Synthesis of annulated oligothiophenes*

V. G. Nenajdenko, E. S. Balenkova, K. Y. Chernichenko, and S. S. Vshivenko*

Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (495) 932 8846. E-mail: nen@acylium.chem.msu.ru

Reactions of 1,1-di(2-naphthyl)-2,2-dichloroethene and 1,1-di(2-benzothienyl)-2,2-dichloroethene with sulfur at 220—225 °C resulted in hitherto unknown oligothiophenes. Tetrathio[6]helicene was synthesized from 1,1-di(3-benzothienyl)-2,2-dichloroethene. Preparative pathway to helicene involving intramolecular ring closure of dithiol derived from 1,1-di-(3-benzothienyl)-2,2-dichloroethene was developed as an alternative to high temperature synthesis.

Key words: 1,1-diaryl-2,2-dichloroethenes, sulfur, diaryl ketones, helicenes, oligothiophenes.

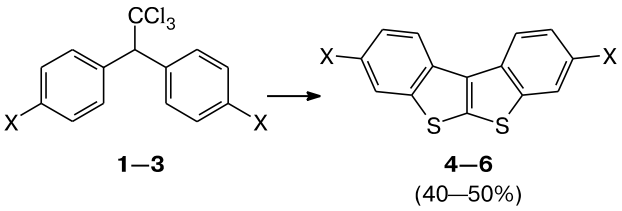
Annulated oligothiophenes are important building blocks toward materials for a wide variety of applications, *e.g.*, electroluminescence,[1] fluorescence, photochromism,[2] non-linear optics.[3] Several thin film transistors based on oligothiophenes exhibit high field-effect charge mobility and on/off ratios.[4] Oligothiophenes were also used for the synthesis of conducting polymers.[5] Recently, in our group the first derivatives of hitherto unknown class of organic compounds, heterocyclic circulenes contaning thiophene or selenophene rings, were synthesized and their potential applications as novel materials were studied.[6] Heterocyclic helicenes with π-donating thiophene rings are of essential interest.[7]

Reaction of halogenated aromatic compounds with sulfur is one of the simplest methods to access fused thiophene compounds.[8] Thus, heating 1,1-diphenyl-2,2,2-trichloroethane (**1**) and its chlorinated (**2**) and brominated (**3**) derivatives with sulfur at 260—270 °C resulted in benzothiopheno[2,3-*b*]benzothiophenes **4—6** in 40—50% yields (Scheme 1).

The mechanism of this reaction is unclear, however, it was assumed that the initial step of the reaction involved thermal removal of hydrogen chloride to give the corresponding dichloroalkene **7**; the intermediate 2-chloro-3-phenylbenzothiophene formed on the initial step of the ring closure was also isolated (Scheme 2).

This versatile and effective approach attracted our attention; therefore, we decided to explore the synthetic scope and potential of the reaction. With the aim to synthesize other fused oligothiophenes, we studied the reaction of various naphthyl- and benzothienyl-substituted 1,1-dichloroethenes with sulfur. We improved the reaction conditions. It was found that the reactions with the corresponding dichloroalkene **7** can be performed at tem-

Scheme 1

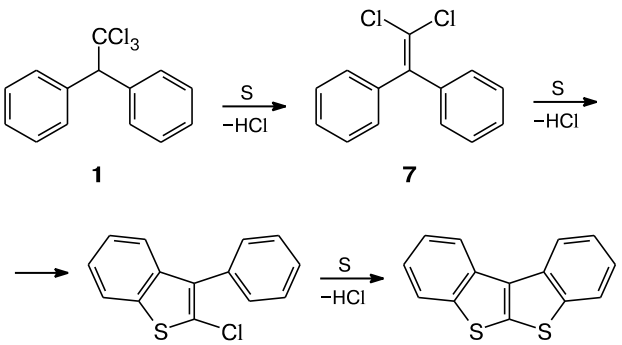


1—3 **4—6** (40—50%)

X = H (**1**, **4**), Br (**2**, **5**), Cl (**3**, **6**)

Reagent and conditions: S, 1,2-dichlorobenzene, 260—270 °C.

Scheme 2



1 **7** **4**

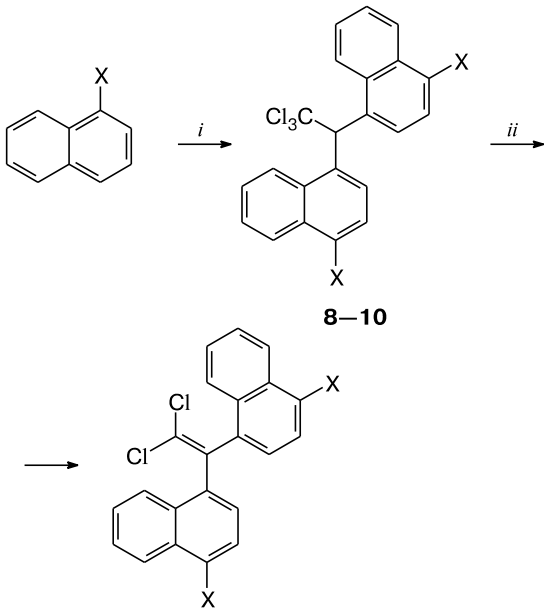
* Based on the Materials of the International Congress on Organic Chemistry dedicated to the 150th anniversary of the Butlerov´s Theory of Chemical Structure of Organic Compounds (September 19—23, 2011, Kazan, Russia).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1441—1447, July, 2012.

peratures lower by 30—40 °C than earlier described giving the target product in the yields higher by 5—10%; however, 2—3-fold longer reaction times were required. To reduce resinification and avoid overheating, 1,2,4-trichlorobenzene boiling at 214 °C was used as a solvent. All these improvements allowed us to increase the yield of benzothiopheno[2,3-*b*]benzothiophene (**4**) to 70%, and its 3,8-dichloro- (**5**) and 3,8-dibromo-substituted derivatives (**6**) to 53 and 50%, respectively. The yields achieved by us were by 10—20% higher than these reported earlier.[8a]

Naphthyl derivatives of 2,2,2-trichloroethanes **8**—**10** were synthesized under conditions used for the synthesis of 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT), namely, by the reaction or arenes with chloral. Refluxing trichlorides with KOH in isopropyl alcohol was found to be the optimal for removal of hydrogen chloride to yield dichloroethanes **11**—**13** (Scheme 3).

