

SHORT
COMMUNICATIONS

Vicarious C-Amination of Nitrobenzene*

O. V. Krylova, V. N. Elokhina, A. S. Nakhmanovich, L. I. Larina, and V. A. Lopyrev

Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, 664033 Russia

Received July 4, 2000

Vicarious nucleophilic substitution of hydrogen is a convenient method of nucleophiles introduction into aromatic [1-3] and heterocyclic [4-7] rings.

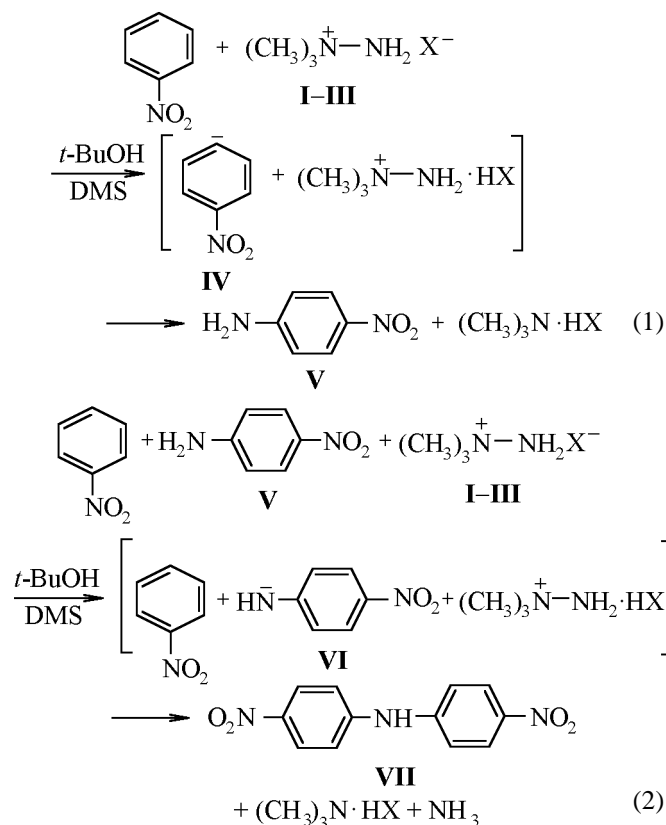
It is known that in reactions of vicarious C-amination of nitrobenzene and its derivatives 1,1,1-trimethylhydrazinium iodide is used as aminating agent in the presence of *t*-BuOK or MeONa. As a result arises a mixture of *o*- and *p*-nitroanilines in 2:1 ratio [8]. In [9] vicarious amination of nitrobenzene was carried out with sulfenamides in DMF in the presence of *t*-BuOK to obtain also a mixture of *o*- and *p*-nitroanilines in an overall yield 69-85%.

We established that the reaction of 1,1,1-trimethylhydrazinium bromide (I), chloride (II), and iodide (III) in anhydrous DMSO in the presence of *t*-BuOK at 20°C yielded not only *p*-nitroaniline (V) but also bis(*p*-nitrophenyl)amine (VII) at any halogen anion in the reagent.

To reveal the formation path of amine VII in the course of the process we attempted to carry out a reaction of *p*-nitroaniline with iodide III in anhydrous DMSO in the presence of *t*-BuOK. However from the reaction mixture only the original *p*-nitroaniline was recovered. In reaction of equimolar quantities of nitrobenzene, *p*-nitroaniline (V), and iodide III under the same conditions we obtained bis(*p*-nitrophenyl)amine (VII) in 60% yield.

Apparently the vicarious C-amination of nitrobenzene includes two parallel reactions.

The first stage of nitrobenzene reaction with halides I-III apparently proceeds via intermediate formation of carbanion IV resulting from leaving of anion X⁻ and through proton elimination from the *para*-position in the nitrobenzene molecule as HX induced by the base. In the second stage of the reac-



X = Br (I), Cl (II), I (III).

tion arises an amino-anion VI that reacts with nitrobenzene to furnish compound VII; here is felt the ammonia odor. *p*-Nitroaniline (V) and bis(*p*-nitrophenyl)amine (VII) were isolated from the reaction mixture by fractional crystallization.

Nitrobenzene reaction with 1,1,1-trimethylhydrazinium bromide (I). To a solution of 2.4 g (0.02 mol) of nitrobenzene in 40 ml of anhydrous DMSO was added slowly at stirring 3.88 g (0.025 mol) of bromide I. The mixture was stirred till complete dissolution, and thereto was added 5.6 g

* The study was carried out under financial support of the Russian Foundation for Basic Research (grant no. 98-03-32899).

