Recl. Trav. Chim. Pays-Bas **114**, 18–21 (1995) 0165-0513/95/01018-04$09.50
SSDI 0165-0513(94)00074-3

Metallation and functionalization of *N*-vinylpyrrole

A.G. Mal'kina [a], **O.A. Tarasova** [a], **H.D. Verkruijsse** [c], **A.C.H.T.M. van der Kerk** [b], **L. Brandsma** [c], **B.A. Trofimov** [a,*]

[a] *Institute of Organic Chemistry of the Russian Academy of Sciences, Siberian Branch, Favorsky Street 1, 664033 Irkutsk, Russia*
[b] *Department of Analytical Molecular Spectroscopy, University of Utrecht, Sorbonnelaan 16, 3584 CA Utrecht, Netherlands*
[c] *Department of Preparative Organic Chemistry of the University, Debye Institute, Padualaan 8, 3584 CH Utrecht, The Netherlands*
(Received September 5, 1994)

Abstract. Metallation of *N*-vinylpyrrole under presumed kinetic conditions, using *n*-butyllithium in THF/hexane mixtures, *n*-butyllithium/*N,N,N',N'*-tetramethylethanediamine in hexane, or *n*-butyllithium/potassium *tert*-butoxide (1:1 molar ratio) in THF/hexane mixtures gives almost equal amounts of derivatives metallated at the α-vinyl or 2-pyrrole position. In the presence of 7–10 mol% diisopropylamine the α-vinyl-lithiated compound is transformed relatively slowly into the pyrrole-lithiated derivative at ~ +30°C. The combined use of catalytic amounts of diisopropylamine and equivalent amounts of *n*-butyllithium and potassium *tert*-butoxide gives rise to a fast and almost complete conversion into the pyrrole-metallated derivative at temperatures in the range −60 to −80°C. A number of 2-substituted *N*-vinylpyrroles have been obtained in good yields by reaction with various electrophilic reagents, in most cases preceded by the addition of anhydrous lithium bromide. *N*-Deprotection is successful only in the case of *N*-vinyl-2-pyrrolecarboxaldehyde.

Introduction

N-Vinylpyrroles have become readily accessible by reaction of oximes or pyrrole derivatives with acetylene[1]. Using the system KOH/dimethyl-sulfoxide, the vinylations can be conveniently carried out at temperatures within the range 90–130°C under atmospheric pressure. Recently[2], we developed a simple procedure for the vinylation of pyrrole itself by this synthetic method, making *N*-vinylpyrrole available in any desired amount. In their search for methods giving access to derivatives of pyrrole, several authors have studied the metallation of *N*-substituted pyrroles[3].

In the present paper we describe the metallation of *N*-vinylpyrrole with strongly basic reagents and subsequent functionalizations with a variety of electrophiles.

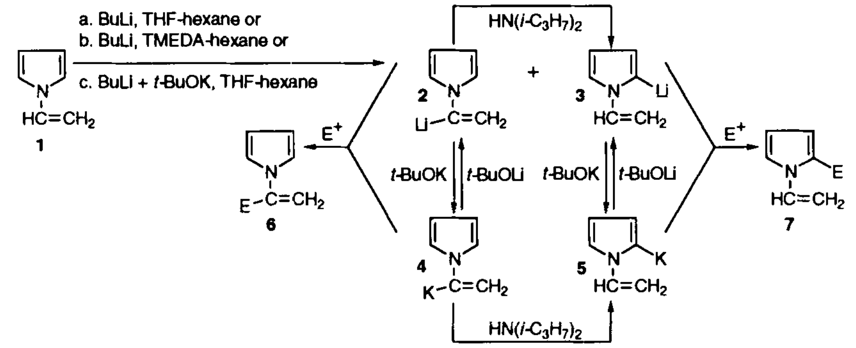
Results and discussion

a. Kinetically controlled metallation (see Scheme 1)

