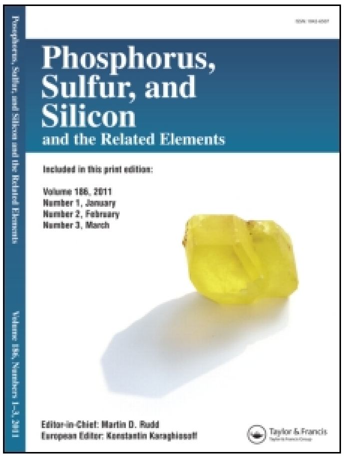


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SILICA PHOSPHORIC ACID/$NaNO_2$ AS A NOVEL HETEROGENEOUS SYSTEM FOR THE COUPLING OF THIOLS TO THEIR CORRESPONDING DISULFIDES

Mohammad Ali Zolfigol[a]; Farhad Shirini[b]; Khosrow Zamani[c]; Efat Ghofrani[a]; Satar Ebrahimi[c]
[a] Chemistry Department, College of Science, Bu-Ali Sina University, Hamadan, Iran [b] Chemistry Department, College of Science, Gilan University, Rasht, Iran [c] Chemistry Department, College of Science, Arak University, Arak, Iran

To cite this Article Zolfigol, Mohammad Ali , Shirini, Farhad , Zamani, Khosrow , Ghofrani, Efat and Ebrahimi, Satar(2004) 'SILICA PHOSPHORIC ACID/$NaNO_2$ AS A NOVEL HETEROGENEOUS SYSTEM FOR THE COUPLING OF THIOLS TO THEIR CORRESPONDING DISULFIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 11, 2177 — 2182

To link to this Article: DOI: 10.1080/10426500490474842

URL: http://dx.doi.org/10.1080/10426500490474842

Phosphorus, Sulfur, and Silicon, 179:2177–2182, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490474842

SILICA PHOSPHORIC ACID/$NaNO_2$ AS A NOVEL HETEROGENEOUS SYSTEM FOR THE COUPLING OF THIOLS TO THEIR CORRESPONDING DISULFIDES

Mohammad Ali Zolfigol,[a] *Farhad Shirini,*[b] *Khosrow Zamani,*[c] *Efat Ghofrani,*[a] *and Satar Ebrahimi*[c]
Chemistry Department, College of Science, Bu-Ali Sina University, Hamadan, Iran;[a] *Chemistry Department, College of Science, Gilan University, Rasht, Iran;*[b] *and Chemistry Department, College of Science, Arak University, Arak, Iran*[c]

(Received March 16, 2003; accepted March 18, 2004)

*Silica phosphoric acid was prepared via reaction of silica chloride (**I**) and phosphoric acid. Thiols can be readily converted to their corresponding thionitrites with a combination of silica phosphoric acid (**II**), wet SiO_2, and sodium nitrite in dichloromethane at room temperature. Disulfides result from the homolytic cleavage of the sulfur–nitrogen bond of the unstable thionitrite and subsequent coupling of the resultant thiyl radicals.*

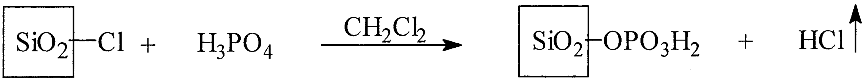
Keywords: Disulfides; silica chloride; silica phosphoric acid; thiols; thionitrites (S-nitrosothiols)

Acids are widely used as catalysts in industry, producing more than 1×10^8 mt/year of products. The most commonly used acids are HF, H_2SO_4, $HClO_4$, and H_3PO_4 (in liquid form or supported on Kieselguhr). Solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and environmentally safe disposal. There is much current research on and general interest in heterogeneous systems because of the importance such systems have in industry and in developing technologies.[1,2] In continuation of our studies on the application of silica resin with acid functional moieties[3]

Financial support for this work from the Research Council of Bu-Ali Sina University, Hamadan, Iran is gratefully acknowledged.

Address correspondence to Mohammad Ali Zolfigol, Chemistry Department, College of Science, Bu-Ali Sina University, P.O. Box 4135, Hamadan 65174, Iran. E-mail: zolfi@basu.ac.ir

we found that silica chloride (**I**) is an excellent source for generation of HCl.[4–6] It is interesting to note that the addition of H_3PO_4 to the silica chloride gives silica phosphoric acid (**II**), and HCl was evolved simultaneously (Scheme 1). Here we wish to report the first example of silica solid acid with phosphoric acid moiety.

