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Ring-opening Reactions of Heterocyclic Organometallics. VI.* The Regio- and Stereospecific Synthesis of Alkylthiovinyl Acetylenes

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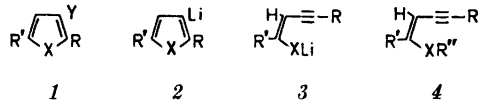
It has been found that 2,5-dialkyl-3-thienyllithium derivatives, prepared through halogen-metal exchange between the corresponding bromo or iodo heterocycles and alkyllithium reagents, ring-open to thioenynes (*3*), which with the alkyl halide formed in the halogen-metal exchange and added in excess give alkylthiovinyl acetylenes (*4*). If the halogen-metal exchange is carried out with phenyllithium, alkylation of *3* can be carried out with other alkylating agents (dimethyl sulfate, ethyl bromoacetate, benzyl chloride).

From ring-opening experiments with 3-bromo-2-ethyl-5-methyl- and 3-bromo-5-ethyl-2-methylthiophene, as well as with 3-bromo-2-*t*-butyl-5-methyl- and 3-iodo-5-*t*-butyl-2-methylthiophene, it was demonstrated that these reactions formally correspond to a strictly regio- and stereospecific addition of thiolates to unsymmetrically substituted diacetylenes. It is also shown that the addition of ethylthiolate to 2,5-heptadiyne is not regiospecific. From 2,4,5-trimethyl-3-thienyllithium a fully substituted vinylacetylenic thioether, which cannot be prepared by thiolate addition to diacetylenes, was obtained.

By-products formed in the ring-opening reactions have been identified.

The synthesis of the thiophenes used as starting materials is described.

Some years ago, we discovered that *2a*, prepared through halogen-metal exchange between 2,5-dimethyl-3-iodoselenophene (*1a*) and ethyllithium, ring-opened even at −70 °C to give *3a*, which was alkylated to yield *4a*, by the ethyl iodide formed in the halogen-metal exchange.[1] We also found that when *2b*, prepared from *1b* and methyllithium, was refluxed in ether for 2 h and then hydrolyzed, a 42 % yield of *4b* was obtained *via* the thiolate *3b*.[2] It followed from experiments with 3-selenienyllithium and 3-thienyllithium in the presence of ethyl bromide, which gave (*Z*)-1-ethylseleno-1-buten-3-yne and (*Z*)-1-ethylthio-1-buten-3-yne, that the ring-opening was stereospecific.[3]



1 *2* *3* *4*

Scheme 1.

a, R=R′=CH_3, R″=C_2H_5, X=Se, Y=I;
b, R=R′=CH_3, R″=CH_3, X=S, Y=I;
c, R=R″=C_2H_5, R′=CH_3, X=S, Y=Br;
d, R=CH_3, R′=R″=C_2H_5, X=S, Y=Br;
e, R=$C(CH_3)_3$, R′=CH_3, R″=C_2H_5, X=S, Y=Br;
f, R=CH_3, R′=$C(CH_3)_3$, R″=C_2H_5, X=S, Y=I.

The formation of *4a* and *4b* formally corresponds to the addition of ethaneselenol and methanethiol respectively to a symmetrically disubstituted diacetylene (*i.e.* 2,4-hexadiyne). The addition of ethanethiol to such diacetylenes under alkaline conditions has been studied by Russian workers.[5–7] In this way *4b* (R″=C_2H_5) was prepared but the stereochemistry of the addition was not discussed. It is known from the work of Truce *et al.*[8,9] that this addition is predominantly *trans* with monoacetylenic compounds. However, it has been shown that in substituted diacetylenes containing one polar group such as carboxyl [10] or hydroxymethyl,[11] the *trans*-stereospecificity of the addition was

* Part V. see Ref. 36.
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*** Taken in part from the Ph.D. thesis of T. Frejd, Lund 1975.

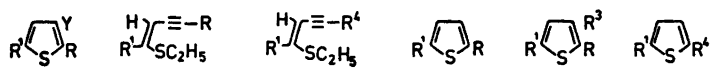
lost, leading to mixtures of *Z*- and *E*-thioenynes. However, the regiospecificity was good and determined by the electronic properties of the substituent, the nucleophile attacking the most electron-deficient terminal carbon of the triple bond array.[10,11] Petrov *et al.*[7] also claimed that ethanethiolate added exclusively to the acetylenic carbon bearing the *t*-butyl and isopropyl group of 6,6-dimethyl-2,4-heptadiyne and 6-methyl-2,4-heptadiyne. (However, *cf.* below.)

Ring-opening reactions. We were therefore interested in investigating the general applicability of the ring-opening reaction for the synthesis of alkylthiovinyl acetylenes, corresponding to a formal regio- and stereospecific addition of thiolates to unsymmetrically disubstituted diacetylenes.

By adding ethyllithium rapidly to *1c* at room temperature, and then adding an excess of ethyl iodide to the reaction mixture, a 60 % yield of *4c* could be isolated. In an analogous way, *1d*, *1e*, and *1f* gave *4d*, *4e*, and *4f*, respectively. The yields obtained are given in Table 1.

We have also found that the addition of ethylthiolate to an unsymmetrically disubstituted diacetylene, in which the two substituents are similar, does not occur regiospecifically. Thus, addition of ethylthiolate to 2,4-heptadiyne, following the procedure of Petrov *et al.*,[7] gave a mixture of 60 % of *4c* and 40 % of *4d* according to GLC analysis. The fact that ethylthiolate shows a weak preference for the methyl bearing carbon of 2,4-heptadiyne, made us therefore doubt the previously mentioned results obtained by Petrov *et al.*[7] These authors claimed that only *4f* was obtained in the addition of ethylthiolate to 6,6-dimethyl-2,4-heptadiyne through an attack on the *t*-butyl carrying carbon. They suggested this structure as they considered the observed methyl long-range coupling to be too small to be that expected for *4e*. They explained this result by assuming that the propagation of the stronger +I-effect of the branched alkyl groups through the π-bond system made the methyl-bearing carbon more electron-rich than the *t*-butyl-bearing carbon. Steric effects on the orientation were not considered. However, we found that the IR spectrum of the product published by these authors was identical with that of *4e* and not of *4f* prepared by

Table 1. Reaction product analysis of the ring-opening experiments on compounds *1c*–*1f* with equivalent amounts of ethyllithium at 21 °C. Reaction time: 4 h. Conditions: A, a fivefold excess of ethyl iodide; B, no ethyl iodide added. Uncalibrated GLC values; isolated yields in parentheses.



