

Synthesis of 1-Nitronaphthalene under Homogeneous Conditions

Yuriy G. Khabarov*, Viacheslav A. Veshnyakov, Ivan A. Snigirev and Ilya I. Pikovskoy
Northern (Arctic) Federal University, Northern Dvina Emb., 17, Archangelsk, Russian Federation

Keywords: 1-nitronaphthalene, naphthalene nitration, nitration, dioxane

Abstract: Various reagents can be used for the nitration of naphthalene ranging from the classical nitrating mixture to unusual reagent systems. In this study, a simple and effective method of nitration of naphthalene using a classical nitrating mixture in 1,4-dioxane is presented. The reaction occurs under homogeneous conditions and GC-MS analysis of the product showed 2 peaks corresponding to 1-nitronaphthalene (96%) and 2-nitronaphthalene (4%). Melting point, UV and IR spectra of the product (isolated in 96-97% yields) correspond to 1-nitronaphthalene.

1 INTRODUCTION

Nitration of naphthalene is often the first stage in the synthesis of such naphthalene derivatives as naphthylamine (Chen *et al.*, 2016), naphthol and aminonaphthalenesulfonic acids which are used in the synthesis of dyes (Booth, 2012).

1-Nitronaphthalene can be synthesized from naphthalene using a classical nitration mixture ($\text{HNO}_3 + \text{H}_2\text{SO}_4$) in a yield of 95% (Fierz-David and Blangey, 1949; Duvalma *et al.*, 1964). In addition, 90% HNO_3 can be used to carry out the reaction in acetonitrile with 85% yield (Wright, 1965). Instead of H_2SO_4 , indium(III) triflate (Yin and Shi, 2006) or lanthanum(III) nitrobenzenesulfonates (Parac-Vogt *et al.*, 2004) can be used as catalysts. Nitration of naphthalene with practically complete conversion can also be carried out on high silica zeolite in petroleum ether with 70% HNO_3 (Bakhvalov and Ione, 1993). The use of zeolites with the NO_2/O_2 system in acetonitrile leads to moderate yields (52-80%) (Shi *et al.*, 2013). A moderate yield of 1-nitronaphthalene (63%) is also obtained with 95% HNO_3 and a mixed catalyst on silica gel without the use of solvents (Shi and Cui, 2003).

$\text{Bi}(\text{NO}_3)_3$, KNO_3 , $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and even NaNO_2 were added into a suspension of silica gel in THF for the nitration of naphthalene, while the yields of 1-nitronaphthalene were 76-88% (Badgular *et al.*, 2007). Cerium ammonium nitrate was also used for nitration of naphthalene with a conversion ratio of more than 98% in a ionic liquid (Dleersnyder *et al.*, 2009). 1-Nitronaphthalene is

formed in a yield of 99% when naphthalene is nitrated with an equimolar mixture of benzyltriphenylphosphonium nitrate and anhydride of methanesulfonic acid without the use of solvents (Hajipour and Ruoho, 2004).

Nitration of naphthalene with acetyl nitrate in a phosphonium ionic liquid gives a 74% yield (Powell *et al.*, 2005). Usually, direct nitration of naphthalene with various reagents leads to the formation of a mixture of 1- and 2-nitronaphthalenes. However, the reaction is sufficiently regioselective, the content of 1-nitronaphthalene in products, as a rule, is 90-92%.

*Ips*o-nitration of naphthalene derivatives makes it possible to obtain individual isomers. Reaction of 1- and 2-naphthylboronic acids with *tert*-butyl nitrite in 1,4-dioxane without catalysts leads to the preparation of 1- and 2-nitronaphthalenes with yields of 75% and 76%, respectively (Wu *et al.*, 2011). A higher yield, 88% for 2-nitronaphthalene, gives nitration with $(\text{CH}_3)_4\text{NNO}_2$ and Cu_2O as a catalyst in acetonitrile (Yan *et al.*, 2012). Mononitroanaphthalenes in yields of 70-82% are formed as a result of catalytic *ip*so-substitution of bromo- or iodo-derivatives of naphthalene with KNO_2 in the presence of copper(II) triflate in DMSO (Amal Joseph *et al.*, 2012). 1-Nitronaphthalene was unexpectedly obtained from 5-nitronaphthylamine by deamination (Srivastava *et al.*, 2011).

The purpose of this research was mononitration of naphthalene using a classical nitrating mixture under homogeneous conditions with 1,4-dioxane as a solvent.

2 EXPERIMENTAL

2.1 Reagents

The following reagent grade commercial chemicals were used: naphthalene, 65% nitric acid, 96% sulfuric acid, 1,4-dioxane and 96% ethanol.

2.2 Synthesis of 1-Nitronaphthalene

Naphthalene (0.50 g, 3.9 mmol) was dissolved in 1,4-dioxane in a 50-ml Erlenmeyer flask. The nitrating mixtures were prepared by mixing concentrated nitric (0.50-1.00 ml, 7.2-14.3 mmol) and sulfuric (0.50-1.00 ml) acids with cooling. The acid mixtures were added to a solution of naphthalene in dioxane and the reaction mixtures were heated under reflux with stirring for various periods of time. Each reaction mixture was transferred to a test tube, cooled, diluted to 25 ml with ice-cold distilled water. The resultant precipitate was isolated by vacuum filtration, washed with ice-cold water until the washings were neutral and dried in a vacuum desiccator at room temperature to produce yellow crystals.

