One-Pot Syntheses of 2-*N*-Alkylamino-, 2-*N*-Phenylamino-2-*N,N*-Dialkylamino-, and 2-*N*-Alkyl-*N*-phenylaminothiophenes

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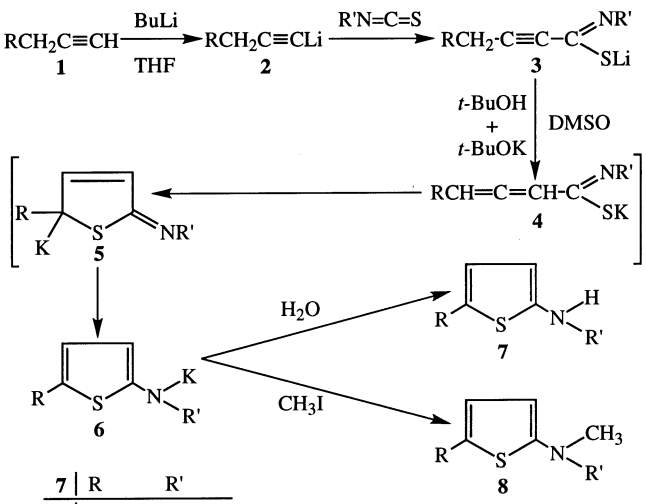
A number of 2-*N*-alkylamino- or 2-*N*-phenylamino-, 2-*N,N*-dialkylamino-, and 2-*N*-alkyl-*N*-phenylaminothiophenes have been prepared in good yields by adding a solution of *tert*-butylalcohol and potassium *tert*-butoxide in dimethylsulfoxide to a solution of the adduct from a lithiated 1-alkyne, $RCH_2C{\equiv}CLi$, or the lithiated allene, *t*BuCH=C=CHLi, and isothiocyanate, R′N=C=S, in tetrahydrofuran and subsequently hydrolyzing the reaction mixture or quenching it with methyl iodide.

Introduction

For simple thiophene derivatives having an amino substituent NRR′ (Rand R′ = H, alkyl or aryl) at the 2-position only a few efficient synthetic methods have been described. About ten years ago we reported in a short paper[1] the synthesis of 5-substituted 2-*N,N*-dialkylaminothiophenes from metallated allenic amines or metallated 1-propynylamines [$H_2C{=}C{=}C(M)NR_2$] with thiocarbonyl compounds such as *tert*-$BuC(=S)SCH_3$ and $(C_2H_5)_2NC(=S)$-SCH_3. A number of 2-*N,N*-dialkylaminothiophenes have been obtained by heating the corresponding thiols with a dialkylamine or a cyclic amine[2]. The *N,N*-disubstituted thiophenes have been used[3] for the synthesis of oligothiophenes that show interesting solvatochromatic phenomena.

Having found[4] that lithiated acetylenes $RCH_2C{\equiv}CLi$ smoothly add to isothiocyanates R′N=C=S with formation of the systems $RCH_2C{\equiv}C{-}C(SLi){=}NR'$, we wondered whether it would be possible under suitable conditions to convert the intermediary adducts into allenic intermediates $RCH{=}C{=}CH{-}C(SLi){=}NR'$ and subsequently to effect ring closure of the latter systems. Hydrolysis or *N*-alkylation finally could afford *N*-substituted or *N,N*-disubstituted thiophenes.

Scheme 1



7	R	R′
a	H	CH_3
b	H	C_2H_5
c	H	i-C_3H_7
d	CH_3	CH_3
e	H	Ph
f	CH_3	Ph
g	OCH_3	Ph

8	R	R′
a	H	CH_3
b	CH_3	CH_3
c	$(CH_3)_2N$	CH_3
d	CH_3	Ph
e	OCH_3	Ph

Results and Discussion

a. Synthesis of 2-Thienylamines from 1-Alkynes

The synthesis of 2-thienylamines was carried out as depicted in Scheme 1.

