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Thiaheterohelicenes 2. Synthesis of Alkylated Thiaheterohelicenes

Jan Larsen and Klaus Bechgaard

Department of Solid State Physics, Macromolecular Chemistry Group, Risø National Laboratory, DK-4000 Roskilde, Denmark

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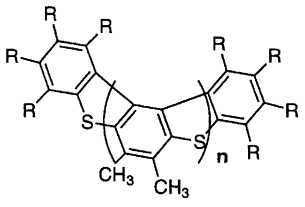
The alkylated thiaheterohelicenes 1,2,3,4,6,7,9,10,11,12-decamethyl-5,8-dithia[5]-helicene **1** and 6,7,9,10,12,13-hexamethyl-5,8,11,14-tetrathia[9]helicene **2** have been prepared by oxidative photolysis of 1,2-diaryl-substituted ethenes. The symmetrical ethenes used in the procedures were prepared by McMurry coupling. Unsymmetrical tetrasubstituted ethenes were obtained by nucleophilic addition of lithium arylates to 3-arylbutan-2-one and dehydration.

In our investigation of thiaheterohelicenes[1] we decided also to synthesize alkylated and peralkylated structures in order to obtain lower oxidation potentials.[2] A second reason was to gain access to potentially very one-dimensional solids, because alkylation will push the expected molecular stacks apart and decrease the interstack electronic interactions. In this paper we report the synthesis of compounds **1** and **2** and attempts to synthesise **3** (see Fig. 1).

McMurry coupling gives high yields and is an excellent tool for the preparation of symmetrically substituted ethenes.[3,4] Our general strategy was to use McMurry coupling to obtain 1,2-diarylated ethenes that were oxidatively photocyclized to give the helicenes. McMurry coupling and cyclizations as used in this paper give access to helicenes with an uneven number of alternating benzene and thiophene units in relatively few steps.

In the present work we also needed tetrasubstituted unsymmetrical ethenes. Normally one would use Wittig–Horner reactions for that purpose, but secondary phosphonate esters are difficult to obtain by the Michaelis–Arbuzov reaction or the Michaelis–Becker reaction. Instead we developed the reaction sequence described in Schemes 2 and 3. The key reaction was a Darzens glycidic ester synthesis which gave access to 3-arylated-butan-2-ones (such as **11**). Nucleophilic attack on the ketone by lithium arylates followed by dehydration gave the desired 1,2-diaryl-1,2-dimethylethenes.



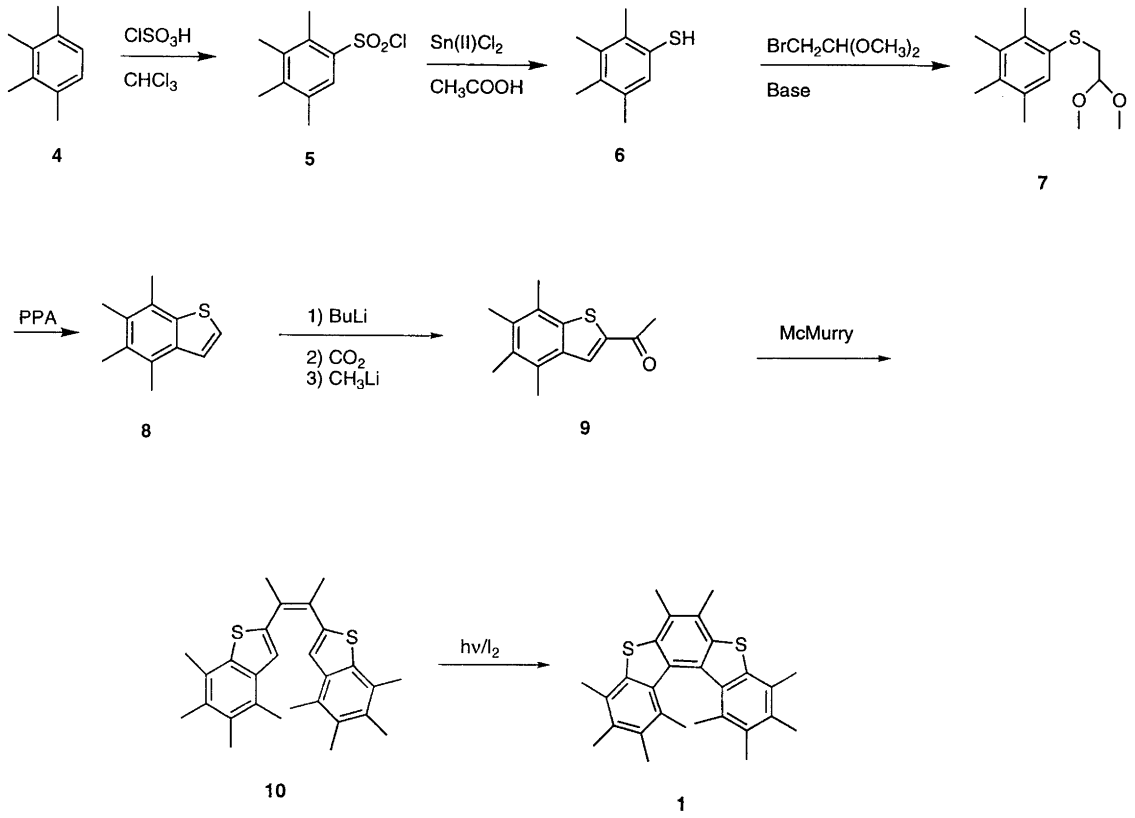
1 : n = 1, R = CH_3
2 : n = 3, R = H
3 : n = 3, R = CH_3