Scheme 3



11—13 (85—95%)

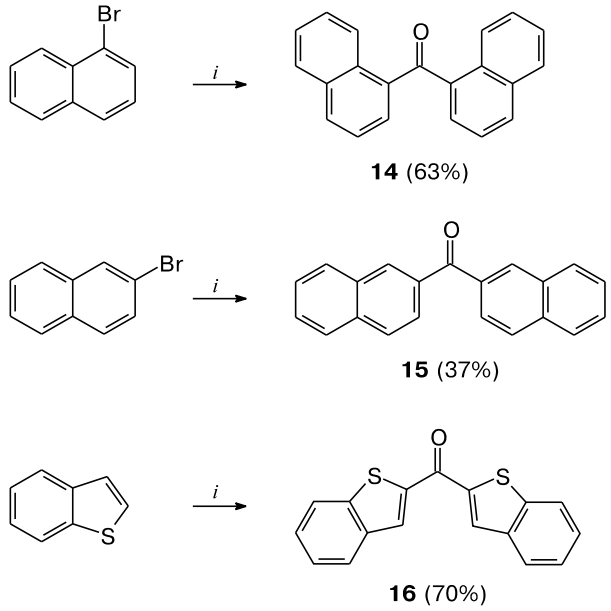
X = OMe (**8**, **11**), Cl (**9**, **12**), F (**10**, **13**)

Reagents: *i*. CCl_3CHO, H_2SO_4; *ii*. KOH, Pr^iOH.

Attempts to synthesize the corresponding 1,1-diaryl-2,2,2-trichloroethanes by the reactions of unsubstituted naphthalene with chloral gave the inseparable mixtures of the isomers. Therefore, the target compounds of this group were accessed from symmetric ketones **14**—**16** (Scheme 4) by transformation of **14**—**16** into the corresponding organometallic derivatives[9] and subsequent olefination[10] of the latter into dichloroethenes.

However, di(3-benzothienyl) ketone (**17**) cannot be accessed from 3-bromobenzothiopehe *via* this procedure.

Scheme 4

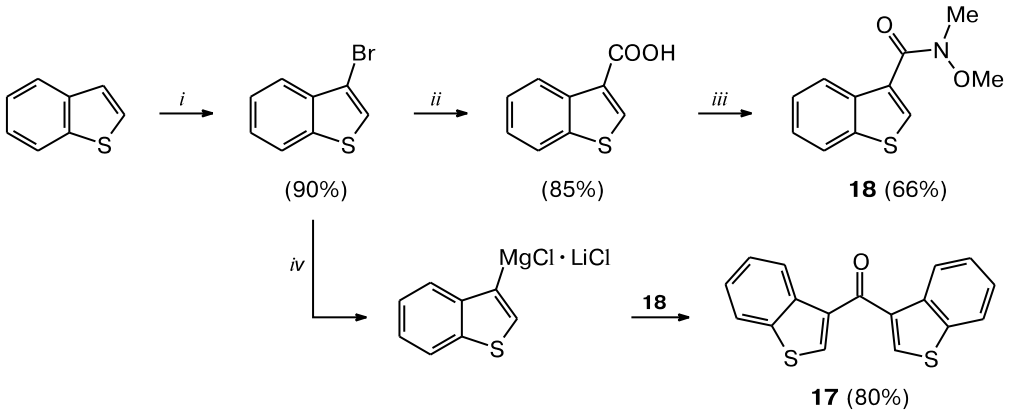


Reagents: *i*. 1) BuLi, 2) Me_2NCOCl, 3) 1 *M* HCl.

A low yield synthesis of di(3-benzothienyl) ketone (**17**) from benzothiophene-3-carbonyl chloride and 3-benzothienylmagnesuim chloride have been described.[11] We modified this procedure and converted 3-benzothiophene carboxylic acid into the corresponding Weinreb amide **18**. The use of amide **18** makes it possible to add only one equivalent of organometallic compound to the carbonyl group. Thus modified procedure allows the synthesis of di(3-benzothienyl) ketone (**17**) from benzothiophene in 40% total yield (Scheme 5).