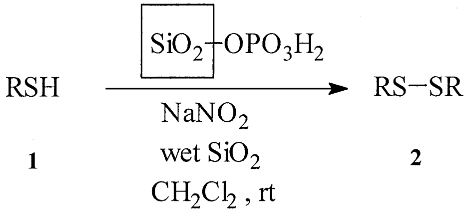


I **II**

SCHEME 1

We were also interested in using reagent (**II**) for the nitrosation of thiols via in situ generation of HNO_2 and NO^+, respectively, when used in conjunction with $NaNO_2$ and wet SiO_2 in an organic solvent (Scheme 1). On the other hand, thionitrites have not been as widely studied as their oxygen counterparts alkyl nitrites, generally because of their reduced stability.[7] However, in recent years there has been much interest generated in the chemistry and biochemistry of nitrosothiols,[7–14] since (1) they are being examined as possible drugs to effect vasodilatation and to reduce platelet aggregation, (2) they are now believed to play an important part in some of the physiological processes involving nitric oxide, and (3) they are being used as a source of thiyl radicals[7] or as nitrosating agents. The vital role of thiols and disulfides in living systems has focused on their interconversion reactions. Intense interest in the chemistry of thionitrites has been generated in connection with the newly discovered remarkable physiological roles of nitric oxide, particularly including vasodilation and cytotoxic action of macrophages. Thiols and thionitrites (S-nitrosothiols) are believed to be involved in processes in vivo, possibly in the mechanism of NO transfer reactions.[11]

The most general reagent is nitrous acid, generated from sodium nitrite and mineral acid in water or in mixed alcohol–water solvents. Other nitrosating agents have been used successfully to synthesize thionitrites, notably alkyl nitrites, nitrosyl salts, dinitrogen trioxide, dinitrogen tetroxide,[7–10] trichloronitromethane,[11] oxalic acid dihydrate,[12] inorganic acidic salts[13] or silica sulfuric acid,[14] and sodium nitrite. Very recently we, among many others, demonstrated that heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions, and minimization of chemical wastes as compared to the liquid-phase counterparts.[13–16] Therefore, we decided to apply silica phosphoric acid (**II**)/$NaNO_2$ as a new heterogeneous system for the oxidation of thiols. We wish to report a simple, cheap, and convenient method for the effective coupling of thiols and production of disulfides under mild and heterogeneous conditions (Scheme 2).



SCHEME 2

Different kinds of thiols were subjected to the coupling reaction in the presence of $NaNO_2$, wet SiO_2 (50% w/w), and silica phosphoric acid (**II**) in dichloromethane. The coupling reactions were performed under mild and completely heterogeneous conditions at room temperature. A bright-red heterogeneous solution was obtained immediately due to the formation of thionitrite. Disulfides result from the homolytic cleavage of the sulfur–nitrogen bond of the unstable thionitrite and subsequent coupling of the resultant thiyl radicals.[11]

Although the reaction occurs without wet SiO_2, the reaction time is very long and the reaction is completed only after several days. Therefore, we think that the presence of wet SiO_2 will act as a media and will provide a heterogeneous effective surface area for in situ generation of HNO_2. It also will make easy workup.

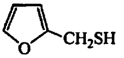
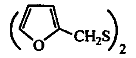
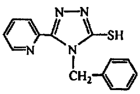
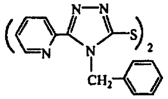
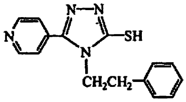
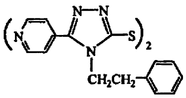
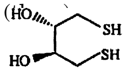
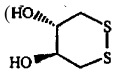
In conclusion, practical and efficient nitrosation–oxidation of thiols was achieved by the present methodology. The cheapness and availability of the reagents, easy procedure, and workup make this method attractive for the organic chemists. We believe that the present methodology addresses the current trend toward green chemistry due to high yields and nontoxic wastes.