Fig. 1.

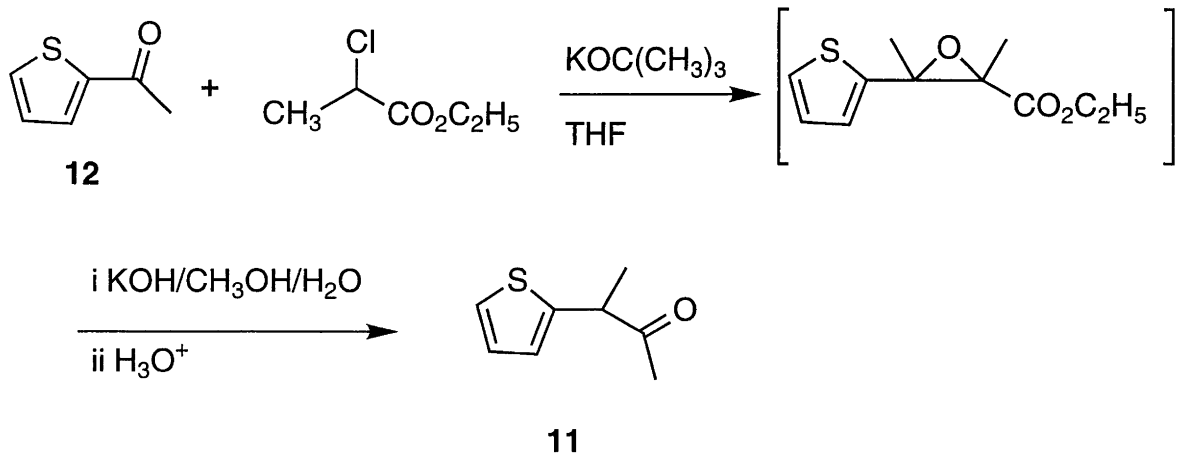
Results and discussion

1,2,3,4,6,7,9,10,11,12-Decamethyl-5,8-dithia[5]helicene, **1**, was synthesized as follows (see Scheme 1). 1,2,3,4-Tetramethylbenzene **4** was chlorosulfonated to **5** and reduced to give the thiol **6**. Alkylation of **6** with bromoacetaldehyde dimethylacetal gave **7**. Ring closure of **7** gave the benzothiophene **8** which was a key intermediate for the permethylated structures. Compound **8** was acetylated via the 2-lithio derivative to give the ketone, **9**. The ketone **9** was coupled to the symmetrical ethylene **10** which, on oxidative photocyclization, gave the thiahelicene **1**. The key intermediate *en route* to compounds **2** and **3** was 3-(thien-2-yl)butanone **11**, which was prepared as follows (see Scheme 2) 2-acetylthiophene **12** and 2-chloropropanoic ethyl ester in a Darzens glycidic ester reaction gave, after hydrolysis and decarboxylation, compound **11**.