2.3 Analytic Methods

Melting points were determined in open capillaries on a Stuart SMP30 melting point apparatus. UV-Vis spectra of products in ethanol solutions were recorded over the wavelength range of 200-500 nm with a Shimadzu UV-1650PC spectrophotometer in 1 cm path length quartz cuvettes relative to ethanol. The IR spectra were recorded over the wavelength range of 4000-600 cm^{-1} on a Shimadzu FTIR-8400S spectrophotometer equipped with a Pike Technologies MIRacle single reflection horizontal ATR accessory with a ZnSe crystal plate.

For GC-MS analysis, a product sample (1 mg) was dissolved in 20 ml HPLC-grade dichloromethane, injection volume was 1 μl with split 5:1. Mass spectra were recorded on a Thermo Scientific Exactive GC Orbitrap mass spectrometer coupled to a TRACE 1310 Gas Chromatograph equipped with TriPlus RSH autosampler. Chromatographic separation was performed on a Thermo Scientific Trace GOLD TG5-SilMS capillary column, 30 m \times 0.25 mm \times 0.25 μm . Helium (99.9999%) was used as a carrier gas with flowrate 1.2 ml/min. The inlet temperature was 280°C. The following thermostat program was used: initial temperature 40°C, hold 2 min, ramp 10°C/min to 280°C, hold 5 min. The mass spectrometer operated

in fullscan mode with 60 000 FWHM mass resolution. Electron ionization (70 eV) was used. Transfer line and ion source temperatures were 280 and 230°C respectively. The control of the mass spectrometer, the collection and preprocessing of the data were performed using Thermo Scientific Xcalibur software. The obtained mass spectra were evaluated using the NIST 14 spectral library by the similarity index (SI).

3 RESULTS AND DISCUSSION

In this study nitration of naphthalene was carried out in homogeneous conditions. Naphthalene was dissolved in 1,4-dioxane and remained in solution when the nitration mixture of various compositions was added and remained homogeneous when heated. During the nitration nitrogen dioxide was evolved in the first 10 min of heating. The product was isolated from the reaction mixture after cooling and addition of water. The yields were the same under the selected synthesis conditions (Table 1).

Table 1: Nitration conditions for naphthalene and product yields.

Reaction condition				Yield (%)	Isomer, %	
Volume, ml			Time (min)		1-nitro	2-nitro
HNO ₃	H ₂ SO ₄	dioxane				
1	1	3	60	97	96.4	3.6
1	1	4	60	96	–	–
1	1	5	60	96	95.8	4.2
0.75	1	5	60	96	95.7	4.3
0.5	1	5	60	97	–	–
1	1	5	50	95	–	–
1	1	5	40	96	–	–
1	0.5	5	60	96	–	–

The isolated products were characterized by their melting point, UV and IR spectra, these results are the same for all samples and correspond to the literature data for 1-nitronaphthalene (Talukder and Kates, 1995; Srivastava et al., 2011). GC-MS analysis was carried out only on 3 samples. The GC-MS analysis showed 2 detectable peaks in the gas chromatographic separation and mass spectra corresponding to 1-nitronaphthalene (retention time 11.38 min, m/z found: 173.04720, SI 797) and 2-nitronaphthalene (retention time 11.89 min, m/z found: 173.04714, SI 699). Calculation of the areas of chromatographic peaks showed that the content of 1-nitronaphthalene in the samples of products is

about 96%, i.e. nitration of naphthalene with a classical nitrating mixture in 1,4-dioxane passes with good regioselectivity. In general, a high regioselectivity of naphthalene nitration is typical in the case of using the classic nitration mixture. (Ikegami and Hiyama, 1954; Alcorn and Wells, 1965). Another advantage of the nitration is the availability of reagents and simplicity of performing the synthesis.

1-Nitronaphthalene: isolated yield 0.65 g (96%), yellow crystalline solid, mp 52.5-53°C [lit. mp 52°C (Talukder and Kates, 1995)]. IR, cm^{-1} : 2831, 1631, 1600, 1568, 1514, 1458, 1439, 1354, 1344, 1261, 1216, 1200, 1173, 1163, 1148, 1141, 1079, 1030, 1000, 978, 961, 953, 930, 914, 872, 861, 815, 804, 787, 759, 726, 655, 628. EIMS: m/z for $[\text{M}^+]$ found: 173.04720. Calc. for $\text{C}_{10}\text{H}_7\text{NO}_2$: 173.0471.

4 CONCLUSIONS

Nitration of naphthalene with a nitrating mixture in 1,4-dioxane occurs under homogeneous conditions. The proposed method for the synthesis of 1-nitronaphthalene is simple and effective. The yield of the product reaches 96-97%. Nitration of naphthalene in 1,4-dioxane has a high regioselectivity. The content of 1-nitronaphthalene and 2-nitronaphthalene in the product is 96 and 4%, respectively.