After preliminary experiments with 1-butyne and methyl isothiocyanate had shown that satisfactory results could be obtained by a one-pot procedure, the addition and cyclization were investigated separately with propyne, 1-butyne, methyl propargyl ether, methyl propargyl sulfide, and *N,N*-dimethyl propargylamine. Thus, the alkynes **1** were lithiated by standard procedures, after which the isothiocyanates were added. The efficiency of formation of the adducts **3** was determined by subsequent quenching with methyl iodide resulting in the formation of the Schiffs bases

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$RCH_2C{\equiv}C-C(SCH_3){=}NR'$. With all of the alkynyllithiums smooth reactions occurred at 20−30°C or slightly elevated temperatures. Addition of methyl iodide gave the expected Schiffs bases in high yields, except in the cases of the reaction of the lithiated methyl propargyl sulfide with isothiocyanates. Initially the latter addition reactions seemed to proceed normally, but after a relatively short period, during the addition of the isothiocyanate, a sudden exothermic reaction took place during which the solution turned very dark brown. Subsequent methylation afforded only intractable tarry material. No better results were obtained when the reactions were carried out at temperatures between 0 and 10°C. *tert*-Butyl isothiocyanate reacted relatively slowly with the lithiated acetylenes. In order to attain 50−60% conversion, it was necessary to heat the reaction mixtures for several hours under reflux. The additions were not noticiably promoted by (catalytic amounts of) copper(I)bromide. In a single case (R = CH_3, R′ = *iso*-C_3H_7) the reaction mixture was quenched with an aqueous solution of ammonium chloride giving the expected thioamide $RCH_2C{\equiv}C-C(=S)NHR'$ in a good yield. The product decomposed vigorously during attempted distillation in a high vacuum, but its identity appeared, except from the IR and NMR spectra, from its conversion into the Schiffs base $RCH_2C{\equiv}C-C(SCH_3){=}NHR'$ in a good yield by addition to an equivalent amount of potasium *tert*-butoxide in THF and subsequent quenching with methyl iodide.

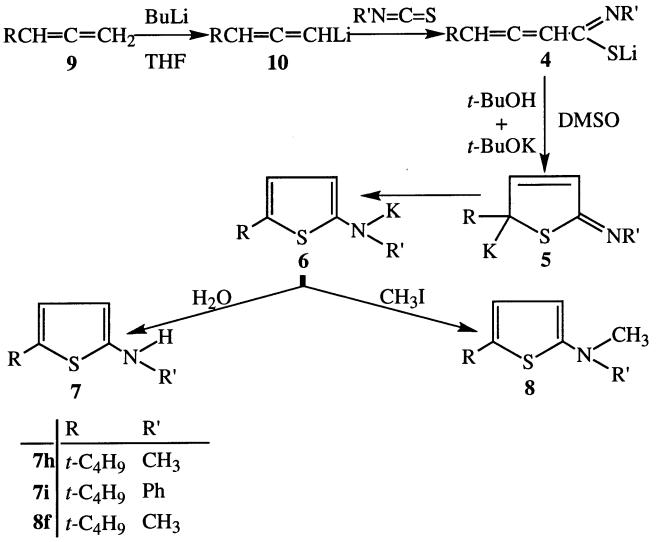
In order to effect cyclization of the intermediates **3**, an equivalent amount of *tert*-butylalcohol and a solution of an equivalent amount of potassium *tert*-butoxide in dimethylsulfoxide were successively added at temperatures between 0 and −10°C, after which the reaction mixtures were gradually warmed. The progress of the conversion was followed by regularly withdrawing samples from the reaction mixtures and quenching them with saturated aqueous ammonium chloride or methyl iodide. The cyclizations were considered to be complete, when in the GLC the peaks ascribed to the methylation products $RCH_2C{\equiv}C-C(SCH_3){=}NR'$ (in the cases of quenching with CH_3I), or other peaks, ascribed to the thioamides $RCH_2C{\equiv}C-C(C=S)NHR'$ or products of hydrolysis of **5** (in the cases of quenching with an ammonium chloride solution) had vanished and replaced by peaks of **8** and **7**, respectively. The one-pot procedures were then terminated by addition of methyl iodide or aqueous ammonium chloride affording **8** and **7** in satisfactory yields. The procedure with methyl propargyl ether and methyl isothiocyanate, however, gave only intractable tarry products. In the case of phenyl isothiocyanate, good results were obtained. Possibly, the adduct $CH_3OCH_2C{\equiv}CC(SLi){=}NCH_3$, can undergo a tele-elimination of methanol initiated by removal of a proton from the $=N-CH_3$ group and resulting in the very unstable cumulenic system $H_2C{=}C{=}C{=}C(SLi)-N{=}CH_2$. Another limitation of the scope of our synthetic method concerns the low stability of the product from the reaction of lithiated *N,N*-dimethyl propargylamine **2** [R = $(CH_3)_2N$] with methyl isothiocyanate (R′ = CH_3) and subsequent hydrolysis. During the removal of the solvent on the rotary evaporator the solution rapidly turned dark and in the last stage a vigorous decomposition reaction occurred resulting in tarry products. If, instead of hydrolysis, methylation with CH_3I was carried out, the stable 2,5-bis-(dimethylamino)thiophene **8c** [R = $(CH_3)_2N$, R′ = CH_3] was obtained in a good yield. Apparently the corresponding derivative **7** is extremely unstable.