In our first attempts at regioselective metallation of *N*-vinylpyrrole **1** this compound was slowly added to solutions of *n*-butyllithium (BuLi) in 1:1 (v/v) mixtures of tetrahydrofuran (THF) and hexane, and of BuLi/*N,N,N',N'*-tetramethylethanediamine (TMEDA) (1:1 molar ratio) in hexane. The progress of the metallation was followed by taking small samples from the reaction mixtures and adding these to a mixture of a large excess of dimethyl disulfide (Me_2S_2) and THF in a reagent tube. After the addition of a small amount of water and pentane the product composition was investigated by gas-liquid chromatography (GLC). This investigation revealed that the metallations proceeded surprisingly fast at room temperature: using base concentrations of ~0.8 to 1.6 mol/l, they were essentially complete after about 15 minutes. In both cases, GLC (and NMR, after synthetic experiments with Me_2S_2), showed almost equal amounts of products substituted at the α-vinyl 2-pyrrole position. The ratio of these derivatives did not change after longer periods of interaction between the basic reagents and vinylpyrrole. We therefore presume that the ratio found corresponds to the relative rates of lithiation at the α-C atom of the vinyl group and the 2-C atom of the pyrrole ring, i.e. it concerns lithiations under kinetic conditions.

As no coordinating properties can be assigned to the vinyl group, we assume that the unusually fast ring metallation (1-methylpyrrole is lithiated much less smoothly in the 2-position under similar conditions[3,7]) is due to electronic activation by the vinyl group.

Experiments on a preparative scale gave, after quenching at −30 to +60°C with Me_2S_2 and other electrophiles a mixture of the two pyrrole derivatives **6a** and **7a** (E = MeS) in excellent yields. It appeared to be impossible to separate compounds **6** and **7** by fractionated distillation as their volatilities are comparable (for structural evidence of the products vide infra).



Scheme 1

Hoping to influence the ratio of the metallic intermediates by a metal effect, we reacted **1** at −80°C with a 1:1-molar solution of BuLi and potassium *tert*-butoxide (^{t}BuOK) in THF and hexane (1:1). However, under these conditions the relative amounts of the methylthio derivatives formed in quench experiments were about the same as in the experiments previously mentioned. "Preparative" methylthiolation afforded the derivatization mixture in excellent yields. A number of experiments with BuLi and ^{t}BuOK or anhydrous LiBr in THF or in diethyl ether as auxiliary reagents gave similar ratios of the two metallic intermediates.

b. Thermodynamically conducted metallations

As the experiments described above did not give any information about thermodynamic preference for either vinylic or ring metallation, we considered the use of a reagent that can transfer the metal atom from the vinyl group to the ring or vice versa through a sequence of proton donation and abstraction. In this way we could possibly arrive at a ratio of the metallic intermediates that corresponds to the thermodynamic ratio. Diisopropylamine was chosen for our experiments for two reasons: firstly, because it has a high kinetic acidity in spite of its high pK value of ~36[4], and, secondly, because its thermodynamic acidity is comparable with the suspected acidities of the α-vinylic and ring protons in **1**. These two properties should ensure an efficient proton (or metal) transfer between the vinylic group and the ring.

Addition (at room temperature) of a small amount of this amine to the solution obtained from **1** and BuLi in THF/hexane indeed resulted in a change of the ratio of the metallated intermediates (as appeared from quenching with Me_2S_2) in favour of the ring-metallated compound. However, this process proceeded only slowly – though almost completely – at +40°C, several hours being necessary. Moreover, the amount of starting compound detected in quench experiments with Me_2S_2 by GLC gradually increased to a synthetically unattractive one, possibly due to proton donation by THF. We next carried out experiments in which 5–10% diisopropylamine was added at −80°C to the metallation mixture obtained at −80°C from **1**, BuLi, and ^{t}BuOK in THF/hexane mixtures. Quench experiments with Me_2S_2 and GLC showed that even after 15 minutes almost complete transformation into the ring-metallated intermediate had occurred ($\leq 5\%$ of vinyl-metallated compound persisted). It has been convincingly shown in previous investigations that proton-transfer reactions involving lithium bases in the presence of equivalent amounts of ^{t}BuOK are much faster[5–7]. Therefore the sequence of proton donation and removal via diisopropylamine leading to the 2-metallated vinylpyrrole **5** and **3** is also expected to proceed more easily in the presence of ^{t}BuOK. We assume that the metallation of **1** with the 1:1 molar mixture of BuLi and ^{t}BuOK and subsequent addition of diisopropylamine leads to an equilibrium mixture of the lithium compounds **2** and **3** and the potassium compounds **4** and **5**.

