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Reduction of 4-Nitrostyrene to 4-Aminostyrene

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Abstract—Reduction of 4-nitrostyrene with Fe^0, Fe^{2+}, and $S_2O_4^{2-}$ was studied. A new method of 4-aminostyrene synthesis was developed.

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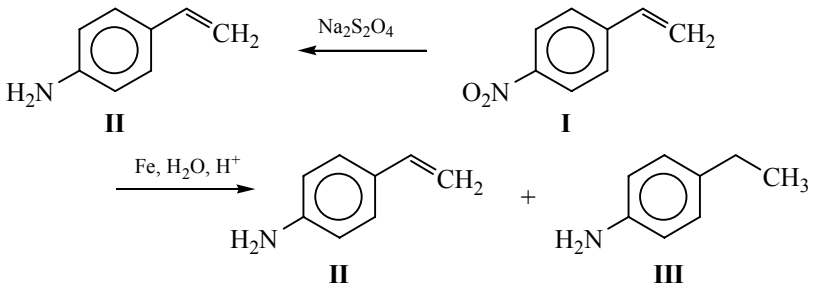
4-Aminostyrene is a compound widely used in organic synthesis as a monomer for the homo- and copolymers design and as a starting material for obtaining other compounds, including monomers [1]. However, at present a very limited number of methods of its synthesis is known.

Most rational ways to produce 4-aminostyrene are dehydration of 2-(4-aminophenyl)ethanol [2] and selective catalytic (Au/Al_2O_3, Au/TiO_2) hydrogenation of 4-nitrostyrene. [3] In the latter case, the process is accompanied by the formation of small amount of 1-amino-4-ethylbenzene whose separation is difficult. Thus, the only known preparative synthesis of 4-aminostyrene is the catalyzed dehydration of 2-(4-aminophenyl)ethanol. Other reduction methods of 4-nitrostyrene are not described in the literature.



We studied the reduction of 4-nitrostyrene with such reducing agents as Fe^0, $Fe(OH)_2$, and $Na_2S_2O_4$.

Classical methods of the reduction of aromatic nitro compounds are often unsuitable for the synthesis of the corresponding amines. The reason may be a specific electron density distribution in the starting nitro compound and the target amino product that determines the features of their reactivity. As a result, in the first case there is ambiguity in the reduction process and in the second, further transformations of amine under the reaction conditions, as well as during the isolation process. 4-Nitrostyrene, as a compound containing strong electron acceptor in the aromatic ring and the polarized conjugated multiple bond, can form under the reduction condition a number of products. Depending on the synthesis method, there is also water addition to form the secondary alcohol. So, boiling of 4-nitrostyrene with an excess of iron in the acidic medium gives initially a mixture of 1-amino-4-styrene and 1-amino-4-ethylbenzene (50:50) in a low yield and is accompanied by a significant tarring due to the probable formation of the cationic homo- and copolymers. The NMR spectrum of the reduction products is shown in Fig. 1.

In the ^1H NMR spectrum of the obtained mixture there are the proton signals of ethyl substituents of compound **III** in the range of 1.0–2.5 ppm. The overlapped signals of the $H^{1,6}$ aromatic protons of both amines and vicinal vinyl proton appear in the range of 6.5–6.7 ppm. A similar spectral pattern was observed

