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SYNTHESIS OF METHYLTHIO-SUBSTITUTED HETEROCYCLES USING THE COMPLEX OF TRIFLUOROMETHANESULFONIC ANHYDRIDE WITH DIMETHYL SULFIDE

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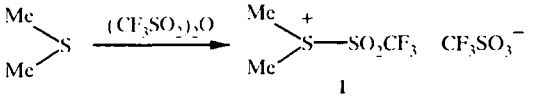
A new method was developed for the electrophilic introduction of methylthio group into a series of aromatic heterocyclic compounds through the hetaryl(dimethyl)sulfonium salts formed in the course of the reaction of the respective heterocycles with the complex of dimethyl sulfide and trifluoromethanesulfonic anhydride. By demethylation with triethylamine it was possible to obtain the methylthio-substituted heterocycles.

Keywords: hetaryl(dimethyl)sulfonium salts, sulfur ylides, methylsulfanyl-substituted hetarenes, trifluoromethylsulfonylsulfonium, electrophilic aromatic substitution.

Since the first report on the production of trifluoromethanesulfonic acid an enormous number of publications have been devoted to the theoretical aspects and synthetic applications of the activation of various organic substrates using trifluoromethanesulfonic anhydride. The unique electronic and nucleophilic characteristics of the triflate group have been studied in detail, are widely known, and determine the extremely wide application of the group in synthetic organic chemistry (e.g., see the review [1]). However, the oxidizing properties of trifluoromethanesulfonic anhydride have been investigated insufficiently. Papers on its use as an oxidizing agent were published comparatively recently [2, 3]. We showed [4] that the oxidation of dimethyl sulfide with trifluoromethanesulfonic anhydride gave a new electrophilic reagent in the form of trifluoromethanesulfonylsulfonium salt (**1**):



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The complex **1** contains two electrophilic sulfur atoms (sulfonium and sulfonate) but reacts with nucleophiles exclusively at the sulfonium center. The reaction of the salt **1** with primary and secondary alcohols gives the corresponding carbonyl compounds, while hydrolysis with aqueous solution of sodium acetate leads to the formation of sulfoxides [4]. We supposed that the reagent could also be used for the production of hetaryl(dimethyl)sulfonium salts from the corresponding heterocycles. Known methods for the production of compounds of this type are based either on the oxidative activation of dimethyl sulfide [5] or on the electrophilic activation of dimethyl sulfoxide [6, 7]. The simplest method for the synthesis of such sulfonium salts through the

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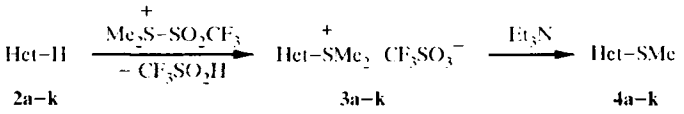
alkylation of aryl alkyl sulfides cannot be considered to be universal since the production of the latter presents a separate synthetic problem [8]. The synthesis of hetaryl(dimethyl)sulfonium salts, based on the oxidative activation of dimethyl sulfide by chlorine or bromine, does not have preparative significance on account of the side oxidation, chlorination, or bromination of the substrate and reaction products [5]. The more universal path to the synthesis of arylsulfonium salts by the reaction of dimethyl sulfoxide with aromatic compounds in the presence of protic acids (HCl, HBr, $HClO_4$) or Lewis acids ($AlBr_3$, $AlCl_3$) makes it possible to bring active aromatic substrates (anisole, azulene) [6, 7] and also thiophene and 2-methylthiophene [9] into the reaction. However, the presence of strong acids in the reaction mixture does not make it possible to conduct the reaction with compounds unstable under acidic conditions. Thus, in spite of the large number of reagents and methods for the production of aryldialkylsulfonium salts the development of "mild" reagents that make it possible to conduct the reaction with labile substrates remains urgent.