In the preparation of compound 6,7,9,10,12,13-hexamethyl-5,8,11,14-tetrathia[9]helicene **2** (see Scheme 3) compound **11** was initially treated with the 2-lithio anion of benzo[*b*]thiophene **12** to give the intermediate alcohol which on treatment with acid gave the ethene **13**. Oxidative photolysis of compound **13** gave **14** which by lithia-



Scheme 1.

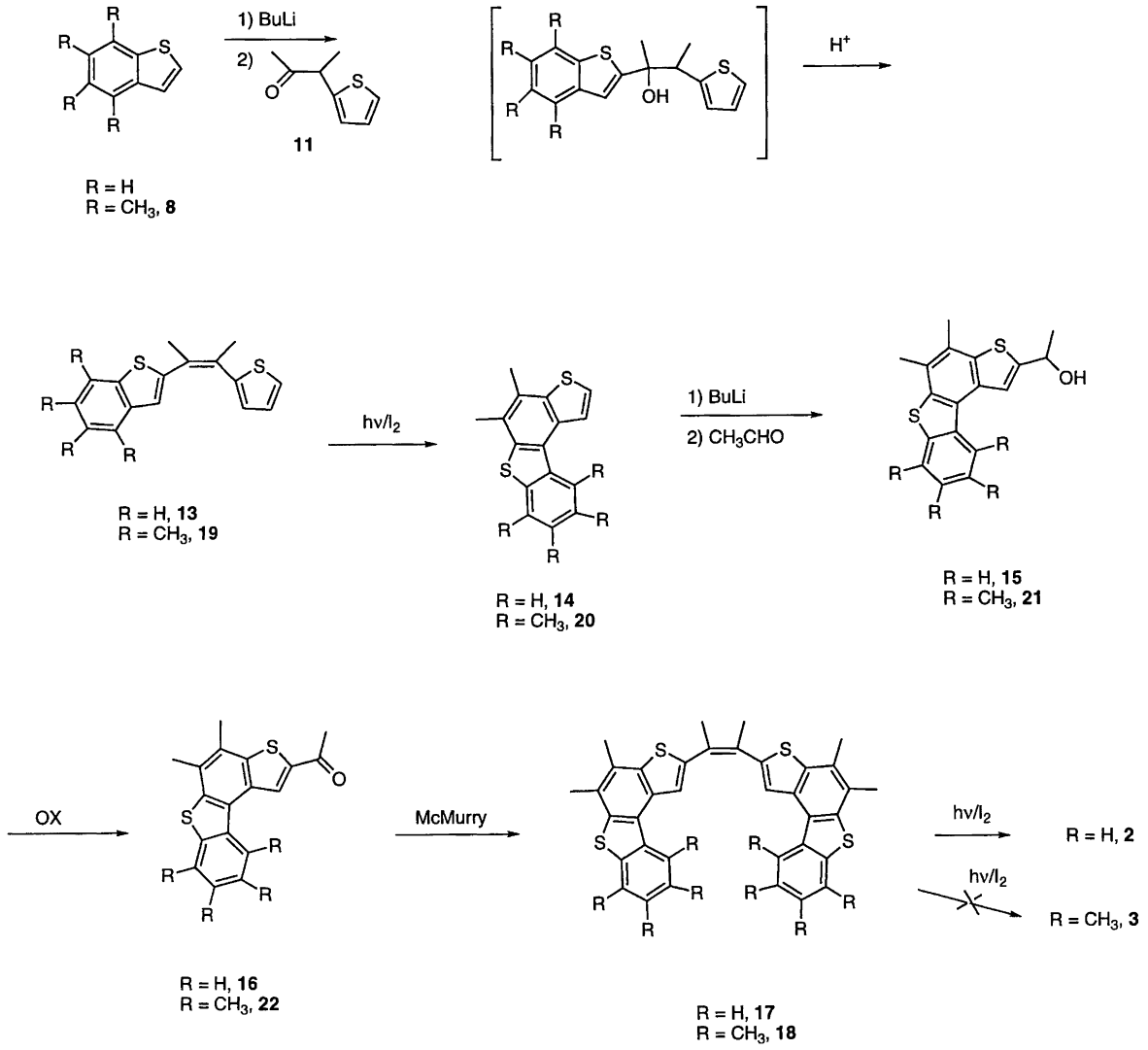


Scheme 2.

tion and treatment with ethanal was converted into the alcohol **15**. Oxidation of **15** gave the corresponding ketone **16**. McMurry coupling of compound **16** gave the ethene **17**. Oxidative photolysis of **17** then gave the desired thiaheterohelicene **2**. An identical sequence (Scheme 3) was used to prepare the permethylated compound **18** through compounds **19–22**. Compound **22** could, however, not be photolysed to give the permethylated helicene **3**.