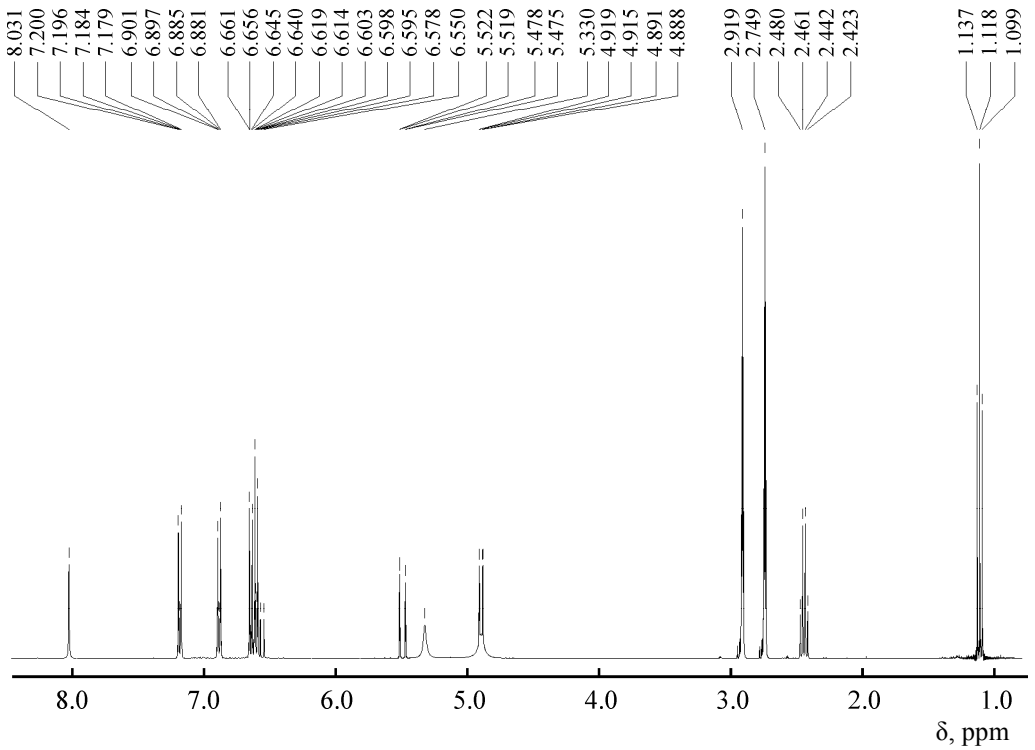


Fig. 1. ^{1}H NMR spectrum (DMF-d_7) of a mixture of amines **II** and **III** isolated at reduction of 1-nitro-4-vinylbenzene with iron.

in the case of dehydration of 1-(4-aminophenyl)ethanol in the presence of weak acids [4].

The reduction of 4-nitrostyrene with iron(II) hydroxide does not lead to the desired result. A complex mixture of amines was obtained containing 4-aminostyrene only in trace amounts.

Analyzing the ^{1}H NMR spectrum of this mixture (Fig. 2) 1-(4-aminophenyl)ethanol was identified as one of the main products as evidenced by the signals at δ, ppm: 1.34 d (3H, CH_3, *J* 6.4 Hz), 4.66 q (1H, CH, *J* 6.4 Hz), and the proton signals of the aromatic ring in the weak field.

In the present work dithionites were found to be the most suitable reducing agents. In particular, when $Na_2S_2O_4$ was used, 4-aminostyrene was obtained in an yield of 25–27%. According to the ^{1}H NMR spectrum of the reaction mixture (Fig. 3), in this case there is no significant amounts of the by-products.

As can be seen from Fig. 3, the ^{1}H NMR spectrum of the reduction product of 4-nitrostyrene contains only signals of the target 4-aminostyrene.

EXPERIMENTAL

4-Nitrostyrene was synthesized as described in [5]. In this work we used: Fe (pure, TU 6-09-2227–81), $FeSO_4·7H_2O$ (chemical grade, GOST 4148–78), 25% NH_3 solution (spectral grade, GOST 24147–80), $Na_2S_2O_4$ (chemical grade), KOH (chemical grade, TU 6-09-02-299–83). Acetone and diethyl ether were used after purification.

The NMR spectra were recorded on a Bruker AVANCE II 400 spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz) using DMF-d_7 and $CDCl_3$ [^{1}H NMR, δ, ppm: 8.031 (CDO) and 7.28, respectively] as solvents. The UV spectra were registered on a SF-256 UVI (LOMO, Russia) spectrophotometer.

