

## Synthesis of 5-[1-(1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrroles

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**Dedicated to academician M. G. Voronkov's 80<sup>th</sup> birthday**  
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### Abstract

The acid-catalysed dimerization of 1-vinyl-2-alkyl- or 1-vinyl-2,3-dialkylpyrroles proves to be a general approach to the synthesis of 5-[1-(1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrroles, a novel family of pyrrole building blocks and intermediates in heterocyclic chemistry.

**Keywords:** 1-Vinylpyrroles, acid-catalyzed dimerization, 5-[1-(1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrroles

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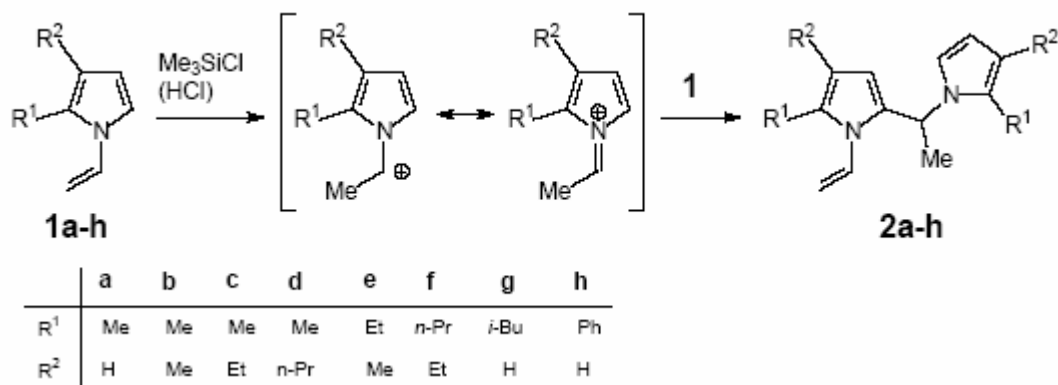
### Introduction

Vinylpyrroles are known as structural units of biologically important natural pigments (e.g. hemoglobin, chlorophyll) and valuable intermediates in pyrrole chemistry.<sup>1,2</sup> Among them, the hetaryl-1-vinylpyrroles are less well explored. The only published method of the synthesis of these compounds appears to be still the reaction of hetaryl alkyl ketoximes with acetylene (the Trofimov reaction)<sup>3-5</sup> performed either as a one-pot procedure (with excess acetylene) or with isolation of corresponding 1*H*-pyrroles followed by vinylation. The knowledge about pyrrolyl-1-vinylpyrroles (vinyldipyrroles) relates to the dimerization of 1-vinyl-4,5,6,7-tetrahydroindole.<sup>6-9</sup> Meanwhile, vinyldipyrroles and vinyl(dipyrrolyl)alkanes are of high interest as monomers for conducting cross-linked polypyrrole networks<sup>10</sup> as well as versatile building blocks for the pyrrole chemistry and for the design of multidentate ligands.

### Results and Discussion

To further contribute in filling this gap, we report on a general approach to the synthesis of 5-[1-(1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrroles **2a–g** by acid-catalyzed dimerization of substituted 1-

vinylpyrroles **1a–g** (Scheme 1).



### Scheme 1

The known examples of the transformation of 1-vinylpyrroles (1-vinylpyrrole, 1-vinylindole, 1-vinylcarbazole) in the presence of Brønsted and Lewis acids involve the formation of charge-transfer complexes and subsequent polymerization across the double bond.<sup>11</sup>

In this study, Me<sub>3</sub>SiCl and HCl (2%) were used as catalysts for the dimerization of 1-vinylpyrrole, the former reacting as supplier of HCl in the presence of moist reactants.

In early studies, only 1-vinyl-4,5,6,7-tetrahydroindole has been dimerized in the same way with Friedel-Crafts catalysts. Therefore, the applicability of this reaction to other 1-vinylpyrroles remained uncertain. The results reported here show that the reaction is general and adds to synthetic tools of pyrrole chemistry.

As expected, the yield of dimers **2a–g** depends on both the reaction conditions and the nature of the pyrrole ring substituents of the starting materials **1a–g**. In the presence of Me<sub>3</sub>SiCl (2%, 20 °C, 24 h) the dimers **2a,b** and **2d** were formed in 38.9–53.0% yield (Table 1). With HCl the major reaction products were oligomers with the only exception of 1-vinylpyrrole **1e** affording the dimer **2e** in 46.1% yield (Table 1).