Conclusions

McMurry coupling was used as to prepare symmetrical tetrasubstituted ethenes. Unsymmetrical 1,2-dimethyl-1,2-diaryl-substituted ethenes were obtained using 3-arylbutan-2-one as the intermediate. Oxidative photolysis as used extensively in this work failed to give compound **3** which can, however, be obtained by direct oxidation of **22**.[5]



Scheme 3.

Experimental

All compounds gave analytical results (C, H, N) within $\pm 0.3\%$ of the theoretical values unless otherwise indicated. Generally ^{1}H NMR and mass spectrometry was used to check the identity of new compounds. In some cases ^{1}H NMR spectra were not obtained owing to limited solubility of the compounds.

Photocyclization: general procedures. Two procedures for the photocyclizations were followed,[6] depending on the solubility of the starting materials.

1. The soluble compounds **10**, **13**, **19**. Approximately 6 g of the starting material were dissolved in 1.8 l of toluene and 0.5 equiv. of I_2 was added. The solution was irradiated with a Q-700 lamp at 20–30°C while air was bubbled through the solution. The irradiation was stopped when no more starting material was visible by TLC (alumina; petrol ether–toluene). The toluene solution was transferred to a conical flask containing sodium dithionite (5 g) and water (200 ml) and stirred for 1–2 h. The organic phase was dried with $MgSO_4$ and evaporated under vacuum to a volume of ca. 150 ml. The residue was filtered through a short column (5 × 10 cm) of alumina (Woelm, basic, super 1), evaporated to dryness and crystallized from heptane unless otherwise stated.

2. The insoluble compounds **17**, **18**. Approximately 0.5–1 g was suspended in 1.8 l of toluene and 0.5 equiv. of I_2 was added. The solution was irradiated with a Q-700 lamp at 50–60°C while air was bubbled through the solution. The irradiation was stopped 2 h after a homogeneous solution was formed. The reaction was worked up as described above, except that toluene was used for the final crystallization.

*1,2,3,4,6,7,9,10,11,12-Decamethyl-5,8-dithia[5]helicene (***1***).* 2,3-Bis(4,5,6,7-tetramethylbenzo[*b*]thiophen-2-yl)but-2-ene **10** was cyclized photochemically to **1** in 58% yield,

according to procedure 1.2 g of compound **10** were used and toluene was used for recrystallization. M.p. > 330°C. MS: *m/z* 430 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.95 (s, 6 H, CH_3), 2.31 (s, 6 H, CH_3), 2.42 (s, 6 H, CH_3), 2.62 (s, 6 H, CH_3), 2.68 (s, 6 H, CH_3).

*6,7,9,10,12,13-Hexamethyl-5,8,11,14-tetrathia[9]helicene (**2**).* 2,3-Bis(4,5-dimethylthieno[3,2-*a*]dibenzothiophen-2-yl)but-2-ene **17** was cyclized photochemically to give **2** in 56% yield, according to procedure 2. M.p. 328–329.5°C. MS: *m/z* 586 (M^+). ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 6 H, CH_3), 2.83 (s, 6 H, CH_3), 2.92 (s, 6 H, CH_3), 6.05 (m, 2 H, Ar), 6.89 (m, 1 H, Ar), 7.48 (d, 1 H, Ar).

*1,2,3,4,-Tetramethylbenzene (**4**)* was obtained from Aldrich and used as received.

*2,3,4,5-Tetramethylbenzenesulfonyl chloride (**5**).* To an ice-cooled solution of 1,2,3,4,-tetramethylbenzene **4** (88.75 g, 0.66 mol) in $CHCl_3$ (700 ml), was added dropwise chlorosulfonic acid (175 ml, 2.6 mol). After 30 min, the reaction was poured onto 1 kg of ice and the organic phase was washed with water (3 × 200 ml), dried with $MgSO_4$ and evaporated to dryness to give the benzenesulfonyl chloride **5** quantitatively. M.p. 72–73°C (Lit.[7] m.p. 72–73°C). ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 6 H, CH_3), 2.35 (s, 3 H, CH_3), 2.68 (s, 3 H, CH_3), 7.75 (s, 1 H, Ar).