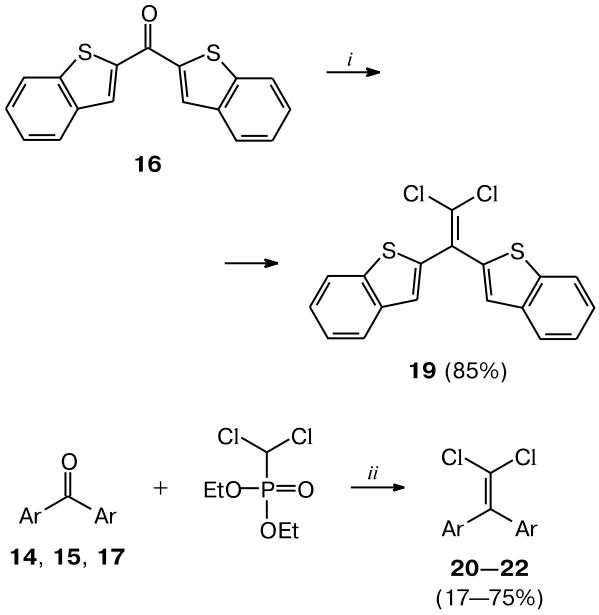
1,1-Di(2-benzothienyl)-2,2-dichloroethene (**19**) was synthesized in 85% yield by the Wittig reaction used previously for the similar aliphatic substrates.[12] However, reactions involving di(3-benzothienyl) ketone (**17**) and dinaphthyl ketones **14** and **15** are more complicated. In the case of di(3-benzothienyl) ketone (**17**), the yield of the target dichloride did not exceed 15—20%. Carrying out the reaction with excesses of triphenylphosphine and CCl_4 did not improve the yield of dichloroalkene. In the case of ketone **14**, no formation of dichloroalkene virtually occurs, which is due apparently to the sensitivity of this reaction to steric demands (the protons in the *peri* position caused significant steric strain). Therefore, 1,1-di(1-naphthyl)-2,2-dichloroethene (**20**), 1,1-di(2-naphthyl)-2,2-dichloroethene (**21**), and 1,1-di(3-benzothienyl)-2,2-dichloroethene (**22**) were synthesized by the reaction of diethyl dichloromethylphosphonate with ketones in the presence of lithium hexamethyldisilazide in the yields of 17, 68, and 75%, respectively. This approach is less sensitive to the steric strains and serves for the synthesis of hindered dichloroalkenes (Scheme 6).[13]

Scheme 5



Reagent and conditions: *i*. Br_2; *ii*. 1) BuLi, 2) CO_2, 3) H_3O^+; *iii*. 1) 1,1-carbonyldiimidazole (CDI), 2) HN(Me)OMe · HCl; *iv*. $Pr^iMgCl \cdot LiCl$, THF, diethyl ether.

Scheme 6

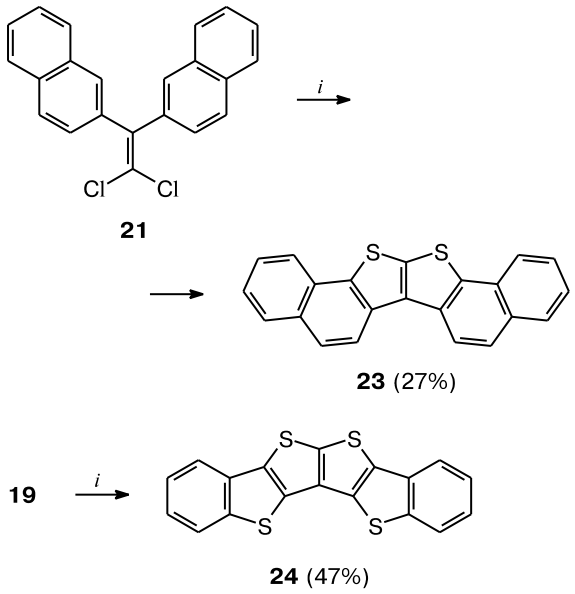


Ar = 1-naphthyl (**14**, **20**), 2-naphthyl (**15**, **21**), 3-benzothienyl (**17**, **22**)

Reagents: *i*. Ph_3P, CCl_4, THF; *ii*. $LiN(TMS)_2$.

Heating either 1,1-di(1-naphthyl)-2,2-dichloroethene (**20**) or substituted 1,1-di(1-naphthyl)-2,2-dichloroethenes **11**—**13** with sulfur at 220—225 °C led to significant resinification of the reaction mixtures and isolation of the target products failed. In contrast to α-naphthyl-substituted dichloroalkenes **11**—**13**, reaction of 1,1-di(2-naphthyl)-2,2-dichloroethene (**21**) with sulfur afforded hitherto unknown naphtho[1,2-*b*]naphtho[2′,1′:4,5]-thieno[3,2-*d*]thiophene (**23**) in 27% yield. Similarly, the reaction of 1,1-di(2-benzothienyl)-2,2-dichloroethene (**19**) with sulfur gave previously unknown benzothiopheno[2″,3″:4′,5′]thieno[3′,2′:4,5]thieno[3,2-*b*]benzothiophene (**24**) in the yield of 47% (Scheme 7).

Scheme 7

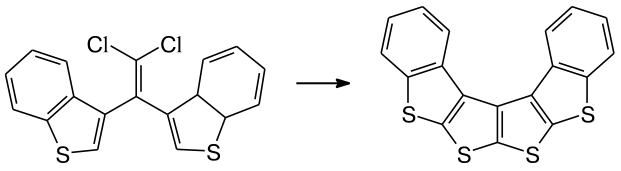


Reagents and conditions: *i*. S, 1,2,4-trichlorobenzene, 220—225 °C.

Reaction of 1,1-di(3-benzothienyl)-2,2-dichloroethene (**22**) with sulfur afforded target hitherto unknown thiophenic helicene, benzothiopheno[3″,2″:4′,5′]thieno-[3′,2′:4,5]thieno[2,3-*b*]benzothiophene (**25**) in 25% yield (Scheme 8).

Low yield of helicene **25** motivated us to elaborate alternative procedure for heterocyclization of dichloroalkenes. We suggested that benzothiophenes could be transformed into target compounds by deprotonation,

Scheme 8

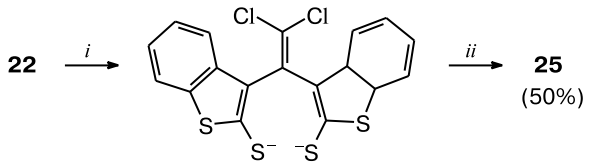


22 **25** (25%)

Reagents and conditions: S, 1,2,4-trichlorobenzene, 220—225 °C.

which benzotiophenes are especially prone, followed by treatment of the resulting lithium salts to give the corresponding thiolates and subsequent ring closure of the latter involving nucleophilic replacement of the chlorine atoms. By this approach, helicene **25** was synthesized from 1,1-di(3-benzothienyl)-2,2-dichloroethene (**22**) in 50% yield (Scheme 9), which is double the yield afforded by heating dichloroalkene with sulfur.

