Chemistry of Heterocyclic Compounds, Vol. 47, No. 10, January, 2012 (Russian Original Vol. 47, No. 10, October, 2011)

DEVINYLATION OF *N*-VINYLPYRROLES USING MERCURY(II) ACETATE

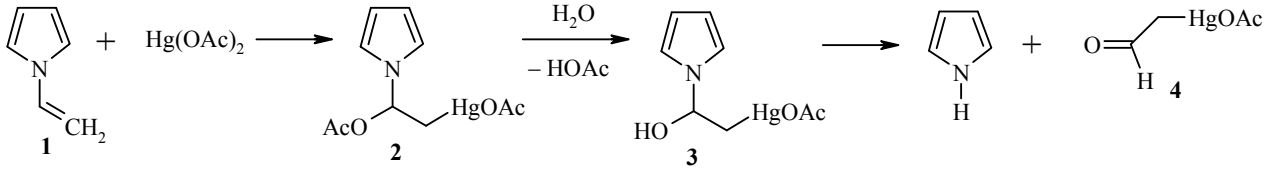
E. Yu. Schmidt[1], A. M. Vasil'tsov[1], N. V. Zorina[1], A. V. Ivanov[1], A. I. Mikhaleva[1], and B. A. Trofimov[1]*

Keywords: mercury(II) acetate, *N*-vinylpyrrole, pyrrole, devinylation.

An *N*-vinyl group is one of the efficient and atom-economic groups for the protection of the NH-function in azoles [1]. Its removal is carried out by different methods: oxidation ($KMnO_4$ [2, 3] or ozonolysis [4, 5]), acid hydrolysis [6-8], or acetomercuration and subsequent treatment with $NaBH_4$ [6-13].

The synthetic use of pyrrole series compounds is limited by the comparatively small set of available NH-pyrroles since their syntheses are generally multistage, labor-intensive, and often demand organometallic reagents which are expensive or hazardous to handle [14, 15]. At the same time, various *N*-vinylpyrroles, in fact protected pyrroles, are prepared from cheap and available ketones and acetylene readily and in high yield *via* the Trofimov reaction [16, 17].

Hence it is clear the need to improve methods of devinylating *N*-vinylpyrroles. Currently the most efficient method involves subsequent treatment of *N*-vinylpyrroles with mercury(II) acetate and sodium borohydride in an aqueous-organic medium. These conditions have obvious preparative and environmental drawbacks, *viz*. the use of large amounts of the highly toxic mercury(II) reagent and a strong reducing agent which many important functional groups (e.g. aldehyde or acyl) will not tolerate. Neither of these actually has a chemical basis. In fact, according to known data for the acetoxymercuration of *O*- and *N*-vinyl derivatives [18, 19], the reaction of *N*-vinylpyrrole (**1**) with mercury(II) acetate must give adduct **2**, hydrolysis of which gives the unstable semiaminal **3** and this decomposes further to pyrrole and acetoxymercury acetaldehyde (**4**).

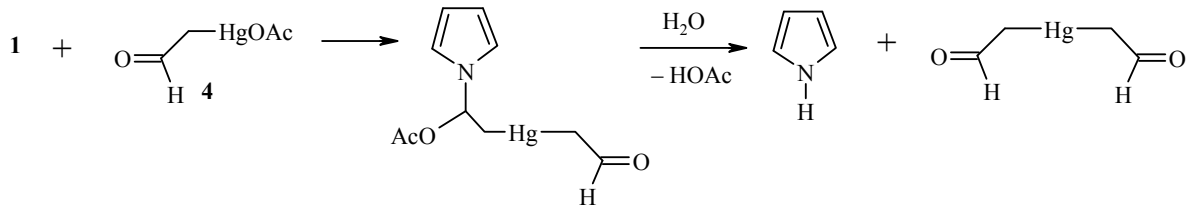


This scheme does not involve the use of an excess of the mercury(II) acetate or any kind of reducing agent. Moreover, the acetoxymercury acetaldehyde (**4**) and/or product of its further hydrolysis, mercury hydroxyacetate (**5**), can mercurate and thus actually devinylate a second molecule of *N*-vinylpyrrole (**1**).

*To whom correspondence should be addressed, e-mail: boris_trofimov@irioch.irk.ru.