*2,3,4,5-Tetramethylbenzenethiol (**6**).* A solution of $SnCl_2$ (380 g, 2.0 mol) in acetic acid (1.7 l) containing 30 ml of water was saturated with HCl, after which 2,3,4,5-tetramethylbenzenesulfonyl chloride **5** (140 g, 0.6 mol) was added in one portion. The reaction mixture reached 80–90°C and was kept at this temperature for 2 h. The mixture was then cooled to ambient temperature and poured into conc. hydrochloric acid (700 ml). The crude product was isolated by filtration and washed with water, dissolved in 10% NaOH (1.5 l) and washed with ether (3 × 300 ml) to remove impurities. The aqueous phase was then poured into conc. hydrochloric acid (500 ml) cooled to 10°C, filtered, washed with water and dried under vacuum over P_2O_5 to yield white crystals of **6** (85 g, 85%). M.p. 67–68°C. ^{1}H NMR ($CDCl_3$): δ 2.13 (s, 3 H, CH_3), 2.18 (s, 6 H, CH_3), 2.27 (s, 3 H, CH_3), 3.16 (s, 1 H, SH), 6.97 (s, 1 H, Ar).

*2,3,4,5-Tetramethylphenyl 2,2-dimethoxyethyl sulfide (**7**).* A solution of 2,3,4,5-tetramethylbenzenethiol **6** (35 g, 0.21 mol), 2-bromoacetaldehyde dimethyl acetal (39 g, 0.23 mol), and potassium carbonate (50 g) in dry acetone (200 ml) was refluxed overnight, cooled, poured into water (500 ml) and extracted with hexane (3 × 150 ml). The hexane was then washed with water (3 × 100 ml), dried with $MgSO_4$ and evaporated to give **7** quantitatively (53.5 g) as an oil. ^{1}H NMR ($CDCl_3$): δ 2.12 (s, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 2.96 (d, 2 H, CH_2), 3.30 (s, 6 H, OCH_3), 4.47 (t, 1 H, CH), 7.10 (s, 1 H, Ar).

*2,3,4,5-Tetramethylphenyl 2,2-dimethoxyethyl sulfide (**7**).* A solution of 2,3,4,5-tetramethylbenzenethiol **6** (35 g, 0.21 mol) and sodium (4.9 g, 0.21 mol) in dry DMF (200 ml) was stirred overnight, or until all the sodium had reacted. 2-Bromoacetaldehyde dimethyl acetal (39 g, 0.23 mol) was then added and the solution was heated to 70–80°C for 1.5 h, cooled and poured into water (500 ml) and extracted with hexane (3 × 150 ml). The hexane was then washed with water (3 × 100 ml) dried with $MgSO_4$ and evaporated to yield **7** quantitatively (53.5 g) as an oil.

*4,5,6,7-Tetramethylbenzo[b]thiophene (**8**).* A 200 ml two-necked bottle was charged with 85% polyphosphoric acid (75 ml) and equipped with an air-cooled downward condenser and a pressure equalizing addition funnel, charged with 2,3,4,5-tetramethylphenyl 2,2-dimethoxyethyl sulfide **7** (10 g, 0.039 mol). The bottle was then immersed in an oil bath preheated to 180°C and evacuated to 10 mmHg. The acetal was added dropwise over a period of 20 min, and the benzo[*b*]thiophene was collected as a white solid in the receiver. The solid was then dissolved in ether and washed with 10% $NaHCO_3$ and water and dried with $MgSO_4$ and evaporated. The solid was dissolved in cyclohexane and filtered through silica gel. Evaporation and crystallized from ethanol yielded white crystals of **8** (6.0 g, 80%). M.p. 124–125°C. ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 6 H, CH_3), 2.47 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 7.25 (d, 1 H, Ar), 7.35 (d, 1 H, Ar). MS: *m/z* 190 (M^+).