After having obtained generally successful results, we have made some attempts to simplify the one-pot procedures by omitting the addition of either *tert*-butylalcohol or potassium *tert*-butoxide. While in the former case the cyclization seemed to proceed somewhat less readily, it was very slow in the absence of *t*BuOK.

b. Synthesis of Thienylamines from tert-Butylallene

From Scheme I it may be concluded that the intermediates with the structures **4** can also be generated by metallating allenes at the terminal carbon atom and subsequently adding an isothiocyanate. Therefore, similar one-pot procedures should be possible with allenic hydrocarbons **9** as starting compounds (Scheme 2).

Scheme 2



	R	R′
7h	*t*-C_4H_9	CH_3
7i	*t*-C_4H_9	Ph
8f	*t*-C_4H_9	CH_3

Allenes **9** (R = alkyl or cycloalkyl) are readily available by the copper(I)-catalyzed reaction of Grignard compounds with propargyl halides[5]. *tert*-Butylallene seemed a suitable substrate for testing the applicability of Scheme II as its lithiation (to give **10**) proceeds regiospecifically[5]. Primary alkylallenes are lithiated for 5−10% at the carbon atom next to the alkyl group. Performing the same sequence of operations as had been done with the 1-alkynes afforded the expected representatives **7** and **8** with R = *t*Bu in fair to good yields.

c. Stability of the Thienylamines Synthesized

In contrast to the parent compound 2-aminothiophene[6], the *N*-monosubstituted thiophenes **7** obtained by our method seem to be fairly thermostable. Nevertheless, after storage (under nitrogen) for a few days at room tempera-

ture, or even after some weeks at −20°C, the refractive indexes had increased considerably, while after redistillation 10−20% of undistillable material, possibly dimers, remained. Like aminothiophene[6] compounds **7** show a high sensitivity towards oxygen. Exposure of the compounds to air caused dark colours within one hour. The *N,N*-disubstituted thiophenes **8** are much more stable.

d. Concluding Remarks

Our one-pot procedures give access to a rather wide variety of 2-*N*-monosubstituted and 2-*N,N*-disubstituted thiophenes, not or less easily available by other methods.

Experimental Section

The isothiocyanates $CH_3N{=}C{=}S$, $C_2H_5N{=}C{=}S$, and $PhN{=}C{=}S$ were commercially available, $(CH_3)_2CH{-}N{=}C{=}S$ was prepared from isopropylamine, acetyl chloride and triethylamine in chloroform[7]. The preparation of *tert*-butylallene, methyl propargyl ether, and *N,N*-dimethyl propargylamine is described in refs.[4][5]. Tetrahydrofuran was dried by shaking with machine-powdered potassium hydroxide and subsequently distilling the filtered liquid from sodium sand/benzophenone. For all reactions dimethylsulfoxide with a water content <1% and potassium *tert*-butoxide free from complexed *tert*-butylalcohol (commercially available) were used. All reactions were carried out under nitrogen in flame-dried glass ware. For cooling a bath with liquid nitrogen (occasional cooling) was used. ^{1}H- and ^{13}C-NMR spectra (300 and 75 MHz, respectively) were recorded on a Bruker AC-300F apparatus, using solutions in deuterochloroform (ca. 20% $^v/_v$).