1 *4* *5, 8* *6, 10* *11, 12* *7, 9*

Starting material	Cond.	Products and yield (%)			
R=C_2H_5, R^1=CH_3, R^4=$CH(CH_3)C_2H_5$, Y=Br					
1c	A	*4c* 75 (60)	*5* 20	*6* 3	*7* 2
	B	*4c* 31	*5* 3	*6* 57	*7* 9
R=CH_3, R^1=C_2H_5, R^4=C_3H_7, Y=Br					
1d	A	*4d* 79 (64)	*8* 11	*6* 8	*9* 2
	B	*4d* 24	*8* 6	*6* 51	*9* 19
R=$C(CH_3)_3$, R^1=CH_3, R^3=C_2H_5, Y=Br					
1e	A	*4e* 90		*10* 10	*11*
	B	*4e* 40		*10* 55	*11* 2
R=CH_3, R^1=$C(CH_3)_3$, R^3=C_2H_5, X=I					
1f	A	*4f* 50 (35)		*10* 4	*12* 46 (33)
	B	*4f* 23		*10* 60	*12* 17

us. Their experiment was repeated and it was found by careful GLC analysis that *4e* was formed exclusively and in 65 % yield. We found that the coupling constant of the ethylenic methyl protons and the ethylenic proton of *4e* was 1.4 Hz (allylic coupling) and that of the acetylenic methyl protons and the ethylenic proton of *4f* was 2.4 Hz.

It is obvious that the ring-opening reactions are of value for the synthesis of the sterically most unfavourable of two possible isomers of alkylthiovinyl acetylenes.

6,6-Dimethyl-2,4-heptadiyne was prepared in 58 % yield by treating *21* with two equivalents of ethereal ethyllithium and ethyl iodide. When the same reagents were applied to 3,4-diiodo-2,5-dimethylthiophene,[13] a 54 % yield of 2,4-hexadiyne was obtained. This type of ring-opening was first observed by Wittig and Rings[14] with 3,4-diiodo-2,5-diphenylthiophene.

Since several by-products were formed in some of the ring-openings, a more detailed product analysis was undertaken in the experiments with *1c–1f*. Two sets of experimental conditions were used: one with an excess (fivefold) of ethyl iodide (A) and the other without added ethyl iodide (B). All experiments were run with one equivalent of ethyllithium per equivalent of haloheterocycle at room temperature for 4 h whereupon water was added. The results are given in Table 1. An excess of ethyl iodide must apparently be used to obtain acceptable yields of *4e–4f*. The dehalogenated heterocycles *6* and *10*, which become the main products if excess ethyl iodide is not used, most probably arise from protonation of the enynethiolates *3c–3f*. Intramolecular addition of the resulting thiols to the triple bond then leads to *6* and *10*. It has been demonstrated by NMR studies that the ring-opening of the 3-thienyllithium derivatives (*2b*, *2e–f*) is complete[15] and it is therefore unlikely that *6* and *10* are formed by protonation of *2c–f*. It is evident that the S_N2 *S*-alkylation of *3c–f* is relatively slow so that, in the absence of excess ethyl iodide, alkylation is far from complete after 4 h.

In the reaction of *1f* large amounts of *12* were formed, and isolated when excess ethyl iodide was used. The reason for this became evident when a kinetic study of the ring-opening reaction was carried out.[15] The ring-opening of *2f* was rather slow, so that Wurtz-Fittig coupling of *2f* with ethyl iodide could successfully compete. This side-reaction could also occur in other cases, where the ring-opening is slow. It should, however, be possible to avoid it by carrying out the halogen-metal exchange with phenyllithium (*cf.* below). It has been previously demonstrated that 2-thienyllithium undergoes Wurtz-Fittig coupling with various alkyl halides.[16] A few percent of the coupling product were also formed in the reaction of *1e*. However, the presence of *11* was only indicated by combined GLC-MS spectrometry. The mass spectrum was rather weak, which made the interpretation of the fragmentation pattern unreliable, and the structure is accordingly uncertain.

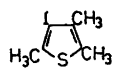
With the ethyl derivatives *1c* and *1d* other types of by-products were observed. Thus in the reaction of *1c* with ethyllithium and excess ethyl iodide, 20 % of *5* and 2 % of *7* were obtained. When equivalent amounts of ethyl iodide were used, the relative amounts were reversed and 3 % of *5* and 9 % of *7* were formed. Similarly, *8* and *9* were formed in the reaction of *1d* and showed the same variation with the amount of ethyl iodide as mentioned above (*cf.* Table 1).

The formation of *5* and *7* is certainly due to deprotonation of a propargylic CH_3 group by ethyllithium or the thienyllithium present, followed by *C*- and *S*-alkylation by ethyl iodide. It is well known that propargylic CH_3 groups are quite acidic.[17] The fact that *7* and *9* are formed in larger amounts when only equivalent amounts of ethyl iodide are used indicates that *C*-alkylation of the propargylic anion is more rapid than *S*-alkylation, the homologous enynethiolates ring-closing to the thiophenes *7* and *9*, upon hydrolysis.