*2-Acetyl-4,5,6,7-tetramethylbenzo[b]thiophene (**9**).* To a solution of 4,5,6,7-tetramethylbenzo[*b*]thiophene **8** (3.8 g, 0.02 mol) in dry THF (75 ml) was added butyllithium (8 ml, 0.02 mol, 2.5 M in hexane) at −70°C. The solution was allowed to warm to −10°C and was then recooled to −70°C. Gaseous CO_2 (excess) was bubbled through the solution over 15 min. After the addition the solution was heated to gentle reflux for 10 min and then recooled to −70°C. Methyllithium (12 ml, 0.03 mol, 2.5 M in hexane) was added. After the addition, the solution was heated to 0°C and poured onto 0.2 l of ice. The aqueous phase was extracted with ether (3 × 75 ml). The combined organic phases were washed with water (2 × 75 ml), dried over $MgSO_4$, evaporated and crystallized from hexane to yield white **9**. Yield 45%, m.p. 176–177°C. ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 7.90 (s, 1 H, Ar).

*2,3-Bis(4,5,6,7-tetramethylbenzo[b]thiophen-2-yl)but-2-ene (**10**).* To dry THF (100 ml) at 0°C under an atmosphere of argon was added dropwise $TiCl_4$ (1.2 ml, 0.011 mol). Zinc dust (1.4 g, 0.021 mol) was added and the solution was refluxed for 2 h. Dry pyridine (0.7 ml) was added and the solution was refluxed. After 30 min, 2-acetyl-4,5,6,7-tetramethylbenzo[*b*]thiophene **9** (2.3 g, 0.01 mol) in dry THF (20 ml) was added and the solution was refluxed overnight. The solvent was removed under reduced pres-

sure and 50 g of ice and conc. HCl (75 ml) were added and the solution stirred for 30 min. The white precipitate was collected, washed with water and dried. The solid was dissolved in toluene and filtered through a short column of silica gel. The solvent was evaporated off to yield white crystals of **10** (2.15 g, 99%), mixture of *E* and *Z*. M.p. 280–283°C. This work-up procedure represents a substantial improvement, because the extraction procedure normally used gives suspensions. ^{1}H NMR ($CDCl_3$): δ 2.23 (s, 6 H, CH_3), 2.28 (s, 6 H, CH_3), 2.31 (s, 6 H, CH_3), 2.32 (s, 6 H, CH_3), 2.35 (s, 6 H, CH_3), 7.14 (s, 2 H, Ar).

*3-(Thien-2-yl)butanone (**11**).* To a solution of 2-acetylthiophene (70.6 g, 0.56 mol) and ethyl 2-chloropropionate (114.8 ml, 0.90 mol) in dry THF (500 ml) at −10°C was added dropwise over 2 h a solution of *t*-BuOK (100 g, 0.9 mol) in dry THF (200 ml). The solution was stirred overnight at room temperature. Ether (200 ml) and $NaHCO_3$ (200 ml) and water (100 ml) were added and the organic phase was further washed with 10% $NaHCO_3$ (3 × 150 ml), water (3 × 150 ml) and brine (2 × 150 ml) and dried over $MgSO_4$. The solvent was evaporated off to yield a slightly yellow-brown oil which was used in the following step without further purification. To the oil was added a solution of KOH (59.4 g, 85% KOH, 0.9 mol) in MeOH (300 ml) and the temperature was kept at 25–30°C until the next day. Ether (300 ml) and water (500 ml) were then added and H_3PO_4 (85%) was added dropwise until the mixture became acidic (ca. 160 ml). Next day hexane (300 ml) was added and the water phase was further extracted with hexane (200 ml). The combined organic phases were washed with water (2 × 100 ml) and $NaHCO_3$ (3 × 100 ml) and brine (2 × 100 ml) and dried over $MgSO_4$. Evaporation of the solvent followed by vacuum distillation afforded **11** as an oil (64 g, 74%), b.p. 95°C (12 mmHg). (Lit.[8] b.p. 150°C, 6 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.47 (d, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 4.01 (q, 1 H, CH), 6.89 (m, 1 H, Ar), 6.95 (m, 1 H, Ar), 7.18 (m, 1 H, Ar).

