ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 4, pp. 614–615. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © B.F. Kukharev, V.K. Stankevich, V.A. Kukhareva, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 4, pp. 607–608.

SHORT COMMUNICATIONS

Synthesis of *N*-Vinylpyrroles from *N*-(2-Hydroxyethyl)pyrroles

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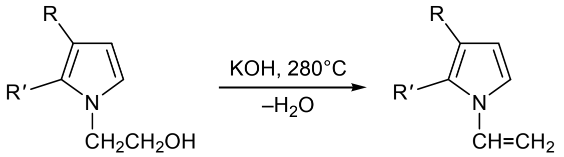
Received September 22, 2010

DOI: 10.1134/S1070428011040257

N-Vinylpyrrole derivatives exhibit versatile biological activity and are promising as monomers and intermediate products in the synthesis of a number of compounds possessing practically important properties [1, 2]. In the recent time, the most convenient method for the preparation of these compounds is based on reaction of ketone oximes with acetylene in the system dimethyl sulfoxide–alkali metal hydroxide (Trofimov reaction) [1, 2]. However, this procedure cannot be used to synthesize *N*-vinylpyrroles from aldehyde oximes because of concurrent dehydration of the latter to form nitriles [3].

We previously reported on the formation of *N*-(2-hydroxyethyl)pyrroles in up to 73% yield as a result of a number of base-catalyzed redox processes, such as oxidation 2,2′-iminodietanol with cyclohexanone [4], cleavage of oxazolidines obtained from carbonyl compounds and 2,2′-iminodietanol [5, 6], and oxidation of these oxazolidines with carbonyl compounds [7].

It is known that some nitrogen-containing heterocyclic compounds having 2-hydroxyethyl substituents are capable of undergoing dehydration by the action of alkali to give the corresponding vinyl derivatives [8]. In the present work we examined dehydration of *N*-(2-hydroxyethyl)-4,5,6,7-tetrahydro-1*H*-indole (**Ia**) to *N*-vinyl-4,5,6,7-tetrahydro-1*H*-indole (**IIa**). We found that *N*-vinylindole **IIa** was formed in 60–68% yield when compound **Ia** was heated over KOH at 280°C. The reaction was accompanied by formation of an appreciable amount of a polymeric product insoluble in water (as still residue). Our attempts to carry out the reaction under reduced pressure almost always resulted in foaming of the alkali melt, its ejection from the flask, and clogging of the descending condenser. The yield of indole **IIa** increased as the moisture content of KOH rose. Therefore, subsequent dehydration experiments were performed with simultaneous supply of water into the reaction mixture. When the amount of water was 10 wt % with respect to **Ia**, the yield of **IIa** reached 96%. Obviously, the reason is formation of a low-boiling azeotrope mixture of **IIa** with water, which shortens its contact with alkali and hampers polymerization.



Ia–Ie **IIa–IIe**

RR′ = $(CH_2)_4$ (**a**), $(CH_2)_5$ (**b**); R = H, R′ = Ph (**c**); R = Me, R′ = Et (**d**); R = *i*-Pr, R′ = H (**e**).

Likewise, from pyrroles **Ib** and **Ic** we obtained *N*-vinyl derivatives **IIb** and **IIc** in 94–97% yield. In the synthesis of low-boiling pyrroles **IId** and **IIe** the process was performed without addition of water and the yield of **IId** and **IIe** was 88–90%. *N*-Vinylpyrroles **IIb**–**IId** were isolated as colorless liquids. The same compounds obtained from ketone oximes and acetylene were described as colored liquids [2].

Initial pyrrole **Ie** was synthesized from the corresponding oxazolidine which was prepared in turn by condensation of isovaleraldehyde with 2,2′-iminodiethanol. Thus the proposed procedure ensures preparation of *N*-vinylpyrroles which cannot be obtained from aldehyde oximes and acetylene. On the other hand, the described procedure is more laborious (it includes three steps), and the yield calculated on the initial ketone is lower by 10–15% than in the synthesis through ketone oximes.

***N*-Vinylpyrroles IIa–IIc** (*general procedure*)**.** A 100-ml steel flask equipped with dosing devices, thermocouple, and descending condenser connected to a receiver was charged with 40 g (0.71 mol) of potassium hydroxide and was heated to 280°C. *N*-(2-Hydroxyethyl)pyrrole **Ia**–**Ic**, 0.1 mol, and water (10 wt %) were supplied simultaneously to the flask over a period of about 1 h. The distillate was treated with 50 ml of diethyl ether, and the organic layer was separated, dried over potassium carbonate, and distilled under reduced pressure.

The synthesis of *N*-vinylpyrroles **IId** and **IIe** was performed in a similar way but without addition of water. The purity of compounds **IIa**–**IIe** was 99.3–99.7% according to the GLC data.

1-Vinyl-4,5,6,7-tetrahydro-1*H*-indole (IIa). Yield 96%, bp 112–113°C (14 mm), d_4^{20} = 1.0010, n_D^{20} = 1.5580; published data [9]: bp 85–86°C (3 mm), d_4^{20} = 1.0010, n_D^{20} = 1.5562.