EXPERIMENTAL SECTION

General

Chemicals were purchased from Fluka, Merck, Riedel-deHaen AG, and Aldrich Chemical companies. Silica chloride was synthesized according to the reported procedures.[4] Disulfides were characterized by comparison of their spectral (IR, ^{1}H-NMR, UV and TLC) and physical data with authentic samples.[8–14,17,18]

TABLE I Coupling of Thiols to Their Corresponding Disulfides with a Combination of Silica Phosphoric Acid (II), $NaNO_2$ (III), and wt. SiO_2 (50% *w*/*w*) in Dichloromethane at Room Temperature

Entry	Substrate 1	Product 2	Time (min)	Yields[b]	Reagent/Substrate[a] II (g)	Reagent/Substrate[a] III (mmol)
1	C_6H_5SH	$(C_6H_5S)_2$	20	99	0.7	2
2	$C_6H_5CH_2SH$	$(C_6H_5CH_2S)_2$	40	91	0.7	2
3	FC_6H_4 SH	$(FC_6H_4\ S)_2$	35	92	0.7	2
4	C_6H_{11} SH	$(C_6H_{11}\ S)_2$	60	99	0.7	2
5	$HOCH_2CH_2$ SH	$(HOCH_2CH_2\ S)_2$	6	85	0.55	2
6	ClC_6H_4 SH	$(ClC_6H_4\ S)_2$	1	70	1.4	2
7	C_4H_9 SH	$(C_4H_9\ S)_2$	30	92	0.8	2
8			25	85	0.7	2
9			10	76[c]	0.7	4
10			10	70[c]	0.7	4
11	 (threo)	 (threo)	25	70[c]	0.7	4

[a] Wet SiO_2: substrate (0.2 g; 1 mmol).
[b] Isolated yields.
[c] Workup with CH_3OH and extracted with (Et_2O/H_2O).

Preparation of Silica Chloride (I)

Thionyl chloride (40 ml) was added to an oven-dried (120°C, vacuum) silica gel (10 g) in a round-bottomed flask (250 ml) equipped with a condenser and a drying tube and refluxed for 48 h. The unreacted thionyl chloride was distilled off. The resulting white-grayish powder was flame-dried and stored in a tightly capped bottle. This silica chloride can be used for months without loosing its activity. It should be noted that the adsorption of water by silica chloride causes its conversion to original silica gel by generation of HCl. The percentage of chloride in the silica chloride was determined by acid-base titration according to the following reaction. The librated HCl was titrated by standard NaOH, and the amount of chloride in silica chloride was calculated.[19]

Preparation of Silica Phosphoric Acid (II)

H_3PO_4 (9.8 g, 0,1 mol) was added to a suspension of silica chloride **I** (94.5 g) in CH_2Cl_2 (200 ml) and vigorously stirred for 2 h. Then the reaction mixture was filtered and the residue washed with CH_2Cl_2 (2 × 50 ml). Silica phosphoric acid was obtained as a white powder.

Typical Experimental Procedure

Silica phosphoric acid **II** (1.4 g), wet SiO_2 (50% *w*/*w*) (0.4 g), and $NaNO_2$ **III** (0.257 g, 4 mmol) were added to a solution of thiophenol ((entry 1) 0.220 g, 2 mmol) in CH_2Cl_2 (10 ml). The resulting mixture was stirred at room temperature. A bright-red heterogeneous solution was obtained immediately. Thionitrites were characterized by comparison of their UV spectra with those reported in the literature.[17,18] Typical spectra are as follows: λ_{max} (CH_2Cl_2): PhSNO, 380, 529, 570 nm. A pale-yellow solution was also obtained after 20 min and then filtered. Dichloromethane was evaporated. The yield was 0.216 g (99%) of crystalline brownish diphenyldisulfide, m.p. 58°C (Lit[17,18] m.p. 58–60°C).

REFERENCES

[1] a) M. A. Zolfigol, D. Habibi, B. F. Mirjalili, and A. Bamoniri, *Tetrahedron Lett.*, **44,** 3345 (2003); b) M. A. Zolfigol, I. Mohammadpoor-Baltork, D. Habibi, B. F. Mirjalili, and A. Bamoniri, *Tetrahedron Lett.*, **44,** 8165 (2003).

[2] J. M. Riego, Z. Sedin, J. M. Zaldivar, N. C. Marziano, and C. Tortato, *Tetrahedron Lett.*, **37,** 513 (1996).