It should be noted that the amount of diisopropylamine is very critical: if too little were used the rate of transformation into the ring-metallated intermediate was low, whereas application of more than 5–10 mol% resulted in a decrease of the yields of the functionalization products, with a relative excess of vinylpyrrole.

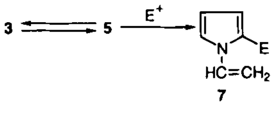
It appeared to be also possible to effect the transformation into the ring-metallated species by using only 20 mol% of ^{t}BuOK, in combination with diisopropylamine. Under these conditions this process proceeded more slowly and higher temperatures (in the region of −25°C) were necessary. Experiments in which the reaction was monitored by quenching small samples with Me_2S_2 showed that, at these higher temperatures, the amount of starting compound gradually increased, possibly as a consequence of protonation by the solvent.

c. Functionalization

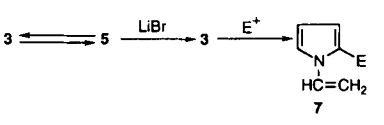
Functionalizations with formation of 2-substituted *N*-vinylpyrroles were carried out according to the following methods:

1. Treatment of **1** with BuLi, equivalent amounts of ^{t}BuOK and catalytic amounts of ^{i}Pr$_2$NH in THF at −80°C for 15–20 min, followed by addition of the electrophilic reagent.
2. As in 1, but with the addition of a 100 mol% excess of LiBr prior to reactions with the electrophile. This addition is assumed to guarantee complete conversion of **5** into **3**.

Procedure 1 (Scheme 2, E = MeS, ^{t}BuC(H)OH, Me_3Si) gave good results in the cases of Me_2S_2, the non-enolizable pivaldehyde $(CH_3)_3C{-}CH{=}O$ and trimethylchlorosilane, but the alkylation with n-butyl bromide gave rise to the predominant formation of a dibutyl derivative (presumably through a sequence of alkylation at the 2-position, metallation of this derivative by **5** at the double bound and introduction of the second butyl group. The reactions with acetone, cyclohexanone and acetaldehyde



Scheme 2



Scheme 3

proceeded especially unsatisfactorily, presumably due to enolate formation. Unexpectedly, the reaction with oxirane did not give any of the 2-hydroxyethyl derivative, but a number of unindentified products.

Procedure 2 (Scheme 3) proceeded with satisfactory results in all cases.

*d. Evidence for the structures of **6** and **7***

As mentioned before, treatment of *N*-vinylpyrrole **1** with a variety of strongly basic reagents under kinetic conditions followed by reaction with electrophiles afforded **6** and **7** in almost equal quantities. In the case of functionalization with Me_2S_2, evidence for the occurrence of **6a** (E = MeS) was provided by treatment of the mixture with an excess of potassium amide in liquid ammonia, resulting in the formation of N-ethynylpyrrole **8** and leaving **7** unchanged. In order to prevent re-addition of thiolate during the work-up, the ammoniacal reaction mixture was treated with an equivalent amount of methyl bromide (at −45°C) which selectively reacted with methanethiolate. Ethynylpyrrole was obtained in a reasonable yield (calculated on the amount of **6a** present in the starting mixtures). This acetylenic compound has recently been synthesized for the first time, starting from pyrrole[8].

