_2$ group is controlled by steric factors.

**Scheme 3**




Ms = $MeSO_2$;
X = $NPr^i_2$ (**2b**), NMePh (**2c**)

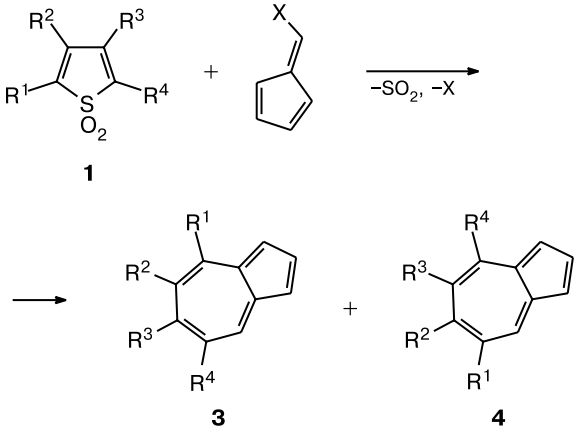
| X | **3f** : **4f** | | δ |
|---|---|---|---|
| $NPr^i_2$ | 1 : 5 | **3f** | 8.44 |
| NMePh | 20 : 1 | **4f** | 9.35 |

An investigation of mixtures obtained in the reactions with fulvenes **2c**—**f** sterically unhindered in position 6 revealed the dominant formation of isomer **3**. For instance, the reaction of compound **1f** with fulvene **2c** gave two regioisomers **3f** and **4f** in the ratio 20 : 1 (see Scheme 3). Obviously, the electronic factors are decisive when fulvene presents no steric hindrances, while the steric factors hinder the formation of a [6+4] cycloadduct.[11b]

By varying the fulvene component **2a**—**f**, we found that fulvenes **2c** and **2e** are the best 6-electron components for this reaction. Starting from these compounds, we obtained in THF and dichloromethane a number of substituted azulenes in moderate yields (Table 2).

All the substituted azulenes **3b**—**g** and **4e**—**g** were obtained for the first time. These functionalized and halogenated azulenes are of both theoretical and application interest, in particular, as precursors in the synthesis of other substituted azulenes.

**Scheme 4**




Thus, we carried out [6+4] cycloaddition reactions with various thiophene dioxides functionalized by elec-

**Table 2.** Azulenes obtained by the reactions of thiophene dioxides **1a**—**g** with fulvenes **2c** and **2e**

| **1** | $R^1$ | $R^2$ | $R^3$ | $R^4$ | X | Solvent | *T*/°C | Yield* (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | **3** | **4** |
| **a** | Cl | Cl | Cl | Cl | MeO | THF | 25 | 11 | — |
| **b** | Cl | H | H | Cl | MeO | $CH_2Cl_2$ | 25 | 19 | — |
| **c** | Br | H | Br | H | N(Me)Ph | $CH_2Cl_2$ | 0—25 | 32 | — |
| **d** | Br | H | H | Br | N(Me)Ph | $CH_2Cl_2$ | 25 | 9 | — |
| **e** | Me | H | H | $CO_2Et$ | N(Me)Ph | THF | −5—0 | 35 | 5 |
| **f** | Cl | H | H | $SO_2Me$ | N(Me)Ph | THF | −5—0 | 40 | 2 |
| **g** | Br | H | H | $SO_2Me$ | N(Me)Ph | THF | −5—0 | 15 | 3 |

* The ratios of products **3** and **4** were determined from the integral intensities of signals in the $^1H$ NMR spectra.

tron-withdrawing groups. We studied for the first time the effect of the fulvene component and chose the optimum conditions for the synthesis of functionalized azulenes. It was demonstrated that the reaction pathway depends on the structures of the starting reagents and can be controlled by both orbital and steric factors.

## Experimental

$^1$H and $^{13}$C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ with $Me_4Si$ as the internal standard. Column chromatography was carried out on silica gel (63—200 mesh, Merck). TLC analysis was carried out on Merck 60 $F_{254}$ plates with hexane—ethyl acetate (3 : 1) as the eluent.

6-Substituted fulvenes **2a**,[10a] **2c**,[10b] **2d**,[10c] **2e**,[10d] and **2f** (see Ref. 10e) were prepared according to known procedures.