Scheme 9



Reagents and conditions: *i*. 1) LDA, 2) S_8; *ii*. DMF, 80 °C, 6 h.

The structures of oligothiophenes synthesized were evaluated by ^{1}H and ^{13}C NMR spectroscopy, UV spectroscopy, and elemental analysis. Considerable difference in chemical shifts of the C(11) protons for helicene **25** (δ_C 8.60) and its linear isomer **24** (δ_C 7.96) is of note. Apparently, this difference is due to that the C(11) protons in helicene are deviated from the molecular plane and are in close spatial proximity. UV spectra of compounds **23**—**25** also exhibit noticeable difference (Fig. 1). Lower extinction coefficient of helicene **25** as compared with oligothiophene **24** can be explained by decrease in conjugation caused by non-planarity of compound **25**. In the case of compound **23** with more fused benzene rings, the extinction coefficient was higher.

In summary, we studied possibility to synthesize polyaromatic compounds with thienothiophenic moiety by the reactions of symmetric 2,2-diaryl-1,1-dichloroethenes with sulfur. This approach allow synthesis of oligothiophenes of both linear and helicene structures. As an alternative to high temperature synthesis, the reaction sequence involving lithiation of benzothienyldichloroalkenes, treatment of the latter with sulfur and subsequent ring closure can be employed. Despite the fact that these approaches can be used to synthesize limited scope of

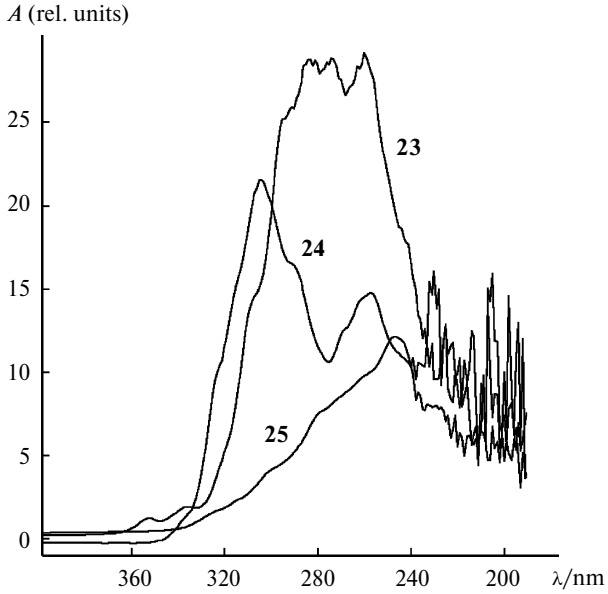


Fig. 1. UV spectra of compounds **23**, **24**, and **25**.

compounds, they are simple straightforward procedures serving for the synthesis of hitherto unknown oligothiophenes.

Experimental

^{1}H and ^{13}C NMR spectra were run on a Bruker Avance 400 spectrometer (working frequencies of 400 and 100 MHz, respectively) in $CDCl_3$ with Me_4Si as internal standard. Mass spectra (70 eV) were recorded on a Shimadzu GCMS-QP5050A instrument. UV spectra were obtained on a Agilent 8453 instrument. TLC was performed on Merck 60 plates; for visualization of the spots, acidified $KMnO_4$ solution, concentrated sulfuric acid or iodine vapors were used. Preparative column chromatography was performed on silica gel (63—200 mesh, Merck). Melting points were determined on a Electrothermal 9100 apparatus. Compounds sensitive to moisture and oxygen were handled under argon. Commercially available reagents (Fluka, Aldrich) were used as purchased, the solvents were distilled prior to use.

Synthesis of 1,1-diaryl-2,2,2-trichloroethanes 8—10 (general procedure). To a vigorously stirred mixture of arene (100 mmol) and chloral (55 mmol), concentrated sulfuric acid (100 mL) was added dropwise maintaining the temperature at 10—15 °C. The mixture was stirred at ambient temperature for 24 h. If after 24 h the reaction did not achieve completion (TLC monitoring), the mixture was heated at 50—60 °C (water bath) for 5—7 h. After completion of the reaction, the mixture was poured into ice water. The organic products were extracted with CH_3Cl, the organic layer was washed with 10% aqueous $NaHCO_3$ (50 mL), brine (50 mL), dried with Na_2SO_4, filtered through a thin layer of silica gel, and concentrated *in vacuo*. The residue was recrystallized from toluene.

2,2,2-Trichloro-1,1-di(4-methoxynaphthyl)ethane (8). Yield 35%, m.p. 255—256 °C (*cf*. Ref. 14: m.p. 257 °C).

2,2,2-Trichloro-1,1-di(4-chloronaphthyl)ethane (9). Yield 40%, m.p. 222—223 °C (*cf*. Ref. 15: m.p. 224 °C).

2,2,2-Trichloro-1,1-di(4-fluoronaphthyl)ethane (10). Yield 65%, m.p. 179—180 °C. Found (%): C, 62.72; H, 3.22. $C_{22}H_{13}Cl_3F_2$. Calculated (%): C, 62.66; H, 3.11. ^{1}H NMR, δ: 6.79 (s, 1 H, CH); 7.18 (t, 2 H, H(3), J = 9.6 Hz); 7.58 (m, 4 H, H(2), H(6)); 8.12 (q, 2 H, H(7), J = 1.0 Hz); 8.19 (d, 2 H, H(5), J = 8.0 Hz); 8.36 (d, 2 H, H(8), J = 8.2 Hz). MS, m/z (I_{rel} (%)): 420 $[M]^+$ (6), 303 $[M - CCl_3]^+$ (100), 302 $[M - CCl_3 - H]^+$ (8), 286 $[M - CCl_3 - H - F]^+$ (14).