The formation of **8** in this elimination reaction proves, not unambiguously, that the starting compound has structure **6a**: the metallation of the vinyl group in **1** could have occurred at the terminal carbon atom affording, upon addition of Me_2S_2, compound **9** which, in principle, also could give **8** in the elimination reaction. We were fortunate to obtain both **6a** and **9** by adding **8** to a solution of MeSNa in liquid ammonia, and subsequently replacing this solvent by ethanol. While the fragmentation pattern of the mass spectra did not allow a conclusion to be made with regard to the structure of the two adducts, the NMR spectrum of the product mixture showed the characteristic signals for the geminal protons in **6a** and the (*Z*)-vicinal protons in **9**.

Most products **7** showed a purity of at least 95%, the main impurity being **6**. The compositions and structures of the products were derived from GLC, ^{1}H-NMR spectroscopy and, in a few representative cases, from the mass spectra. Compound **7** E = Me is identical to a sample prepared by the Trofimov reaction[9].

e. Experiments directed to the removal of the vinyl group

Gonzales et al.[10] described a method for the removal of the CH_2CH_2Cl group from ring-substituted pyrroles, involving abstraction of HCl by a base and the subsequent treatment of the intermediary *N*-vinylpyrrole derivative with acid. We applied this acid treatment to our compounds **7**, but the deprotection was only successful in the case of **7**, E = CH = O (*Gonzales* et al. also obtained this aldehyde). All of the other derivatives **7** were converted into intractable tars or amorphous solids. (It may also be concluded from the article of *Gonzales* that this deprotonation method has a limited scope.)

Experimental

a. General

All operations were performed under an inert atmosphere. *n*-Butyllithium (BuLi) was purchased from Chemetall, Frankfurt am Main, Germany, as a 1.6 molar solution in hexane. Potassium *tert*-butoxide (^{t}BuOK) was also commercially available. Lithium bromide was dried by heating the commercially available anhydrous salt for 45 min (batches of ≤ 40 g) at 150°C in a vacuum of 1 to 15 mmHg, using a 500-ml round-bottomed flask. Dry THF was made by shaking the solvent with machine-powdered potassium hydroxide (50 g/l) and distilling the filtered liquid from sodium sand in the presence of benzophenone. NMR-spectra were recorded on a Varian EM 390 spectrometer (20% solutions in CCl_4, Me_4Si δ 0 ppm, as internal standard). All gas chromatogramms were made on a Varian 3400 gas chromatograph with a 15 m capillary column, internal diameter 0.53 mm, with a 1.5 μm DB-5 coating.

b. Functionalizations according to procedure 1

A 500-ml round-bottomed three-necked flask, fitted with a thermometer/gas-inlet combination, a mechanical stirrer and a gas outlet was purged with dry nitrogen. Subsequently a solution of 60 mmol of BuLi in 37 ml of hexane (1.6 molar solution) was placed in the flask. After cooling to below 0°C, 40 ml of THF was added, followed by 50 mmol of *N*-vinylpyrrole. The temperature of the reaction mixture was allowed to rise to *ca.* 10°C, then the mixture was cooled to −90°C (occasional cooling in a bath with liquid nitrogen). A solution of 60 mmol of ^{t}BuOK in 25 ml of THF was added over ~ 30 seconds while keeping the temperature between −80 and −60°C. After 5 min, a mixture of 7 mmol of diisopropylamine and 3 ml of THF was added at −80°C. A test experiment (a 1-ml sample of the reaction mixture was added to a mixture of 0.2 g of Me_2S_2 and 1 ml of THF after which GLC was performed) showed that after 15 to 20 min the ratio of the ring-metallated and α-vinyl-metallated intermediates had become optimal (at least 95:5). Me_2S_2, pivaldehyde (Me_3CCHO) or Me_3SiCl (70 mmol, freshly distilled) was added in one portion at −80°C with vigorous stirring. The cooling bath was removed and the temperature allowed to rise to −10°C. Water (100 ml) was then added and extraction with pentane was carried out. After washing the extracts with water and drying the extracts over anhydrous sodium sulfate, the solvent was removed under reduced pressure. Distillation afforded the derivatives.