While continuing the investigations on the reactivity of the complex **1** we studied its reaction with a series of heteroaromatic compounds. The reaction takes place under mild conditions in methylene chloride at cooling and leads to the corresponding aryl(dimethyl)sulfonium salts **3a-k**. In most cases one regioisomer, i.e., the product from electrophilic substitution at the most nucleophilic carbon atom of the heterocycle, is formed. Only in the reactions with benzothiophene (**2e**) and N-methylpyrrole (**2g**), in which positions 2 and 3 of the heterocyclic ring are sterically accessible and comparable in activity, the isomeric sulfonium salts are detected spectrally as impurities.

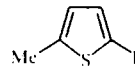
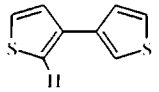
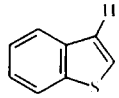
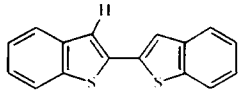
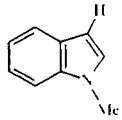
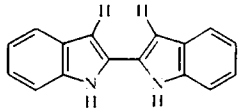
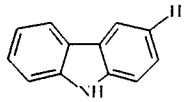
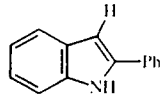
In order to obtain hetaryl methyl sulfides we investigated the possibility of demethylating the salts. Earlier [10] dimethyl sulfide was used for the mild demethylation of dimethylvinylsulfonium salts, but in this case the reaction took place slowly at room temperature. It was therefore more expedient to use the stronger nucleophile – triethylamine, the reaction with which takes place at an acceptable rate under mild conditions. The excess of triethylamine can be easily removed from the reaction mixture. The methylthio group can be introduced into the heterocyclic compound in a single stage without the previous isolation of the sulfonium salts.



With the proposed reagent it is possible to conduct the reaction under significantly more acidic conditions than previously described. Thus, in contrast to the structurally similar complex of dimethyl sulfoxide with trifluoromethanesulfonic anhydride widely used for introduction of dimethylsulfonium group into aromatic substrates [11], where the strong trifluoromethanesulfonic acid is formed in the reaction medium, the significantly weaker trifluoromethanesulfinic acid is released during the reaction of the complex **1**. However, we were unable to obtain the individual compounds from the acid-labile heterocycles of the furan series; strong resinification was observed. In some cases the sulfonium salts were not obtained in the pure form on account of the complexity of purification and the insufficient stability. However, the respective sulfides can be synthesized without the intermediate isolation of sulfonium salts. Moreover, the reaction of the complex **1** with biindole **2i** leads to the formation only of the product from double substitution – sulfide **4i** even at high dilution, at low temperature, and using an excess of the substrate. Such a reaction path is probably due to the extremely high reactivity of biindole **2i** in electrophilic substitution.

During an attempt to demethylate the sulfonium salt **3k**, obtained from 2-phenylindole, by the action of triethylamine sulfonium ylide **5k** was obtained instead of the expected sulfide. In spite of the fact that bases (NaH, KOH) are necessary for the production of ylides in the case of the usual alkylsulfonium salts [12], the dimethyl-substituted derivatives of pyrrole and indole exhibit enhanced NH acidity, and the respective ylides can be formed under the influence of weaker bases [13, 14]. Thus, other less basic nucleophiles are required for the production of the desired sulfide from the salt **3h**. Earlier thiourea was used for the demethylation of cyclic sulfonium salts containing carbonyl function labile under basic conditions [15]. In fact, the demethylation of compound **3h** with thiourea under acidic conditions gives the corresponding sulfide with a yield of 84% (scheme).

TABLE 1. The Synthesis of Hetaryl(dimethyl)sulfonium Salts and Hetaryl Methyl Sulfides*