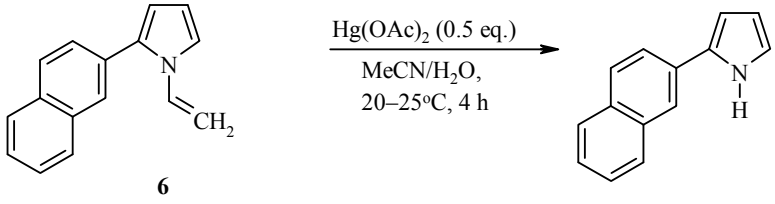
[1]A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky St., Irkutsk 664033, Russia.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1570-573, October, 2011. Original article submitted July 22, 2011.



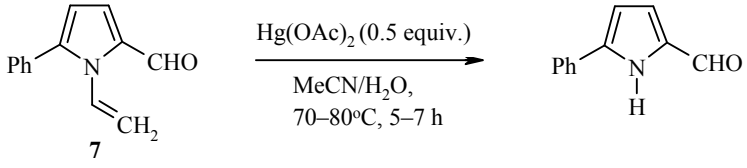
Hence 0.5 mol of the mercury(II) acetate should be sufficient to devinylate 1 mol of the *N*-vinylpyrrole (**1**) and the use of sodium borohydride is unnecessary.

Experimental verification in the case of the 2-(2-naphthyl)-*N*-vinylpyrrole (**6**) and 5-phenyl-*N*-vinylpyrrole-2-carbaldehyde (**7**) confirmed this proposal. Hence treatment of *N*-vinylpyrrole **6** with 0.5 equivalents of mercury(II) acetate in aqueous acetonitrile for 4 h at room temperature converted it to the corresponding NH-pyrrole in virtually quantitative yield.



6

Pyrrole **7** with mercury(II) acetate (50 mol%) in aqueous acetonitrile at 70-80ºC loses the vinyl group after 5-7 h to form NH-pyrrole.



7

Devinylation of pyrrole **7** and subsequent treatment with $NaBH_4$ lead to reduction of the aldehyde group to give the 2-hydroxymethyl derivative (room temperature, 1-2 h).

Hence it has been shown for the first time that *N*-vinylpyrroles can be readily and efficiently devinylated under mild conditions using only 50 mol% of mercury(II) acetate (in place of the previously used threefold excess) and without any kind of reducing agent. The novel method opens up the possibility of preparing different NH-pyrroles from *N*-vinylpyrroles (or their mixtures with NH-pyrroles) which are readily synthesized from ketones and acetylene [20, 21].

^1H and ^{13}C NMR spectra were recorded on a Bruker 400 DPX spectrometer (400 and 100 MHz respectively) using $CDCl_3$ with HMDS (δ 0.05 ppm) as internal standard.

Devinylation of 2-(2-Naphthyl)-*N*-vinylpyrrole (6). 2-(2-Naphthyl)-*N*-vinylpyrrole (**6**) (0.22 g, 1 mmol) was dissolved in acetonitrile (10 ml), $Hg(OAc)_2$ (0.16 g, 0.5 mmol) and water (5 ml) were added, and the product was stirred at room temperature. After 4 h the reaction mixture was diluted with water, NaCl (~1.5 g) was added, and then extracted with diethyl ether (4×10 ml). The ether extracts were combined, washed

with water (3×10 ml), and dried over potassium carbonate. After removal of ether the residue was chromatographed on an alumina column (eluent hexane and ether, 2:1) to give pure 2-(2-naphthyl)pyrrole in 98% yield with physicochemical properties and spectroscopic parameters in agreement with those published in [22].

Devinylation of 5-Phenyl-*N*-vinylpyrrole-2-carbaldehyde (7). 5-Phenyl-*N*-vinylpyrrole-2-carbaldehyde (**7**) (0.20 g, 1 mmol) was dissolved in acetonitrile (10 ml), $Hg(OAc)_2$ (0.16 g, 0.5 mmol) and water (5 ml) were added, and the product was stirred at 70-80ºC using a reflux condenser. After 5 h the reaction mixture was diluted with water, NaCl (~2 g) was added, and the product was extracted with diethyl ether (4×12 ml). The ether extracts were combined, washed with water (3×10 ml), and dried over potassium carbonate. After removal of ether the residue was chromatographed on an alumina column (eluent benzene) to give pure 5-phenylpyrrole-2-carbaldehyde in 65% yield with physicochemical properties and spectroscopic parameters identical to those published in [23].