Synthesis of 1-amino-4-vinylbenzene. *a*. To 6.20 g (0.0416 mol) of 4-nitrostyrene was added 9.29 g (0.1663 mol) of granulated Fe and 19 ml of HCl aqueous solution prepared from 1.3 ml of concentrated HCl. Then the mixture was refluxed for 3 h, while tarring was observed. Then to the reaction mixture was added 5.0 g of Na_2CO_3, and the volatiles were removed. The distillate was acidified with HCl to pH 5.0–5.5 at shaking. The resulting emulsion was extracted with two portions of diethyl ether. The extract was dried over $CaCl_2$, and the solvent was removed in a vacuum. 0.71 g of the starting 4-nitrostyrene were obtained. Then to an aqueous solution of 4-ethyl- and 4-vinylphenylammonium

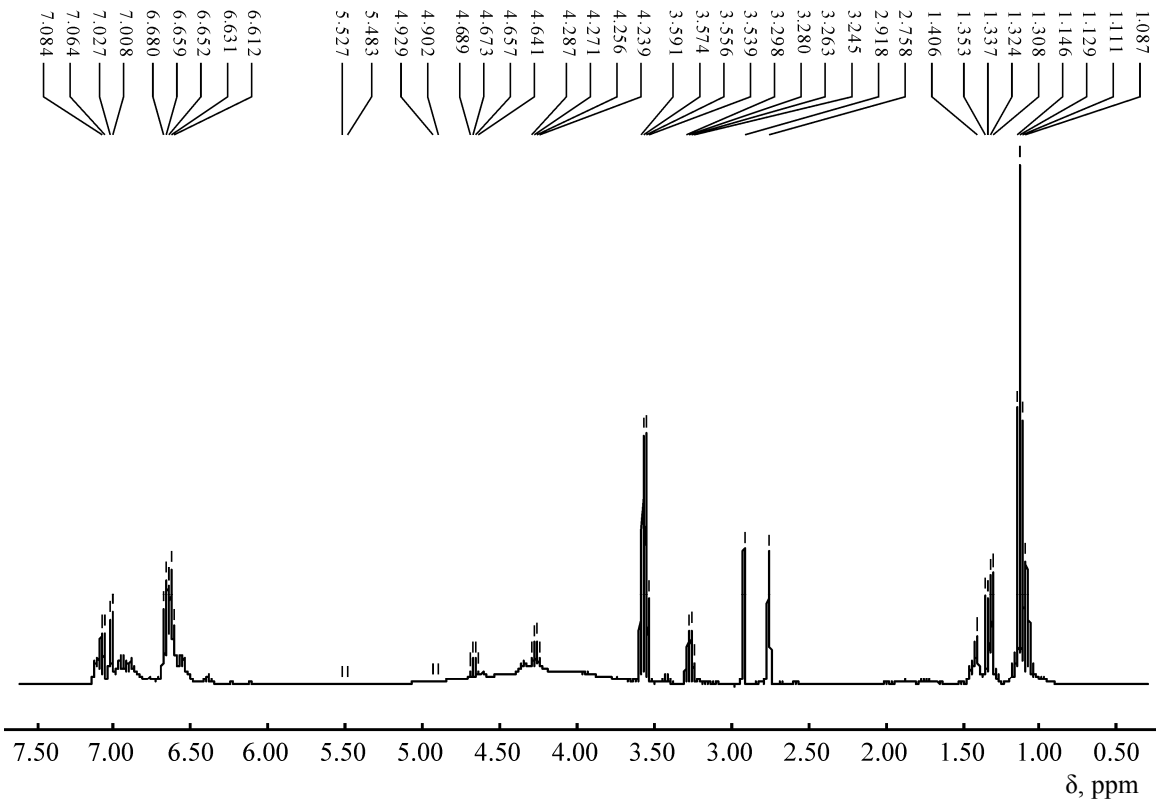


Fig. 2. ^{1}H NMR spectrum (DMF-d_7) of the products of 4-nitrostyrene reduction with $Fe(OH)_2$ (the signals at δ 1.11–1.15 and 3.54–3.59 ppm correspond to diethyl ether admixture in the sample).