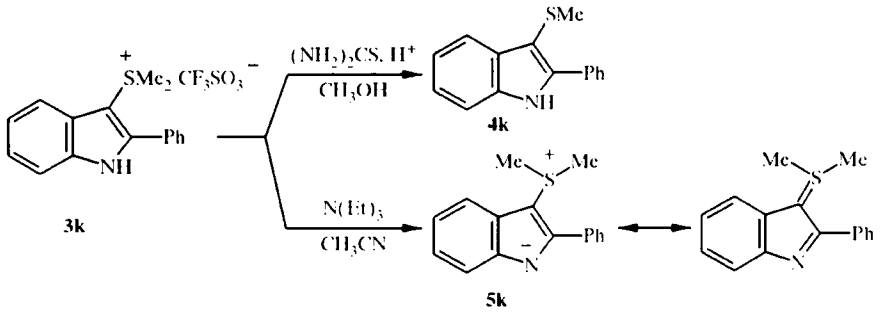
Compound	Heterocycle Het H	Sulfonium salt Het S^+Me_2 $CF_3SO_3^-$	Yield, %	Sulfide*[2] Het SMe	Yield, %
2a		3a	78	4a	76
2b		3b	83	4b	75
2c		3c	82	4c	50
2d		3d	87	4d	45
2e		3e	65	4e	81
2f		3f	81	4f	88
2g		3g	70	4g	43
2h		3h		4h	45
2i		3i		4i	46
2j		3j	83	4j	61
2k		3k	78	4k	84

* The hydrogen atom substituted by the dimethylsulfonium group is indicated.

*[2] In the reactions without isolation of the respective sulfonium salts the total yield of sulfide is indicated.

Thus, the reaction of the complex of dimethyl sulfide and trifluoromethanesulfonic anhydride with a series of heteroaromatic compounds was studied. On the basis of the reaction a new method was developed for the electrophilic introduction of methyl group into a series of aromatic heterocyclic compounds through the demethylation of the initially formed hetaryl(dimethyl)sulfonium salts by the action of triethylamine or, in the case of the derivatives of indole with increased NH acidity, by the action of thiourea in an acidic medium.

Scheme



EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on Varian VXR-400 and Bruker AMX 300 spectrometers (100 and 75 MHz for ^{13}C) in deuterochloroform, hexadeuteroacetone, and trideuteroacetonitrile with TMS as internal standard. Thin-layer chromatography was conducted on Silufol UV-254 plates with acidified potassium permanganate solution and iodine vapor as developers. Preparative chromatography was carried out with Merck silica gel (230-400 mesh). Trifluoromethanesulfonic anhydride was obtained by the method [1] from trifluoromethanesulfonic acid (Merck).

Synthesis of Hetaryl(dimethyl)sulfonium Trifluoromethanesulfonates (General Procedure). Dimethyl sulfide (0.37 ml, 5 mmol) was added to solution of trifluoromethanesulfonic anhydride (0.84 ml, 5 mmol) in absolute methylene chloride (50 ml) under stirring and cooling to -40°C. A white precipitate of the complex formed immediately. After 15 min solution of the respective heteroaromatic compound (5 mmol) in absolute dichloromethane (20 ml) was added dropwise to the reaction mixture with cooling to -40°C. The temperature of the mixture was raised to -20°C, and it was left for 0.25-4 h until the reaction was complete (monitored by TLC). The solvent was evaporated under vacuum at room temperature to a quarter of the initial volume. The sulfonium salt was then precipitated with ether, washed, and dried in a vacuum desiccator. The product was purified by reprecipitation from acetonitrile with ether.

Dimethyl(3-methyl-2-thienyl)sulfonium Trifluoromethanesulfonate (3a). Yield 78%; mp 110-111°C. ^1H NMR spectrum (trideuteroacetonitrile, δ, ppm): 8.00 (1H, d, ^3J = 5.2 Hz, 5-H); 7.08 (1H, d, ^3J = 5.2 Hz, 4-H); 3.21 [6H, s, $(CH_3)_2S^+$]; 2.43 (3H, s, CH_3). ^{13}C NMR spectrum (trideuteroacetonitrile, ppm): 151.58 ($C_{(5)}$); 136.91 ($C_{(4)}$); 132.13 ($C_{(3)}$); 122.61 (q, $^1J_{CF}$ = 320.6 Hz, CF_3SO_3); 117.66 ($C_{(2)}$); 32.59 [$(CH_3)_2S^+$]; 15.24 (CH_3). Found, %: C 30.55; H 3.63. $C_8H_{11}F_3O_3S_2$. Calculated, %: C 31.16; H 3.60.

