Ring-opening Reactions of Heterocyclic Organometallics. X.*  
Phenyl- and N,N-Dimethylaminomethyl-substituted 3-Thienyllithium Derivatives  

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The usefulness of the ring-opening of phenyl substituted 3-thienyllithium derivatives for the synthesis of substituted alkylthiovinyl acetylenes is demonstrated. The stability of 2,N,N-dimethylaminomethyl-3-methyl-3-thienyllithium (20) towards ring-opening is ascribed to intramolecular chelation. On the other hand, 5,N,N-dimethylaminomethyl-2-methyl-3-thienyllithium smoothly ring-opened to give (Z)-1-(N,N-dimethylamino)-2-ethylthio-2-hexen-4-yne (23) in 50% yield, upon ethylation. This gives additional evidence for the usefulness of this reaction for the preparation of otherwise difficultly accessible alkylthiovinyl acetylenes.

In recent papers, we have demonstrated that 2,5-dialkyl-3-thienyllithium derivatives ring-open at room temperature to lithium enynethiolates, while 2,5-dialkyl-3-selenenyllithium derivatives even at -70 °C undergo the corresponding reactions to lithium enyneselenolates.1,4 We have also found that strong -1-substituents such as Cl or OCH₃ in the 2-position of 3-thienyllithium derivatives have a stabilizing influence so that ring-opening does not occur.2 As mentioned previously,2 intermolecular complexation of the organolithium derivative to the free electron pair of the -1-substituent could possibly also contribute to the stabilization of the above-mentioned 3-thienyllithium derivatives. We were therefore interested in studying the effect on ring-opening of a substituent which makes intramolecular chelation possible, and have chosen the dimethylaminomethyl group for this purpose.

With a weaker -1-substituent such as methylthio in the 2-position ring-opening took place.3 It seemed therefore reasonable that 2-phenyl-substituted 3-thienyllithium derivatives should also ring-open, as C₆H₅ has a weaker inductive effect than SCH₃, judging from Swain's and Lupton's F-values4 (F = 0.139 and 0.332, respectively). Therefore, in order to elucidate the scope and limitation of the ring-opening for

![Scheme 1](image)

Scheme 1. Product analysis of the reaction between different phenyl substituted 3-halothiophenes and ethyllithium in the presence of a fivefold excess of ethyl bromide. Reaction conditions: 4 h at +21 °C, then hydrolysis. Uncalibrated GLC values. Figures within parentheses represent isolated yields.
the stereospecific synthesis of substituted alklythiovinyl acetylenes, we have studied some phenyl-substituted 3-thiencyllithium derivatives.

**Phenyl substituted 3-thiencyllithium derivatives.** As expected, when 1, 2, and 3 were treated in the standard way with ethereal ethyllithium followed by ethyl bromide at room temperature and hydrolysis after 4 h, ring-opening occurred (Scheme 1). However, the relatively large amounts of dehalogenated heterocycles formed, such as 35% of 7 from the reaction of 2 and 20% of 4 from 3, indicated that the corresponding thiencylithium derivatives were rather stable or that the enynethiolates were slowly alkylated. If the ring-cleavage is slow, such lithium derivatives would also have greater opportunity to undergo Wurtz-Fittig couplings. The formation of 5 from 1, 8 from 2, and 10 from 3 was indicated by combined GLC-MS, but since the fragmentation patterns (MS) of these compounds were not conclusive their structures are uncertain. For preparative purposes, the ring-opening of 1 and 3 with ethyllithium appears useful, since 47% of 6 and 55% of 11 could be isolated. In the reaction of 3, also a small amount of 12 was formed through ethylation at the propargylic methyl group. The assignment of structure 12 was based on its mass spectrum, which showed similar features to that of (Z)-3-ethythio-3-nonen-5-yn, e.g., the prominent peak at M−57 and the relatively high abundance of m/z = 91 (C7H3+), tropylum. However, it was more difficult to isolate 9 formed from the reaction of 2 with ethyllithium and ethyl bromide, since its properties were too similar to those of some by-products. In order to suppress the formation of these by-products, halogen-metal exchange was carried out with phenyllithium. In such a case it is most convenient to use iodothiophenes in order to achieve a rapid reaction. The enynethiolates formed were then methylated with dimethyl sulfate. In this way, a 69% yield of 15, was obtained from 13, a 50% yield of 16 from 14 and a 63% yield of 17 from 2.