Increasing the size of the 3-substituent of the pyrrole **1** (H < Me < *n*-Pr) gave higher yields of dimers **2** (Table 1). Peculiar exceptions are 3-ethyl-2-methyl-1-vinylpyrrole **1c** and 2-(isobutyl)-1-vinylpyrrole **1g**, which did not react and were almost completely recovered from the reaction mixture (95–99%). Attempts to prepare the dimers **2c** and **2g** by increasing the reaction time (up to 48 h) or with higher Me<sub>3</sub>SiCl concentration (up to 4%) failed. Low yields (0.8–3.4%) of **2c** and **2g** were obtained only at a reaction temperature at 50 °C or with HCl (Table 1). In 1-vinylpyrrole **1h** the phenyl substituent prevented the dimerization under the above conditions, and only oligomers were formed exclusively.

The 5-[1-(1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrroles **2a–g** are colorless or light-yellow liquids that were distilled under reduced pressure; the physico-chemical properties are listed in Table 2.

**Table 1.** Dimerization of 1-vinylpyrroles **1** at room temperature

| R <sup>1</sup> | R <sup>2</sup> | <b>1</b> | Catalyst <sup>a</sup>             | Time [h] | <b>2</b> | Yield [%] |          |
|----------------|----------------|----------|-----------------------------------|----------|----------|-----------|----------|
|                |                |          |                                   |          |          | <b>2</b>  | Oligomer |
| Me             | H              | <b>a</b> | Me <sub>3</sub> SiCl              | 24       | <b>a</b> | 38.9      | 21.4     |
| Me             | H              | <b>a</b> | HCl                               | 24       | <b>a</b> | 17.0      | 60.0     |
| Me             | Me             | <b>b</b> | Me <sub>3</sub> SiCl              | 24       | <b>b</b> | 48.4      | 19.0     |
| Me             | Me             | <b>b</b> | HCl <sup>b,c</sup>                | 24       | <b>b</b> | 20.2      | 75.3     |
| Me             | Et             | <b>c</b> | Me <sub>3</sub> SiCl              | 24       | <b>c</b> | Trace     | 5.0      |
| Me             | Et             | <b>c</b> | Me <sub>3</sub> SiCl              | 48       | <b>c</b> | Trace     | 6.3      |
| Me             | Et             | <b>c</b> | Me <sub>3</sub> SiCl <sup>c</sup> | 48       | <b>c</b> | Trace     | 54.2     |
| Me             | Et             | <b>c</b> | Me <sub>3</sub> SiCl              | 16e      | <b>c</b> | 0.8       | 24.8     |
| Me             | Et             | <b>c</b> | HCl                               | 24       | <b>c</b> | 3.4       | 62.6     |
| Me             | <i>n</i> -Pr   | <b>d</b> | Me <sub>3</sub> SiCl              | 24       | <b>d</b> | 53.0      | 20.0     |
| Et             | Me             | <b>e</b> | Me <sub>3</sub> SiCl              | 24       | <b>e</b> | Trace     | 5.0      |
| Et             | Me             | <b>e</b> | HCl                               | 24       | <b>e</b> | 46.1      | 17.2     |
| <i>n</i> -Pr   | Et             | <b>f</b> | Me <sub>3</sub> SiCl              | 24       | <b>f</b> | 8.8       | 7.4      |
| <i>i</i> -Bu   | H              | <b>g</b> | Me <sub>3</sub> SiCl <sup>d</sup> | 24       | <b>g</b> | Trace     | 0.3      |
| <i>i</i> -Bu   | H              | <b>g</b> | Me <sub>3</sub> SiCl              | 16       | <b>g</b> | Trace     | 3.8      |
| <i>i</i> -Bu   | H              | <b>g</b> | HCl                               | 24       | <b>g</b> | 2.6       | 49.2     |
| Ph             | H              | <b>h</b> | Me <sub>3</sub> SiCl              | 24       |          | 0         | 100      |

<sup>a</sup> Catalyst concentration 2%. <sup>b</sup> Exothermic reaction, up to 70 °C. <sup>c</sup> 36% Aqueous solution. <sup>d</sup> 4% Me<sub>3</sub>SiCl. <sup>e</sup> Reaction temperature 50 °C.