Dimethyl(5-methyl-2-thienyl)sulfonium Trifluoromethanesulfonate (3b). Yield 83%; mp 114-116°C. The ^1H NMR spectrum was identical with the spectrum described for dimethyl(5-methyl-2-thienyl)sulfonium perchlorate [9]. ^{13}C NMR spectrum (trideuteroacetonitrile): 153.93 ($C_{(5)}$); 140.07 ($C_{(4)}$); 128.35 ($C_{(3)}$); 121.97 (q, $^1J_{CF}$ = 318.2 Hz, CF_3SO_3); 118.99 ($C_{(2)}$); 32.70 [$(CH_3)_2S^+$]; 16.10 ppm (CH_3).

Dimethyl[3-(3'-thienyl)-2-thienyl]sulfonium Trifluoromethanesulfonate (3c). Yield 82%; oil. ^1H NMR spectrum (trideuteroacetonitrile, δ, ppm): 8.13 (1H, d, ^3J = 5.3 Hz, 5-H); 7.20 (1H, dd, ^4J = 2.9 Hz, ^4J = 1.4 Hz, 2'-H); 7.61 (1H, dd, ^3J = 5.1 Hz, ^4J = 2.9 Hz, 4'-H); 7.39 (1H, d, ^3J = 5.3 Hz, 4-H); 7.36 (1H, dd, ^3J = 5.1 Hz, ^4J = 1.4 Hz, 5'-H); 3.24 [6H, s, $(CH_3)_2S^+$]. ^{13}C NMR spectrum (trideuteroacetonitrile, ppm): 148.71 ($C_{(2)}$); 137.39 ($C_{(5)}$); 133.71 ($C_{(4)}$); 131.26 ($C_{(4')}$); 129.69 ($C_{(3')}$); 128.93 ($C_{(5')}$); 128.69 ($C_{(3)}$); 128.52 ($C_{(2')}$); 124.00 (q, $^1J_{CF}$ = 312.3 Hz, CF_3); 33.16 [$(CH_3)_2S^+$]. Found, %: C 34.55; H 3.00. $C_{11}H_{11}F_3O_3S_4$. Calculated, %: C 35.09; H 2.95.

Dimethyl(3-phenyl-2-thienyl)sulfonium Trifluoromethanesulfonate (3d). Yield 87%; oil. ^1H NMR spectrum (deuterochloroform, ppm): 8.17 (1H, d, ^3J = 5.3 Hz, 4-H); 7.56-7.45 (5H, m, 2',3',4',5',6'-H); 7.35 (1H, d, ^3J = 5.3 Hz, 5-H); 3.22 [6H, s, $(CH_3)_2S^+$]. ^{13}C NMR spectrum (deuterochloroform, ppm): 154.56 ($C_{(3)}$); 137.55 ($C_{(5)}$); 133.43 ($C_{(1')}$); 131.48 ($C_{(4')}$); 130.54 ($C_{(4)}$); 130.23 ($C_{(2')}$ and $C_{(6')}$); 130.04 ($C_{(3')}$ and $C_{(5')}$); 129.92 ($C_{(2)}$); 21.19 [$(CH_3)_2S^+$]. Found, %: C 41.72; H 3.54. $C_{13}H_{11}F_3O_3S_3$. Calculated, %: C 42.15; H 3.54.

1-Benzothiophen-3-yl(dimethyl)sulfonium Trifluoromethanesulfonate (3e). Yield 65%; mp 109-111°C. ^{1}H NMR spectrum (trideuteroacetonitrile, ppm): 8.81 (1H, s, 2-H); 8.04 (1H, d, ^3J = 8.0 Hz, 4-H); 8.01 (1H, d, ^3J = 8.5 Hz, 7-H); 7.65-7.56 (2H, m, 5-H and 6-H); 3.42 [6H, s, $(CH_3)_2S^+$]. ^{13}C NMR spectrum (trideuteroacetonitrile, ppm): 140.36 (C_{3a}); 137.61 (C_2); 135.09 (C_{7a}); 127.10 (C_5 or C_6); 126.91 (C_5 or C_6); 124.17 (C_7); 122.02 (q, $^1J_{CF}$ = 319.2 Hz, CF_3SO_3); 121.06 (C_4); 119.05 (C_3); 29.40 [$(CH_3)_2S^+$]. Found, %: C 37.89; H 3.25. $C_{11}H_{11}F_3O_3S_2$. Calculated, %: C 38.36; H 3.22.