**6-Diisopropylaminofulvene (2b).** A mixture of diisopropylformamide (12.9 g, 0.1 mol) and dimethyl sulfate (12.6 g, 0.1 mol) was stirred under argon at 60 °C for 6 h. The resulting viscous mass was added dropwise under argon at 20 °C to stirred cyclopentadienylsodium[10a] (8.8 g, 0.1 mol) in THF (45 mL). Stirring was continued at room temperature for an additional 1 h and poured into ice water (200 mL). The product was extracted with ether (3×50 mL). The combined extracts were dried over $Na_2SO_4$ and concentrated *in vacuo*. The residue was recrystallized from hexane to give compound **2b** (7.2 g, 41%) as dark yellow crystals, m.p. 63—64 °C. $^1$H NMR, δ: 1.33, 1.35 (both s, 6 H each, MeCHMe); 3.77, 4.83 (both br.s, 1 H each, MeCHMe); 6.32, 6.43 (both m, 1 H each, H(2), H(5)); 6.56 (m, 2 H, C(3), C(4)); 7.25 (s, 1 H, H(1)). $^{13}$C NMR, δ: 19.9, 24.0, 46.8, 51.1, 113.4, 115.3, 118.7, 125.3, 125.6, 144.5. Found (%): C, 81.24; H, 10.55. $C_{12}H_{19}N$. Calculated (%): C, 81.30; H, 10.80.

**Synthesis of azulenes 3a—g and 4e—g (general procedure).** A solution of fulvene **2c** or **2e** (0.01 mol; see Table 2) in dichloromethane or THF (2 mL) was added to a solution or suspension of thiophene dioxide **1** (0.01 mol) in the same solvent (5 mL). The reactions with the most reactive thiophene dioxides **1e—f** were carried out at an ice-bath temperature, gradually raising the temperature to ambient for completion of the reaction. The rest of the reactions were carried out at 25 °C. The completion of the reaction was determined by TLC. The reaction duration was 15—20 h for halothiophene dioxides **1a—d** and 2—3 h for thiophene dioxides **1e—g** containing electron-withdrawing substituents. The solvent was removed *in vacuo* and the target azulenes were isolated by chromatography with hexane as the eluent.

**4,5,6,7-Tetrachloroazulene (3a).** The yield was 11%, m.p. 133—134 °C (*cf.* Ref. 9c: m.p. 137—139 °C). $^1$H NMR, δ: 7.34 (dd, 1 H, $J$ = 5.9 Hz, $J$ = 1.2 Hz); 7.70 (m, 1 H); 7.90 (t, 1 H, $J$ = 7.8 Hz, $J$ = 5.9 Hz, $J$ = 3.9 Hz); 8.49 (s, 1 H).

**4,7-Dichloroazulene (3b).** The yield was 19%, m.p. 55—57 °C. $^1$H NMR, δ: 7.27 (d, 1 H, H(5), $J$ = 12.0 Hz); 7.41 (dd, 1 H, H(1), $J$ = 2.6 Hz, $J$ = 1.2 Hz); 7.63, 7.66 (both d, 1 H each, H(6), H(8), $J$ = 12.0 Hz, $J$ = 1.2 Hz); 7.96 (m, 1 H, H(2)); 8.44 (d, 1 H, H(3), $J$ = 2.6 Hz). $^{13}$C NMR, δ: 119.6; 120.9; 122.9; 128.3; 134.0; 135.1; 136.6; 137.5; 139.4; 141.6; Found (%): C, 60.50; H, 2.82. $C_{10}H_6Cl_2$. Calculated (%): C, 60.95; H, 3.07.

**4,6-Dibromoazulene (3c).** The yield was 32%, m.p. 64—65 °C. $^1$H NMR, δ: 7.46, 7.50 (both dd, 1 H each, H(5), H(7), $J$ = 2.8 Hz, $J$ = 1.2 Hz, $J$ = 12.0 Hz, $J$ = 1.2 Hz); 7.62 (d, 1 H, H(1), $J$ = 1.2 Hz); 7.91 (m, 1 H, H(2)); 7.98 (d, 1 H, H(8), $J$ = 12.0 Hz); 8.01 (s, 1 H, H(3)). $^{13}$C NMR, δ: 122.7, 123.9, 125.8, 130.8, 131.8, 132.9, 134.6, 136.0, 137.6, 138.3. Found (%): C, 41.71; H, 1.83. $C_{10}H_6Br_2$. Calculated (%): C, 42.00; H, 2.11.