The evidence for the formation of *5* was only its mass spectrum and its slightly longer GLC retention time compared to *4c*. The compound *8*, on the other hand, was isolated and gave a satisfactory ^1H NMR spectrum showing the propyl grouping. Its mass and IR spectra also confirmed the structure. The formation of *9* was proven by comparing its mass spectrum with literature data as well as by comparing its retention time (GLC) with that of an authentic sample. In the case of *7*,

only the mass spectrum was taken as evidence for its formation. The mass spectrum of the isomeric *16* was, however, quite different from that of *7*.

In order to demonstrate that 3-thienyllithium derivatives with substituents in the 4-position could also be utilized for the synthesis of thioenynes, *13* was treated with ethyllithium and ethyl iodide at room temperature. As expected, *14* was formed (50 %). During the progress of this work, Jakobsen [4] reported the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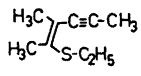
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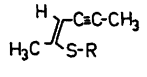
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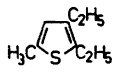
a R = $CH_2C_6H_5$
b R = CH_2CO_2H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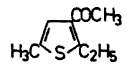
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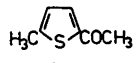
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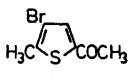
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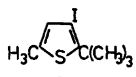
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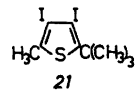
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ring-opening of 4-methyl-3-thienyllithium in the presence of butyl bromide, which afforded (*Z*)-1-butylthio-2-methyl-1-buten-3-yne. These results show the synthetic possibility of preparing thioenynes with substituents in all positions. It should be pointed out that compounds like the above-mentioned thioenynes cannot be synthesized by adding thiolates to diacetylenes, but more elaborate routes must be used.

It should be stressed that our approach is not limited to the use of alkylating agents corresponding to the alkyl halide formed in the halogen-metal exchange. Thus the reaction of *1b* with ethereal phenyllithium at room temperature yielded *2b*, which ring-opened smoothly to *3b*, which of course does not react with iodobenzene. Addition of dimethyl sulfate gives a 63 % yield of *4b*. This yield is higher than that obtained if *1b* is reacted only with methyllithium (42 %).[2] In this connection it should be mentioned that halogen-metal exchange between 2,5-dimethyl-3-bromothiophene and methyllithium is slow. After 21 h at room temperature only 10 % halogen-metal exchange took place and 90 % of the starting bromo derivative was recovered. Obviously methyllithium is not suitable for exchange with bromoarenes. This has previously been observed in the benzene series. [18] When benzyl chloride was added to the ethereal solution of *3b* a 52 % yield of *15a* [19] was obtained. With ethyl bromoacetate *3b* gave a 58 % yield of *15b* after hydrolysis of the initially formed ethyl ester.

Syntheses of starting materials. Compound *1c* [12] was used for the synthesis of *16*, which was needed as a reference compound. Halogen-metal exchange between *1c* and butyllithium at −70 °C followed by *N*,*N*-dimethylacetamide gave *17* in 42 % yield. The relatively low yield is probably due to steric hindrance from the ethyl group, leading to deprotonation of the *N*,*N*-dimethylacetamide by the thienyllithium derivative.[21] Wolff-Kishner reduction [22] of the acetyl derivative *17* then gave the desired diethyl derivative. Starting from 2-*t*-butylthiophene, *1e* was prepared in the same way as *1c* according to the procedure of Lantz and Hörnfeldt.[12] Also *1d* was prepared according to Ref. 12 by bromination of *18* with bromine and aluminium trichloride to give *19*, followed by Wolff-Kishner reduction.

By again following the description of Lantz and Hörnfeldt,[12] *1f* was synthesized from *10* by the iodine-iodic acid method.[23] It was found that a mixture containing 90 % of *1f* and 10 % of its isomer *20* was formed (GLC). A convenient way of eliminating *20* was to treat the mixture with 0.2 equivalent of butyllithium followed by hydrolysis. In this way *1f* was obtained free from the isomer although some of it (10 %) was lost. It is possible that less than 0.2 equivalent of butyllithium is necessary, as it can be expected that the iodine of *20* being *ortho* to the *t*-butyl group, is the most reactive one, due to release of steric strain, when the iodine is replaced by lithium. Such effects have been observed in halogen-metal exchange of some alkylsubstituted bromothiophenes.[24] It was also possible to achieve diiodination of *10* with the iodine-iodic acid method. Prolonged reaction at 80 °C with two equivalents of iodine-iodic acid gave a 43 % yield of *21*.

2,3,5-Trimethylthiophene was prepared from *1b*[13] by halogen-metal exchange with butyllithium at −70 °C followed by reaction with dimethyl sulfate. Iodination with iodine-iodic acid then gave *13* in 59 % yield.

A number of workers have prepared 2,4-heptadiyne by several methods.[25–27] However, the yields were low and this compound was first fully characterized in 1965.[27] The synthesis of diacetylene from 1,4-dichloro-2-butyne has been described by Armitage *et al.*,[28] who used sodium amide in liquid ammonia for the elimination of hydrogen chloride. The alkylation of the diacetylene anion gave various mono- and disubstituted diacetylenes, depending on the conditions. A detailed description of the preparation of 1,3-hexadiyne starting from 1,4-dichloro-2-butyne has been given by Brandsma.[29] By subsequent anion formation of 1,3-hexadiyne with butyllithium in hexane followed by methyl iodide in hexamethylphosphoric triamide we obtained 2,4-heptadiyne in 59 % yield.