These results give additional evidence for the preparative usefulness of the ring-opening of 3-thiencyllithium derivatives for the preparation of substituted alklythiovinyl acetylenes, corresponding to a stereo- and regiospecific addition of alkylthiolates to unsymmetrically disubstituted diacetylenes. In the cleavage of the lithium derivatives of 2, a fully substituted alklythiovinyl acetylene is obtained, which should be more difficult to prepare by other routes.

**N,N-Dimethylaminomethyl-substituted 3-thiencyllithium derivatives.** The effect of a 2,N,N-dimethylaminomethyl group in stabilizing 3-thiencyllithium is indicated in Scocum and Gierer’s work (which appeared when our work was in progress) in which it was found that 18 was metalated in the 3-position by butyllithium at room temperature. The lithium compound was trapped with benzophenone, which gave a 65% yield of 19. The possibility for the lithium compound to ring-open was not mentioned. We could, however, show by 1H NMR spectroscopy that no vinyl hydrogen absorption was present even after 12 h at room temperature in an experiment in which 20 was sealed in an NMR tube and the vinyl region was scanned at different times. The thiencyllithium derivative was prepared through halogen-metal

![Chemical structure](image)

**Scheme 2.** Isolated yields of enyne-methylthioethers when some phenyl substituted 3-iodothiophenes were treated with phenyllithium at +21 °C for 4 h, followed by dimethyl sulfate.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>13</td>
<td>69%</td>
</tr>
<tr>
<td>14</td>
<td>50%</td>
</tr>
<tr>
<td>2</td>
<td>63%</td>
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exchanged between 21 and ethyllithium in ether. In a parallel experiment it was shown that only 18 was formed upon hydrolysis after 4 h. Thus in this case the Wurtz-Fittig coupling did not interfere.

That intramolecular chelation was of importance in the stabilization of 20 was evident from the facile opening taking place when the N,N-dimethylaminomethyl function was situated in the 5-position. Thus 22 gave a 50% yield of 23 when treated with ethyllithium and ethyl bromide at room temperature for 4 h. It thus seems clear that both strongly electron-attracting groups, and substituents giving intramolecular chelates of suitable geometry, can stabilize 3-thienyl lithium derivatives.

**Synthesis of starting material.** Starting from the known 3,5-dibromo-2-phenylthiophene, 6 prepared through bromination of 2-phenylthiophene, I was obtained by halogen-metal exchange with butyllithium followed by reaction with dimethyl sulfate. Halogen-metal exchange between I and butyllithium at -70 °C followed by reaction with iodine gave 13 in good yield.

Compound 2 was prepared from the known 2,5-dimethyl-3-phenylthiophene 7 by iodination with the iodine/iodic acid method. In order to prepare 3, we started from 3,5-dibromo-2-methylthiophene, which upon reaction with butyllithium and cyclohexanone gave 3-bromo-5-(1-cyclohexenyl)-2-methylthiophene. This compound was then aromatized in the usual way with chloranil to give 3. Substance 14 was obtained through halogen-metal exchange between 3 and butyllithium at -70 °C followed by reaction with iodine.

The compound 21 was prepared in the following manner: 24 16 was metalated in the 5-position with lithium diisopropylamide in ether (cf. Ref. 11). Upon reaction with solid carbon dioxide, 25 was obtained in 65% yield. Via the acid chloride, 25 was transformed to 26, which upon LiAlH₄ reduction gave 21. In a similar way, starting from 27, 28 was prepared via the acid chloride. Reduction gave 22 in 72% yield. The acid 27 was obtained by treating 3,5-dibromo-2-methylthiophene with butyllithium at -70 °C followed by solid carbon dioxide.

The structures of starting materials and products isolated in the reactions described in this paper were evident from their spectroscopical properties (IR, NMR and mass spectra) and elemental analyses (cf. Experimental part).

