

SHORT
COMMUNICATIONS

Oxidative Devinylation of *N*-Vinylpyrroles

B. A. Trofimov, E. Yu. Shmidt, A. I. Mikhaleva, N. V. Zorina, and E. Yu. Senotrusova

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: boris_trofimov@irioch.irk.ru

Received January 19, 2008

DOI: 10.1134/S1070428008080277

N-Vinylpyrroles are reactive building blocks for the synthesis of various compounds of the pyrrole series [1–7], medical agents [8, 9], pesticides [10], repellents [11], epoxy resins [12], light-sensitive [13, 14] and semiconducting polymers [15], and materials for optoelectronics [6, 16]. *N*-Vinylazoles (including *N*-vinylpyrroles) are used as azoles with protected NH functionality in a number of important syntheses, in particular in the preparation of antiphlogistic drugs [17]. Removal of the vinyl protection can be achieved by hydrolysis [18], mercuration followed by reduction with NaBH₄ [19] (*N*-vinylpyrroles), ozonolysis [20] (*N*-vinylimidazoles), and oxidation with KMnO₄ [21] (*N*-vinylpyrazoles). From the preparative viewpoint, the most attractive is oxidative elimination of the *N*-vinyl group by the action of potassium permanganate, which was recently described for di- and tri-bromo-*N*-vinylpyrazoles [21].

Devinylation of *N*-vinylpyrroles involves the strongest difficulties due to high reactivity of pyrrole ring toward oxidants and electrophiles. Therefore, it seemed to be very important to elucidate whether devinylation of *N*-vinylpyrroles with KMnO₄ is possible, taking into account that the known ability of pyrrole ring to undergo oxidation [22] could give rise to undesirable side processes.

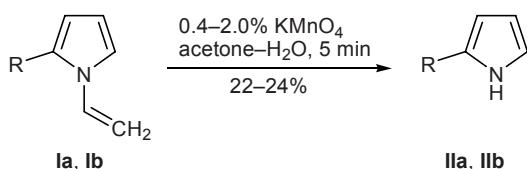
Our experiments showed that some *N*-vinylpyrroles are capable of losing the vinyl group with conservation

of the pyrrole ring on treatment with a dilute (0.4–2.0%) aqueous solution of potassium permanganate over a period of a few minutes. The reactions occurred at –20 to 20°C, and the yield (unoptimized) of the corresponding NH-pyrroles was 22–24%. The efficiency of the process depends on the structure of the initial *N*-vinylpyrrole. For example, only traces of the corresponding NH derivative were obtained from *N*-vinyl-4,5,6,7-tetrahydroindole (according to the ¹H NMR data), though the substrate was consumed completely. Obviously, in this case successful devinylation requires even milder conditions (lower temperature, shorter time, and smaller oxidant concentration).

Our attempts to perform devinylation in a heterogeneous system (benzene, diethyl ether, 2% KMnO₄, room temperature), as well as in an aqueous dispersion (1% KMnO₄) were unsuccessful: 70–94% of the initial *N*-vinylpyrrole was recovered from the reaction mixture. Nevertheless, it is obvious that further optimization could lead to the development of a convenient express procedure for devinylation of *N*-vinylpyrroles.

Devinylation of 2-phenyl-1-vinyl-1*H*-pyrrole (Ia). A solution of 0.2 g (1.18 mmol) of pyrrole **Ia** in 20 ml of acetone was cooled to –20°C, and 0.56 g (3.55 mmol) of a freshly prepared 2% aqueous solution of potassium permanganate was added under stirring. The mixture turned colorless within 5 min, and MnO₂ separated as an amorphous material. The mixture was diluted with 15 ml of water and extracted with diethyl ether (3 × 15 ml), the combined extracts were washed with water (3 × 15 ml) and dried over potassium carbonate, and the solvent was removed to leave 0.04 g (24%) of pyrrole **IIa** whose physical constants were consistent with published data [2].

Devinylation of 2-(2-naphthyl)-1-vinyl-1*H*-pyrrole (Ib). A freshly prepared 2% aqueous solution of



R = Ph (**a**), 2-naphthyl (**b**).

potassium permanganate, 0.43 g (2.73 mmol) was added to a solution of 0.2 g (0.91 mmol) of pyrrole **Ib** in 10 ml of acetone under stirring at room temperature. The mixture turned colorless within 5 min, the precipitate of MnO₂ was filtered off and washed with acetone (3×5 ml), acetone was removed from the filtrate, and the aqueous solution was extracted with ethyl acetate (3×10 ml). The extract was washed with water (3×10 ml) and dried over potassium carbonate, and the solvent was distilled off to obtain 0.04 g (22%) of pyrrole **IIb**. The physical constants of the product were in agreement with published data [2].

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 06-03-08051-ofi) and by the Foundation for Support of Russian Science.