chlorides was added a cooled solution of KOH to the strongly alkaline reaction. The amines were extracted with diethyl ether, the extract was dried over KOH and evaporated in a vacuum. Yield 0.25 g of a mixture of 1-amino-4-styrene and 1-amino-4-ethylbenzene with a slight prevalence of the latter. ^{1}H NMR spectrum, δ, ppm: 1.118 t (3H, CH_3, *J* 7.6 Hz), 2.45 q (2H, CH_2, *J* 7.6 Hz), 5.33 br.s [2H, NH_2, **II**], 4.90 br.s [2H, NH_2, **III**], 4.90 d.d (1H, *cis*-H, *J* 10.9, *J* 1.3 Hz), 5.50 d.d (1H, *trans*-H, *J* 17.6, *J* 1.3 Hz), 6.58 q (1H, *vic*-H, *J* 10.9 Hz), 6.61 d [2H, 2,6-Ar, *J* 8.4 Hz, **III**], 6.65 d [2H, 2,6-Ar, *J* 8.5 Hz, **II**], 6.89 d [2H, 3,5-Ar, *J* 8.3 Hz, **III**], 7.19 d [2H, 3,5-Ar, *J* 8.5 Hz, **II**].

b. To a solution of 2.24 g (0.015 mol) of distilled 4-nitrostyrene in 100 ml of acetone was added 50 ml of H_2O and 19.70 g (0.113 mol) of $Na_2S_2O_4$. Then the mixture was vigorously stirred for 10 min. The brown solution becomes colorless after 2 min, and the mixture was warmed to about 45°C. The reaction mixture was cooled and diluted with 150 ml of diethyl ether and 50 ml of H_2O. The organic layer was separated and extracted with water (2×150 ml, 2×150 ml). The ether-acetone solution was dried over Na_2SO_4 and decanted. The desiccant was washed with 40 ml of diethyl ether. The organic solutions were combined, and the solvent was removed on a rotary evaporator in a vacuum. To the residue 8 ml of H_2O was added. After stirring, to the mixture 5 ml of diethyl ether was added. Then the mixture was quantitatively transferred to a separating funnel using 5 ml of ethyl ether. To a liquid in a funnel was added another 10 ml of diethyl ether, and the mixture was separated. The ether solution was dried over KOH. The solution was decanted, filtered off, and evaporated in a vacuum. Yield 0.44 g (24.6%), liquid crystallizing when cooling. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.72 br.s (2H, NH_2), 5.09 d.d (1H, *cis*-H, *J* 10.9, *J* 1.3 Hz), 5.59 d.d (1H, *trans*-H, *J* 17.6, *J* 1.3 Hz), 6.65 q (1H, *vic*-H, *J* 10.9 Hz), 6.66 d (2H, 2,6-Ar, *J* 8.5 Hz), 7.26 d (2H, 3,5-Ar, *J* 8.5 Hz).

c. To a mixture of 1.08 g (0.0072 mol) of 4-nitrostyrene, 48.2 ml of acetone and 24.1 ml of H_2O was added 9.50 g (0.0546 mol) of $Na_2S_2O_4$. The mixture was stirred for 10 min. After 1 min the intermediate products formation was completed. Then the reaction mixture was cooled and diluted with 25 ml of diethyl