**4,7-Dibromoazulene (3d).** The yield was 9%, m.p. 89 °C. $^1$H NMR, δ: 7.27 (d, 1 H, H(5), $J$ = 12.0 Hz); 7.41 (dd, 1 H, H(1), $J$ = 2.6 Hz, $J$ = 1.2 Hz); 7.63, 7.66 (both d, 1 H each, H(6), H(8), $J$ = 12.0 Hz, $J$ = 1.2 Hz); 7.96 (m, 1 H, H(2)); 8.44 (d, 1 H, H(3), $J$ = 2.6 Hz). $^{13}$C NMR, δ: 118.3, 119.9, 121.1, 125.4, 130.0, 137.3, 137.9, 138.9, 140.1, 142.7. Found (%): C, 41.91. H, 1.99. $C_{10}H_6Br_2$. Calculated (%): C, 42.00. H, 2.11.

**7-Ethoxycarbonyl-4-methylazulene (3e) and 4-ethoxycarbonyl-7-methylazulene (4e).** Azulene **3e**. The yield was 35%. $^1$H NMR, δ: 1.12—1.20 (m, 3 H, $MeCH_2$); 1.40 (s, 3 H, Me); 4.20—4.35 (m, 1 H, $CH_2O$); 7.51, 7.68 (both dd, 1 H each, $J_1$ = 7.2 Hz, $J_2$ = 7.0 Hz); 7.57, 7.59 (both d, 1 H each, $J$ = 4.0 Hz, $J$ = 4.0 Hz); 7.84 (m, 1 H); 8.40 (m, 1 H). Azulene **4e**. $^1$H NMR, δ: 1.12—1.20 (m, 3 H, $MeCH_2$); 1.44 (s, 3 H, Me); 4.20—4.35 (m, 1 H, $CH_2O$); 7.55, 7.71 (both dd, 1 H each, $J_1$ = 7.2 Hz, $J_2$ = 7.0 Hz); 7.65, 7.69 (both d, 1 H each, $J$ = 4.0 Hz); 7.84 (m, 1 H); 8.40 (m, 1 H). Found (%): C, 78.21. H, 6.89. $C_{14}H_{14}O_2$. Calculated (%): C, 78.48. H, 6.59.

**4-Chloro-7-methylsulfonylazulene (3f) and 7-chloro-4-methylsulfonylazulene (4f).** Azulene **3f**. The yield was 40%. $^1$H NMR, δ: 3.33 (s, 3 H, $MeSO_2$); 4.95 (dd, 1 H, H(5), $J_1$ = 5.5 Hz, $J_2$ = 1.3 Hz); 6.39, 6.58 (both m, 1 H each); 6.71 (dd, 1 H, H(6), $J_1$ = 5.5 Hz, $J_2$ =1.3 Hz); 6.98 (d, 1 H, H(2), $J$ = 4.5 Hz); 8.44 (s, 1 H). Azulene **4f**. $^1$H NMR, δ: 3.29 (s, 3 H, $MeSO_2$); 4.87 (dd, 1 H, H(5), $J_1$ = 5.7 Hz, $J_2$ = 1.0 Hz); 6.19, 6.47 (both m, 1 H each); 6.68 (dd, 1 H, H(6), $J_1$ = 5.7 Hz, $J_2$ = 1.0 Hz); 6.81 (d, 1 H, H(2), $J$ = 4.2 Hz); 9.35 (s, 1 H). Found (%): C, 54.71; H, 3.67. $C_{11}H_9ClO_2S$. Calculated (%): C, 54.89; H, 3.77.

**4-Bromo-7-methylsulfonylazulene (3f) and 7-bromo-4-methylsulfonylazulene (4g).** Azulene **3g**. The yield was 15%. $^1$H NMR, δ: 3.30 (s, 3 H, $MeSO_2$); 4.71 (dd, 1 H, H(5), $J_1$ = 5.5 Hz, $J_2$ = 1.2 Hz); 6.25, 6.38 (both m, 1 H each); 6.55 (dd, 1 H, H(6), $J_1$ = 5.9 Hz, $J_2$ = 1.0 Hz); 6.94 (d, 1 H, H(2), $J$ = 4.2 Hz); 7.71 (s, 1 H). Azulene **4g**. $^1$H NMR, δ: 3.29 (s, 3 H, $MeSO_2$); 4.89 (dd, 1 H, H(5), $J_1$ = 5.5 Hz, $J_2$ = 1.3 Hz); 6.20, 6.41 (both m, 1 H each); 6.63 (dd, 1 H, H(6), $J_1$ = 5.9 Hz, $J_2$ = 1.0 Hz); 6.90 (d, 1 H, H(2), $J$ = 4.2 Hz); 9.66 (s, 1 H). Found (%): C, 46.11; H, 3.22. $C_{11}H_9BrO_2S$. Calculated (%): C, 46.33; H, 3.18.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32024-a) and the Foundation for Assistance to Russian Science.