**EXPERIMENTAL**

**General remarks.** (See Ref. 2).

**3-Bromo-5-methyl-2-phenylthiophene (1).** To 50.0 g (0.157 mol) of 3,5-dibromo-2-phenylthiophene 6 in 250 ml of ether, 115 ml (0.161 mol) of 1.40 M butyllithium in hexane was added at -70 °C followed by 20.5 g (0.163 mol) of dimethyl sulfate in 100 ml of ether. The temperature was kept below -65 °C. When the addition was complete, the reaction mixture was stirred at -70 °C for 4 h, whereupon it was allowed to reach room temperature. Conc. ammonium hydroxide was added and the ethereal layer was washed with 2 N HCl, water and dried. Evaporation and distillation gave 22.3 g (56%) of the title compound, b.p. 116-120 °C/N. NMR (CHCl₃): δ 7.1–7.7 (C₆H₅, m, 5 H); 6.60 (4-H, q, 1 H); 2.33 (5-CH₃, d, 3 H). J₉H₅₇₂₄ = 11 Hz. [Found: C 52.12; H 3.60; Br 31.60; S 12.61. Calc. for C₇H₅Br₂S (253.16): C 52.19; H 3.58; Br 31.56; S 12.67.]

**3-Iodo-5-methyl-2-phenylthiophene (13).** To a solution of 8.3 g (0.035 mol) of I in 100 ml of ether, 25 ml (0.035 mol) of 1.40 M butyllithium in hexane was added at -70 °C, followed by 8.9 g (0.035 mol) of iodine in 100 ml of ether. The reaction mixture was allowed to reach room temperature, whereupon it was poured onto aq. sodium thiosulfate. The organic layer was washed with water to neutral reaction, and dried. Evaporation of the solvent yielded 8.7 g of crude 13, which was distilled to give 5.4 g (54%) of the title compound, b.p. 118–119 °C/N. NMR (CHCl₃): δ 7.15–7.65 (C₆H₅, m, 5 H); 6.66 (4-H, q, 1 H); 2.38 (5-CH₃, d, 3 H). J₉H₅₇₂₄ = 11 Hz. [Found: C 43.98; H 3.04; S 10.78. Calc. for C₇H₅I₂S (300.16): C 44.02; H 3.02; S 10.68.]

**3-Iodo-2,5-dimethyl-4-phenylthiophene (2).** A mixture of 5.00 g (26.6 mmol) of 2,5-dimethyl-3-phenylthiophene, 4 3.6 g (14 mmol) of iodine, 1.2 g (6.8 mmol) of iodic acid, 15 ml of acetic acid, 20 ml of water, 15 ml of CCl₄ and 0.1 ml of conc. H₂SO₄ was stirred vigorously at 60 °C for 4.5 h. After cooling, the reaction mixture was poured into aqueous sodium thiosulfate and extracted with CCl₄. The organic portions were washed with water, dried and the solvent was evaporated. The crystalline residue, 7.5 g (90%), was recrystallized from hexane in the cold (-25 °C) giving 6.5 g (70%) of the pure title compound, m.p. 63–66 °C. NMR (C₆D₆): δ 7.1–7.5 (C₆H₅, m, 5 H); 2.40 (CH₃, s, 3 H); and 2.27 (CH₂, s, 3 H). [Found: C 45.90; H 3.60; S 10.16. Calc. for C₁₃H₁⁵I₂S (314.19): C 45.87; H 3.53; S 10.21.]

3-Bromo-2-methyl-5-phenylthiophene (3). To 25.6 g (0.100 mol) of 3,5-dibromo-2-methylthiophene in 250 ml of ether, 100 ml (0.110 mol) of 1.10 M butyllithium in hexane was added at −70 °C. After 0.5 h 10.0 g (0.102 mol) of cyclohexanone in 100 ml of ether was added and the mixture was allowed to reach room temperature, whereupon 100 ml of 5 N HCl was added. After stirring for 0.5 h the etheral layer was washed with water and dried. Evaporation yielded 25.0 g of crude 3-bromo-5-(1-cyclohexenyl)-2-methylthiophene, which was aromatized with 40 g (0.18 mol) of DDQ in 400 ml of refluxing benzene for 2.5 h. The mixture was cooled and filtered and the filter was washed with benzene several times. The filtrate was washed repeatedly with 5 N NaOH solution and finally with water. Evaporation of the solvent and recrystallization from ethanol-water yielded 12.9 g (51 %) of the title compound, m.p. 72–73 °C. NMR (CDCl3): δ 7.00 (4-H, s, 1 H), 7.15–7.6 (C6H5, 5 H), 2.37 (2-CH3, s, 3 H). [Found: C 52.16; H 3.51; Br 31.57; S 12.71. Calc. for C10H8Br2S: C 52.16; H 3.58; Br 31.56; S 12.67.]