[3] M. A. Zolfigol, F. Shirin, A. Ghorbani Choghamarani, and I. Mohammadpoor-Baltork, *Green Chem.*, **4,** 562 (2002) and references cited therein.

[4] a) F. Mohanazadeh, A. R. Momeni, and Y. Rangbar, *Tetrahedron Lett.*, **33,** 6127 (1994); b) H. Firouzabadi, N. Iranpoor, B. Karimi, and H. Hazarkhani, *Synlett.*, 263 (2000).

[5] M. A. Zolfigol, M. Torabi, and S. E. Mallakpour, *Tetrahedron*, **57,** 8381 (2001).

[6] M. A. Zolfigol, F. Shirini, and A. Ghorbani-Choghamarani, *Synth. Commun.*, **32,** 1809 (2002).

[7] a) D. L. H. Williams, *Supplement F2: The Chemistry of Amino, Nitroso, Nitro and Related Groups* (John Wiley & Sons Ltd, London, 1996), pp. 665–682 and references cited therein; b) L. K. Keefer and D. L. H. Williams, *Methods in Nitric Oxide Reseach* (John Wiley & Sons Ltd, 1996), pp. 509–519.

[8] a) D. L. H. Williams, *Transition Met. Chem.*, **21,** 189 (1996); b) P. H. Beloso and D. L. H. Williams, *Chem. Commun.*, 89 (1997); c) D. R. Nobel, H. R. Swift, and D. L. H. Williams, *Chem. Commun.*, 2317 (1999); d) A. P. Munro and D. L. H. Williams, *Can. J. Chem.*, **77,** 550 (1999); e) A. P. Munro and D. L. H. Williams, *J. Chem. Soc. Perkin Trans.*, **2,** 1989 (1999); f) A. J. Holmes and D. L. H. Williams, *Chem. Commun.*, 1711 (1998); g) S. Amado, A. P. Dicks, and D. L. H. Williams, *J. Chem. Soc. Perkin Trans.*, **2,** 1869 (1998); h) P. J. Coupe and D. L. H. Williams, *J. Chem. Soc. Perkin Trans.*, **2,**

1057 (1999); i) D. L. H. Williams, *Acc. Chem. Res.*, 869 (1999); j) J. M. Fukuto and L. J. Ignarro, *Acc. Chem. Res.*, 149 (1997); j) S. Goldstein and G. Czapski, *J. Am. Chem. Soc.*, **118,** 3419 (1996); k) S. Raghavan, A. Rajender, S. C. Joseph, and M. A. Rasheed, *Synth. Commun.*, **31,** 1477 (2001); l) B. d'Roy, A. D. M. Hardemare, and M. Fontecave, *J. Org. Chem.*, **59,** 7019 (1994).

[9] S. Oae, Y. H. Kim, and D. Fukushima, *Chem. Lett.*, 893 (1977).

[10] A. Cornelis, N. Depaye, A. Gerstmans, and P. Laszlo, *Tetrahedron. Lett.*, **24,** 3103 (1983).

[11] A. Demir, A. C. Igdir, and A. S. Mahasneh, *Tetrahedron*, **55,** 12399 (1999).

[12] M. A. Zolfigol, D. Nematollahi, and S. E. Mallakpour, *Synth. Commun.*, **29,** 2277 (1999).

[13] M. A. Zolfigol, *Synth. Commun.*, **30,** 1593 (2000).

[14] M. A. Zolfigol, *Tetrahedron*, **57,** 9509 (2001) and references cited therein.

[15] M. A. Zolfigol, M. H. Zebarjadian, G. Chehardoli, S. E. Mallakpour, and M. Shamsipur, *Tetrahedron*, **57,** 1627 (2001).

[16] F. Shirini, M. A. Zolfigol, B. Mallakpour, S. E. Mallakpour, and A. R. Hajpour, *Tetrahedron Lett.*, **43,** 1555 (2002).

[17] N. Iranpoor, H. Firouzabadi, and M. A. Zolfigol, *Synth. Commun.*, **28,** 367 (1998).

[18] H. Firouzabadi, N. Iranpoor, and M. A. Zolfigol, *Synth. Commun.*, **28,** 1179 (1998).

[19] M. A. Zolfigol, T. Madrakian, E. Ghaemi, A. Afkhami, S Azizian, and S. Afshar, *Green Chem.*, **4,** 611 (2002).