LETTERS TO THE EDITOR

OLIGOMERIZATION OF N-VINYLPYRROLES UNDER THE ACTION OF SODIUM METAL

B. A. Trofimov, L. V. Morozova,
A. I. Mikhaleva, É. I. Brodskaya,
M. V. Markova, S. E. Korostova,
N. I. Golovanova, and D.-S. D. Taryashinova

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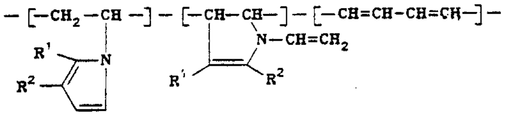
N-Vinylpyrroles are polymerized under the action of radicals, cations and electron-acceptors [1-3]. Recently, a new, unexpected route for the conversion of N-vinylpyrroles was discovered in the presence of Brønsted and Lewis acids [1, 4].

There is no information in the literature on the conversion of N-vinylpyrroles in the presence of alkaline reagents. It is usual to assume that substances of this class are stable under nucleophilic conditions since vinylation of pyrroles is most effectively carried out in strongly basic media at elevated temperatures [1, 5].

We here report for the first time that N-vinylpyrroles (1-vinyl-4,5,6,7-tetrahydroindole, 1-vinyl-2-phenylpyrrole, 1-vinyl-2,3-dimethylpyrrole) undergo oligomerization under the action of sodium metal at 190°C.

It has been shown, on the basis of a study of the IR, UV, PMR, and ESR spectra, that the reaction takes place with entrainment of both the N-vinyl group of the monomer and the endocyclic double bond of the pyrrole ring and leads to the formation of oligomers which include the fragments mentioned and a short polyene chain which is formed as a result of detachment of pyrrole NH.



I – III

I R^1-R^2=$(CH_2)_4$; II R^1=Ph, R^2=H; III R^1=R^2=Me

The monomers were purified by vacuum fractionation [1] and the purity monitored by GLC.

To 3.00 g (0.02 mole) 1-vinyl-4,5,6,7-tetrahydroindole was added 0.15 g sodium, the mixture heated 12 h at 190°C and the unreacted sodium then removed by decantation. The reaction product was isolated by reprecipitation from 1,4-dioxane into ethanol, washed with the precipitant and with water and dried. Yield 1.09 g (36%) oligomer as a cream-colored powder with mol. wt. 900. Under the same conditions but without the sodium, the yield was 10-12%. PMR spectrum (C_6D_6) (ppm): 1.77, 2.66 ppm (cyclohexane ring protons), 5.84, 6.19 (C—H protons of the pyrrole ring), 3.53 (N—CH protons of the polymer chain). IR spectrum (cm^{-1}): 695, 705, 1290, 1365, 1480, 1580 (pyrrole ring), 3090, 1640, 960, 850 (N-vinyl group [1]), 1580 (broad band) ($[-CH{=}CH-]_n$) [6]. UV spectrum (in 1,4-dioxane), λ_{max} nm ($\varepsilon \cdot 10^{-3}$): 208 (4.3), 264 (3.7).

LITERATURE CITED

1. B. A. Trofimov and A. I. Mikhaleva, N-Vinylpyrroles [in Russian], Nauka, Novosibirsk (1985), p. 260.
2. M. Biswas, J. Macromol. Sci., Rev. Macromol. Chem., C14, 1 (1976).
3. B. A. Trofimov, A. I. Mikhaleva, and L. V. Morozova, Usp. Khim., 54, 1034 (1985).
4. B. A. Trofimov, L. V. Morozova, M. V. Sigalov, A. I. Mikhaleva, and M. V. Markova, Makromol. Chem., 188, 2251 (1987).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, p. 1420, October, 1989. Original article submitted January 12, 1989.

0009-3122/89/2510-1190$12.50

5. M. F. Shostakovskii, G. G. Skvortsova, and E. S. Domnina, Usp. Khim., 38, 892 (1969).
6. E. M. Popov and G. A. Kogan, Usp. Khim., 37, 256 (1968).