[2-(1-Benzothiophen-2-yl)-1-benzothiophen-3-yl](dimethyl)sulfonium Trifluoromethanesulfonate (3f). Yield 81%; mp 163-165°C. ^{1}H NMR spectrum (trideuteroacetonitrile): 8.25 (1H, d, ^3J = 7.85 Hz, 4-H); 8.12 (1H, d, ^3J = 8.18 Hz, 4'-H); 8.00 (1H, d, ^3J = 6.2 Hz, 7'-H); 7.98 (1H, d, ^3J = 6.2 Hz, 7'-H); 7.88 (1H, s, 3'-H); 7.71-7.60 (2H, m, 5-H and 5'-H); 7.52-7.48 (2H, m, 6-H and 6'-H); 3.45 [6H, s $(CH_3)_2S^+$]. ^{13}C NMR spectrum (trideuteroacetonitrile, ppm): 151.78; 142.37; 140.69; 140.40; 136.09; 131.73; 109.93 (7C arom. quat.); 129.91; 128.36; 128.23; 127.99; 126.93; 126.34; 125.40; 123.39 (9CH arom.); 28.04 [2C, $(CH_3)_2S^+$]. Found, %: C 47.57; H 3.12. $C_{19}H_{13}F_3O_3S_4$. Calculated, %: C 47.88; H 3.17.

Dimethyl(1-methyl-1H-pyrrol-2-yl)sulfonium Trifluoromethanesulfonate (3g). Yield 70%; mp 110-112°C. The ^{1}H NMR spectrum was identical with the spectrum described for dimethyl(1-methyl-1H-pyrrol-2-yl)sulfonium perchlorate [14]. ^{13}C NMR spectrum (deuterochloroform, ppm): 131.62 (C_5); 122.03 (q, $^1J_{CF}$ = 321.3 Hz, CF_3); 118.07 (C_4); 112.32 (C_3); 110.70 (C_2); 35.63 (NCH_3); 32.36 [$(CH_3)_2S^+$].

Dimethyl(9H-carbazol-3-yl)sulfonium Trifluoromethanesulfonate (3j). Yield 83%; oil. ^{1}H NMR spectrum (deuterochloroform, ppm): 8.65-7.23 (7H, m, arom.); 7.03 (1H, s, NH); 3.27 [6H, s, $(CH_3)_2S^+$]. ^{13}C NMR spectrum (deuterochloroform, ppm): 143.78 (C_{9a}); 141.70 (C_{8a}); 128.70 (C_3); 127.62 (C_2); 127.21 (C_{4a}); 127.02 (C_5); 126.23 (C_{4b}); 124.27 (C_4); 121.72 (C_8); 121.64 (C_6); 114.17 (C_1); 112.81 (C_8); 30.68 [$(CH_3)_2S^+$]. Found, %: C 47.53; H 3.77. $C_{15}H_{14}F_3NO_3S_2$. Calculated, %: C 47.74; H 3.74.

Dimethyl(2-phenyl-1H-indol-3-yl)sulfonium Trifluoromethanesulfonate (3k). Yield 78%; mp 147-149°C. The ^{1}H NMR spectrum was identical with the spectrum described for dimethyl(2-phenyl-1H-indol-3-yl)sulfonium iodide [16]. ^{13}C NMR spectrum (hexadeuteroacetone, ppm): 148.14 (C_{7a}); 138.20 (C_2); 131.18 ($C_{1'}$); 130.56 (2C, $C_{2'}$, $C_{6'}$); 129.88 (2C, $C_{3'}$, $C_{5'}$); 129.34 (C_{3a}); 125.57 (C_5 or C_6); 125.22 (C_5 or C_6); 123.43 (C_4); 121.91 (q, $^1J_{CF}$ = 318.9 Hz, CF_3SO_3); 119.51 (C_7); 114.74 ($C_{4'}$); 28.65 [$(CH_3)_2S^+$].