Mass spectra were extensively used for molecular weight determination and for distinguishing between alkylthiophenes and the isomeric vinylacetylenic thioethers. The molecular ion fragment was the base peak for most of the enyne thioethers. Exception to this rule was found for *8* (base peak at M − 57). However, the molecular ion was still 89 rel. %, which is not in agreement with the fragmentation of propylthiophenes or ethylthiophenes. These compounds should give base peaks at M − 29 and M − 15, respectively.[30] It is well known that most simple alkylthiophenes give a base peak due to β-cleavage,[31] with a molecular ion of relatively low abundance (20 − 40 %). Accordingly, it was no problem to differentiate between alkylthiophenes and enyne thioethers when all compounds formed in the reactions were not isolated. Quite abundant fragments of the ethylthioenynes were those originating from the CH_3CS ion and from the loss of SC_2H_5. The above mentioned fragmentations were almost negligible for the alkylthiophenes. The fragment at *m/e* 91 ($C_7H_7^+$, tropylium) was prominent for enyne thioethers with seven-carbon chains, while this was not so in the cases of the isomeric thiophenes.

EXPERIMENTAL

General remarks. All experiments with organometallic compounds were performed under a dry oxygen-free nitrogen atmosphere and in solvents (ether, hexane) which were dried and distilled from sodium wire. The nitrogen gas was bubbled through a wash bottle with a basic pyrogallol solution to remove oxygen and then a wash bottle with conc. sulfuric acid to remove moisture. Hexamethylphosphoric triamide (HMPA) was purified according to Ref. 32. Dimethyl sulfate (DMS) and dimethylformamide (DMF) were used freshly distilled, and the iodobenzene (used for the phenyllithium preparations) was distilled twice with an efficient column.

The ethereal organometallic reagents (C_2H_5Li, C_6H_5Li and C_4H_9Li) were all titrated on the total base content with 0.1 M HCl and the real titre of the ethyllithium and butyllithium solutions was obtained by the double titration procedure.[33]

GLC analyses were performed with a Perkin-Elmer 900 gas chromatograph or a Varian 1400 gas chromatograph, both equipped with flame ionization detectors. The areas of the peaks of the gas chromatograms were evaluated with a Varian 480 digital integrator connected to the PE 900 or simply by the triangle approximation. It appeared that the discrepancy between the two methods was less than ±5 rel. %, which was considered small, since calibration was not performed in any case. However, the chromatograms could be reproduced within ±2 rel. %, and therefore fairly accurate comparisons of changes in the product distributions could be made. The columns were made of stainless steel (2.0 mm i.d., 1.9 m), and nitrogen was used as carrier gas (flow rate 35 ml/min). The carriers for the stationary phases were Chrom. W (80/100, for NPGS and BDS), Gas Chrom. Q (80/100, for OV 17 and OV 1) and Diatomite C1Q (100/120, for SE 30). For preparative GLC a Perkin-Elmer F 21 preparative gas chromatograph was used, equipped with a 20 % BDS column (8.0 mm i.d., 2.7 m).

Mass spectra were recorded on an LKB 9000 mass spectrometer with an ionization energy of 70 eV. ^1H NMR spectra were in most cases recorded on a Varian A-60 NMR spectrometer, and in a few cases on a Varian XL 100-15 NMR spectrometer. IR spectra were recorded on a Perkin-Elmer Grating Infrared spectrometer. The melting points were determined with a Reichert melting point microscope and are uncorrected. Elemental analyses were performed by the Department of Analytical Chemistry at the University of Lund, Miss Ilse Beetz, Mikroanalytisches Laboratorium, Kronach, West Germany and by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, West Germany.

The isolations of the pure acetylenic derivatives were in most cases performed by TLC. Glass plates with an activated 1 mm silica gel layer (Kieselgel GF 254 nach Stahl, 10–40 μ, Merck) were used, and the crude products were applied on the plates as 50 % acetone solutions by the aid of a Camag Chromatocharger. The zones were made visible with a UV lamp (360 nm) and eluted with ether. The purity of the substances was checked with VPC, NMR and elemental analyses.

3-Acetyl-2-ethyl-5-methylthiophene (17). A solution of 10.2 g (49.7 mmol) of 3-bromo-2-ethyl-5-methylthiophene (*1e*) in 100 ml of ether was cooled to −70 °C, and 42 ml (55 mmol) of 1.30 M butyllithium in hexane was added. The mixture was stirred for 1 h at this temperature, whereupon 4.8 g (55 mmol) of *N,N*-dimethylacetamide in 50 ml of ether was added. The reaction mixture was allowed to reach room temperature, stirred overnight and poured into 5 N HCl/ice. After stirring for 1 h, the aqueous layer was extracted with ether and the ethereal portions were washed with water and dried. Evaporation of the solvent and distillation gave 3.5 g (42 %) of the title compound, b.p.$_{0.6}$ 60–65 °C. NMR (CCl_4): δ 6.90 (q, 1 H, 4-H), 2.33 (s, $COCH_3$), 2,40 (bs, 5-CH_3), 3.08 (q, 2 H, 2-C_2H_5), 1.25 (t, 3 H, 2-C_2H_5). $J_{4H,5CH_3}$ = 1.0 Hz; $J_{CH_2-CH_3}$ = 7.0 Hz. [Found: C 63.5; H 7.34; S 19.0. Calc. for $C_{10}H_{12}OS$ (168.26): C 64.25; H 7.19; S 19.06].

2,3-Diethyl-5-methylthiophene (16). A mixture of 3.5 g (21 mmol) of *17* and 5 ml of 99.5 % hydrazine hydrate in 20 ml of ethylene glycol was gradually heated to 140 °C. Water and hydrazine were distilled off. After cooling, 5 g of KOH pellets was added and the mixture was heated to 90–110 °C until the nitrogen evolution ceased (2 h), whereupon the mixture was cooled and poured into 200 ml of 2 N HCl and extracted with ether. The ethereal portions were washed with water and dried. Evaporation and distillation gave 0.6 g (19 %) of the title compound, b.p.$_{12}$ 94–96 °C. Mass spectrum: *m/e* = 154, 35 % (M^+); *m/e* = 139, 100 % ($[M-15]^+$). NMR (CCl_4): δ 6.32 (q, 1 H, 4-H), 2.33 (d, 5-CH_3), 2.2–2.8 and 0.9–1.4 (C_2H_5). $J_{4H,5CH_3}$ = 1.4 Hz. [Found: C 70.13; H 9.05; S 20.65. Calc. for $C_9H_{14}S$ (154.28): C 70.07; H 9.15; S 20.78].