Synthesis of 1,1-diaryl-2,2-dichloroethenes 11—13 (general procedure). To a solution of 1,1-diaryl-2,2,2-trichloroethane (30 mmol) in Pr^{i}OH (0.5 L), a solution of KOH (60 mmol) in anhydrous MeOH (10 mL) was added. The resulting mixture was refluxed until completion of the reaction (TLC monitoring) and poured into water (1 L). The precipitate formed was filtered off, washed with water, dried, and recrystallized from toluene.

2,2-Dichloro-1,1-di(4-methoxynaphthyl)ethene (11). Yield 85%, m.p. 176—178 °C (*cf.* Ref. 14: m.p. 180 °C).

2,2-Dichloro-1,1-di(4-chloronaphthyl)ethene (12). Yield 87%, m.p. 188—189 °C (*cf.* Ref. 15: m.p. 190 °C).

2,2-Dichloro-1,1-di(4-fluoronaphthyl)ethene (13). Yield 95%, m.p. 177—178 °C. Found (%): C, 68.50; H, 3.30. $C_{22}H_{12}Cl_2F_2$. Calculated (%): C, 68.59; H, 3.14. ^{1}H NMR, δ: 7.07 (br.s, 2 H, H(3)); 7.31 (br.s, 2 H, H(4)); 7.65—7.78 (m, 4 H, H(6), H(7)); 8.20—8.34 (m, 2 H, H(5), H(8)). ^{13}C NMR, δ: 109.2 (d, C(3), J = 20.5 Hz); 121.4 (d, C(5), J = 5.1 Hz); 124.2 (d, C(4a), J = 16.1 Hz); 125.3 (C(2), C(8)); 126.5 (C(6), C(7)); 128.0 (C(1), C(8a)); 131.2 (CCl_2); 133.6 ($\underline{C}$=CCl_2); 158.6 (d, C(4), J = = 249.6 Hz). MS, m/z (I_{rel} (%)): 384 $[M]^+$ (61), 351 $[M - CF - 2H]^+$ (20), 349 $[M - Cl]^+$ (47), 348 $[M - HCl]^+$ (13), 313 $[M - 2Cl]^+$ (100), 310 $[M - C_6H_4 + 2H]^+$ (19).

Di(1-naphthyl) ketone (14). To an ice-cold solution of 1-bromonaphthalene (20.7 g, 100 mmol) in anhydrous diethyl ether (300 mL), 2.5 *M* BuLi in hexane (40 mL, 100 mmol) was added, the mixture was warmed to 15—20 °C, and kept at this temperature for 2 h. Then, the mixture was cooled to −50 °C and a solution of *N,N*-dimethylcarbamoyl chloride (5.5 g, 51 mmol) in anhydrous diethyl ether (30 mL) was added over a period of 2—3 min. The reaction mixture was warmed to −30 °C over 3 h and kept at this temperature for 2 h. Then, the mixture was allowed to warm to 0 °C and 1 *M* HCl (100 mL) was added. The organic layer was separated, the aqueous phase was extracted with dichloromethane (3×30 mL). The combined organics were dried with Na_2SO_4, the solvent was removed *in vacuo*. Recrystallization of the residue from benzene afforded 17.8 g (63%) of di(1-naphthyl) ketone **14**, m.p. 104—104.5 °C (*cf.* Ref. 16: m.p. 103 °C).

Di(2-naphthyl) ketone (15). To an ice-cold solution of 2-bromonaphthalene (15.4 g, 74.4 mmol) in anhydrous diethyl ether (200 mL), 2.5 *M* BuLi in hexane (30 mL, 75 mmol) was added, the mixture was warmed to 15—20 °C and kept at this temperature for 3 h. Then the reaction mixture was cooled to −50 °C and a solution of *N,N*-dimethylcarbamoyl chloride (4.08 g, 37.9 mmol) in anhydrous diethyl ether (30 mL) was added over a period of 2—3 min. The temperature was allowed to rise to ambient and the mixture was stirred for 16 h. Then 1 *M* HCl (100 mL) was added, the organic layer was separated, the aqueous phase was extracted with AcOEt (3×50 mL). The combined organics were dried with Na_2SO_4, the solvent was removed *in vacuo*. Recrystallization of the residue from hexane—ethyl acetate afforded 3.8 g (36.6%) of di(2-naphthyl) ketone **15**, m.p. 160—161.5 °C (*cf.* Ref. 17: m.p. 163 °C).

Di(2-benzothienyl) ketone (16). To a solution of benzothiophene (10 g, 75 mmol) in anhydrous diethyl ether (150 mL) cooled to −20 °C, 2.5 *M* BuLi in hexane (30 mL, 75 mmol) was added over a period of 30 min. The mixture was warmed to 0 °C and kept for 1.5 h. Then, the mixture was re-cooled to −55 °C and a solution of *N,N*-dimethylcarbamoyl chloride (4 g, 37 mmol) in anhydrous diethyl ether (20 mL) was added within 2—3 min. The mixture was allowed to warm to 0 °C over 3.5—4 h and quenched with 1 *M* HCl (70 mL). The organic layer was separated, the aqueous layer was extracted with diethyl ether. The combined organics were dried with Na_2SO_4, the solvent was removed *in vacuo*. Recrystallization of the residue from toluene afforded 7.72 g (70%) of di(2-benzothienyl) ketone **16**, m.p. 170.5—171 °C (*cf.* Ref. 18: m.p. 172—174 °C).