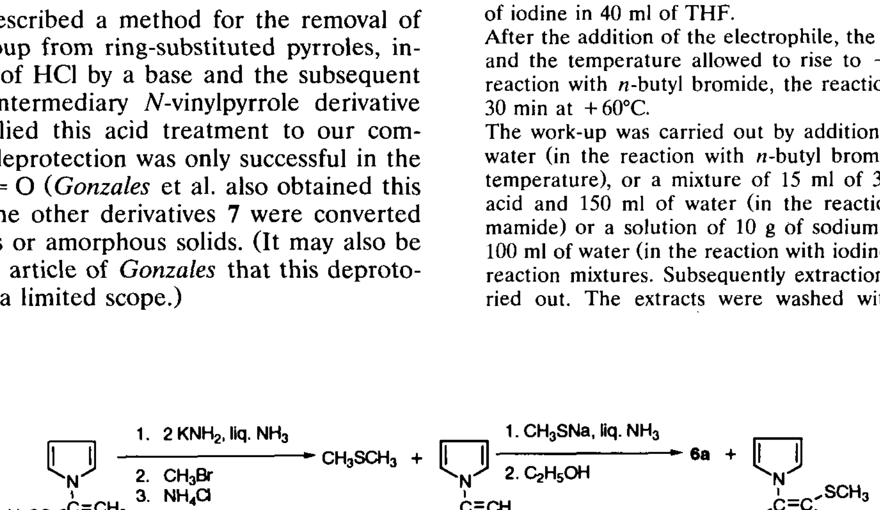
c. Functionalizations according to procedure 2

After test experiments had shown that (after 15 to 20 min) the thermodynamic metallation of **1** with BuLi, ^{t}BuOK and diisopropylamine at −80 to −60°C had proceeded to completion, a solution of 10 g (excess) of lithium bromide in 30 ml of THF was added at −80°C with vigorous stirring.

After 10 min, the following compounds were added in one portion with vigorous stirring: 70 mmol of freshly distilled acetaldehyde; a mixture of 100 mmol of oxirane and 20 ml of THF; 70 mmol of dry acetone; 60 mmol of cyclohexanone; 60 mmol of freshly distilled benzaldehyde; 70 mmol of dry *N*,*N*-dimethylformamide; 150 mmol of *n*-butyl bromide; 70 mmol of methyl iodide; a solution of 60 mmol of iodine in 40 ml of THF.

After the addition of the electrophile, the cooling bath was removed and the temperature allowed to rise to −20°C. In the case of the reaction with *n*-butyl bromide, the reaction mixture was heated for 30 min at +60°C.

The work-up was carried out by addition (at −20°C) of 100 ml of water (in the reaction with *n*-butyl bromide after cooling to room temperature), or a mixture of 15 ml of 30% aqueous hydrochloric acid and 150 ml of water (in the reaction with *N*,*N*-dimethylformamide) or a solution of 10 g of sodium thiosulfate ($Na_2S_2O_3$) in 100 ml of water (in the reaction with iodine) to the vigorously stirred reaction mixtures. Subsequently extractions with pentane were carried out. The extracts were washed with water and dried over



Scheme 4

anhydrous sodium sulfate. After removal of the solvents under reduced pressure (in the case of the reaction with methyl iodide the greater part of solvent was first distilled off under normal pressure) the remaining liquid was distilled.
The iodine derivative appeared to be very unstable (explosive decomposition during an attempted distillation).