3-Iodo-2-methyl-5-phenylthiophene (14) was prepared in a way analogous to that used for the isomeric 4-halo-2-methyl derivative 13, from 3.00 g (0.0119 mol) of 3 in 75 ml of ether, 10 ml (0.012 mol) of 1.20 M butyllithium in hexane and 3.2 g (0.013 mol) of iodine dissolved in 75 ml of ether. Thus 3.56 g of a crystalline crude product was obtained, which was recrystallized from ethanol to give the title compound, m.p. 65–66 °C, 2.16 g (60 %). NMR (CCl4): δ 7.1–7.6 (C6H5, m, 5 H), 7.08 (4-H, s, 1 H), 2.45 (2-CH3, s, 3 H). [Found: C 44.1; H 2.99; I 41.8. Calc. for C10H6I2S: C 44.02; H 3.02; I 42.48.]

3-Bromo-5-methyl-2-thioephenoxyacetic acid (16). To 24.0 g (0.297 mol) of disopropylamine in 100 ml of ether, 180 ml (0.240 mol) of 1.50 M butyllithium in hexane was added. After 10 min, 35.4 g (0.200 mol) of 4-bromo-2-methylthiophene in 100 ml of ether was added rapidly at room temperature. The reaction mixture was poured onto solid carbon dioxide in ether after 45 min and extracted with aq. 2 N NaOH. Upon acidification with 5 N HCl, 29.1 g (56 %) of the title compound was isolated, which was sufficiently pure to use in synthetic work according to NMR. Recrystallization from ethanol-water gave the pure acid, m.p. 205–206 °C. NMR (acetone-d6): δ 6.93 (4-H, q, 1 H), 2.53 (5-CH3, d, 3 H), 9.10 (COOH). JCH-SH = 1.0 Hz. [Found: C 32.63; H 2.30; S 14.55. Calc. for C6H10O4S (221.07): C 32.60; H 2.30; S 14.50.]

3-Bromo-2-(N,N-dimethylcarboxamido)-5-methylthiophene (26). To a solution of 17.9 g (0.150 mol) of thionyl chloride in 50 ml of ether, 22.1 g (0.100 mol) of 25 was added in portions, followed by 2 ml of pyridine. The mixture was refluxed with stirring for 2.5 h, whereupon the solvent, together with the excess of thionyl chloride, was evaporated. The residue (white needles) was dissolved in 100 ml of anhydrous benzene and dimethylamine was added through the reaction mixture (ice cooling). When 20 g of dimethylamine had been introduced, the reaction mixture was filtered and the filter was washed several times with ether. The filtrate was evaporated and the residue dissolved in ether. The organic layer was washed with 2 N HCl, 2 N NaOH, water and dried. After evaporation and distillation, 11.8 g (48 %) of the pure amide was obtained, b.p. 84 °C, 21 °C IR: C = O 1630 cm⁻¹. NMR (CCl4): δ 6.55 (4-H, q, 1 H), 2.45 (5-CH3, d, 3 H); 2.98 (NCH3, s, 6 H). JCH-SH = 1.1 Hz. [Found: C 38.75; H 4.05. Calc. for C6H14BrNOS (248.14): C 38.72; H 4.06.]

3-Bromo-2-(N,N-dimethylaminomethyl)-5-methylthiophene (21). To 1.05 g (0.0277 mol) of LiAlH4 in 25 ml of ether, 10.0 g (0.0403 mol) of 26 in 25 ml of ether was added. When the addition was complete, the reaction mixture was refluxed for 3 h and 25 ml of water was added. The reaction mixture was filtered and the filter was washed with ether. The filtrate was dried over KOH pellets, evaporated and distilled (some decomposition), which gave 5.0 g (53 %) of the title compound, b.p. 69–73 °C. NMR (CCl4): δ 6.49 (4-H, q, 1 H), 2.43 (5-CH3, s, 2 H), 2.20 (NCH3, s, 6 H), JCH-SH = 1.0 Hz. [Found: C 41.12; H 5.14; S 13.65. Calc. for C6H14BrNOS (234.16): C 41.04; H 5.17; S 13.69.]