1. *Lithiation of 1-Alkynes or tert-Butylallene and Subsequent Reaction with Isothiocyanates [Preparation of Solutions of* **3** *(Scheme 1) or* **4** *(Scheme 2)]:* In a 500-ml round-bottomed, three-necked flask equipped with a gas inlet-thermometer combination, a mechanical stirrer and a dropping funnel-outlet combination, was placed a solution of 0.11 mol of *n*BuLi in ca. 70 ml of hexane. THF (70 ml) was added with cooling below 0°C. For the lithiation of the acetylenes the solution was cooled to −60°C, after which the acetylene (0.12 mol, propyne and 1-butyne as a mixture with 30 ml of THF, cooled at −50°C) was added within a few seconds. In the cases of propyne and dimethyl propargylamine suspensions were formed, the other acetylenes gave clear or almost clear (1-butyne) solutions. The lithiation of *tert*-butylallene was carried out by adding the allene (0.13 mol) in one portion at −65°C and subsequently stirring the reaction mixture for an additional half hour at −25 to −30°C. A clear solution was formed. Immediately after the addition of the acetylenes, the solutions or suspensions were warmed to +10°C and the isothiocyanate (0.10 mol) was added in one portion ($CH_3N{=}C{=}S$ in admixture with 10 ml of THF). The temperature of the mixtures was allowed to rise without external cooling. The reactions with the soluble acetylides proceeded rapidly within the range 20 to 35°C, in the cases of lithiated propyne and dimethyl propargylamine smooth conversions were observed after heating to 35 or 40°C. The reactions were terminated by stirring for an additional 15 min at 35 to 40°C or 45 to 50°C (lithiated propyne and dimethyl propargylamine). In all cases yellow or light-brown ($PhN{=}C{=}S$) solutions were formed. Lithiated *tert*-butylallene is much more reactive, therefore the temperature was kept between −85 and −100°C during the addition of the isothiocyanates (over 10 min). After the addition the temperature was allowed to rise (without external cooling) to −20°C.

2. *Preparation of the 2-N-Alkylamino- and 2-N-Phenylaminothiophenes* (**7**) *(Schemes 1 and 2):* The solution of **3** (Scheme 1) or **4** (Scheme 2) prepared as described in exp. *1* was brought at −15°C. *tert*-Butylalcohol (0.13 mol, in admixture with a few ml of diethyl ether) and a solution of 0.11 mol of potassium *tert*-butoxide in 50 ml of DMSO were successively added over a few sec. The reaction mixtures gradually turned dark-brown upon increasing the temperature. The reactions were followed by withdrawing small aliquots (ca. 1 ml), adding them to a mixture of 3 ml of diethyl ether and 3 ml of saturated aqueous ammonium chloride and making a gas-liquid chromatogram of the organic layer. After taking a sample, the reaction mixture was kept at −15°C during the times needed for GLC. After GLC had indicated completion of the conversions, the reaction mixtures were cooled to 0°C, then 150 ml of an aqueous solution of 30 g of ammonium chloride was added with vigorous stirring. The aqueous layer was extracted four times with small portions of a 1:1 mixture of ether and pentane. The combined organic solutions were washed twice with aqueous ammonium chloride (30 g / 150 ml), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. After one flash distillation at 1 mm Hg or lower pressure through a very short Vigreux column the products were carefully redistilled. Reaction times and temperatures, global indications of distillation temperatures in °C/mm Hg, and spectral data are mentioned below.

2-N-Methylaminothiophene (**7a**) *(Scheme 1):* Reaction time 40 min at 48°C; b.p. 50°C/1 mm Hg, (ref.[8] 88−92°C/15 mm Hg), n_D^{20} 1.5830, yield 65% (purity 96% GLC). − ^{1}H NMR: δ = 2.87 (s, 3 H), 3.80 (br.s, 1 H), 6.01 (dd, *J* = 3.6 and 1.4, 1 H), 6.46 (dd, 1 H), 6.74 (dd, *J* = 5.5, 1 H). − ^{13}C NMR: δ = 34.26, 103.08, 110.11, 126.21, 156.43. − C_5H_7NS (113.18): calcd. C 53.06, H 6.23, N 12.38, S 28.33; found C 53.10, H 6.09, N 12.44, S 28.50.

2-N-Ethylaminothiophene (**7b**) *(Scheme 1):* Reaction time 25 min at 50°C, b.p. 65°C/15 mm Hg, (ref.[8] 82−85°C/2−3 mm Hg), n_D^{20} 1.5630, yield 72% (purity 99.9% GLC). − ^{1}H NMR: δ = 1.26 (t, 3 H), 3.16 (q, *J* = 7.2, 2 H), 3.75 (br.s, 1 H), 6.04 (dd, *J* = 3.6 and 1.4, 1 H), 6.74 (dd, *J* = 5.5, 1 H), 6.46 (dd, 1 H). − ^{13}C NMR: δ = 14.77, 42.66, 103.81, 110.16, 126.11, 155.18. − C_6H_9NS (127.21): calcd. C 56.65, H 7.13, N 11.01, S 25.21; found C 56.54, H 7.18, N 11.01, S 25.10.