REFERENCES

1. A. C. Spivey and S. J. Woodhead, *Annu. Rep. Prog. Chem., Sect. B: Org. Chem.*, **94**, 77 (1998).
2. B. Iddon, J. E. Tønder, M. Hosseini, and M. Begtrup, *Tetrahedron*, **63**, 56 (2007).
3. B. A. Trofimov, E. Yu. Schmidt, A. I. Mikhaleva, N. V. Zorina, and E. Yu. Senotrusova, *Zh. Org. Khim.*, **44**, 1258 (2008).
4. Y. L. Chen, K. G. Hedberg, and K. J. Guarino, *Tetrahedron Lett.*, **30**, 1067 (1989).
5. D. J. Hartley and B. Iddon, *Tetrahedron Lett.*, **38**, 4647 (1997).
6. B. A. Trofimov, S. E. Korostova, A. I. Mikhaleva, L. N. Sobenina, and A. N. Vasil'ev, *Khim. Geterotsikl. Soedin.*, 1631 (1982). [*Chem. Heterocycl. Comp.*, **18**, 1257 (1982)].
7. C. Gonzalez, R. Greenhouse, R. Tallabs, and J. M. Muchowski, *Can. J. Chem.*, **61**, 1697 (1983).
8. B. A. Trofimov, S. E. Korostova, S. E. Shevchenko, A. I. Mikhaleva, and N. L. Matel', *Zh. Org. Khim.*, **32**, 897 (1996).
9. A. V. Varlamov, L. G. Voskresenskii, T. N. Borisova, A. I. Chernyshev, and A. N. Levov, *Khim. Geterotsikl. Soedin.*, 683 (1999). [*Chem. Heterocycl. Comp.*, **35**, 613 (1999)].
10. T. N. Borisova, N. Bonifas, L. G. Voskresenskii, A. I. Chernyshev, A. V. Varlamov, and A. P. Krapivko, *Khim. Geterotsikl. Soedin.*, 1709 (2004). [*Chem. Heterocycl. Comp.*, **40**, 1477 (2004)].
11. I. K. Petrushenko, V. I. Smirnov, K. B. Petrushenko, E. Yu. Schmidt, N. V. Zorina, Yu. Yu. Rusakov, A. M. Vasil'tsov, A. I. Mikhaleva, and B. A. Trofimov, *Zh. Obshch. Khim.*, **77**, 1307 (2007).
12. R. Torregrosa, I. M. Pastor, and M. Yus, *Tetrahedron*, **63**, 947 (2007).
13. E. Yu. Schmidt, B. A. Trofimov, A. I. Mikhaleva, N. V. Zorina, N. I. Protsuk, K. B. Petrushenko, I. A. Ushakov, M. Yu. Dvorko, R. Méallet-Renault, G. Clavier, Thanh Truc Vu, Ha Thanh Thao Tran, and R. B. Pansu, *Chem. Eur. J.*, **15**, 5823 (2009).
14. R. A. Jones and G. P. Bean, *The Chemistry of Pyrroles*, Academic Press, New York (1977).
15. A. Gossauer, in *Houben-Weyl Methoden der Organischen Chemie*, Vol. E6a/1, Thieme, Stuttgart (1994), p. 556.
16. Z. Rappoport and J. F. Liebman (editors.), *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids*, Wiley, Chichester (2008), p 241.
17. Z. Wang, in: *Comprehensive Organic Name Reactions and Reagents*, Part 3, Wiley, London (2009), p. 2793.
18. R. W. Martin, *Anal. Chem.*, **21**, 921 (1949).
19. P. Vatsulik, *The Chemistry of Monomers* [in Russian], Vol. 1,Mir, Moscow (1960), p. 239.
20. E. Yu. Schmidt, A. I. Mikhaleva, A. B. Zaitsev, A. M. Vasil'tsov, and N. V. Zorina, *ARKIVOC*, vii, 11 (2005).

21. A. I. Mikhaleva, E. Yu. Schmidt, A. V. Ivanov, A. M. Vasil'tsov, E. Yu. Senotrusova, and N. I. Protsuk, *Zh. Org. Khim.*, **43**, 236 (2007).
22. S. E. Korostova, B. A. Trofimov, L. N. Sobenina, A. I. Mikhaleva, and M. V. Sigalov, *Khim. Geterotsikl. Soedin.*, 1351 (1982). [*Chem. Heterocycl. Comp.*, **18**, 1043 (1982)].
23. A. Padwa, J. Smolanoff, and A. Tremper, *J. Am. Chem. Soc.*, **97**, 4682 (1975).