3-Bromo-2-methyl-5-thioephenoxyacetic acid (27). To 46.3 g (0.181 mol) of 3,5-dibromo-2-methylthiophene in 200 ml of ether, 140 ml (0.186 mol) of 1.33 M butyllithium in ether was added at −70 °C. The mixture was stirred for 20 min, whereupon it was poured onto solid carbon dioxide in ether. The ethereal phase was extracted with 2 N NaOH and the alkaline portions were acidified with 5 N HCl, which gave 35.2 g of the crude acid. Recrystallization from acetic acid:water gave the pure title compound, m.p. 197–200 °C, 30.2 g (75 %). NMR (acetone-d6): δ 7.60 (4-H, s, 1 H), 2.47 (2-CH3, s, 3 H). [Found: C 32.70; H 2.30; Br 36.08; S 14.52. Calc. for C6H14BrO2S (221.07): C 32.60; H 2.28; Br 36.14; S 14.50.]

3-Bromo-5-(N,N-dimethylcarboxamido)-2-methylthiophene (28) was prepared in analogy with its isomer (26) from 35.2 g (0.159 mol) of 27 to give after work-up and distillation, 29.0 g (74 %) of the title compound; b.p. 114–145 °C IR: C = O 1625 cm⁻¹. NMR (CCl4): δ 7.08 (4-H, s, 1 H); 2.38 (2-CH3, s, 3 H); 3.10 (NCH3, s, 6 H). [Found: C 38.30; H 4.11; S 12.85. Calc. for C6H14BrNOS (248.14): C 38.72; H 4.06; S 12.92.]

3-Bromo-5-(N,N-dimethylaminomethyl)-2-methylthiophene (22) was prepared in analogy with its isomer 21 from 27.2 g (0.110 mol) of 28 to yield 18.7 g (73 %), b.p. 85–87 °C. NMR (CCl4): δ 6.65 (4-H, s, 1 H); 3.47 (5-CH3, s, 2 H); 2.37 (2-CH3, s, 3 H); 2.20 (NCH3, s, 6)
General method for the ring-opening of 3-lithioheterocycles (G). See Ref. 2.

(Z)-2-Ethylthio-5-phenyl-2-penten-4-yn (6). The general method G was followed. From 5.06 g (0.0200 mol) of I in 50 ml of ether, 28 ml (0.021 mol) of 0.76 M ethereal ethyllithium and 10.9 g (0.100 mol) of ethyl bromide, 3.23 g of crude product was obtained. Combined GLC-MS analysis (column OV 17, 3 %, 100–230 °C, 12 °C/min) of the washed and dried ethereal reaction mixture showed three compounds, namely 2-methyl-5-phenylthiophene (d) (m/e = 174; calc. for C₉H₈S = 174), 3-ethyl-5-methyl-2-phenylthiophene (δ) (m/e = 202; calc. for C₁₃H₁₄S = 202), and δ (m/e = 202; calc. for C₁₃H₂₄S = 202) (see Scheme 1). After distillation, 1.9 g (47 % of the title compound was obtained, bp₁; H₂O = 150–110 °C.

IR: C=C 2190 cm⁻¹, NMR (CCl₄): δ 2.00 (1-H, d, 3 H); 5.57 (3-H, q, 1 H); 7.1–7.6 (C₆H₅, m, 5 H); [SC(H₂)]; 2.80 (q, 2 H) and 1.23 (t, 3 H). J₁,₂ = 1.4 Hz, J₄,₅ = 7.0 Hz. [Found: C 76.9; H 7.01; S 15.7. Calc. for C₁₃H₂₄S (202.32): C 77.18; H 6.98; S 15.85.]

