Dimerization of 1-vinyl-4,5,6,7-tetrahydroindole in the presence of acids

L. V. Morozova,* A. I. Mikhaleva, M. V. Markova, L. N. Sobenina, and B. A. Trofimov

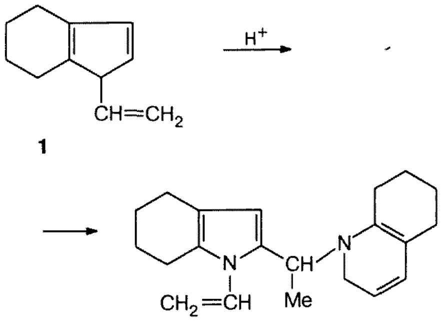
Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 460 331

In the presence of Brönsted and Lewis acids, 1-vinyl-4,5,6,7-tetrahydroindole is transformed into its dimer, 1-vinyl-2-[1-(4,5,6,7-tetrahydroindolyl)ethyl]-4,5,6,7-tetrahydroindole, and polymers containing units of the dimer and segments of oxidized tetrahydroindole cycles.

Key words: 1-vinylpyrroles, Brönsted and Lewis acids, reactions of the pyrrole ring.

Reactions of *N*-vinylpyrroles and *N*-vinylindoles with halogens, hydrogen halides, organylchlorosilanes, and stannanes give charge transfer complexes, which subsequently polymerize at the double bond.[1–3]

We previously showed[4–6] that the transformation of 1-vinyl-4,5,6,7-tetrahydroindole (**1**) in the presence of various acids follows a fundamentally different pathway to give its dimer, 1-vinyl-2-[1-(4,5,6,7-tetrahydroindolyl)-ethyl]-4,5,6,7-tetrahydroindole (**2**). Dimer **2** is the product of electrophilic replacement of the hydrogen atom at the α-position of the pyrrole ring in one molecule of **1** by an immonium cation formed from a second molecule of **1**.



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In the present work, with the purpose of discovering the optimum conditions for synthesizing dimer **2**, we used a series of Brönsted and Lewis acids, including alkylhalosilanes, metal (tin, iron, and titanium) chlorides, boron trifluoride etherate, and diverse mineral and organic acids. The majority of these catalysts proved to be insufficiently effective: the reaction gives a small yield of dimer **2** and is accompanied by the formation of deeply colored oligomeric products (Table 1).

The yields of oligomers (molecular masses 1000—2000) range within 10—30 % and reach 70 % only in the presence of HNO_3. Typical catalysts of ionic polymerization (BF_3OEt_2, $FeCl_3$, or $SnCl_4$) not only cause no dimerization but also have low activity with respect to polymerization. For example, only traces of compound **2** are formed in the case of BF_3OEt_2.

According to IR and NMR spectral data,[7] the structure of polymers incorporates repeating fragments of dimer **2** and products of subsequent transformations involving the pyrrole ring. The resulting polymers are paramagnetic: the ESR spectrum contains a signal typical of polymers with a system of conjugated bonds (the concentration of paramagnetic centers is $4.2 \cdot 10^{16}$ spins g^{-1}, $\Delta H = 9.7$ Oe).

Polymeric layers sensibilized with 2,4,7-trinitrofluorenone are electrophotographically charged by corona discharge to a potential of 280—340 V. The integral electrophotographic sensitivity is $(0.13 \div 1.7) \cdot 10^{-4}$ lux^{-1} s^{-1}.

When the reaction is carried out in acetic acid (with its three- to fivefold excess), dimer **2** is formed in a quantitative yield, and no specific purification methods are required.

It is known that *N*-vinylpyrroles are characterized by the existence of competition between the double bond and the α-position of the pyrrole ring as objects for electrophilic attack.[8] It was likely that cation **3** formed from dimer **2** would undergo intramolecular cyclization to give pentacyclic product **4**.

However, as shown by spectral studies (IR, NMR), compound **4** is not formed, possibly because of a sharp decrease in reactivity of the pyrrole ring, which results from the strong electron-withdrawing effect of the second pyrrole ring bearing a positive charge.

Attempts to carry out the reaction between compound **1** and ethyl vinyl ether, whose cation can, in principle, attack the α-position of the pyrrole ring, did

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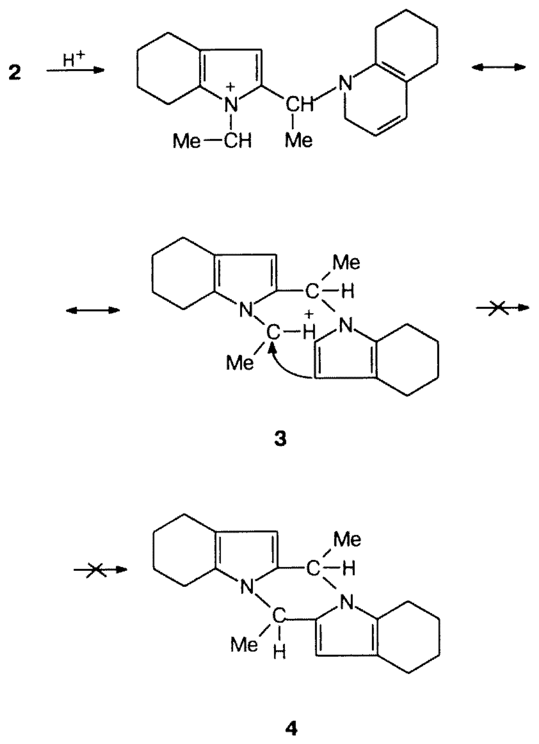
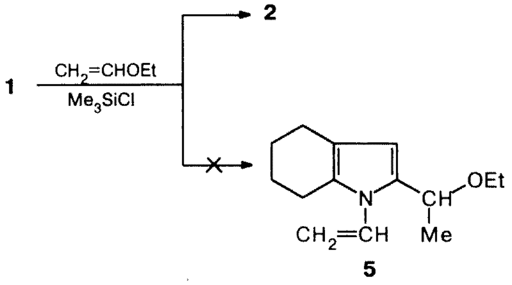