## References

1. K.-P, Zeller, in *Houben-Weyl; Methoden der organischen Chemie*, Georg Thieme, Stuttgart, 1985; Vol. **V/2c**, 127 pp.
2. (a) T. Zieliński, M. Kedziorek, and J. Jurczak, *Tetrahedron Lett.*, 2005, **46**, 6231; (b) M. Lamberto, C. Pagba, P. Piotrowiak, and E. Galoppini, *Tetrahedron Lett.*, 2005, **46**, 4895.

3. S. Ito, S. Kikuchi, N. Morita, and T. Asao, *J. Org. Chem.*, 1999, **64**, 5815.
4. (a) T. Asao, S. Ito, and N. Morita, *Tetrahedron Lett.*, 1988, **29**, 2839; (b) D. A. Colby and T. D. Lash, *J. Org. Chem.*, 2002, **67**, 1031; (c) O. K. Abou-Zied, *Spectrochim. Acta, Part A*, 2005, **62**, 245.
5. (a) F. A. Andersen and D. R. Teufel, *Int. J. Toxicol.*, 1999, **18**, 27; (b) M. Guarrera, L. Turbino, and A. Rebora, *J. Eur. Acad. Dermatol. Venerol.*, 2001, **15**, 486.
6. (a) K. Ziegler and K. Hafner, *Angew. Chem.*, 1955, **67**, 301; (b) L. T. Scott, M. A. Minton, and M. A. Kirms, *J. Am. Chem. Soc.*, 1980, **102**, 6311; (c) M. Yasunami, S. Miyoshi, N. Kanegae, and K. Takase, *Bull. Chem. Soc. Jpn*, 1993, **66**, 892; (d) S. Carret, A. Blanc, Y. Coquerel, M. Berthod, A. E. Greene, and J.-P. Deprés, *Angew. Chem., Int. Ed. (Engl.)*, 2005, **44**, 5130.
7. (a) V. G. Nenajdenko, A. E. Gavryushin, and E. S. Balenkova, *Tetrahedron Lett.*, 2001, **42**, 4397; (b) V. G. Nenajdenko, A. M. Moiseev, and E. S. Balenkova, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2144 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2241].
8. (a) V. G. Nenajdenko, A. M. Moiseev, and E. S. Balenkova, *Tetrahedron,* 2005, **61**, 10880; (b) V. G. Nenajdenko, A. M. Moiseev, and E. S. Balenkova, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 2117 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2182]; (c) A. M. Moiseev, V. G. Nenajdenko, and E. S. Balenkova, *Tetrahedron*, 2006, **61**, 4139.
9. (a) S. E. Reiter, L. C. Dunn, and K. N. Houk, *J. Am. Chem. Soc.*, 1977, **99**, 4199; (b) D. Mukherjee, L. C. Dunn, and K. N. Houk, *J. Am. Chem. Soc.*, 1979, **101**, 251; (c) K. Kanematsu, H. Kazunobu, and D. Hirokazu, *Heterocycles*, 1981, **16**, 1145; (d) Y. Lu, D. M. Lemal, and J. P. Jasinski, *J. Am. Chem. Soc.*, 2000, **122**, 2440; (e) J. Nakayama, *Bull. Soc. Chem. Jpn,* 2000, **73**, 1; (f) Y. Lou, J. Chang, J. Jorgensen, and D. M. Lemal, *J. Am. Chem. Soc.*, 2002, **124**, 15302.
10. (a) K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *Organic Syntheses*, John Wiley & Sons, New York, 1973, Coll. Vol. **5**, p. 431; (b) P. Rademacher, R. Stolevik, and W. Lüttke, *Angew. Chem., Int. Ed. (Engl.)*, 1968, **10**, 806; (c) N. F. Bondar´, E. V. Koroleva, T. N. Omel´chenko, and A. A. Akhrem, *Zh. Org. Khim.*, 1981, **17**, 2333 [*J. Org. Chem. USSR*, 1981, **17**, 2084]; (d) I. Gupta and P. Yates, *Synth. Commun.*, 1982, **13**, 1007; (e) G. Nzabamwita, B. Kolani, and B. Jousseaume, *Tetrahedron Lett.*, 1989, **30**, 2207.
11. (a) K. N. Houk, J. K. George, and R. E. Duke, *Tetrahedron*, 1974, **30**, 523; (b) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, 1973, **95**, 7301.

*Received November 18, 2005;*
*in revised form January 17, 2006*