5-t-Butyl-3-iodo-2-methylthiophene (1f). From 45.8 g (0.297 mol) of 2-*t*-butyl-5-methylthiophene (*10*), 27.9 g (0.110 mol) of iodine, 13.9 g (0.0790 mol) of iodic acid, 150 ml of acetic acid, 60 ml of water, 60 ml of CCl_4 and 2 ml of conc. H_2SO_4, 84.0 g of a crude product was obtained, following the procedure described in Ref. 12. The product contained 90 % of the title compound and 10 % of its isomer 2-*t*-butyl-3-iodo-5-methylthiophene (*20*), according to combined GLC-MS analysis (column OV 1, 3 %, 100–210 °C, 10 °C/min). Distillation gave 64.0 g of material still containing *20*, b.p.$_{12}$ 129–130 °C. To a solution of 60.0 g (0.214 mol) of the distillate in 250 ml of ether, 31 ml (0.043 mol) of 1.40 M butyllithium was added at −70 °C. After 30 min the reaction mixture was hydrolyzed with methanol. The usual work-up and distillation gave 35.6 g (43 %) of isomer-free *1f*, b.p.$_{12}$ 128–129 °C, n_D^{20} 1.5704 (lit.[12] b.p.$_{10}$ 120–122 °C, n_D^{20} 1.5715).

5-t-Butyl-3,4-diiodo-2-methylthiophene (21). A mixture of 15.4 g (0.0998 mol) of *10*, 20.6 g (0.0811 mol) of iodine, 7.90 g (0.0449 mol) of iodic acid, 40 ml of acetic acid, 15 ml of water, 20 ml of CCl_4 and 1.0 ml of conc. H_2SO_4 was stirred vigorously at 80 °C for 8 h and worked up as described for *13* below. After distillation, 17.3 g (43 %) of the title compound was obtained, b.p.$_{0.01}$ 113–123 °C, n_D^{20} = 1.6430. NMR (CCl_4): δ 2.48 (s, 3 H, CH_3), 1.48 (s, 9 H, $C(CH_3)_3$). [Found: C 26.70; H 3.02. Calc. for $C_9H_{12}I_2S$ (406.07): C 26.62; H 2.98].

A forerun, 7.3 g, b.p.$_{0.01}$ 65–75 °C, was mainly 5-*t*-butyl-3-iodo-2-methylthiophene (*1f*) (NMR).

2,3,5-Trimethylthiophene. A solution of 50.0 g (0.210 mol) of 2,5-dimethyl-3-iodothiophene [13] (*1b*) in 100 ml of ether was cooled to −70 °C, and 146 ml (0.22 mol) of 1.5 M butyllithium in hexane was added, followed by 27.7 g (0.220 mol) of dimethyl sulfate in 100 ml of ether (very slowly). The mixture was stirred at −70 °C for 1.5 h, whereupon the cooling bath was removed and the reaction mixture was allowed to reach room temperature. Conc. ammonium hydroxide was added and the ethereal layer was separated, washed with 2 N HCl, water and dried. Evaporation and distillation gave 14.9 g (56 %) of the title compound, b.p. 161–163 °C (lit.[34] b.p. 163 °C).

4-Iodo-2,3,5-trimethylthiophene (13). A mixture of 12.6 g (0.100 mol) of 2,3,5-trimethylthiophene, 35 ml of acetic acid, 40 ml of water, 35 ml of CCl_4, 4.40 g (0.025 mol) of iodic acid and 4 drops of conc. H_2SO_4 was warmed to 40 °C, whereupon 12.7 g (0.0500 mol) of iodine was added in portions (vigorous stirring). When the addition was complete, the temperature was raised to 60 °C. After 2 h the reaction mixture was poured into aqueous sodium thiosulfate and extracted with CCl_4. The organic portions were washed with water, dried, evaporated and distilled, giving 15.0 g (59 %) of the title compound, b.p.$_{0.7}$ 67–68 °C. NMR (CCl_4): δ 2.07 (s, 3 H, CH_3) and 2.30 (bs, 6 H, CH_3). [Found: C 33.41; H 3.63; S 12.75. Calc. for C_7H_9IS (252.12): C 33.35; H 3.60; S 12.72].

General method for the ring-opening of 3-lithioheterocycles (G)

Nitrogen gas was supplied for 30 min to the predried, hot (110 °C) apparatus, consisting

of a three-necked round-bottomed flask fitted with a condenser (drying tube, $CaCl_2$), stirrer, dropping funnel and a neck for the gas inlet. The dropping funnel was also supplied with nitrogen gas. The 3-halo heterocyclic compound was dissolved in ether and ethereal ethyllithium was added rapidly. After 10 min, an excess of ethyl bromide or iodide was added all at once, and the reaction mixture was kept at +21 °C (room temperature) for 4 h. The reaction mixture was hydrolyzed with water and the aqueous phases were extracted three times with ether. The collected ethereal portions were washed with water to neutral reaction and dried with $MgSO_4$. After the evaporation of the solvent the crude product was purified by distillation or by TLC.