**Table 2.** Physico-chemical properties of 5-[1-(1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrroles **2a-f**

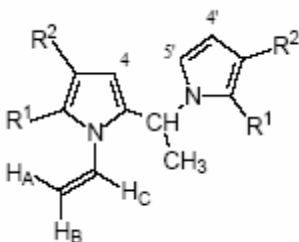
| <b>2</b> | bp [°C (mm Hg)]          | <i>d</i> <sub>4</sub> <sup>20</sup> | <i>n</i> <sub>D</sub> <sup>20</sup> | Elemental analysis: calcd/found [%] |             |             | M <sup>+</sup> |
|----------|--------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------|-------------|----------------|
|          |                          |                                     |                                     | C                                   | H           | N           |                |
| <b>a</b> | 112–112.5 (2)            | 1.0136                              | 1.5440                              | 78.46/78.20                         | 8.47/8.32   | 13.07/13.26 | 213            |
| <b>b</b> | 123–125 (2) <sup>a</sup> | 1.0036                              | 1.5420                              | 79.29/79.12                         | 9.15/9.40   | 11.56/11.37 | 241            |
| <b>c</b> | 125–126 (0.1)            | 0.9691                              | 1.5338                              | 79.95/79.98                         | 9.69/9.80   | 10.36/10.29 | 269            |
| <b>d</b> | 127–128 (0.1)            | 0.9584                              | 1.5294                              | 80.48/80.62                         | 10.13/9.96  | 9.39/9.42   | 297            |
| <b>e</b> | 137–140 (2)              | 0.9790                              | 1.5358                              | 79.95/80.48                         | 9.69/9.70   | 10.36/10.30 | 269            |
| <b>f</b> | dec <sup>b</sup>         | 0.9670                              | 1.5305                              | 80.93/80.58                         | 10.49/10.20 | 8.58/8.36   | -              |

<sup>a</sup> Crystals upon storage, mp 25.5–28.5 °C. <sup>b</sup> Decomposed during fractionation.

The structure of the dimers **2** was deduced from <sup>1</sup>H NMR spectra exhibiting the signals of the CH-CH<sub>3</sub> moiety at δ 5.09–5.17 and 1.60–2.57, respectively, along with those of the pyrrole and

vinyl group signals (Table 3). MS and IR spectra (Tables 2 and 4) are also in agreement with structure **2**. According to the IR study of *N*-vinylpyrroles,<sup>1</sup> all absorptions observed in the IR spectra of **2a–h** (Table 4) prove the non-planar conformation of the *N*-vinylpyrrole moiety, lacking any indication of the planar conformation. There is no band at 1590 cm<sup>-1</sup> assigned to the planar conformation.<sup>1</sup> The band assigned to  $\tau_{\text{CH=}}$  (960 cm<sup>-1</sup>) has shifted to higher frequency at 970–980 cm<sup>-1</sup>, with narrower and less intense appearance; the  $\omega_{\text{CH}_2=}$ -band (860 cm<sup>-1</sup>) has shifted to 870–880 cm<sup>-1</sup>, is narrow and reduced in intensity with a shoulder at 850 cm<sup>-1</sup>. Also the  $\omega_{\text{CH=}}$ -band (585 cm<sup>-1</sup>) has shifted to 600–630 cm<sup>-1</sup> with a shoulder at 585 cm<sup>-1</sup>. The band at 520 cm<sup>-1</sup> is absent.