Transformations of Sulfonium Salts to Sulfides (General Procedure). To solution of the sulfonium salt (2 mmol) in acetonitrile (10 ml), cooled to 0°C, with stirring triethylamine (1.4 ml, 10 mmol) was added. The temperature of the reaction mixture was slowly raised to room temperature, and the mixture was kept for 1 h. The solvent was evaporated under vacuum, the residue was treated with ether, and the ether solution was passed through a column of silica gel. After distillation of the solvent the sulfide was in some cases purified further by chromatography (eluent hexane–ethyl acetate, 9:1).

3-Methyl-2-(methylthio)thiophene (4a). Yield 76%; oil. The ^{1}H NMR data were identical with published data [17]. ^{13}C NMR spectrum (deuterochloroform, ppm): 141.08 (C_3); 130.24 (C_2); 129.82 (C_4); 126.46 (C_5); 21.54 (CH_3S); 14.31 (CH_3).

5-Methyl-2-(methylthio)thiophene (4b). Yield 75%; oil. The ^{1}H and ^{13}C NMR spectral data were identical with published data [18].

2-Methylthio-3-(3'-thienyl)thiophene (4c). Yield 50%; oil. ^{1}H NMR spectrum (deuterochloroform, ppm): 7.68 (1H, dd, ^4J = 3.0 Hz, ^4J = 1.4 Hz, 2'-H); 7.53 (1H, ^3J = 5.1 Hz, ^4J = 1.4 Hz, 5'-H); 7.61 (1H, dd, ^3J = 5.1 Hz, ^4J = 3.0 Hz, 4'-H); 7.28 (1H, d, ^3J = 5.5 Hz, 5-H); 7.19 (1H, d, ^3J = 5.5 Hz, 4-H); 2.41 (3H, s, CH_3S). ^{13}C NMR spectrum (deuterochloroform, ppm): 137.38 (C_3); 135.92 ($C_{3'}$); 131.07 (C_2); 129.03 ($C_{5'}$); 127.63 (C_4); 126.18 ($C_{2'}$); 126.05 ($C_{4'}$); 122.53 (C_5); 21.13 (CH_3S). Found, %: C 50.95; H 3.78. $C_9H_8S_3$. Calculated, %: C 50.90; H 3.80.

2-Methylthio-3-phenylthiophene (4d). Yield 45%; oil. ^{1}H NMR spectrum (deuterochloroform, ppm): 7.6 (2H, m, 2'-H, and 6'-H); 7.46 (2H, m, 3'-H and 5'-H); 7.38 (1H, m, 4'-H); 7.33 (1H, d, ^3J = 5.3 Hz, 4-H); 7.02 (1H, d, ^3J = 5.3 Hz, 5-H); 2.41 (3H, s, CH_3S). ^{13}C NMR spectrum (deuterochloroform, ppm): 142.94 (C_3); 135.50 ($C_{1'}$); 131.72 (C_2); 129.37 ($C_{4'}$); 128.56 ($C_{2'}$ and $C_{6'}$); 128.00 ($C_{3'}$ and $C_{5'}$); 127.00 (C_4); 125.91 (C_5); 21.19 (CH_3S). Found, %: C 64.14; H 4.89. $C_{11}H_{10}S_2$. Calculated, %: C 64.03; H 4.89.

3-Methylthio-1-benzo[*b*]thiophene (4e). Yield 81%; oil. The ^{1}H and ^{13}C NMR spectral data were identical with published data [19].

2-(1-Benzothiophen-2-yl)-3-(methylthio)benzo[*b*[thiophene (4f). Yield 88%; mp 108-110°C. ^{1}H NMR spectrum (deuterochloroform, ppm): 7.99 (1H, d, ^3J = 7.93 Hz, 4-H); 7.83-7.67 (3H, m, H arom.); 7.45-7.28 (4H, m, H arom.); 7.37 (1H, s, 3'-H); 2.33 (3H, s, CH_3). ^{13}C NMR spectrum (deuterochloroform, ppm): 141.39; 140.89; 140.34; 138.67; 137.72; 135.59; 124.62 (7C quat. arom.); 125.54; 125.05; 124.99; 124.80; 124.57; 124.32; 123.73; 123.38; 122.03; 123.38; 122.01 (9CH arom.); 19.17 (CH_3S). Found, %: C 65.45; H 3.84. $C_{17}H_{12}S_3$. Calculated, %: C 65.34; H 3.87.