(Z)-2-Methylthio-2-hexen-4-yne (4b). To 100 ml (0.10 mol) of 1.0 M ethereal phenyllithium, 23.8 g (0.100 mol) of *1b* in 100 ml of ether was added at room temperature. After 1/2 h, 13.9 g (0.110 mol) of dimethyl sulfate in 50 ml of ether was slowly added. Ammonia was added after 1 h and the ethereal layer was washed with water, 2 N HCl and water to neutral reaction. After drying and evaporation of the solvent, the residue was distilled, to yield 7.9 g (63 %) of the title compound with the same properties as described previously (NMR, IR, m.p.).[2]

The reaction between 2,5-dimethyl-3-bromothiophene and methyllithium. A solution of 15.0 g (0.0785 mol) of 2,5-dimethyl-3-bromothiophene in 100 ml of ether was cooled to −70 °C, whereupon 100 ml (0.0810 mol) of 0.81 M methyllithium was added dropwise, followed by 5.68 g (0.0400 mol) of methyl iodide. The mixture was then allowed to reach room temperature. A sample was poured onto solid carbon dioxide in ether but no carboxylic acid could be isolated. After 21 h, water was added to the reaction mixture and the ethereal layer was washed with water and dried. GLC analysis (column BDS, 10 %, 105 °C) showed, upon comparison of the retention times with authentic samples, that the starting material amounted to ~90 % and compound *4b* to ~10 %. IR of the evaporated crude product: C≡C 2220 cm⁻¹.

(Z)-2-Hexen-4-yne-2-ylthioacetic acid (15b). To 100 ml (0.100 mol) of 1.0 M phenyllithium, 23.8 g (0.100 mol) of *1b* in 100 ml of ether was added at room temperature. After 1/2 h the reaction mixture was forced over (with nitrogen gas) to a dropping funnel and added to a solution of 16.7 g (0.100 mol) of ethyl bromoacetate in 100 ml of ether (water cooling). The reaction mixture was stirred for 1 h at room temperature, whereupon it was poured into 500 ml of 2 N NaOH and stirred for 2 h. The aqueous layer was separated, extracted with ether and acidified with 5 N HCl. An oil precipitated, which subsequently crystallized. Thus, 10.7 g of the crude title compound was collected by filtration. The pure acid, 9.8 g (58 %), was obtained after recrystallization from ethanol:water, m.p. 84.5 −86.5 °C. IR: C=O 1700 cm⁻¹, C≡C 2210 cm⁻¹. NMR ($CDCl_3$): δ 5.50 (m, 1 H, 4-H), 2.08 (m, $C=CCH_3$), 2.01 (bd, $C\equiv CCH_3$), 3.65 (s, 2 H, $-CH_2-$), 11.87 (s, 1 H, COOH). [Found: C 56.51; H 5.95; S 18.83. Calc. for $C_8H_{10}O_2S$ (170.23): C 56.45; H 5.92; S 18.84].

(Z)-2-Benzylthio-2-hexen-4-yne (15a). With the same amounts of reagents as above, the title compound was prepared by replacing ethyl bromoacetate with 13.9 g (0.110 mol) of benzyl chloride in 50 ml of ether. The reaction mixture was stirred overnight and was subsequently hydrolyzed. The ethereal layer was washed with water and dried. After evaporation of the solvent, the residue was distilled to give 10.5 g (52 %) of *15a*, b.p. $_{2.0}$ 141 − 142 °C, m.p. 53 − 55 °C (lit.[19] m.p. 55 °C). IR: C≡C 2220 cm⁻¹. NMR (CCl_4): δ 7.0 − 7.5 (m, 5 H, C_6H_5), 3.97 (s, 2 H, $-CH_2-$), 5.32 (m, 1 H, 3-H), 1.93 (bs, 6 H, 1-H and 6-H).

(Z)-2-Ethylthio-2-hepten-4-yne (4c). The general method G was followed. From 10.3 g (0.0500 mol) of 3-bromo-2-ethyl-5-methylthiophene (*1c*) in 100 ml of ether, 100 ml (0.060 mol) of 0.60 M ethereal ethyllithium and 39.0 g (0.250 mol) of ethyl iodide, 4.6 g (60 %) of the title compound was obtained by distillation, b.p.$_{13}$ 106 − 107 °C. Combined GLC-MS analysis (column BDS, 10 %, 130 °C) of the washed and dried reaction mixture showed the following compounds: *4c* (*m/e* = 154; calc. for $C_9H_{14}S$ = 154), *(Z)*-2-ethylthio-6-methyl-2-octen-4-yne (*5*) (*m/e* = 182; calc. for $C_{11}H_{18}S$ = 182), 2-ethyl-5-methylthiophene (*6*) (*m/e* = 126; calc. for $C_7H_{10}S$ = 126) and 2-*sec*-butyl-5-methylthiophene (*7*) (*m/e* = 154; calc. for $C_9H_{14}S$ = 154). See Table 1, condition A. IR: C≡C 2220 cm⁻¹. NMR (CCl_4): δ 1.99 (m, 3 H, 1-H), 5.32 (m, 1 H, 3-H), 2.32 (bq, 6-H), 1.37 − 1.05 (7-H), 2.81 and 1.37 − 1.05 (q, *S*-C_2H_5). $J_{SCH_2-CH_3} = J_{6H,7H} = 7.0$ Hz. [Found: C 70.10; H 9.13; S 20.71. Calc. for $C_9H_{14}S$ (154.28): C 70.07; H 9.15; S 20.78]. The reaction was repeated, but ethyl iodide was not added to the reaction mixture, which changed the component distribution of the reaction product as shown in Table 1, condition B.

(Z)-3-Ethylthio-3-hepten-5-yne (4d). The general method G was followed, and the same amounts of reagents as in the preceding experiment were used. Thus, 4.9 g (64 %) of *4d*, b.p.$_{2.0}$ 74 − 75 °C was obtained from 3-bromo-5-ethyl-2-methylthiophene (*1d*). Combined GLC-MS analysis (column BDS, 10 %, 130 °C) of the washed and dried reaction mixture showed the following compounds: *4d* (*m/e* = 154; calc. for $C_9H_{14}S$ = 154), *(Z)*-3-ethylthio-3-nonen-5-yne (*8*) (*m/e* = 182; calc. for $C_{11}H_{18}S$ = 182), 2-ethyl-5-methylthiophene (*6*) (*m/e* = 126; calc. for $C_7H_{10}S$ = 126) and 2-ethyl-5-propylthiophene (*9*) (*m/e* = 154; calc. for $C_9H_{14}S$ = 154). See Table 1, condition A. IR: C≡C 2220 cm⁻¹.