(0.05 mol) of dry *t*-BuOK. Immediately the reaction mixture became bright red. The mixture was stirred at 20°C for 4 h, then poured on ice, acidified to pH 3 with 10% hydrochloric acid. The mixture was cooled to 0°C, the separated precipitate was filtered off, the filtrate was extracted with ethyl acetate (3 × 20 ml), the extract was washed with 40 ml of water and dried with MgSO₄. The ethyl acetate was evaporated in a vacuum to dryness, and the residue was combined with the previously obtained precipitate. The combined solids were dissolved in MeOH, filtered, the filtrate was cooled to 0°C, and the precipitated *p*-nitroaniline (**V**) was filtered off. Yield of nitroamine **V** 0.55 g (20%), mp 147°C (mp 146–147°C [10]). The residue insoluble in methanol was dried on filter and recrystallized from DMF–dioxane mixture (3:1). Yield of bis(*p*-nitrophenyl)amine (**VII**) 0.7 g (14%), mp 216–217°C (mp 216°C [11]). In reaction prolonged to 40 h was isolated only amine **VII** in 47% yield. In reaction performed in superbasic medium (KOH–DMSO) yield of nitroamine **V** was 30%, of compound **VII** 13%.

Compound VII. IR spectrum (ν , cm⁻¹): 1320, 1580, 3300. ¹H NMR spectrum (DMSO-*d*₆, δ , ppm): 9.92 s (1H, NH), 7.35–8.20 m (8H, ³*J*_{HH} 9.5 Hz). ¹⁵N NMR spectrum (DMSO-*d*₆, δ _N, ppm): -271.84 (NH), -10.7 (NO₂). Found, %: C 55.48; H 3.52; N 16.30. C₁₂H₉N₃O₄. Calculated, %: C 55.60; H 3.47; N 16.22.

Nitrobenzene reaction with 1,1,1-trimethylhydrazinium chloride (**II**) was carried out in a similar way for 4 h. From 2.46 g (0.02 mol) of nitrobenzene and 2.76 g (0.025 mol) of chloride **II** we obtained 0.8 g (29%) of compound **V** and 0.4 g (8%) of compound **VII**.

Nitrobenzene reaction with 1,1,1-trimethylhydrazinium iodide (III) was carried out in a

similar way for 4 h. From 2.46 g (0.02 mol) of nitrobenzene and 5.05 g (0.025 mol) of iodide **III** we obtained 0.5 g (18%) of compound **V** and 0.6 g (13%) of compound **VII**. In reaction carried out for 10 h the yields of compounds **V** and **VII** were 8 and 19% respectively. In 40 h was obtained only compound **VII** in 47% yield.

Nitrobenzene reaction with *p*-nitroaniline and 1,1,1-trimethylhydrazinium iodide (III) was carried out in a similar way for 10 h. From 2.46 g (0.02 mol) of nitrobenzene, 2.76 g (0.02 mol) of *p*-nitroaniline, and 5.05 g (0.025 mol) of iodide **III** we obtained 3.1 g (60%) of compound **VII**.

REFERENCES

1. Makosza, M. and Ludwiczak, S., *Synthesis*, 1986.
2. Makosza, M. and Ludwiczak, S., *J. Org. Chem.*, 1984, vol. 49, p. 4562.
3. Makosza, M., Danikiewicz, W., and Wojciechowski, K., *Lieb. Ann.*, 1987, pp. 711–715.
4. Lopyrev, V.A., Elokhina, V.H., Krylova, O.V., Hakhmanovich, A.S., Larina, L.I., Sorokin, M.S., and Vokin, A.I., *Khim. Geterotsikl. Soed.*, 1999, no. 9, pp. 1254–1256.
5. Bernard, M.K., *Polish J. Chem.*, 1997, vol. 71, pp. 1413–1420.
6. Bernard, M.K., Makosza, M., Szafran, B., and Wrzeciono, U., *Lieb. Ann.*, 1989, pp. 545–549.
7. Suwinski, J. and Swierczek, K., *Tetrahedron*, 1993, vol. 49, pp. 5339–5350.
8. Pagoria, P.F., Mitchell, A.R., and Schmidt, R.D., *J. Org. Chem.*, 1996, vol. 61, pp. 2934–2935.
9. Makosza, M. and Bialecki, M., *J. Org. Chem.*, 1992, vol. 57, pp. 4784–4785.
10. *Beilst. H.*, vol. 12, p. 711.
11. *Beilst. H.*, vol. 12, p. 716.