**Table 3.** <sup>1</sup>H NMR data of 5-[1-(1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrroles **2a–h**.



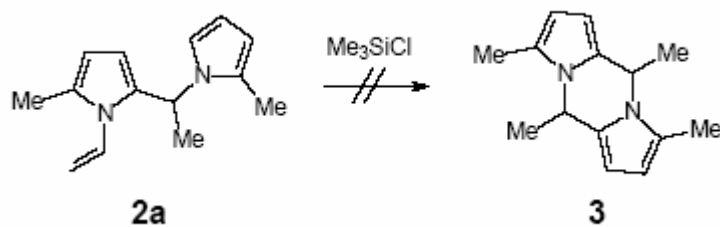
|          |                 | $\delta\text{H}$ |                   |                               |                       |   |   |                 |                              |  |  |
|----------|-----------------|------------------|-------------------|-------------------------------|-----------------------|---|---|-----------------|------------------------------|--|--|
| <b>2</b> | HA <sup>a</sup> | HB <sup>b</sup>  | HC <sup>a,b</sup> | 4-H,<br>4'-<br>H <sup>c</sup> | 5'-<br>H <sup>c</sup> | R <sup>1</sup>  | R <sup>2</sup>  | CH <sup>d</sup> | CH <sub>3</sub> <sup>d</sup> |  |  |
| <b>a</b> | 4.96            | 4.78             | 6.24              | 5.95                          | 6.32                  | CH <sub>3</sub> 2.20  | H 5.84  | 5.17            | 1.62                         |  |  |
| <b>b</b> | 4.89            | 4.75             | 6.05              | 5.84                          | 6.28                  | CH <sub>3</sub> 2.12  | CH <sub>3</sub> 2.00  | 5.13            | 1.60                         |  |  |
| <b>c</b> | 4.89            | 4.70             | 6.12              | 5.88                          | 6.29                  | CH <sub>3</sub> 2.09  | CH <sub>3</sub> 1.15 <sup>d</sup><br>CH <sub>2</sub> 2.41 <sup>d</sup>                                      | 5.15            | 1.61                         |  |  |
| <b>d</b> | 4.85            | 4.66             | 6.09              | 5.80                          | 6.25                  | CH <sub>3</sub> 1.60  | CH <sub>3</sub> 0.87 <sup>d</sup><br>CH <sub>2</sub> 0.92 <sup>d</sup><br>CH <sub>2</sub> 2.35 <sup>d</sup> | 5.12            | 2.57                         |  |  |
| <b>e</b> | 4.80            | 4.93             | 6.05              | 5.80                          | 6.22                  | CH <sub>3</sub> 1.10 <sup>d</sup><br>CH <sub>2</sub> 2.55 <sup>d</sup>                                      | CH <sub>3</sub> 1.64  | 5.14            | 2.00                         |  |  |
| <b>f</b> | 4.86            | 4.45             | 6.13              | 5.68                          | 6.89                  | CH <sub>3</sub> 0.95 <sup>d</sup><br>CH <sub>2</sub> 1.06 <sup>d</sup><br>CH <sub>2</sub> 2.50 <sup>d</sup> | CH <sub>3</sub> 1.40 <sup>d</sup><br>CH <sub>2</sub> 1.55 <sup>d</sup>                                      | 5.09            | 1.60                         |  |  |
| <b>g</b> | 5.12            | 4.60             | 6.15              | 5.74                          | 6.97                  | CH <sub>3</sub> 1.10 <sup>d</sup><br>CH 2.43 <sup>d</sup><br>CH <sub>2</sub> 1.54 <sup>d</sup>              | CH <sub>3</sub> 5.80  | 5.14            | 1.76                         |  |  |

<sup>a</sup>  $J_{\text{AC}} = 15.7\text{--}16.0$  Hz. <sup>b</sup>  $J_{\text{BC}} = 8.9\text{--}9.2$  Hz;  $J_{\text{AB}} = 0.8$  Hz. <sup>c</sup>  $J_{4,5'} = 2.9\text{--}3.2$  Hz. <sup>d</sup>  $J = 6.9\text{--}7.1$  Hz.

It is conceivable to further cyclize the dipyrrolylethanes **2a–g** in the manner shown in Scheme 2, and the feasibility of this transformation has been checked. The reaction was carried out in very diluted solutions (0.5 g **2a** in 200 mL hexane) at 20 °C in the presence of Me<sub>3</sub>SiCl (4.8% and 16%) during 170 h. Cyclization did not occur, the tricyclic diazine derivative **3** was not detected, only the starting material **2a** was recovered (Scheme 2).

**Table 4.** IR data of 5-[1-(1-pyrrolyl)ethyl]-1-vinylpyrroles **2a–g**

|          |   |
|----------|---|
| <b>2</b> | $\nu$ [m <sup>-1</sup> ] (neat)   |
| <b>a</b> | 610 w, 630 w, 708 s, 750, 780, 880, 980 w, 1090, 1150 w, 1220 s, 1280 s, 1370, 1410 s, 1520, 1640, 2840 s, 2900 s, 3100 w   |
| <b>b</b> | 610, 630, 710 s, 790, 890, 910, 970, 1020 w, 1040 w, 1060 w, 1110, 1170, 1200, 1310 s, 1350, 1370, 1420, 1490, 1510, 1640, 2860 s, 2910 s, 2970 s, 3090 w             |
| <b>c</b> | 630, 690 s, 710 w, 870, 910, 970, 1040 w, 1150, 1210, 1260, 1300 s, 1370, 1420, 1480 s, 1530 w, 1620, 2850, 2910 s, 2950 s, 3090 w                                    |
| <b>c</b> | 620, 690, 708, 870, 890, 910, 970, 1040 w, 1100, 1210, 1250, 1300 s, 1330, 1370, 1420, 1480, 1500 w, 1640, 2860, 2910 s, 2960 s, 3090 w                               |
| <b>e</b> | 610, 660, 680, 708, 790, 890 w, 970, 1030, 1050, 1100, 1160, 1200, 1250, 1290, 1310 s, 1330 w, 1370, 1420, 1440, 1480, 1500, 1640, 2860 s, 2920 s, 2960 s, 3010, 3090 |
| <b>f</b> | 600, 690, 700, 790 w, 870, 930, 970, 1100, 1150 w, 1190, 1200, 1260, 1290, 1320 w, 1370, 1450, 1480, 1630, 2850 s, 2900 s, 2940 w                                     |
| <b>g</b> | 630, 700, 780 w, 820, 880, 970, 1000 w, 1080 w, 1100 w, 1170, 1210, 1280, 1370, 1420, 1460, 1630, 2870, 2930, 2950 s  |