2-Methylthio-1-H-pyrrole (4g). Yield 43%; oil. The ^{1}H and ^{13}C NMR spectral data were identical with published data [20].

1-Methyl-3-(methylthio)-1H-indole (4h). Yield 45%; oil. ^{1}H NMR spectrum (trideuteroacetonitrile, ppm): 7.89 (1H, d, 4-H); 7.38-7.27 (3H, m, 5-H, 6-H, and 7-H); 7.17 (1H, s, 7-H); 3.68 (3H, s, CH_3); 2.47 (3H, s, CH_3S). ^{13}C NMR spectrum (trideuteroacetonitrile, ppm): 137.30 ($C_{(7a)}$); 132.57 ($C_{(2)}$); 129.41 ($C_{(3a)}$); 122.30 ($C_{(5)}$ or $C_{(6)}$); 119.94 ($C_{(5)}$ or $C_{(6)}$); 119.28 ($C_{(4)}$); 109.78 ($C_{(7)}$); 105.99 ($C_{(3)}$); 32.72 (CH_3); 20.66 (CH_3S). Found, %: C 67.26; H 6.12. $C_{10}H_{11}NS$. Calculated, %: C 67.75; H 6.25.

3,3'-Di(methylthio)-2,2'-biindole (4i). Yield 46%; mp 222-224°C. ^{1}H NMR spectrum (deuterochloroform, ppm): 11.33 (2H, s, 2NH); 7.81 (2H, d, ^3J = 7.7 Hz, 7-H, 7'-H); 7.50 (2H, d, ^3J = 7.8, 4-H, 4'-H); 7.34-7.22 (4H, m, 5-H, 6-H, 5'-H, 6'-H); 2.44 (6H, s, $2CH_3S$). ^{13}C NMR spectrum (deuterochloroform, ppm): 135.59 (2C, $C_{(7a)}$, $C_{(7'a)}$); 131.73 (2C, $C_{(3a)}$, $C_{(3'a)}$); 129.77 (2C, $C_{(2)}$, $C_{(2')}$); 123.73; 120.83; 118.87; 111.54; 104.04 (2C, $C_{(4)}$, $C_{(4')}$); 20.33 (2C, $2CH_3S$). Found, %: C 66.47; H 4.99. $C_{18}H_{16}N_2S_2$. Calculated, %: C 66.63; H 4.97.

3-Methylthio-9H-carbazole (4j). Yield 61%; mp 113-117°C. Published data: mp 117-119°C [21]. ^{1}H NMR spectrum (deuterochloroform, ppm): 8.04-7.97 (3H, m, arom., NH); 7.40-7.17 (5H, m, arom.); 2.52 (6H, s, CH_3S). ^{13}C NMR spectrum (deuterochloroform, ppm): 139.67 ($C_{(9a)}$); 138.17 ($C_{(8a)}$); 127.76 ($C_{(2)}$); 127.36 ($C_{(4a)}$); 126.08 ($C_{(3)}$); 123.94 ($C_{(4a)}$); 122.48 ($C_{(4b)}$); 121.12 ($C_{(4)}$); 120.26 ($C_{(5)}$); 119.51 ($C_{(6)}$); 111.22 ($C_{(1)}$); 110.68 ($C_{(8)}$); 18.84 (CH_3S). Found, %: C 73.11; H 5.23. $C_{13}H_{11}NS$. Calculated, %: C 73.20; H 5.20.

3-(Dimethyl-λ^4-sulfanylidene)-2-phenyl-3H-indole (4k). Yield 84%; mp 177-178°C. Published data: mp 125-129°C [16]. The ^{1}H and ^{13}C NMR spectral data were identical with published data [16].

3-Methylthio-2-phenyl-1H-indole (4l). The compound was obtained from the sulfonium salt (**3k**) by the method [15]. Yield 85%; mp 110-112°C. Published data: mp 106-107°C [22].

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