1-Vinyl-4,5,6,7,8-hexahydro-1*H*-cyclohepta[*b*]-pyrrole (IIb). Yield 97%, bp 120–121°C (14 mm), d_4^{20} = 0.9940, n_D^{20} = 1.5555; published data [1]: bp 93–94°C (1 mm), d_4^{20} = 0.9937, n_D^{20} = 1.5560.

2-Phenyl-1-vinyl-1*H*-pyrrole (IIc). Yield 94%, bp 93–94°C (1 mm), d_4^{20} = 1.0451, n_D^{20} = 1.6195; published data [10]: bp 94°C (1 mm), d_4^{20} = 1.0443, n_D^{20} = 1.6190.

2-Ethyl -3-methyl-1-vinyl-1*H*-pyrrole (IId). Yield 88%, bp 46–48°C (3 mm), d_4^{20} = 0.9161, n_D^{20} = 1.5175; published data [11]: bp 59–60°C (6 mm), d_4^{20} = 0.9158, n_D^{20} = 1.5175.

3-Isopropyl-1-vinyl-1*H*-pyrrole (IIe). Yield 90%, bp 95–97°C (100 mm), d_4^{20} = 0.8936, n_D^{20} = 1.5108. IR spectrum, ν, cm^{-1}: 3090, 3055 (=C–H), 1635, 1510, 1495 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.19 d (6H, Me, ^3J = 5.9 Hz), 2.79 m (1H, CH), 4.60 d.d (1H, *trans*-CH$_2$=, ^2J = 0.9, $^3J_{trans}$ = 15.8 Hz), 4.96 d.d (1H, *cis*-CH$_2$=, ^2J = 0.9, $^3J_{cis}$ = 8.9 Hz), 6.09 d (1H, 4-H, ^3J = 2.7 Hz), 6.63 d (1H, 5-H, ^3J = 2.7 Hz), 6.69 d.d (1H, 1-CH, $^3J_{cis}$ = 8.9, $^3J_{trans}$ = 15.8 Hz), 6.73 s (1H, 2-H). Found, %: C 79.74; H 9.77; N 10.21. $C_9H_{13}N$. Calculated, %: C 79.95; H 9.69; N 10.36.

The ^{1}H NMR spectrum was recorded on a Bruker DPX-400 spectrometer (400 MHz) in $CDCl_3$ at 26°C using hexamethyldisiloxane as internal reference. The IR spectrum (film) was obtained on a Specord 75IR instrument. Initial *N*-(2-hydroxyethyl)pyrroles **Ia**–**Ie** were synthesized by condensation of the corresponding carbonyl compounds with 2,2′-iminodiethanol according to the procedure described in [12], followed by cleavage of *N*-(2-hydroxyethyl)oxazolidines thus formed as reported in [6].

REFERENCES

1. Trofimov, B.A. and Mikhaleva, A.I., *N-Vinilpirroly* (*N*-Vinylpyrroles), Novosibirsk: Nauka, 1984.
2. Trofimov, B.A., *Geteroatomnye proizvodnye atsetilena* (Heteroatom Acetylene Derivatives), Moscow: Nauka, 1981, p. 165.
3. Trofimov, B.A., Mikhaleva, A.I., Korostova, S.E., Balabanova, L.N., and Vasil’ev, A.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, p. 690.
4. Kukharev, B.F. and Atavin, A.S., *Zh. Org. Khim.*, 1974, vol. 10, p. 670.
5. Kukharev, B.F. and Atavin, A.S., *Khim. Geterotsikl. Soedin.*, 1973, p. 1580.
6. Kukharev, B.F., Stankevich, V.K., and Kukhareva, V.A., *Khim. Geterotsikl. Soedin.*, 1986, p. 533.
7. Kukharev, B.F., Stankevich, V.K., and Kukhareva, V.A., *Khim. Geterotsikl. Soedin.*, 1984, p. 700.
8. Kolesnikov, G.S., *Sintez vinil’nykh proizvodnykh aromaticheskikh i geterotsiklicheskikh soedinenii* (Synthesis of Vinyl Derivatives of Aromatic and Heterocyclic Compounds), Moscow: Akad. Nauk SSSR, 1960.
9. Mikhaleva, A.I., Trofimov, B.A., and Vasil’ev, A.N., *Khim. Geterotsikl. Soedin.*, 1979, p. 197.
10. Trofimov, B.A., Korostova, S.E., Balabanova, L.N., Mikhaleva, A.I., and Vasil’ev, A.N., *Khim. Geterotsikl. Soedin.*, 1978, p. 489.
11. Mikhaleva, A.I., Trofimov, B.A., and Vasil’ev, A.N., *Zh. Org. Khim.*, 1979, vol. 15, p. 602.
12. Neelakantan, L., *J. Org. Chem.*, 1971, vol. 36, p. 2256.