*2-(Benzo[b]thiophen-2-yl)-3-(thien-2-yl)but-2-ene (**13**).* To a solution of benzo[*b*]thiophene (27.0 g, 0.20 mol) in dry THF (100 ml) was added butyllithium (80 ml, 0.20 mol, 2.5 M in hexane) at −70°C. The solution was allowed to warm to −10°C and was then recooled to −30°C. 3-(2-Thienyl)butanone (34.0 g, 0.22 mol) in dry THF (100 ml) was added dropwise. After the addition, the solution was allowed to reach room temperature and then poured onto 0.5 l of ice. The aqueous phase was extracted with ether (3 × 100 ml) and the combined organic phases were washed with $NaHCO_3$ (2 × 100 ml), water (2 × 100 ml) and brine (100 ml). After drying with $MgSO_4$ evaporation gave 2(benzo[*b*]thiophen-2-yl)-3-(2-thienyl)-butan-2-ol as an oil that crystallized upon standing. M.p. 78–82°C. The product was dissolved in toluene (300 ml), *p*-toluenesulfonic acid (2 g) was added and water was removed with a Dean–Stark apparatus. After 3 h the solution was cooled and the organic phase washed with 10% $NaHCO_3$ (2 × 100 ml), water (2 × 100 ml) and brine (100 ml) and dried with $MgSO_4$. After evaporation under vacuum the solid was dissolved in 100 ml hexane and filtered through 10 cm of silica gel and the solvent was evaporated off to give **13** as a slightly yellow oil, yield 46.4 g (91.2%). The oil, which consisted of *E* and *Z* isomers crystallized upon standing. M.p. ca. 50°C and after recrystallizes from MeOH, m.p. 72–73°C. ^{1}H NMR ($CDCl_3$: δ 2.25 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 7.08 (m, 2 H, Ar), 7.14 (s, 1 H, Ar), 7.32 (m, 3 H, Ar), 7.73 (d, 1 H, Ar), 7.80 (d, 1 H, Ar).

*4,5-Dimethylthieno[3,2-a]dibenzothiophene (**14**).* 2-(Benzo[*b*]thiophen-2-yl)-3-(2-thienyl)but-2-ene **13** was cyclized photochemically to **14** in 75% yield, according to procedure 1. M.p. 125.5–126.5°C. MS: *m/z* 290 (M^+). ^{1}H NMR ($CDCl_3$): δ 2.60 (s, 3 H, CH_3), 2.90 (s, 3 H, CH_3), 7.47 (m, 2 H, Ar), 7.60 (d, 1 H, Ar), 7.90 (m, 1 H, Ar), 8.18 (d, 1 H, Ar), 8.45 (m, 1 H, Ar).

*1-(4,5-Dimethylthieno[3,2-a]dibenzothiophen-2-yl)ethanol (**15**).* To a solution of 4,5-dimethylthieno[3,2-*a*]dibenzothiophene **14** (9.9 g, 0.037 mol) in dry THF (500 ml) was added butyllithium (16.5 ml, 0.040 mol, 2.5 M in hexane) at −70°C. The solution was allowed to warm to −10°C and was then recooled to −70°C. Acetaldehyde (2.3 ml, 0.040 mol) was added dropwise. After the addition, the solution was heated to 0°C and poured onto 0.1 l of ice. The aqueous phase was extracted with ether (3 × 50 ml). The combined organic phases were washed with water (2 × 50 ml), dried over $MgSO_4$, evaporated and crystallized from hexane to yield white **15** (11.0 g, 95%), m.p. 200–205°C (decomp.). ^{1}H NMR ($CDCl_3$): δ 1.78 (d, 3 H, CH_3), 2.50 (s, 1 H, OH), 2.64 (s, 3 H, CH_3), 2.66 (s, 3 H, CH_3), 5.38 (q, 1 H, CH), 7.48 (m, 2 H, Ar), 7.95 (d, 1 H, Ar), 8.08 (s, 1 H, Ar), 8.48 (d, 1 H, Ar).