Benzothiophene-3-carboxylic acid. To a solution of 3-bromobenzothiophene[19] (21.3 g, 100 mmol) in anhydrous diethyl ether (250 mL) cooled to −70 °C, 2.5 *M* BuLi in hexane (40 mL, 100 mmol) was added over a period of 5 min and the mixture was stirred at −70 °C for 30 min. The resulting suspension of 3-benzothienyllithium was added to a mixture of excess crashed CO_2 in anhydrous diethyl ether (250 mL) and then the reaction mixture was poured into 2 *M* HCl (400 mL). The organic layer was separated, the aqueous phase was extracted with diethyl ether (150 mL). The combined organics were washed with 2 *M* KOH (3×150 mL). The basic solution was acidified with diluted HCl. Crystals were collected and recrystallized from toluene to give 15.2 g (85%) of benzothiophene-3-carboxylic acid, m.p. 175—176 °C (*cf.* Ref. 20: m.p. 178—178.5 °C).

***N*-Methoxy-*N*-methylbenzothiophene-3-carboxamide (18).** To a stirred solution of benzothiophene-3-carboxylic acid (7.13 g, 40 mmol) in $CHCl_3$ (50 mL), 1,1-carbonyldiimidazole (7.78 g, 48 mmol) was added portionwise. After gas evolution ceased, the mixture was stirred for 15 min and *N,O*-dimethylhydroxylamine (4.68 g, 48 mmol) was slowly added. The reaction mixture was stirred for 18 h, then water (50 mL) was added and stirring was continued for 15 min. The organic layer was separated, washed with 10% HCl, 10% aqueous NaOH, water, dried with Na_2SO_4, and filtered through a short layer of silica gel. Removal of the solvent *in vacuo* afforded 5.9 g (66.7%) of *N*-methoxy-*N*-methylbenzothiophene-3-carboxamide **18**, yellowish oil. Found (%): C, 59.23; H, 5.22. $C_{11}H_{11}NO_2S$. Calculated (%): C, 59.71; H, 5.01. ^{1}H NMR, δ: 3.41 (s, 3 H, NCH_3); 3.58 (s, 3 H, OCH_3); 7.38 (t, 1 H, H(6), J = 8.0 Hz); 7.44 (t, 1 H, H(5), J = 8.0 Hz); 7.87 (d, 1 H, H(7), J = 8.0 Hz); 8.05 (s, 1 H, H(2)); 8.25 (d, 1 H, H(4), J = 8.0 Hz).

Di(3-benzothienyl) ketone (17). To a solution of 3-bromobenzothiophene (9.62 g, 45 mmol) in anhydrous THF (30 mL), 2.25 *M* suspension of $Me_2CHMgCl \cdot LiCl$ (21.2 mL, 48 mmol) in diethyl ether was added under argon and the mixture was stirred for 18 h. Then *N*-methoxy-*N*-methylbenzothiophene-3-carboxamide **18** (5 g, 23 mmol) in anhydrous THF (10 mL) was added and stirring was continued for 24 h. The reaction mixture was diluted with saturated aqueous NH_4Cl (5 mL) and water (40 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organics were dried with Na_2SO_4 and the solvent was removed *in vacuo*. Recrystallization of the residue from toluene afforded 5.3 g (79.7%) of di(3-benzothienyl) ketone **17**, m.p. 166—168 °C (*cf.* Ref. 14: 167—167.5 °C).

Synthesis of 1,1-diaryl-2,2-dichloroethenes 20—22 from diaryl ketones (general procedure). To 2.5 *M* BuLi in hexane (8.8 mL, 2.2 mmol) cooled to −78 °C, a solution of hexamethyl-

disilazane (3.9 g, 2.4 mmol) in THF (20 mL) was slowly added. The reaction mixture was slowly warmed to 0 °C and re-cooled to −78 °C, subsequently a mixture of diethyl dichloromethylphosphonate (4.42 g, 2 mmol) and diaryl ketone (2 mmol) in THF (50 mL) was added dropwise. The mixture was stirred at −78 °C for 10 min and at ambient temperature for 16 h. The reaction was quenched with saturated aqueous NH_4Cl and the mixture was extracted with diethyl ether (3×30 mL). The organic layer was washed with water, dried with Na_2SO_4, the solvent was removed *in vacuo*, the residue was passed through a short layer of silica gel (elution with hexane—dichloromethane, 1 : 1).

2,2-Dichloro-1,1-di(1-naphthyl)ethene (20). Yield 17%. ^{1}H NMR, δ: 7.41 (m, 2 H, H(2)); 7.60 (m, 2 H, H(3)); 7.73 (m, 2 H, H(7)); 7.83 (d, 2 H, H(5), J = 7.7 Hz); 7.92 (d, 2 H, H(6), J = 7.7 Hz); 8.40 (m, 2 H, H(8)).[14]

2,2-Dichloro-1,1-di(2-naphthyl)ethene (21). Yield 68%. ^{1}H NMR, δ: 7.44 (dd, 2 H, H(7), H(8), J = 6.8 Hz, J = 1.8 Hz); 7.49—7.54 (m, 4 H, H(6), H(9)); 7.82—7.88 (m, 8 H, H(1), H(5), H(10), H(12)).[14]

2,2-Dichloro-1,1-di(3-benzothienyl)ethene (22). Yield 75%, m.p. 128.5—129 °C. Found (%): C, 59.60; H, 3.00. $C_{18}H_{10}Cl_2S_2$. Calculated (%): C, 59.84; H, 2.79. ^{1}H NMR, δ: 7.35—7.40 (m, 4 H, H(5), H(6)); 7.53 (s, 2 H, H(2)); 7.67—7.71 (m, 2 H, H(4)); 7.87—7.91 (m, 2 H, H(7)). ^{13}C NMR, δ: 122.9 (CCl_2); 123.1 (C(2)); 124.6 (C(7)); 124.6 (C(5)); 126.2 ($\underline{C}$=CCl_2); 126.8 (C(6)); 129.4 (C(4)); 133.7 (C(3a)); 136.9 (C(3)); 147.0 (C(7a)). MS, m/z (I_{rel} (%)): 360 $[M]^+$ (61), 326 $[M - S - H]^+$ (8), 325 $[M - Cl]^+$ (20), 324 $[M - HCl]^+$ (12), 289 $[M - 2\ Cl]^+$ (100), 288 $[M - 2\ Cl - H]^+$ (24).

