Asian Journal of Chemistry Vol. 19, No. 6 (2007), 4661-4664

Silica Sulfuric Acid as an Efficient Reagent for Bamberger Rearrangement of Phenyl Hydroxylamine Derivatives in Solvent-Free Conditions

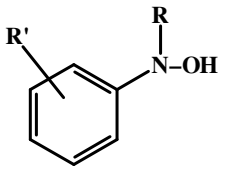
RASHID BADRI* and MOHAMMAD REZA SHUSHIZADEH
Chemistry Department, College of Science, Chamran University
61357-4-3169 Ahvaz, Iran
Fax: (98)(611)3337009; E-mail: rashidbadri@yahoo.com

Phenyl hydroxylamines undergo Bamberger rearrangement in the presence of silica sulfuric acid under solvent-free conditions to afford the corresponding 4-amino phenol derivatives in high yields.

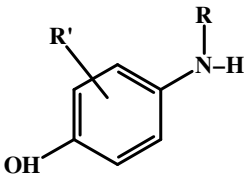
Key Words: Phenyl hydroxylamines, Silica sulfuric, Non-solvent, Bamberger rearrangement.

INTRODUCTION

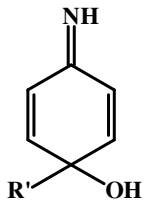
4-Aminophenol derivatives are important intermediates in the preparation of several analgesic and antipyretic drugs such as paracetamol, acetanilide and phenacetin[1]. It is well known that phenyl hydroxylamine derivatives **I** readily rearrange to their corresponding 4-amino phenol derivatives **II** in aqueous solution. The reaction was discovered by Bamberger[2] and called the Bamberger rearrangement.



I



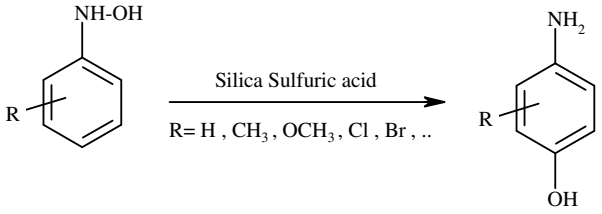
II



III

Bamberger showed that in aqueous sulfuric acid the parent compound (R = R′ = H) gave 4-amino phenol. In ethanol as solvent 2- and 4-amino ethyl esters were isolated and when hydrochloric acid was used 2- and 4-chloroamine derivatives were obtained[1,3]. For R′ as 4-Me, the initial product was the iminocyclohexadienol **III**, which was then converted to quinone by hydrolysis[4]. This rearrangement was also observed in reactions such as reduction of nitroaromatic compounds, oxidation of aromatic amines and some biologically significant processes[5,6]. This rearrangement is sensitive to steric effects[7], pH and occurs by an SN^1 mechanism[8] in which water, or

other groups such as halogen and alkoxyl serve as the attacking nucleophiles. The use of silica sulfuric acid as a stable solid acid was found to be a versatile good reagent for replacement of sulfuric acid in some organic transformations[9-11].



EXPERIMENTAL

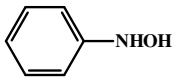
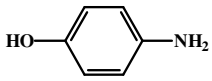
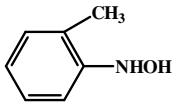
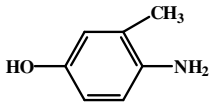
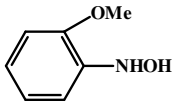
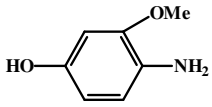
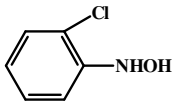
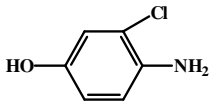
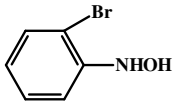
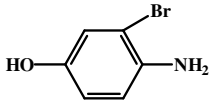
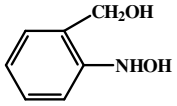
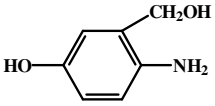
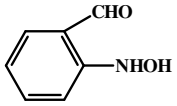
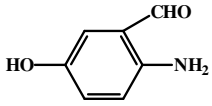
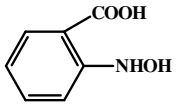
Silica sulfuric acid was prepared according to the reported procedure[9]. Products were characterized by comparison of their spectra (IR, ^{1}H NMR) and physical data with authentic samples[12]. The purity determination of products and reaction monitoring were accomplished by TLC on silica gel polygram SIGL/UV254 plates. Melting points were uncorrected. The IR spectra were recorded on Bomem FT-IR spectrometer. ^{1}H NMR spectra were taken on a 400 MHz Bruker spectrometer.

General procedure for conversion of phenylhydroxyl amines to 4-amino phenols: The reaction was carried out by mixing the phenyl hydroxylamine (4 mmol), silica sulfuric acid (1.5 g) and silica gel (3 g, for better grinding). The mixture was ground at ambient temperature for the specified of time (Table-1). The progress of reaction was monitored by TLC. After the reaction was complete, ether (30 mL) as solvent was added and the solid was filtered off. The ether solution was washed with 5 % sodium hydrogen carbonate (10 mL),water (2 × 10 mL) and dried over anhydrous magnesium sulfate and filtered. The solvent evaporated under reduced pressure to give the product which was purified by silica gel plates or column chromatography over silica gel.