NMR (CCl_4): δ 1.38–0.97 (1-H), 2.25 (q, 2-H), 5.39 (m, 1 H, 4-H), 1.98 (d, 7-H), 2.80 (q, 2 H) and 1.38–0.97 (*S*-C_2H_5). $J_{SCH_2-CH_3} = J_{1H,3H} = 7.0$ Hz. [Found: C 70.21; H 9.17; S 20.65. Calc. for $C_9H_{14}S$ (154.28): C 70.07; H 9.15; S 20.78].

During the distillation, a few mg of almost pure (*Z*)-3-ethylthio-3-none-5-yne (*8*) was collected at 88–89 °C, 2.0 mmHg. NMR (benzene, XL-100 spectrum): δ 1.18–0.87(1-H), 2.06 (q, 2-H), 5.54 (m, 4-H), 2.22 (t, d, 7-H), 1.63 –1.34 (pent, 8-H), 1.15–0.87 (9-H), 2.61 (q) and 1.15–0.87 (*S*-C_2H_5). The small splitting of the signal originating from the terminal $-CH_2-$ group of the propyl group (7 H) was 2.3 Hz. The experiment was repeated, but no ethyl iodide was added to the reaction mixture, which changed the component distribution of the reaction product as shown in Table 1, condition B.

(Z)-2-Ethylthio-6,6-dimethyl-2-hepten-4-yne (4e). The general method G was followed. From 4.66 g (0.0200 mol) of 3-bromo-2-*t*-butyl-5-methylthiophene (*1e*) in 50 ml of ether, 38 ml (0.023 mol) of 0.60 M ethereal ethyllithium and 15.6 g (0.100 mol) of ethyl iodide, 3.13 g (86 %) of crude *4e* was obtained. Combined GLC-MS analysis (column SE 30, 3 % 100 –200 °C, 10 °C/min) showed the following compounds: 2-*t*-butyl-5-methylthiophene (*10*) ($m/e = 154$; calc. for $C_9H_{14}S = 154$) and *4e* ($m/e = 182$; calc. for $C_{11}H_{18}S = 182$). See Table 1, condition A. Isolation of *4e* through distillation was unsuccessful due to vigorous foaming and therefore a pure sample was obtained through preparative TLC (1 mm silica gel, hexane, R_F 0.35–0.16); n_D^{21} 1.5110. IR: C≡C 2220 and 2190 cm^{-1}, C=C 1585 cm^{-1}. NMR (CCl_4): δ 1.97 (d, 3 H, 1-H), 5.34 (q, 1 H, 3-H), 1.25 (s, $C(CH_3)_3$), 2.83 (q, 2 H) and 1.1–1.3 (*S*-C_2H_5). $J_{1H,3H} = 1.4$ Hz. [Found: C 72.50; H 10.00; S 17.52. Calc. for $C_{11}H_{18}S$ (182.33): C 72.46; H 9.95; S 17.59].

The experiment was repeated, but no ethyl iodide was added to the reaction mixture, which changed the component distribution of the reaction product as shown in Table 1, condition B.

(Z)-3-Ethylthio-2,2-dimethyl-3-hepten-5-yne (4f) *and 5-t-butyl-3-ethyl-2-methylthiophene* (12). The general method G was followed. From 28.0 g (0.100 mol) of 5-*t*-butyl-3-iodo-2-methylthiophene (*1f*) in 200 ml of ether, 200 ml (0.11 mol) of 0.55 M ethereal ethyllithium and 78.0 g (0.500 mol) of ethyl iodide, 16.6 g (91 %) of a crude mixture of *4f* and *12* was obtained. Combined GLC-MS analysis (column SE 30, 3 %, 100–200 °C, 10 °C/min) of the washed and dried reaction mixture showed the presence of the following compounds: 2-*t*-butyl-5-methylthiophene (*10*) ($m/e = 154$; calc. for $C_9H_{14}S = 154$), *12* ($m/e = 182$; calc. for $C_{11}H_{18}S = 182$) and *4f* ($m/e = 182$; calc. for $C_{11}H_{18}S = 182$). See Table 1, condition A.

Also in this experiment, distillation was unsuitable due to foaming. Compound *12* was obtained pure by preparative GLC (column BDS, 20 %, 100–200 °C, 10 °C/min). Thus, 5.00 g of the crude product gave 1.8 g (33 %) of *12*. NMR (CCl_4): δ 6.35 (s, 4-H), 2.23 (s, 2-CH_3), 1.30 (s, $C(CH_3)_3$), 2.40 (q) and 1.13 (t, 3-C_2H_5). $J_{CH_2-CH_3} = 7$ Hz. [Found: C 72.2; H 9.88; S 17.6. Calc. for $C_{11}H_{18}S$ (182.33): C 72.46; H 9.95; S 17.59].

Compound *4f* was obtained pure by preparative TLC (1 mm silica gel, hexane, R_F 0.52 –0.64). Compound *12* had R_F 0.18–0.36, but was not isolated in this way. Thus, 1.00 g of the crude product gave 0.38 g (35 %) of *4f*, $n_D^{21} = 1.5149$. IR: C≡C 2220 and 2040 cm^{-1}, C=C 1580 cm^{-1}. NMR (CCl_4): δ 1.14 (s, $C(CH_3)_3$), 5.75 (q, 1 H, 4-H), 1.99 (d, 3 H, 7-H), 2.98 (q, 2 H) and 1.09–1.33 (*S*-C_2H_5). $J_{SCH_2-CH_3} = 7.5$ Hz; $J_{4H,7H} = 2.4$ Hz. [Found: C 72.2; H 9.87; S 17.3. Calc. for $C_{11}H_{18}S$ (182.33): C 72.46; H 9.95; S 17.59].