TETRAHALOTETRAAZAFULVALENES – NEW STRONG ELECTRON ACCEPTORS

S. G. Dedik, V. D. Orlov,
A. S. Édzhinya, V. Yu. Khodorkovskii, and
O. Ya. Neiland

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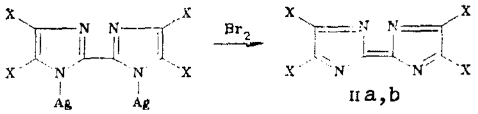
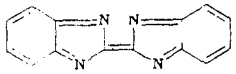
It was deduced in [1] on the basis of quantum chemical calculations that bis(imidazole-2-ylidene) – tetraazafulvalene and its derivatives – which had not so far been reported, should possess high acceptor ability and could be used as a component of organic metals and semiconductors. With the object of studying their electron-acceptor properties we have prepared, for the first time, tetrachloro- and tetrabromotetraazafulvalene (IIa,b) together with the dibenzo-derivative (III) the preparation of which has been described previously [2] but its acceptor properties have not been studied.



I

IIa,b

I, IIa X=Cl, b X=Br



III

Tetrachlorotetraazafulvalene (IIa). To a suspension of the silver salt Ia [3] (0.005 mole) in 100 ml CH_2Cl_2 at −30°C was added, with vigorous stirring, a solution of 0.005 mole bromine in 20 ml CH_2Cl_2. The mixture was stirred for 30 min and then warmed to 20°C and filtered. The filtrate was evaporated to a volume of 10 ml and the dark brown needles filtered off in an atmosphere of argon and dried in vacuum. Yield 60%, decomp 145-147°C. UV spectrum (in CH_3CN), λ_{max} nm (log ε): 345 (4.56), 363 (4.63). IR spectrum (nujol mull) (cm^{-1}): 1510, 1465, 1215, 1140, 1120, 1050, 860, 655, 530. Mass spectrum, m/z: 270 (M^+). Compound IIb was prepared in a similar manner in 55% yield, dark brown needles, decomp. 200°C. UV spectrum (in CH_3CN), λ_{max} nm (log ε) 369 (4.58), 387 (4.62). IR spectrum (KBr) (cm^{-1}): 1490, 1455, 1175, 1135, 1120, 1105, 985, 870, 660. Elemental analysis gave results corresponding to the calculated. Compounds IIa and IIb under the action of an equivalent quantity of $NH_2OH \cdot HCl$ in CH_3CN formed 4,4'-5,5'-tetrahalodiimidazolyls; tetraazafulvalene IIa is somewhat unstable to the action of atmospheric oxygen. From cyclic voltammetry data in CH_3CN solution against Ag/AgCl, compound III is a weak electron acceptor comparable in strength to naphthoquinone. Two reversible reduction peaks were observed at potentials $E_1^{red} = -0.65$ V; $E_2^{red} = -1.28$ V; $\Delta E_{1,2} = 0.63$ V which points to the exceptionally high stability of the anion-radical (log K = 10.68). For compounds IIa,b only one quasi-reversible reduction peak was observed at 0.30 and 0.38 V, respectively. Thus the derivatives IIa, b are acceptors similar in strength to tetrafluorotetracyanoquinodimethane. The properties of the ion-radical salts and charge-transfer complexes based on compounds IIa and IIb have been studied.

LITERATURE CITED

1. I. V. Krivoshei, V. E. Umanskii, O. M. Tsyguleva, and A. L. Boiko, Abstracts of papers, VI All-Union Conference on Charge-Transfer Complexes and Ion-Radical Salts, Chernogolovka (1984), p. 63.
2. V. H. M. Hill, J. Org. Chem., 28, 1931 (1963).
3. K. Lehmstedt and H. Rolker, Berichte, 76, 879 (1943).

A. M. Gor'kii State University, Kharkov 310077. Riga Polytechnic Institute, Riga 226048.
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