*2-Acetyl-4,5-dimethylthieno[3,2-a]dibenzothiophene (**16**).* To a solution of 1-(4,5-dimethylthieno[3,2-*a*]dibenzothiophen-2-yl)ethanol **15** (9.4 g, 0.03 mol) in CH_2Cl_2 (50 ml) was added pyridinium dichromate (15.8 g, 0.045 mol). The next day ether (100 ml) was added and the solution was filtered. The organic phase was washed with 2 M hydrochloric acid (3 × 50 ml) followed by water (2 × 50 ml) and dried over $MgSO_4$. The organic phase was reduced under vacuum to a volume of 50 ml and filtered through a short silica gel column. The solvent was evaporated off and the solid crystallized from heptane to yield white **16** (8.7 g, 94%). M.p. 227–228°C. ^{1}H NMR ($CDCl_3$): δ 2.60 (s, 6 H, CH_3), 2.75 (s, 3 H, CH_3), 7.53 (m, 1 H, Ar), 7.95 (d, 1 H, Ar), 8.41 (d, 1 H, Ar), 8.65 (s, 1 H, Ar).

*2,3-Bis(4,5-dimethylthieno[3,2-a]dibenzothiophen-2-yl)but-2-ene (**17**).* Same procedure as for compound **10** except that the ketone 2-acetyl-4,5-dimethylthieno[3,2-*a*]dibenzothiophene **16** (0.011 mol) was added as a solid and

that the filtration through the short column was omitted. Quantitative yield. M.p. > 330°C. MS: *m/z* 588 (M^+).

*2,3-Bis(4,5,7,8,9,10-hexamethylthieno[3,2-a]dibenzothiophen-2-yl)but-2-ene (**18**).* The same procedure was followed as for compound **10** except that the ketone 2-acetyl-4,5,7,8,9,10-hexamethylthieno[3,2-*a*]dibenzothiophene **22** (0.011 mol) was added as a solid and that the filtration through the short column was omitted. Quantitative yield. M.p. > 330°C. MS: *m/z* 700 (M^+).

*2-(4,5,6,7-Tetramethylbenzo[b]thiophen-2-yl)-3-(thien-2-yl)-but-ene (**19**).* As for compound **13**. 4,5,6,7-Tetramethylbenzo[*b*]thiophene **8** (0.10 mol) gave **19** in 89% yield. M.p. 117–117.5°C. ^{1}H NMR ($CDCl_3$): δ 2.25 (s, 6 H, CH_3), 2.26 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.40 (s, 6 H, CH_3), 6.82 (m, 2 H, Ar), 7.05 (m, 2 H, Ar).

*4,5,7,8,9,10-Hexamethylthieno[3,2-a]dibenzothiophene (**20**).* 2-(4,5,6,7-Tetramethylbenzo[*b*]thiophen-2-yl)-3-(thien-2-yl)butene **19** was cyclized photochemically to **20** in 76% yield, according to procedure 1. M.p. 234–236°C. ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 6 H, CH_3), 2.59 (s, 3 H, CH_3), 2.66 (s, 3 H, CH_3), 2.68 (s, 3 H, CH_3), 2.79 (s, 3 H, CH_3), 7.46 (d, 1 H, Ar), 7.87 (d, 1 H, Ar).

*1-(4,5,7,8,9,10-Hexamethylthieno[3,2-a]dibenzothiophen-2-yl)ethanol (**21**).* As for compound **15**, 4,5,7,8,9,10-hexamethylthieno[3,2-*a*]dibenzothiophene **20** (0.025 mol) gave **21** in 92% yield. M.p. 164–170°C. ^{1}H NMR ($CDCl_3$): δ 1.70 (d, 3 H, CH_3), 2.41 (s, 6 H, CH_3), 2.52 (s, 1 H, OH), 2.58 (s, 3 H, CH_3), 2.62 (s, 6 H, CH_3), 2.77 (s, 3 H, CH_3), 5.28 (q, 1 H, CH), 7.72 (s, 1 H, Ar).

*2-Acetyl-4,5,7,8,9,10-hexamethylthieno[3,2-a]dibenzothiophene (**22**).* As for compound **16**, 1-(4,5,7,8,9,10-hexamethylthieno[3,2-*a*]dibenzothiophen-2-yl)ethanol **21** (0.020 mol) gave **22** in 93% yield. M.p. 236–238°C. ^{1}H NMR ($CDCl_3$): δ 2.43 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 2.66 (s, 3 H, CH_3), 2.68 (s, 3 H, CH_3), 2.71 (s, 3 H, CH_3), 2.83 (s, 3 H, CH_3), 8.51 (s, 1 H, Ar).

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