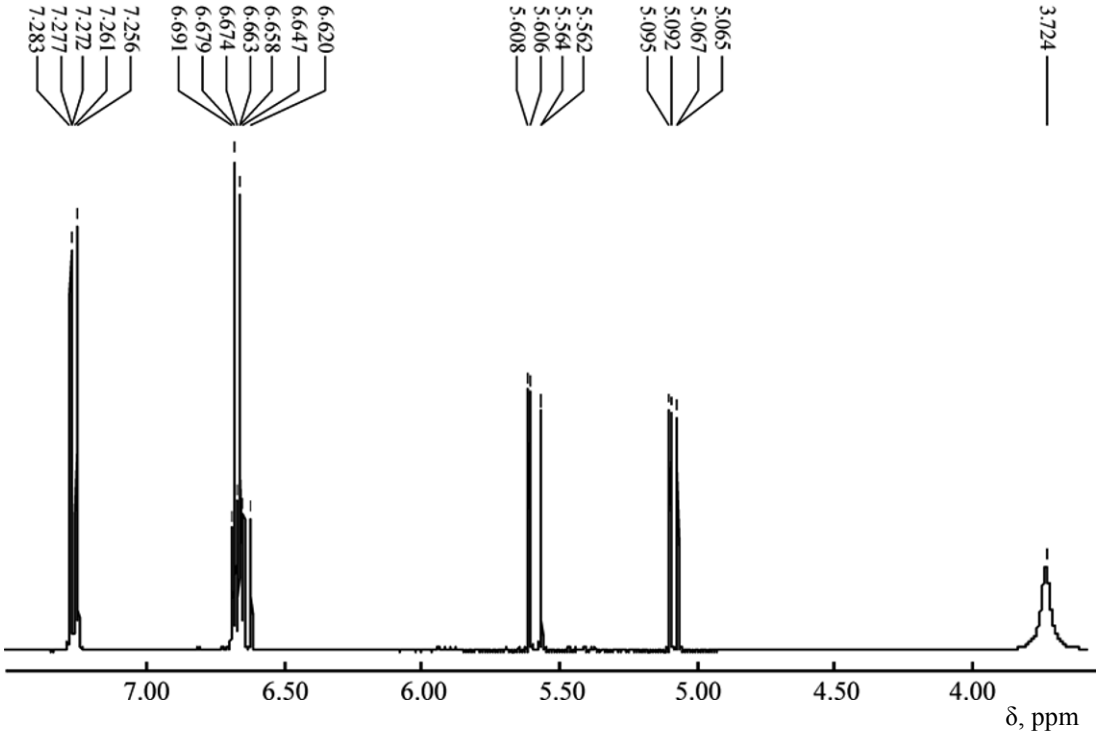


Fig. 3. ^{1}H NMR spectrum ($CDCl_3$) of the products of 4-nitrostyrene reduction with sodium dithionite.

ether. The precipitate was filtered off, washed with 25 ml of diethyl ether, and concentrated. 4-Aminostyrene was extracted from a suspension with 100 ml of diethyl ether. The organic layer was separated, and the aqueous layer was extracted with 50 ml of diethyl ether. The obtained extracts were combined, dried over KOH, and concentrated. Yield 0.23 g (26.7%), colored liquid crystalizing when cooling. Then the product was purified by distillation. To a distillate was added a CH_3COOH excess. A 4-nitrostyrene impurity was extracted with diethyl ether. The free base was isolated by treating with a KOH solution excess and extracted with diethyl ether. The extract was dried over KOH and concentrated in a vacuum. Yield 0.08 g. UV spectrum, λ_{max}, nm: 275.91 (methanol).

Reduction of 4-nitrostyrene with iron(II) hydroxide. To a hot solution of 97.17 g (0.3497 mol of $FeSO_4$) of $FeSO_4 \cdot 7H_2O$ in 195 ml of H_2O was added with stirring a warm solution of 7.45 g (0.0500 mol) of 4-nitrostyrene in a mixture of 15 ml of ethanol and 1 ml of 25% NH_3 solution. Then to the reaction mixture was added by portions with stirring 50 ml of 25% NH_3 solution (up to pH 9). The mixture was refluxed for 5 min. a part of the reduction products was distilled off. A liquid was decanted and filtered. The residue was extracted with ethanol. Then ethanol was evaporated. The extract, filtrate, and distillate were combined and acidified with HCl to pH 5–6. The insoluble admixtures were extracted with diethyl ether. An aqueous solution was filtered and alkalinized with KOH solution to pH 12–13. The precipitate formed. The obtained colored mixture was extracted with diethyl ether. After the solvent removal, 2.52 g of an amines mixture was obtained as a viscous transparent yellow liquid, which does not crystallize at –21°C.

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