REFERENCES

- Trofimov, B.A., Mikhaleva, A.I., Morozova, L.V., Vasil'ev, A.N., and Sigalov, M.V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, p. 269.
- Trofimov, B.A. and Mikhaleva, A.I., *N-Vinylpirrolyl (N-Vinylpyrroles)*, Novosibirsk: Nauka, 1984, p. 264.
- Trofimov, B.A., *Pyrroles. Part 2. The Synthesis, Reactivity, and Physical Properties of Substituted Pyrroles*, Jones, R.A., Ed., New York: Wiley, 1992, p. 131.
- Butler, R.N., Cunningham, H.A.G.D., and McArdle, P., *J. Chem. Soc., Perkin Trans. 1*, 1993, p. 883.
- Morozova, L.V., Mikhaleva, A.I., Markova, M.V., Sobennina, L.N., and Trofimov, B.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1996, p. 423.
- Trofimov, B.A., Schmidt, E.Yu., Mikhaleva, A.I., Vasil'tsov, A.M., Zaitsev, A.B., Smolyanina, N.S., Senotrusova, E.Yu., Afonin, A.V., Ushakov, I.A., Petrushenko, K.B., Kazheva, O.N., Dyachenko, O.A., Smirnov, V.V., Schmidt, A.F., Markova, M.V., and Morozova, L.V., *Eur. J. Org. Chem.*, 2006, p. 4021.
- Mikhaleva, A.I., Zaitsev, A.B., Ivanov, A.V., Schmidt, E.Yu., Vasil'tsov, A.M., and Trofimov, B.A., *Tetrahedron Lett.*, 2006, vol. 47, p. 3693.
- Minakova, T.T., Morozova, L.V., Mikhaleva, A.I., and Trofimov, B.A., USSR Inventor's Certificate no. 539901, 1976; *Ref. Zh., Khim.*, 1977, no. 18S334P.
- Zhavrid, S.V., Shashikhina, M.N., Gribkova, N.V., Kazak, N.F., Mikhaleva, A.I., Trofimov, B.A., Vasil'ev, A.N., Zhungietu, G.I., Rekhter, M.A., Radul, O.M., Vlad, L.A., Bukhanyuk, S.M., and Zorin, L.M., *Khim.-Farm. Zh.*, 1983, p. 25.
- Morozova, L.V., Mikhaleva, A.I., Markova, M.V., Molchanov, O.Yu., and Putan, T.V., *Khimiya i primenenie pestitsidov* (Chemistry and Application of Pesticides), Moscow, 1990, p. 7.
- Massel', G.I., Rozhkov, A.S., Mikhaleva, A.I., Vasil'ev, A.N., and Trofimov, B.A., *Lesnoi Zh.*, 1984, p. 94.
- Minakova, T.T., Morozova, L.V., Usmanova, T.A., Mikhaleva, A.I., and Trofimov, B.A., USSR Inventor's Certificate no. 653269, 1979; *Ref. Zh., Khim.*, 1980, no. 4S324P.
- Morozova, L.V., Mikhaleva, A.I., Korostova, S.E., and Filimonova, I.L., *Elektronika organicheskikh materialov* (Electronics of Organic Materials), Moscow: Nauka, 1985, p. 305.
- Morozova, L.V., Mikhaleva, A.I., and Myachina, G.F., *Zh. Prikl. Khim.*, 1987, vol. 60, p. 1193.
- Vasil'tsov, A.M., Schmidt, E.Yu., Mikhaleva, A.I., Zorina, N.V., Zaitsev, A.B., Petrova, O.V., Krivdin, L.B., Petrushenko, K.B., Ushakov, I.A., Pozo-Gonzalo, C., Pomposo, J.A., and Grande, H.-J., *Tetrahedron*, 2005, vol. 61, p. 7756.
- Khulugurov, V.M., Bryukvina, L.I., Petrushenko, K.B., Mikhaleva, A.I., Vasil'tsov, A.M., Sobenina, L.N., Schmidt, E.Yu., and Zaitsev, A.B., *Dokl. Ross. Akad. Nauk*, 2005, vol. 402, p. 353.
- Gonzalez, C., Greenhouse, R., Tallabs, R., and Muchowski, J.M., *Can. J. Chem.*, 1983, vol. 61, p. 1697.
- Trofimov, B.A., Korostova, S.E., Mikhaleva, A.I., Sobennina, L.N., and Vasil'ev, A.N., *Khim. Geterotsikl. Soedin.*, 1982, p. 1631.
- Trofimov, B.A., Korostova, S.E., Shevchenko, S.E., Mikhaleva, A.I., and Matel', N.L., *Russ. J. Org. Chem.*, 1996, vol. 32, p. 865.
- Hartley, D.J. and Iddon, B., *Tetrahedron Lett.*, 1997, vol. 38, p. 4647.
- Iddon, B., Tonder, J.E., Hosseini, M., and Begtrup, M., *Tetrahedron*, 2007, vol. 63, p. 56.
- Jones, R.A. and Bean, G.P., *The Chemistry of Pyrroles*, London: Academic, 1977.