2-N-Isopropylaminothiophene (**7c**) *(Scheme 1):* Reaction time 40 min at 45°C, b.p. 56°C/1 mm Hg, n_D^{20} 1.5438, yield 78% (purity 99.5% GLC). − ^{1}H NMR: δ = 1.22 (d, 6 H), 3.45 (m, *J* = 6.3, 1 H), 3.60 (br.s, 1 H), 6.04 (dd, *J* = 3.6 and 1.4, 1 H), 6.47 (dd, 1 H), 6.71 (dd, *J* = 5.5, 1 H). − ^{13}C NMR: δ = 22.91, 49.40, 105.48, 110.84, 126.06, 154.18.

2-N-Methylamino-5-methylthiophene (**7d**) *(Scheme 1):* Reaction time 30 min at 45°C, b.p. 60°C/1.5 mm Hg, n_D^{20} 1.5645, yield 61% (purity 100% GLC). − ^{1}H NMR: δ = 2.34 (d, *J* = 1.1, 3 H), 2.83 (s, 3 H), 3.65 (br.s, 1 H), 5.80 (d, *J* = 2.6, 1 H), 6.36 (dd, *J* = 3.6 and 1.1, 1 H). − ^{13}C NMR: δ = 15.03, 34.23, 102.86, 123.33, 124.81, 154.02. − C_6H_9NS (127.21): calcd. C 56.65, H 7.13, N 11.01, S 25.21; found C 56.73, H 7.00, N 11.08, S 25.15.

2-N-Phenylaminothiophene (**7e**) *(Scheme 1):* Reaction time 30 min at 42°C, b.p. 110°C/0.5 mm Hg, n_D^{20} 1.6555, yield 63% (purity 98.3% GLC). − ^{1}H NMR: δ = 5.61 (br.s, 1 H), 6.74 (ddd, *J* = 0.8, 1.4, 3.6), 6.86 (m), 6.89 (m,), 6.90 (dd, *J* = 5.8), 6.94 (dd), 7.24 (m). − ^{13}C NMR: δ = 114.44, 119.00, 119.09, 119.72, 125.77, 129.24, 145.81, 145.89. − $C_{10}H_9NS$ (175.25): calcd.68.54, H 5.18, N 7.99, S 18.30; found C 68.35, H 5.20, N 8.00, S 18.41.

2-N-Phenylamino-5-methylthiophene (**7f**) *(Scheme 1):* Reaction time 15 min at 40°C, b.p. 120°C/0.5 mm Hg, n_D^{20} 1.6335, yield 85% (purity 100% GLC). − ^{1}H NMR (CCl_4): δ = 2.44 (d, *J* = 0.8, 3 H), 5.2 (br.s, 1 H), 6.53−6.58 (m), 6.79−6.86 (m), 7.21 (m). −

^{13}C NMR: δ = 15.69, 114.66, 119.29, 120.56, 123.26, 129.15, 134.47, 142.76, 146.50. − $C_{11}H_{11}NS$ (189.28): calcd. 69.80, H 5.86, N 7.40, S 16.94; found C 69.79, H 5.85, N 7.37, S 16.90.

2-N-Phenylamino-5-methoxythiophene (**7g**) *(Scheme 1):* Reaction time 15 min at 45°C, b.p. 155°C/0.5 mm Hg, n_D^{20} 1.6266, yield 55% (purity 99% GLC). − ^{1}H NMR: δ = 3.88 (s, 3 H), 5.35 (br.s, 1 H), 5.99 (d, *J* = 3.9, 1 H), 6.48 (d, 1 H), 6.70−6.86 (m, 4 H), 7.20 (m, 1 H). − ^{13}C NMR: δ = 59.81, 101.57, 113.71, 119.16, 121.41, 129.14, 131.58, 147.28, 161.92. − $C_{11}H_{11}NOS$ (205.28): calcd. C 64.36, H 5.40, N 6.82, S 15.62; found C 64.21, H 5.40, N 6.84, S 15.67.