The experiment was repeated, but no ethyl iodide was added to the reaction mixture, which changed the component distribution as shown in Table 1, condition B.

(Z)-2-Ethylthio-3-methyl-2-hexen-4-yne (14). The general method G was followed. From 10.0 g (0.0397 mol) of 4-iodo-2,3,5-trimethylthiophene (*13*) in 100 ml of ether, 67 ml (0.040 mol) of 0.60 M ethereal ethyllithium and 21.8 g (0.200 mol) of ethyl bromide, 5.50 g of crude product was obtained. Distillation gave 3.12 g (51 %) of *14*, b.p.$_{0.6}$ 52–54 °C. IR: C≡C 2220 and 2040 cm^{-1}. NMR (CCl_4): δ 1.82 (s, 3 H, CH_3), 1.97 (bs, 6 H, CH_3), 2.72 (q, 2 H) and 1.21 (t, 3 H, *S*-C_2H_5). $J_{SCH_2-CH_3} = 7$ Hz. [Found: C 70.00; H 9.10; S 20.85. Calc. for $C_9H_{14}S$ (154.28): C 70.07; H 9.15; S 20.78].

2,4-Heptadiyne. To a solution of 14.0 g (0.179 mol) of 1,3-hexadiyne [29] in 100 ml of ether, 130 ml (0.185 mol) of 1.42 M butyllithium in hexane was added at –50 °C followed by 28.5 g (0.200 mol) of methyl iodide after 10 min. The reaction was followed by GLC (column OV 17, 3 %, 70–150 °C, 10 °C/min) of hydrolyzed samples. Since no conversion had occurred after 1/2 h, 50 ml of dry HMPA was added. An exothermic reaction took place and the starting material was completely consumed 5 min after the addition of HMPA. The reaction mixture was poured into ice-water, extracted with ether, and dried. The ethereal solution was filtered and 50 ml of decalin was added. The ether was distilled off at ordinary pressure, whereupon the pressure was lowered to 100 mmHg. A fraction was collected between 60 and 70 °C, and it was redistilled to give 9.2 g (56 %) of the title compound, b.p.$_{70-90}$ 75–85 °C (lit.[26] b.p.$_{32}$ 59–60 °C). NMR (CCl_4): δ 1.90 (t, 3 H, 1-H), 2.25 (q with fine structure, 2 H, 6-H), 1.17 (t, 3 H, 7-H). $J_{1H,6H} = 1.0$ Hz; $J_{6H,7H} = 7.0$ Hz.

The addition of ethanethiolate to 6,6-dimethyl-2,4-heptadiyne. A mixture of 1.10 g (9.17 mmol)

of 6,6-dimethyl-2,4-heptadiyne, 1.13 g (18.2 mmol) of ethanethiol and 0.11 g of KOH in 4 ml of methanol was heated to 120 °C for 3.5 h in a 10 ml Pyrex ampoule. The reaction mixture was poured into water, which was extracted several times with ether. GLC analysis (column OV 1, 3 %, 110–260 °C, 10 °C/min) of the dried ethereal solution showed mainly one component (~70 %) with the same retention time as *4e* together with 30 % of starting material. Evaporation of the solvent and the remaining starting material yielded 1.1 g (65 %) of crude *4e*. NMR (CCl_4) of the crude product was identical with that of *4e* but different from that of *4f*. The same was true for an IR spectrum.

The addition of ethanethiolate to 2,4-heptadiyne. With the same method as in the preceding experiment, a mixture of *4c* and *4d* in the proportions 60:40 (GLC, column OV 17, 3 %, 80–200 °C, 10 °C/min) was obtained from 3.69 g (40.1 mmol) of 2,4-heptadiyne, 5.0 g (81 mmol) of ethanethiol and 0.3 g of KOH in 6 ml of methanol. The identification of the components was performed by comparison of the retention times (GLC) with those of authentic samples of *4c* and *4d* ("mixing" analysis). Evaporation of the solvent and the remaining starting material gave 3.7 g (52 %) of crude product.

6,6-Dimethyl-2,4-heptadiyne. To 12.2 g (0.0300 mol) of 2-*t*-butyl-3,4-diiodo-5-methylthiophene (*21*) in 100 ml of ether, 100 ml (0.065 mol) of 0.65 M ethereal ethyllithium was added at −70 °C followed by 4.7 g (0.030 mol) of ethyl iodide. After 1 h, the reaction mixture was allowed to reach room temperature and kept there for 4 h, whereupon it was poured onto solid carbon dioxide in ether. No carboxylic acid could be isolated from the basic extracts upon acidification. The neutral ethereal phase was dried and the solvent was removed by distillation at ordinary pressure. The title compound was obtained at reduced pressure, b.p.$_{14}$ 57–59 °C, 2.1 g (58 %). n_D^{22} 1.4780 (lit.[7] b.p.$_{10}$ 51–51.5 °C, n_D^{20} 1.4802). IR: C≡C 2195, 2155 and 2040 cm^{-1} (lit.[7] 2192, 2151 and 2030 cm^{-1}).

2,4-Hexadiyne. With the same procedure as in the preceding experiment, the title compound was obtained from 36.4 g (0.100 mol) of 3,4-diiodo-2,5-dimethylthiophene[18] in 1 l of ether, 250 ml (0.20 mol) of 0.80 M ethereal ethyllithium and 15.6 g (0.100 mol) of ethyl iodide. The dried neutral ethereal extract was concentrated to half its volume and the residue was cooled to −70 °C, whereupon the crystals were collected by suction. Repeated concentration of the filtrates and cooling gave a total of 5.0 g (54 %) of the title compound, m.p. 67–68 °C (lit.[35] 66–67 °C).

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