ACKNOWLEDGEMENTS

The work was performed using the instrumentation of Core Facility Center "Arktika" of Northern (Arctic) Federal University (project RFMEFI59417X0013).

REFERENCES

- Alcorn, P.G.E., Wells P.R., 1965. Nitration of the methylnaphthalenes. *Australian Journal of Chemistry*, 18(9), 1377-1389.
- Amal Joseph, P.J., Priyadarshini, S., Lakshmi Kantam, M., Maheswaran, H., 2012. Copper catalyzed ipso-nitration of iodoarenes, bromoarenes and heterocyclic haloarenes under ligand-free conditions. *Tetrahedron Letters*, 53(12), 1511-1513.
- Badgujar, D.M., Talwar, M.B., Asthana, S.N., Mahulikar, P.P., 2007. Environmentally benign synthesis of aromatic nitro compounds using silica supported inorganic nitrates. *Journal of Scientific and Industrial Research*, 66(3), 250-251.
- Bakhvalov, O.V., Ione, K.G., 1993. A method of nitration of naphthalene. RU 2079482.
- Booth, G., 2012. Naphthalene derivatives. In: *Ullmann's encyclopedia of industrial chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, pp. 678-699.
- Chen, Z., Zhang, W., Lu, M., Li, M., Zhang, S., 2016. Preparation of naphthylamine by catalytic hydrogenation over palladium/mesoporous carbon. *Shiyou Huagong/Petrochemical Technology*, 45(12), 1449-1454.
- Dleersnyder, K., Schaltin, S., Fransaer, J., Binnemans, K., Parac-Vogt, T.N., 2009. Ceric ammonium nitrate (CAN) as oxidizing or nitrating reagent for organic reactions in ionic liquids, *Tetrahedron Letters*, 50(32), 4582-4586.
- Duvalma, M., Pirvulescu, I.V., Bota, T.D., 1964. Procédé de préparation de nitro-1-naphtalène par nitration de naphtalène. Fr 1352613.
- Fierz-David, H.E., Blangey, L., 1949. *Fundamental processes of dye chemistry*. Interscience Publishers, Inc. New York.
- Hajipour, A.R., Ruoho, A.E., 2004. A fast and mild method for nitration of aromatic rings. *Phosphorus, Sulfur and Silicon and the Related Elements*, 179(2), 221-226.
- Ikegami, H., Hiyama, H., 1954. Relation of Nitration Temperature of Naphthalene and β -Isomer Contents. *The Journal of the Society of Chemical Industry, Japan*, 57(4), 332-333.
- Parac-Vogt, T.N., Pachini, S., Nockemann, P., Hecke, K.V., Meervelt, L.V., Binnemans, K., 2004. Lanthanide(III) Nitrobenzenesulfonates as New Nitration Catalysts: The Role of the Metal and of the Counterion in the Catalytic Efficiency. *European Journal of Inorganic Chemistry*, (22), 4560-4566.
- Powell, B.D., Powell, G.L., Reeves, P.C., 2005. Phosphonium ionic liquids as solvents for nitration reactions of arenes. *Letters in Organic Chemistry*, 2(6), 550-553.
- Shi, C., Peng, X., Tai, Y., Dong, X., Wang, H., 2013. Zeolite-assisted regioselective mononitration of naphthalene with nitrogen dioxide/molecular oxygen. *Research on Chemical Intermediates*, 39(7), 3151-3156.
- Shi, M., Cui, S.-C., 2003. Electrophilic Aromatic Nitration Using a Mixed Catalyst of Lithium, Molybdenum, Ytterbium on Silica Gel. *Advanced Synthesis and Catalysis*, 345(12), 1329-1333.
- Srivastava, N., Shukla, M., Saha, S., 2011. An unusual way to synthesize 1-nitronaphthalene from 1-amino-5-nitronaphthalene. *African Journal of Pharmacy and Pharmacology*, 5(4), 542-546.
- Talukder, M., and Kates, C.R., 1995. Naphthalene derivatives. In: *Howe-Grant, M. (ed.) Kirk-Othmer encyclopedia of chemical technology*, 4th ed., Vol. 16. Wiley, New York, p. 491.
- Wright, O.L., 1965. Nitration process. US 3221062.

- Wu, X.-F., Schranck, J., Neumann, H., Beller, M., 2011. Convenient and mild synthesis of nitroarenes by metal-free nitration of arylboronic acids. *Chemical Communications*, 47(46), 12462+12463.
- Yan, G., Zhang, L., Yu, J., 2012. Copper-Catalyzed Nitration of Arylboronic Acids with Nitrite Salts Under Mild Conditions: An Efficient Synthesis of Nitroaromatics. *Letters in Organic Chemistry*, 9(2), 133-137.
- Yin, W.-P., Shi, M., 2006. Indium triflate as a recyclable catalyst for the nitration of aromatic compounds without a halogenated solvent. *Journal of Chemical Research*, (9), 549-551.