(Z)-1-Ethylthio-1-phenyl-1-penten-3-yne (11). The general method G was followed. From 5.06 g (0.0200 mol) of 3 in 59 ml of ether, 5.06 g (0.0201 mol) of 0.70 M ethereal ethyllithium and 7.80 g (0.0500 mol) of ethyl iodide, 3.52 g of a crude product was obtained. Combined GLC-MS analysis (column OV 17, 3 %, 200–290 °C, 12 °C/min) showed the presence of four compounds, namely δ (m/e = 174; calc. for C₁₀H₁₁S = 174), 3-ethyl-2-methyl-5-phenylthiophene (10) (m/e = 202; calc. for C₁₂H₁₄S = 202) and (Z)-1-ethylthio-1-phenyl-1-hepten-3-yne (12) (m/e = 230; calc. for C₁₃H₂₂S = 230) (see Scheme 1). TLC (1 mm silica gel, hexane) gave 1.50 g of the crude product gave 0.94 g (55 %) of the title compound (R₁, H₂O = 0.2–0.4). IR: C=C = 2215 and 2040 cm⁻¹, NMR (CCl₄): δ 7.69 (2-H, q, 1 H); 2.05 (5-H, d, 3 H); 5.20 (q, 2 H) and 1.08 (t, 3 H). J₁,₂ = 2.40 Hz, J₄,₅ = 7.0 Hz. [Found: C 77.10; H 7.01; S 15.85. Calc. for C₁₃H₂₄S (202.32): C 77.18; H 6.98; S 15.85.]

(Z)-2-Ethylthio-3-phenyl-2-hepten-4-yne (9). The general method G was followed. From 2.00 g (6.37 mmol) of 2 in 30 ml of ether, 14 ml (6.40 mmol) of 0.46 M ethereal ethyllithium and 3.27 g (30.0 mmol) of ethyl bromide, 0.90 g of crude product was obtained. Combined GLC-MS analysis (column OV 17, 3 %, 100–290 °C, 10 °C/min) of the washed and dried reaction mixture showed the presence of three compounds, namely 2,5-dimethyl-3-phenylthiophene (7) (m/e = 188; calc. for C₁₀H₁₃S = 188), 3-ethyl-2,5-dimethyl-4-phenylthiophene (8) (m/e = 216; calc. for C₁₃H₁₄S = 216), and 9 (m/e = 216; calc. for C₁₃H₂₄S = 216) (see Scheme 1). TLC (1 mm silica gel, hexane) gave two fractions; Z 1 (0.25 g, R₁ = 0.30–0.54), which according to NMR and GLC analysis consisted of 7 and S 2 (0.15 g, 12 %, R₁, H₂O = 0.12–0.05), which was the crystalline title compound. Recrystallization from hexane at -25 °C gave 6, m.p. 58–60 °C. IR: C=C 2110 and 2040 cm⁻¹. NMR (CCl₄): δ 2.02 (1-H, 6-H, bs, 6 H); 5.20 (C₆H₅, m, 5 H); [SC(H₂)]; 2.83 (q, 2 H) and 1.32 (t, 3 H). J₁,₂ = 7 Hz. [Found: C 77.79; H 7.46; S 14.77. Calc. for C₁₃H₁₄S (216.35): C 77.72; H 7.45; S 14.82.]

(Z)-2-Methylthio-5-phenyl-2-penten-4-yn (15). To 1.50 g (5.00 mmol) of 13 in 25 ml of ether, 5.0 ml (5.60 mmol) of 1.0 M phenyllithium was added (with a syringe) at room temperature and in a glove-box supplied with dry oxygen-free nitrogen. After 4 h, 0.63 g, (5.0 mmol) of dimethyl sulfate in 10 ml of ether was added and the reaction mixture was hydrolyzed with 10 ml of conc. ammonium hydroxide solution another hour. The mixture was washed with 2 N HCl and water to neutral reaction and dried. After evaporation of the ether and lower-boiling substances (e.g. iodobenzene), 0.90 g of crude product remained, which was chromatographed (TLC, 1 mm silica gel, hexane) to give 0.65 g (69 %) of the title compound. IR: C=C 2185 cm⁻¹, NMR (CCl₄): δ 2.10 (1-H, d, 3 H); 5.54 (3-H, q, 1 H); 7.1–7.6 (C₆H₅, m, 5 H); 2.57 (SCH₃, s, 3 H). J₁,₂ = 1.4 Hz. [Found: C 76.44; H 6.39; S 17.15. Calc. for C₁₃H₁₄S (188.29): C 76.55; H 6.42; S 17.03.]