2-N-Methylamino-5-tert-butylthiophene (**7h**) *(Scheme 2):* Reaction time 60 min at 45°C, b.p. 90°C/2 mm Hg, n_D^{20} 1.5323, yield 43% (purity 99% GLC). − ^{1}H NMR: δ = 1.32 (s, 9 H), 2.84 (s, 3 H), 3.65 (br.s, 1 H), 5.80 (d, *J* = 3.8, 1 H), 6.41 (d, 1 H). − ^{13}C NMR: δ = 32.23, 34.00, 34.21, 102.30, 119.36, 142.34, 153.52. − $C_9H_{15}NS$ (169.29): calcd. C 63.85, H 8.93, N 8.27, S 18.94; found C 63.95, H 8.80, N 8.30, S 18.90.

2-N-Phenylamino-5-tert-butylthiophene (**7i**) *(Scheme 2):* Reaction time 40 min at 48°C, b.p. 135°C/0.5 mm Hg, n_D^{20} 1.5948, yield 87% (purity 100% GLC). − ^{1}H NMR: δ = 1.40 (s, 9 H), 5.30 (br.s, 1 H), 6.58 (d, *J* = 3.9, 1 H), 6.63 (d, 1 H), 6.82−6.89 (m, 4 H), 7.23 (m, 1 H). − ^{13}C NMR: δ = 32.23, 34.00, 34.21, 102.30, 119.36, 142.54, 153.52. − $C_{14}H_{17}NS$ (231.36): calcd. C 72.768, H 7.41, N 6.05, S 13.86; found C 72.63, H 7.30, N 6.12, S 13.94.

The IR spectra of the *N*-monosubstituted thiophenes showed inter alia an absorption at approximately 3390 cm^{-1} (NH).

3. *Preparation of 2-N,N-Disubstituted Thiophenes* (**8**) *(Schemes 1 and 2):* For the lithiation of the acetylenes or *tert*-butylallene, the addition of the lithio compounds to the isothiocyanates and the cyclization of the adducts the procedure described in exps. *1* and *2* was followed. The cyclization reaction was monitored by quenching 1-ml samples of the reaction mixtures with aqueous ammonium chloride, followed by gas liquid chromatography of the organic layers. In a few cases quenching with methyl iodide gave a clearer indication of the progress of the cyclizations. After completion of the cyclization the reaction mixture was cooled to −5°C and methyl iodide (30 g, large excess) was added over 10 min while gradually allowing the temperature of the reaction mixture to rise to <25°C. After the addition the reaction mixture was stirred for 5 min at 50°C, then 150 ml of an aqueous solution of 30 g ammonium chloride was added. The products were isolated as described for compounds **7** in exp. *2*.

2-N,N-Dimethylaminothiophene (**8a**) *(Scheme 1):* Reaction time 1 h at 50−55°C, b.p. 70°C/10 mm, (ref.[9] 66−69°C/9 mm Hg), n_D^{20} 1.5560, yield 67% (purity 96.3% GLC). − ^{1}H NMR: δ = 2.97 (s, 6 H), 5.99 (dd, *J* = 3.9 and 1.4, 1 H), 6.56 (dd, 1 H), 6.85 (dd, *J* = 6.0, 1 H). − ^{13}C NMR (75 MHz): δ = 43.11, 102.61, 110.22, 126.44, 159.51. − C_6H_9NS (127.21): calcd. C 56.65, H 7.13, N 11.01, S 25.21; found C 56.38, H 7.16, N 11.08, S 25.31.

2-N,N-Dimethylamino-5-methylthiophene (**8b**) *(Scheme 1):* Reaction time 30 min at 40°C, b.p. 80°C/10 mm Hg, n_D^{20} 1.5426, yield 74% (purity 93.1% GLC), (ref.[9] b.p.75°C/10 mm Hg, n_D^{24} 1.5425). − ^{1}H NMR: δ = 2.3 (d, *J* = 1.0, 3 H), 2.94 (s, 6 H), 5.80 (d, *J* = 3.6, 1 H), 6.36 (dq, 1 H). − ^{13}C NMR: δ = 14.56, 43.17, 102.71, 123.55, 124.86, 157.37. − $C_7H_{11}NS$ (141.24): calcd. C 59.53, H 7.85, N 9.92, S 22.70; found C 59.41, H 7.75, N 9.97, S 22.65.