Synthesis of benzothiopheno[2,3-*b*]benzothiophenes 4—6 and 23—25 (general procedure). A mixture of 1,1-diaryl-2,2-dichloroethene (1 mmol) and sulfur (2 mmol) in 1,2,4-trichlorobenzene (0.6—0.8 mL) was heated at 220—225 °C for 8—48 h. The reaction mixture was cooled down, pounded and dissolved in refluxing toluene (100—200 mL). The solution was cooled, the crystals formed were filtered off and recrystallized from toluene.

Benzothiopheno[2,3-*b*]benzothiophene (4). Yield 70%, m.p. 140—141 °C (*cf.* Ref. 8: m.p. 138—139 °C).

3,8-Dibromobenzothiopheno[2,3-*b*]benzothiophene (5). Yield 50%, m.p. 280—282 °C (*cf.* Ref. 8: m.p. 283—284 °C).

3,8-Dichlorobenzothiopheno[2,3-*b*]benzothiophene (6). Yield 53%, m.p. 265—266 °C (*cf.* Ref. 8: m.p. 268 °C).

Naphtho[1,2-*b*]naphtho[2′,1′:4,5]thieno[3,2-*d*]thiophene (23). Yield 27%, m.p. 355—356.5 °C. UV ($CHCl_3$), λ_{max}/nm (ε): 260, 280. ^{1}H NMR, δ: 7.53 (t, 2 H, J = 6.0 Hz); 7.61 (t, 2 H, J = 6.0 Hz); 7.95 (d, 2 H, J = 10.0 Hz); 8.00 (d, 2 H, J = 8.0 Hz); 8.08 (d, 2 H, J = 10.0 Hz); 8.50 (d, 2 H, J = 8.0 Hz). ^{13}C NMR spectrum of compound **23** was not recorded because of its low solubility. MS, m/z (I_{rel} (%)): 340 $[M]^+$ (100), 170 $[M]^{2+}$ (40).

Benzothiopheno[2″,3″:4′,5′]thieno[3′,2′:4,5]thieno[3,2-*b*]benzothiophene (24). Yield 47%, m.p. 313—314.5 °C. Found (%): C, 61.38; H, 2.48. $C_{18}H_8S_4$. Calculated (%): C, 61.33; H, 2.29. UV ($CHCl_3$), λ_{max}/nm (ε): 257, 304. ^{1}H NMR, δ: 7.42 (t, 2 H, H(3), H(10), J = 8.0 Hz); 7.50 (t, 2 H, H(4), H(9), J = 8.0 Hz); 7.90 (d, 2 H, H(5), H(8), J = 8.0 Hz); 7.96 (d, 2 H, H(2), H(11), J = 8.0 Hz). ^{13}C NMR, δ: 120.6 (C(5), C(11)); 124.2 (C(2), C(14)); 124.6 (C(3), C(13)); 125.1 (C(4), C(12)); 127.7 (C(1), C(15)); 128.5 (C(6), C(8)); 133.2 (C(7), C(9)); 136.1 (C(16), C(18)); 136.3 (C(8)); 141.8 (C(17)). MS, m/z (I_{rel} (%)): 352 $[M]^+$ (100), 176 $[M]^{2+}$ (63).

Benzothiopheno[3″,2″:4′,5′]thieno[3′,2′:4,5]thieno[2,3-*b*]benzothiophene (25). Yield 25%, m.p. 244.5—245 °C. Found (%): C, 61.52; H, 2.27. $C_{18}H_8S_4$. Calculated (%): C, 61.33; H, 2.29. UV ($CHCl_3$), λ_{max}/nm (ε): 245. ^{1}H NMR, δ: 7.44 (t, 2 H, H(3), H(10), J = 7.7 Hz); 7.57 (t, 2 H, H(5), H(9), J = 7.7 Hz); 7.94 (d, 2 H, H(5), H(8), J = 8.0 Hz); 8.60 (d, 2 H, H(2), H(11), J = 8.0 Hz). ^{13}C NMR, δ: 123.4 (C(5), C(11)); 123.9 (C(2), C(14)); 124.0 (C(3), C(13)); 124.4 (C(4), C(12)); 130.8 (C(1), C(15)); 132.7 (C(6), C(8)); 133.0 (C(7), C(9)); 139.5 (C(16), C(18)); 140.1 (C(8)); 143.2 (C(17)).

Benzothiopheno[3″,2″:4′,5′]thieno[3′,2′:4,5]thieno[2,3-*b*]benzothiophene (25). To a solution of diisopropylamine (0.408 g, 4.02 mmol) in anhydrous THF (40 mL) cooled to −30 °C, 2.5 *M* BuLi in hexane (1.6 mL, 4 mmol) was added dropwise. The mixture was stirred until temperature raised to 0 °C and re-cooled to −78 °C, then powdered sulfur (0.128 g, 4 mmol) was added followed by slow addition of a solution of 2,2-dichloro-1,1-di(3-benzothienyl)ethene **22** (0.722 g, 2 mmol) in anhydrous THF (5 mL). The mixture was stirred at −78 °C for 1 h and at ambient temperature for 16 h. The reaction mixture was concentrated *in vacuo*. To the residue, anhydrous DMF (50 mL) was added and the mixture was heated at 80 °C for 6 h with stirring. The reaction was quenched with saturated aqueous NH_4Cl (50 mL) and the mixture was extracted with CH_2Cl_2 (3×100 mL). The organic layer was dried with Na_2SO_4, the solvent was removed *in vacuo*. Column chromatography of the residue (SiO_2, elution with hexane—CH_2Cl_2, 1 : 1) afforded 0.351 g (50%) of benzothiopheno[3″,2″:4′,5′]thieno[3′,2′:4,5]thieno[2,3-*b*]benzothiophene (**25**). Physicochemical parameters and spectral properties of compound **25** are in agreement with that of the sample synthesized by the general procedure (see above).