1-Vinyl-2-(methylthio)pyrrole (**7a**) B.p. 80°C/15 mmHg; n_D^{20} 1.5766; yield 70%. ^{1}H-NMR: 7.2–7.5 (d.d.), 4.65 (d), 5.05 (d) (vinylic protons); 2.18 (SCH_3); 7.10 (m), 6.30 (m), 6.15 (m) (ring protons). Mass spectrum: exact mass 139.0456 (calcd. 139.0456).

1-Vinyl-2-(trimethylsilyl)pyrrole (**7b**) B.p. 79°C/15 mmHg; n_D^{20} 1.5085; yield 75%. ^{1}H-NMR: 6.8–7.1 (d.d.), 4.55 (d), 5.10 (d) (vinylic protons); 0.3 ($SiMe_3$); 7.15 (m), 6.15 (m), 6.30 (m) (ring protons). Mass spectrum: exact mass 165.0952 (calcd. 165.0974).

1-Vinyl-2-butylpyrrole (**7c**) B.p. 93°C/15 mmHg; n_D^{20} 1.5041; yield 72%. ^{1}H-NMR: 6.6–6.9 (d.d.), 4.90 (d), 4.50 (d) (vinylic protons); 1.50 (m), 2.50 (t) (butyl protons); 6.79 (m), 5.96 (m), 5.76 (m) (ring protons).

1-Vinyl-2-iodopyrrole (**7d**) Not distilled because of thermal instability, however, the crude product (yield ~90%) showed a reasonable purity (~90%) by GLC and NMR. ^{1}H-NMR: 6.8–7.1 (q); 5.06 (d), 4.70 (d) (vinylic protons); 7.10 (m). 6.30 (m), 6.16 (m) (ring protons).

1-Vinyl-2-methylpyrrole (**7e**) B.p. 47°C/15 mmHg; n_D^{21} 1.5220; yield 65%. ^{1}H-NMR: 6.6–6.9 (d.d.), 4.93 (d), 4.48 (d) (vinylic protons); 2.13 (CH_3, broadened signal); 6.7 (m), 5.90 (m), 5.73 (m) (ring protons). The spectrum is identical to that of a sample prepared according to Ref. 9.

1-Vinyl-2-formylpyrrole (**7f**) B.p. 85°C/15 mmHg; n_D^{20} 1.5862; yield 74%. ^{1}H-NMR: 9.57 (s) (formyl proton); 7.8–8.1 (d.d.), 5.20 (d), 4.78 (d) (vinylic protons); 7.32 (m), 6.87 (m), 6.25 (m) (ring protons). Mass spectrum: exact mass 121.0517 (calcd. 121.0528).

1-Vinyl-(2-hydroxymethyl)pyrrole (**7g**) B.p. 110°C/15 mmHg; n_D^{20} 1.5525; yield 65%. ^{1}H NMR: 6.7–7.1 (d.d.), 4.50 (d), 4.55 (d) (vinylic protons); 4.28 (s) (CH_2); 6.8 (m), 5.9 (m) (ring protons). Mass spectrum: exact mass 123.0642 (calcd. 123.0684).

1-Vinyl-2-(1-hydroxyethyl)pyrrole (**7h**) B.p. 130°C/ 15mm Hg; n_D^{20} 1.5435; yield 73%. ^{1}H-NMR: 6.8 (m) (a-vinylic proton and ring proton 5); 4.97 (d), 4.59 (d) (vinylic protons); 6.0 (m), 5.8 (m) (ring protons); 3.60 (t) (CH_2OH); 2.7 (t) (CH_2). Mass spectrum: exact mass 137.0843 (calcd. 137.0841).

1-Vinyl-2-(2-hydroxyethyl)pyrrole (**7i**) B.p. 109°C/15 mmHg; n_D^{21} 1.5360; yield 69%. ^{1}H-NMR: 7.0–7.3 (d.d.), 4.97 (d), 4.55 (d) 4.60 (d), (vinylic protons and CH-O); 6.87 (m), 5.95 (m) (ring protons); 1.35 (d) (CH_3). Mass spectrum: exact mass 137.0849 (calcd. 137.0841).