(Z)-1-Methylthio-1-phenyl-1-penten-3-yne (16). This compound was prepared by the same method and on the same scale as the preceding experiment from 14. The crude product (0.60 g) was purified by TLC (1 mm silica gel, hexane), giving 0.47 g (50 %) of the title compound. IR: C=C 2220 cm⁻¹, NMR (CCl₄): δ 6.85 (2-H, q, 1 H); 2.05 (5-H, d, 3 H); 7.1–7.6 (C₆H₅, m, 5 H); 2.03 (SCH₃, s, 3 H). J₁,₂ = 2.4 Hz. [Found: C 76.50; H 6.40; S 17.13. Calc. for C₁₃H₁₄S (188.29): C 76.55; H 6.42; S 17.03.]

(Z)-2-Methylthio-3-phenyl-2-hepten-4-yne (17). As in the preceding experiment, compound 17 was prepared from 2. The crude product (0.85 g) was purified as above, which gave the title compound, 0.64 g (63 %), m.p. 84–86 °C. IR: C=C 2200 cm⁻¹, NMR (CCl₄): δ 2.00 (1-H, 6-H, bs, 6 H); 7.17 (C₆H₅, s, 5 H); 2.32 (SCH₃, s, 3 H). [Found: C 77.74; H 7.01; S 15.80. Calc. for C₁₃H₂₄S (202.32): C 77.18; H 6.98; S 15.85.]

The stability of 2-([N,N-dimethylaminomethyl]-5-methyl-3-thienylithium. 2f (0.117 g, 0.500 mol) was introduced into an NMR tube. The tube was sealed with a plastic cap and cooled to -70 °C, whereupon 0.50 ml of 1.0 M ethyllithium was injected through the cap by a syringe and the tube was sealed off with a glassblower’s torch. The vinyl region was scanned every two hours during 12 h, but no traces of vinylc protons were observed.
2-(N,N-Dimethylaminomethyl)-5-methylthiophene. The general method G was followed. From 2.34 g (0.0100 mol) of 2I in 30 ml of ether, 13 ml (0.010 mol) of 0.80 M ethereal ethyllithium and 5.45 g (0.0500 mol) of ethyl bromide, 1.40 g (90%) of the crude title compound was obtained after evaporation of the solvent. GLC (column OV 17, 3%, 100–250 °C, 20°/min) showed only one component. IR: no acetylenic absorptions. Distillation gave the pure title compound, b.p. 88–89 °C, nD20 = 1.5170. (Lit. b.p. 88–89 °C, nD20 = 1.5150.) NMR (CCl4): δ 6.53 (3-H, bd); 4.4 (4-H, d, q); 2.43 (5-CH3, bs, 3 H); 3.48 (-CH2-), s, 2 H; 2.20 (NCH3, s, 6 H). JH,H = 3.2 Hz; JH,HCH = 1.0 Hz.

(Z)-1-(N,N-dimethylamino)-2-ethylthio-2-hexen-1-yl-ene (23). The general method G was followed. From 10.0 g (0.0427 mol) of 22 in 75 ml of ether, 75 ml (0.045 mol) of 0.80 M ethereal ethyllithium and 16.4 g (0.150 mol) of ethyl bromide, 7.6 g of a crude product was obtained. The title compound was obtained pure by distillation, b.p. 76–80 °C, 3.8 g (49%). (Extensive decomposition took place during the distillation.) IR: C=CH 2220 cm⁻¹. NMR (CCl4): δ 2.97 (1-H, bs, 2 H); 5.53 (3-H, m, 1 H); 1.98 (6-H, d, 3 H); 2.17 (NCH3, s, 6 H); (SC2H4H) 2.97 (q, 2 H) and 1.25 (t, 3 H). JH,H = 2.4 Hz; JSC2H4H = 7.2 Hz. [Found: C 65.44; H 9.29; S 17.39. Calc. for C14H16NS (183.32): C 65.52; H 9.35; S 17.49.]

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