not give the expected 2-ethoxyethyl-1-vinyl-4,5,6,7-tetrahydroindole (**5**) under any of the conditions used (the **1** : ether ratio was 1 : 1—1 : 10, the amount of Me_3SiCl catalyst was 1—5 %). The vinyl ether was retained almost completely, while **1** was transformed into **2** under these conditions.



Experimental

IR spectra of the products synthesized were recorded on an IR-75 spectrometer in KBr. ^1H NMR spectra were recorded on a Tesla BS-567 instrument (100 MHz) using $SiMe_4$ as the internal standard.

Dimerization of 1-vinyl-4,5,6,7-tetrahydroindole. Method A. Dimethyldichlorosilane (0.03 g) was added to compound **1** (3.00 g, 20 mmol). After 50 h, the reaction mixture was dissolved in hot hexane and filtered from insoluble polymers. Cooling gave crystals (1.95 g, 65 %) of 1-vinyl-2-[1-(4,5,6,7-tetrahydroindolyl)ethyl]-4,5,6,7-tetrahydroindole (**2**), m.p. 114 °C. The ^1H NMR and IR spectra were identical to those reported previously.[6]

A similar procedure was used with other catalysts (see Table 1).

B. AcOH (5.00 g, 83.0 mmol) was added at 20 °C to compound **1** (1.00 g, 6.6 mmol). The reaction mixture was stirred for 1 h and neutralized with a saturated solution of Na_2CO_3. The crystals that precipitated were washed with water on a filter and dried to give 0.98 g (98 %) of dimer **2**, m.p. 114 °C.

Treatment of ethyl vinyl ether with 1. Trimethylchlorosilane (0.04 g) was added to a mixture of compound **1** (1.00 g, 6.6

Table 1. Oligomerization of 1-vinyl-4,5,6,7-tetrahydroindole

Catalyst	Amount of catalyst (mass. %)	Reaction time /h	Yield of dimer **2** (%)	Yield of oligomers (%)
HCl[a]	2	48	46	10
HCl[b]	2	48	20	14
H_2SO_4	2	50	17	25
HNO_3[c]	1	0.01	Traces	70
AcOH	1	50	Traces	5
AcOH	Threefold excess	2	88	6
AcOH	Fivefold excess	2	98	Traces
$FeCl_3$	2	50	Traces	8
$TiCl_4$	2	50	Traces	6
$SnCl_4$	4	50	Traces	6
$SiCl_4$	2	50	15	15
Et_3SiCl	2	50	68	23
Me_2SiCl_2	2	50	65	27
$Me_2EtSiCl$	2	50	32	30
BF_3OEt_2	1	50	Traces	5

[a] 1 *N* solution in dioxane. [b] 1 *N* aqueous solution. [c] Boiling up, instantaneous polymerization.

mmol) and ethyl vinyl ether (1.00 g, 1.4 mmol). The reaction mixture was stirred at 20 °C and kept for 50 h. Evacuation returned 0.96 g (96 %) of the starting ether. Dimer **2** was identified in the reaction mixture (TLC, ^{1}H NMR).

References

1. B. A. Trofimov and A. I. Mikhaleva, *N-Vinilpirroly* [*N-Vinylpyrroles*], Nauka (Siberian Branch), Novosibirsk, 1984 (in Russian).
2. M. Biswas, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1976, **C 14**, 1.
3. B. A. Trofimov, *Adv. Heterocycl. Chem.*, 1990, **51**, 177.
4. B. A. Trofimov, A. I. Mikhaleva, and L. V. Morozova, *Usp. Khim.*, 1985, **54**, 1034 [*Russ. Chem. Rev.*, 1985, **54** (Engl. Transl.)].
5. L. V. Morozova, A. I. Mikhaleva, and M. V. Sigalov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* [*Bull. Sib. Branch Acad. Sci. USSR, Div. Chem. Sci.*], 1986, 128 (in Russian).
6. L. V. Morozova and A. I. Mikhaleva, *Khim. Geterotsikl. Soedin.*, 1987, 479 [*Chem. Heterocycl. Compd.*, 1987 (Engl. Transl.)].
7. B. A. Trofimov, L. V. Morozova, M. V. Sigalov, A. I. Mikhaleva, and M. V. Markova, *Macromol. Chem.*, 1987, **88**, 2251.
8. B. A. Trofimov, in *Pyrroles. Part Two: The Synthesis, Reactivity, and Physical Properties of Substituted Pyrroles*, Ed. A. Jones, New York, Wiley, Inc., 1992, 131.

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