1-Vinyl-2-(3-hydroxy-2,2-dimethylpropyl)pyrrole (**7j**) B.p. 120°C/15 mmHg; n_D^{20} 1.5185; yield 71%. ^{1}H-NMR: 7.0–7.3 (d.d.), 5.05 (d), 4.55 (d) (vinylic protons); 6.83 (m), 6.0 (m) (ring protons); 4.35 (s) (H-C-O); 0.9 (s) (^{t}butyl). Mass spectrum: exact mass 179.1316 (calcd. 179.1310).

1-Vinyl-2(a-hydroxybenzyl)pyrrole (**7k**) M.p. 70–71°C (hexane); yield 80%. ^{1}H-NMR: 7.3 (m) (phenyl); 6.9–7.2 (d.d.), 4.95 (d), 4.65 (d) (vinylic protons); 5.70 (s) (H-C-O); 6.9 (m), 5.97 (m), 5.70 (m) (ring protons). Mass spectrum: exact mass 199.0995 (calcd. 199.0997).

1-Vinyl-2-(1-hydroxy-1-methylethyl)pyrrole (**7l**) M.p. 73–74°C (pentane); yield 88%. ^{1}H-NMR: 7.5–7.8 (d.d.), 4.90 (d), 4.50 (d) (vinylic protons); 6.80 (m), 5.85 (m) (ring protons); 1.53 (s) (CH_3). Mass spectrum: exact mass 151.0991 (calcd. 151.0997).

1-Vinyl-2-(1-hydroxycyclohexyl)pyrrole (**7m**) M.p. 74–75°C (pentane); yield 80%. ^{1}H-NMR: 7.5–7.8 (d.d.), 4.95 (d), 4.55 (d) (vinylic protons); 6.80 (m), 5.95 (m) (ring protons); 1.6 (m) (CH_2). Mass spectrum: exact mass 191.1343 (calcd. 191.1310).

d. Kinetic metallation of 1 *and subsequent functionalization with dimethyl disulfide (Me_2S_2)*

To a mixture of 0.20 mol of **1** and 120 ml of THF, a solution of 0.20 mol of n-butyllithium in 126 ml of hexane was added over 15 min, while keeping the temperature of the reaction mixture at 20–25°C. After an additional 45 min, the solution was cooled to −40°C and 0.22 mol of Me_2S_2 was added in one portion with vigorous stirring. Five minutes after this addition, 100 ml of water was added, also with vigorous stirring. The upper layer was dried over potassium carbonate. The liquid remaining, after concentration of the solution in vacuo, was distilled through a 20-cm Vigreux column to give a mixtureof **6a** and **7a** (ratio ~45:55). ^{1}H-NMR-spectrum of **6a**: 2.14 (SCH_3); 4.75 (d), 5.15 (d) (vinylic protons); 6.10 (m), 6.85 (m) (ring protons).

e. Treatment of the mixture of 6a *and* 7a *with potassium amide in liquid ammonia: conversion of* 6a *into N-ethynylpyrrole* 8