2,5-Bis(dimethylamino)thiophene (**8c**) *(Scheme 1):* Reaction time 10 min at 15°C, b.p. 80°C/0.7 mm Hg, n_D^{20} 1.5561, yield 73% (purity 97.5% GLC). − ^{1}H NMR: δ = 2.75 (s, 12 H), 5.69 (s, 2 H). − ^{13}C NMR: δ = 44.19, 104.28, 149.21. − $C_8H_{14}N_2S$ (170.28): calcd. C 56.43, H 8.29, N 16.45, S 18.83; found C 56.30, H 8.24, N 16.50, S 18.94.

2-N-Methyl-N-phenylamino-5-methylthiophene (**8d**) *(Scheme 1):* Reaction time 15 min at 40°C, b.p. 110°C/1 mm Hg, n_D^{20} 1.6131, yield 85% (purity 100% GLC). − ^{1}H NMR: δ = 2.40 (d, 3 H), 3.25 (s, 3 H), 6.47 (d, *J* = 3.6, 1 H), 6.50 (dq, *J* = 1.0, 1 H), 6.80 (m), 6.86 (m, 4 H), 7.19 (m, 1 H). − ^{13}C NMR: δ = 15.85, 41.70, 115.07, 119.05, 120.60, 123.11, 128.77, 134.96, 149.34, 150.48. − $C_{12}H_{13}NS$ (203.31): calcd. 70.89, H 6.45, N 6.89, S 15.77; found C 70.90, H 6.35, N 6.94, S 15.78.

2-N-Methyl-N-phenylamino-5-methoxythiophene (**8e**) *(Scheme 1):* Reaction time 10 min at 40°C, b.p. 130°C/0.6 mm Hg, n_D^{20} 1.6085, yield 80% (purity 100% GLC). − ^{1}H NMR: δ = 3.22 (s, 3 H), 3.82 (s, 3 H), 5.93 (d, *J* = 3.9), 6.41 (d, 1 H), 6.78 (m, 4 H), 7.19 (m, 1 H). − ^{13}C NMR: δ = 41.56, 59.68, 101.15, 114.06, 118.56, 120.89, 128.75, 139.19, 149.47, 162.12. − $C_{12}H_{13}NOS$ (219.31): calcd. C 65.72, H 5.98, N 6.39, S 14.62; found C 65.75, H 5.91, N 6.42, S 14.60.

2-N,N-Dimethylamino-5-tert-butylthiophene (**8f**): Reaction time 20 min at 60°C, b.p. 70−75°C/1 mm Hg, n_D^{20} 1.5242, yield 62% (purity 93.1% GLC), (ref.[1] b.p. 55°C/0.1 mm Hg, n_D^{20} 1.5219). − ^{1}H NMR: δ = 1.31 (s, 9 H), 2.82 (s, 6 H), 5.68 (d, *J* = 3.6, 1 H), 6.42 (d, 1 H). − $C_{10}H_{17}NS$ (183.32): calcd. C 65.52, H 9.35, N 7.64, S 17.49; found C 65.38, H 9.30, N 7.70, S 17.53.

[1] R.L.P. de Jong, L. Brandsma, *J. Organometal. Chem.* **1986**, *316*, C21−C23.
[2] H. Hartmann, S. Scheithauer, *J. Prakt. Chem.* **1969**, *311*, 827−843.
[3] [3a] F. Effenberger, F. Würthner, F. Steybe, *J. Org. Chem.* **1995**, *60*, 2082−2091. − [3b] F. Effenberger, F. Würthner, *Angew. Chem.* **1993**, *105*, 742−744; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 719−721.
[4] L. Brandsma, *Preparative Acetylenic Chemistry*, 2nd ed., Elsevier, Amsterdam, **1988**.
[5] L. Brandsma, H.D. Verkruijsse, *Synthesis of Acetylenes, Allenes and Cumulenes*, A Laboratory Manual, Elsevier, Amsterdam, **1981**.
[6] D.L. Eck, G.W. Stacy, *J. Heterocycl. Chem.* **1969**, *6*, 147−151.
[7] N.A. Nedolya, to be published; compare B.A. Trofimov, M.G. Voronkov, N.A. Nedolya, V.V. Gerasimova *Chem. Abstr.* **1988**, *109*, 230297a (U.S.S.R. SU 1,384,576).
[8] W. Steinkopf, *Justus Liebigs Ann. Chem.* **1914**, *403*, 17−44.
[9] E.B. Pedersen, S.-O. Lawesson, *Tetrahedron* **1974**, *30*, 875−878.
[97254]