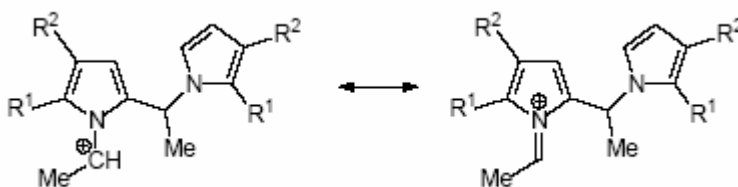


### Scheme 2

The reason for this failure cannot be just steric hindrance caused by an unfavorable conformation. Also the reactivity of the *N*-alkyl-pyrrole ring toward intramolecular electrophilic substitution may be decreased considering the strong electron-withdrawing effect of neighboring positively charged pyrrole ring transmitted through the sp<sup>3</sup> carbon atom by inductive (non-conjugative) effect as well as by a “through-space” polarization of the neighboring uncharged pyrrole ring (Scheme 3).

The decreased reactivity of the *N*-vinyl group of **2a–h** is also manifests by the fact that

dimers **2** cannot add phenols in the presence of  $\text{CF}_3\text{COOH}$ , whereas the corresponding monomers **1** form the corresponding 1-(1-aryloxyethyl)pyrroles in up to 60% yields.<sup>12</sup> This may be caused also by the lack of conjugation between the *N*-vinyl and the pyrrole moieties due to their noncoplanarity. This seems to be supported by the above mentioned changes in the IR spectra,<sup>9</sup> and by  $^1\text{H}$  NMR evidence. The proton signals of the vinyl  $\text{CH}_2$  group are shifted downfield by 0.4 ppm relative to the signals in pyrroles **1a–h** (Table 3). As has been shown for the dimer of 1-vinyl-4,5,6,7-tetrahydroindole<sup>9</sup> (with the  $^{13}\text{C}$  signal of the vinyl  $\beta$ -C shifted downfield by 10.4–11 ppm), this is the largest downfield shift known for these nuclei in the 1-vinylpyrroles series; correspondingly, this reflects the strongest deviation from coplanarity and conjugation.



**Scheme 3**

## Experimental Section

**General Procedures.** Spectra (films) were run on a Specord IR-75 spectrometer;  $^1\text{H}$  NMR spectra of  $\text{CDCl}_3$  solutions with TMS as an internal standard were recorded on a Tesla BS-567 instrument (100 MHz). Mass spectra were run on an LKB 2091 CMC-MS spectrometer, ionization energy 60 eV, SE-30 phase, ion source temperature 250 °C.

### 2-Methyl-5-[1-(2-methyl-3-propyl-1*H*-pyrrol-1-yl)ethyl]-3-propyl-1-vinyl-1*H*-pyrrole (**2d**).

**Typical procedure.** To 2-methyl-3-propyl-1-vinyl-1*H*-pyrrole (**1d**) (3.00 g, 20.1 mmol) was added with stirring chloro(trimethyl)silane (0.06 g, 0.5 mmol), and the reaction mixture was allowed to stand at room temperature for 24 h. The resultant dark-red resin was extracted with diethyl ether ( $3 \times 30$  mL), and 0.1 M KOH in ethanol (0.02 mL) was added to the extract for binding the catalyst. The extract was washed with water ( $4 \times 100$  mL) until neutral reaction and dried with  $\text{K}_2\text{CO}_3$ . The ether was stripped off, and the reaction mixture was distilled in vacuum to give **2d** (1.59 g, 53%). The distillation residue (a dark-brown resin of oligomer) was dried until constant weight (0.6 g, 20%).

The dimerization of other 1-vinylpyrroles **1** was analogous (Table 1). Dimers 3-ethyl-5-[1-(3-ethyl-2-propyl-1*H*-pyrrol-1-yl)ethyl]-2-propyl-1-vinyl-1*H*-pyrrole (**2f**) and 2-isobutyl-5-[1-(2-isobutyl-1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrrole (**2g**) were isolated by column chromatography

on aluminum oxide with hexane as eluent. Experimental and spectral data of 5-[1-(1*H*-pyrrol-1-yl)ethyl]-1-vinyl-1*H*-pyrroles **2a–f** are listed in Tables 2–4. Due to the low yield of dimer **2g** the structure was determined by the <sup>1</sup>H NMR spectrum only (Table 3).

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