References

1. O. K. Kim, H. Y. Woo, K. S. Lee, K. S. Kim, K. S. Shim, C. Y. Kim, *Synth. Met.,* 2001, **121**, 1607.
2. G. M. Tsivgoulis, J. M. Lehn, *Angew. Chem., Int. Ed.*, 1995, **34**, 1119.
3. O. K. Kim, A. Fort, M. Barzoukas, M. Blanchard-Desce, J. M. Lehn, *J. Mater. Chem.*, 1999, **9**, 2227.
4. X. C. Li, H. Sirringhous, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat, R. H. Friend, *J. Am. Chem. Soc.*, 1998, **120**, 2206.
5. M. Fujitsuka, T. Sato, A. Watanabe, O. Ito, T. Shimidzu, *Chem. Lett.*, 1996, 285.
6. (a) K. Yu. Chernichenko, V. V. Sumerin, R. V. Shpanchenko, E. S. Balenkova, V. G. Nenajdenko, *Angew. Chem.*, *Int. Ed.*, 2006, **45**, 7367; (b) K. Yu. Chernichenko, E. S. Balenkova, V. G. Nenajdenko, *Mendeleev Commun.*, 2008, **18**, 171; (c) A. Dadvand, F. Cicoira, K. Yu. Chernichenko, E. S. Balenkova, R. M. Osuna, V. H. Jolin, F. Rosei, V. G. Nenajdenko, D. F. Perepichka, *Chem. Commun.*, 2008, 5354; (d) O. Ivasenko, J. M. MacLeod, K. Chernichenko, E. Balenkova, R. V. Shpanchenko, V. G. Nenajdenko, F. Rosei, D. F. Perepichka, *Chem. Commun.*, 2009, 1192; (e) S. S. Bukalov, L. A. Leites, K. A. Lyssenko, R. R. Aysin, A. A. Korlyukov, J. V. Zubavichus, K. Chernichenko, E. S. Balenkova, V. G. Nenajdenko, M. Yu. Antipin, *J. Phys. Chem. A.*, 2008, **112**, 10949; (f) K. Chernichenko, N. Emelyanov, I. Gridnev, V. G. Nenajdenko, *Tetrahedron*, 2011, **67**, 6812.

7. (a) V. G. Nenajdenko, V. V. Sumerin, K. Yu. Chernichenko, E. S. Balenkova, *Org. Lett.*, 2004, **6**, 3437; (b) R. Osuna, R. P. Ortiz, M. C. R. Delgado, V. G. Nenajdenko, V. V. Sumerin, E. S. Balenkova, V. Hernández, J. T. L. Navarrete, *ChemPhysChem.*, 2007, 745; (c) A. Rajca, H. Wang, M. Pink, S. Rajca, *Angew. Chem., Int. Ed.*, 2000, **39**, 4481.
8. (a) M. G. Voronkov, T. V. Lapina, *Khim. Geterotsikl. Soedin.*, 1965, 342 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1965, **1**, 224]; (b) M. G. Voronkov, V. E. Udre, *Khim. Geterotsikl. Soedin.*, 1965, 683 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1965, **1**, 458]; (c) M. G. Voronkov, V. E. Udre, E. P. Popova, *Khim. Geterotsikl. Soedin.*, 1967, 1003 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1967, **3**, 784]; (d) M. G. Voronkov, V. E. Udre, *Khim. Geterotsikl. Soedin.*, 1966, 527 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1966, **2**, 394]; (e) M. G. Voronkov, V. E. Udre, *Khim. Geterotsikl. Soedin.*, 1968, 43 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1968, **4**, 33].
9. P. Lucas, N. El Mehdi, H. H. Anh, D. Belanger, L. Breau, *Synthesis*, 2000, 1253.
10. (a) V. N. Korotchenko, V. G. Nenajdenko, A. V. Shastin, E. S. Balenkova, *Russ. Chem. Rev.*, 2004, **73**, 957 [*Usp. Khim.*, 2004, **73**, 1039]; (b) V. G. Nenajdenko, V. N. Korotchenko, A. V. Shastin, E. S. Balenkova, *Russ. Chem. Bull.* (*Int. Ed.*), 2004, **53**, 1034 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 991].
11. G. Komppa, S. Weckman, *J. Prakt. Chem.*, 1933, **138**, 109.
12. H. Rezaei, J. F. Normant, *Synthesis*, 2000, 109.
13. V. Mouries, R. Waschbuesch, J. Carran, P. Savignac, *Synthesis*, 1998, 271.
14. C. Broquet-Borgel, *Ann. Chim.*, 1958, **13**, 204.
15. O. Stephenson, W. A. Waters, *J. Chem. Soc.*, 1946, 339.
16. N. S. Nudelman, P. Outumuro, *J. Org. Chem.*, 1982, **47**, 4347.
17. E. Beckmann. O. Liesche, E. Correns, *Ber. Dtsch. Chem. Ges.*, 1923, **56**, 341.
18. E. Fischer, J. Larsen, J. B. Christensen, M. Fourmigue, H. G. Madsen, N. Harrit, *J. Org. Chem.*, 1996, **61**, 6997.
19. W. H. Cherry, W. Davies, B. C. Ennis, Q. N. Porter, *Aust. J. Chem.*, 1967, **20**, 313.
20. M. W. Farrar, R. Levine, *J. Am. Chem. Soc.*, 1950, **72**, 443.

Received May 23, 2012;
in revised form June 27, 2012