A solution of 0.18 mol of potassium amide in 200 ml of liquid ammonia was prepared from potassium in the presence of a 50 mg of iron(III) nitrate in a 1-l round-bottomed three-necked flask, fitted with a mechanical stirrer, a gas outlet and a gas-inlet/dropping-funnel combination. The mixture of **6a** and **7a** (containing ~45% **6a**) (0.2 mol, dissolved in 50 ml of dry ether) was added dropwise over 10 min with efficient stirring. After completion of the addition the reaction mixture was cooled in a bath at −50°C, while passing nitrogen through the flask. A mixture of methyl bromide (0.09 mol) and dry ether (50 ml) was added dropwise over 15 min, then the cooling bath and the gas outlet were removed and finely powdered ammonium chloride (0.15 mol) was added in small portions over 10 min, with efficient stirring, while continuing the stream of nitrogen. The ammonia was then removed by warming the flask in a water bath at 35–40°C. Dry ether (100 ml) was added to the salty residue. After warming the suspension for an additional 15 min at ~35°C, it was filtered on a sintered-glass funnel, and the salt was rinsed well with ether. The greater part of the ether was slowly distilled off under nitrogen at atmospheric pressure through a 40-cm Vigreux column (temperature of the bath was not higher than 100°C during the last stage of the distillation). *N*-Ethynylpyrrole, together with a small amount of ether was obtained by evacuating the flask and collecting the volatile material in a receiver cooled to −70°C. Redistillation of the contents of the receiver under nitrogen through a 20 cm Vigreux column gave N-ethynylpyrrole, b.p. 108–110°C/760 mmHg; n_D^{20} 1.513; yield 65% (calculated on **6a** in the starting mixture). The NMR spectral data corresponded with those given in Ref 8.

f. Addition of sodium methanethiolate to ethynylpyrrole: formation of 6a *and* 9

In 100 ml of anhydrous liquid ammonia was dissolved 0.05 mol (1.2 g) of sodium. Me_2S_2 (0.025 mol, 2.4 g) was added dropwise with magnetic stirring. Subsequently ethynylpyrrole (0.05 mol, 4.6 g) was added in one portion. After practically all the ammonia had evaporated, 50 ml of 100% ethanol was added and the mixture was warmed for 30 min at 30°C. Working up occurred by addition of 200 ml of water, extraction with pentane and removal of this solvent under reduced pressure. Careful distillation of the remaining liquid afforded one fraction, b.p. 78–90°C/15 mmHg (yield ~80%), consisting of **6a** and **9** (ratio ~5:2). Exact mass of **9** 139.0449 (calcd. 139.0456). The ^{1}H-NMR spectrum of **9** showed the vinylic protons in the *Z*-position adjacent to the MeS group (5.22 ppm) and the pyrrole ring (6.55 ppm). The ring protons appeared at the same positions as for **6a** (6.10 and 6.85, multiplets), the MeS signal appeared at 2.26 ppm.

References

[1] *B.A. Trofimov*, Vinylpyrroles in The Chemistry of Heterocyclic Compounds, Vol. 48, part 2, p. 131, *R.A. Jones*, ed., John Wiley, (1992).

[2] *O.A. Tarasova, A.G. Mal'kina, L. Brandsma* and *B.A. Trofimov*, Synth. Commun. **24**, 2035 (1994).

[3] *M. Gharpure, A. Stoller, F. Bellamy, G. Firnau* and *V. Snieckus*, Synthesis 1079, (1991) and references mentioned therein.

[4] *R.R. Fraser* and *T.S. Mansour*, J. Org. Chem. **49**, 3442, (1984).

[5] *L. Lochmann, J. Pospisil* and *D. Lim*, Tetrahedron Lett. 255, (1966); *M. Schlosser*, J. Organometal. Chem. **8**, 9, (1967).

[6] *M. Schlosser*, Polare Organometalle, Springer-Verlag, Heidelberg, (1973).

[7] *L. Brandsma* and *H.D. Verkruijsse*, Preparative Polar Organometallic Chemistry, Vol I, Springer-Verlag, Heidelberg, (1978).

[8] *M.S. Paley, D.O. Frazier, H. Abeledeyem, S.P. McManus* and *S.E. Zutaut*, J. Amer. Chem. Soc. **114**, 3247, (1992).

[9] *A.I. Mikhaleva, B.A. Trofimov* and *A.N. Vasil'ev*, Zh. Org. Khim. **15**, 602, (1979) (Russ.); Chem. Abstr. **91**, 56738, (1979).

[10] *C. Gonzalez, R. Greenhouse, R. Tallabs* and *J.M. Machowski*, Can. J. Chem. **61**, 1697, (1973).