RESULTS AND DISCUSSION

In continuation of our studies on the solid state reaction, we wish here to report the use of silica sulfuric acid for preparation of aminophenol derivatives *via* Bamberger rearrangement. Thus, the different phenyl hydroxylamines were prepared from corresponding nitrobenzene derivatives by reduction procedure using ammonium chloride-zinc dust mixture as reducing agent in distilled water[13]. Then each prepared phenyl hydroxylamine (4 mmol) was mixed with proper amount of silica sulfuric acid (4 mmol H^+) and a few grams more of silica gel in an agate mortar and pestle and the mixture was ground at ambient temperature for appropriate time (15-45 min). The results are summarized in Table-1.

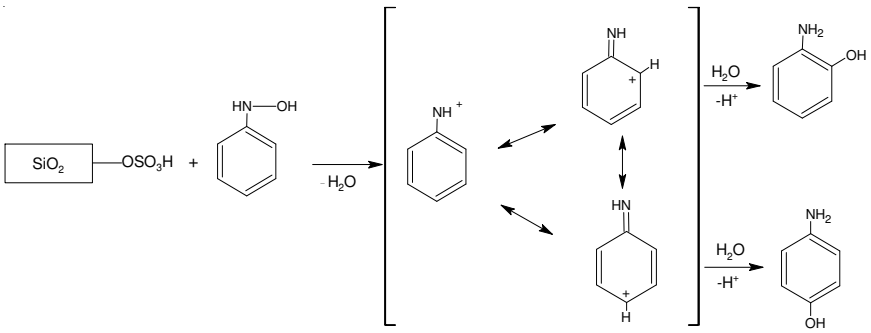
TABLE-1
BAMBERGER REARRANGEMENT OF PHENYL HYDROXYLAMINES TO 4-AMINO PHENOL DERIVATIVES IN THE PRESENCE OF SILICA SULFURIC ACID UNDER SOLVENT-FREE CONDITIONS AT ROOM TEMPERATURE[a,b]

Substrate	Time (min)	Yield (%)	Product	m.p. (ºC)
	20	89		183
	17	92		175
	15	95		210
	25	87		160
	35	85		150
	40	60		120
	45	79		201
	120	–	–	–

[a]All products were confirmed by comparison with authentic samples (IR, ^{1}H NMR and TLC); [b]Yield refer to pure isolated products.

As Table-1 indicates, the reaction was completed within (15-45) min in moderate to high yields (60-95 %). Nearly all the yields obtained by this non-solvent procedure are much better than those obtained in aqueous conditions[13]. It is noteworthy that the presence of activating groups such as -OMe and -Me increase the yield of rearrangement (Table-1) while the deactivating groups decrease the yield of product (Table-1). Also no *ortho*

amino phenols were observed during this procedure and 2-hydroxylamino-benzoic acid was unreactive under the same reaction condition. The possible mechanism of rearrangement under non-solvent condition could be as outlined in **Scheme-I**.



Scheme-I

In conclusion the rearrangement of phenyl hydroxylamines under non-solvent conditions to 4-hydoxyamines is a mild, simple and environmentally safe reaction and silica sulfuric acid is an inexpensive and efficient reagent for this transformation.

REFERENCES

1. S. Mitchell, Analgesics, Antipyretic and Anti-inflammatory Agent, Kirk-Othmer Encyclopedia of Chemical Technology, Wiley-Interscience: New york, Vol. 2, edn. 3, p. 580 (1992).
2. E. Bamberger, *Ber.*, **27**, 1347 (1894); **27**, 1548 (1894); **33**, 3600 (1900).
3. E. Bamberger and J. Lagutt, *Ber.*, **31**, 1500 (1898).
4. E. Bamberger, *Ber.*, **28**, 245 (1895).
5. L.A. Strenson and R.E. Gmmans, *Bioorg. Chem.*, **4**, 58 (1975).
6. D.A. Fidler, J.S. Logan and M.M. Boudakin, *J. Org. Chem.*, **26**, 4014 (1961).
7. T. Sone, K. Homamoto, Y. Seigi, S. Shinkai and O. Manabe, *J. Chem. Soc. Perkin Trans. II*, 1596 (1981).
8. T. Sone, Y. Tokuda, T. Sakai, S. Shinkai and O. Manabe, *J. Chem. Soc. Perkin Trans. II*, 298 (1981).
9. B.F. Mirjalili, M.A. Zolfigol, A. Bamoniri and A.J. Zarei, *Chin. Chem. Soc.*, **51**, 509 (2004).
10. A.R. Hajipour, A. Zarei, L. Khazdooz, S.A. Pourmousavi and A.E. Ruoho, *Bull. Korean Chem. Soc.*, **26**, 808 (2005).
11. A.R. Hajipour, B.F. Mirjalili, A. Zarei, L. Khazdooz and A.E. Ruohv, *Tetrahedron Lett.*, **45**, 6607 (2004).
12. R.L. Shriner and R.C. Fuson, The Systematic Identification of Organic Compounds, John Wiley & Sons Inc., edn. 5 (1964).
13. B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith and A.R. Tetchell, A.I. Vogel's: Textbook of Practical Organic Chemistry, edn. 4, p. 722, 723 (1978).

(*Received*: 17 July 2006; *Accepted*: 24 April 2007) AJC-5605