Pergamon

Tetrahedron Letters 39 (1998) 8505–8508

TETRAHEDRON
LETTERS

Hypervalent Tris(catecholato)silicate derived from Rice Husk Ash

V.Chandrasekhar*, **S.Nagendran, Samiksha and G.T.Senthil Andavan**

Department of Chemistry, Indian Institute of Technology, Kanpur – 208 016, India.

Received 5 August 1998; accepted 1 September 1998

Abstract: *Rice husk ash with a particle size distribution between 2 and 7μm reacts with catechol and sodium methoxide in methanol to afford the tris(catecholato)silicate,* $Na_2[Si(o\text{-}C_6H_4O_2)_3]$ ***1***.

Recently it has been shown that hypervalent five and six-coordinate anionic silicon compounds can be utilised as synthons for the generation of a variety of organo silicon compounds[1-2] and even organophosphorus and sulphur compounds[3]. Traditionally, organo silicon compounds have been synthesised from silicon halides which are prepared commercially by the 'direct' process of Rochow[4]. More recently there have been efforts to utilise cheap and easily available silicon sources such as silica and silica gel for the preparation of reactive glycolato and catecholato silicates[5-7].

We report in this paper the results of our study on the utilisation of rice husk ash (RHA) as the silicon source for the preparation of the six coordinate hypervalent dianionic silicon compound $Na_2[Si(o\text{-}C_6H_4O_2)_3]$ **1**. It was of interest to see if rice husk, an enormous waste product in most agricultural countries, can be effectively converted into value added organo silicon compounds. To the best of our knowledge there have been no examples in literature on the preparation of organo silicon compounds from RHA, although there are reports on its use as a silicon source for the assembly of zeolites[8].

Rice husk has been fired in the open and then subsequently at 1000°C in an oven to afford RHA-1 which has been shown to be an essentially pure crystabolite form of silica by X-ray diffraction. RHA-1 has been thoroughly ground to afford RHA-2. Particle size distribution (PSD) studies on RHA-1 and RHA-2 reveal that in the former the majority of the particles are between 50 to 100μm (Figure). In order to compare the reactivity of RHA-1 and RHA-2 in terms of their PSD, we also chose to study TLC grade silica gel, which had a distribution between 5 and 50μm. The reactions of these three silicon sources were carried out with catechol and sodium methoxide in methanol by adopting a procedure described previously[7]. While RHA-2 and TLC grade silica gel afforded the hypervalent compound **1** in good yields[9], the reaction with RHA-1 was very slow

---

* **e.mail: vc@iitk.ac.in**

0040-4039/98/$ - see front matter © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)01849-8

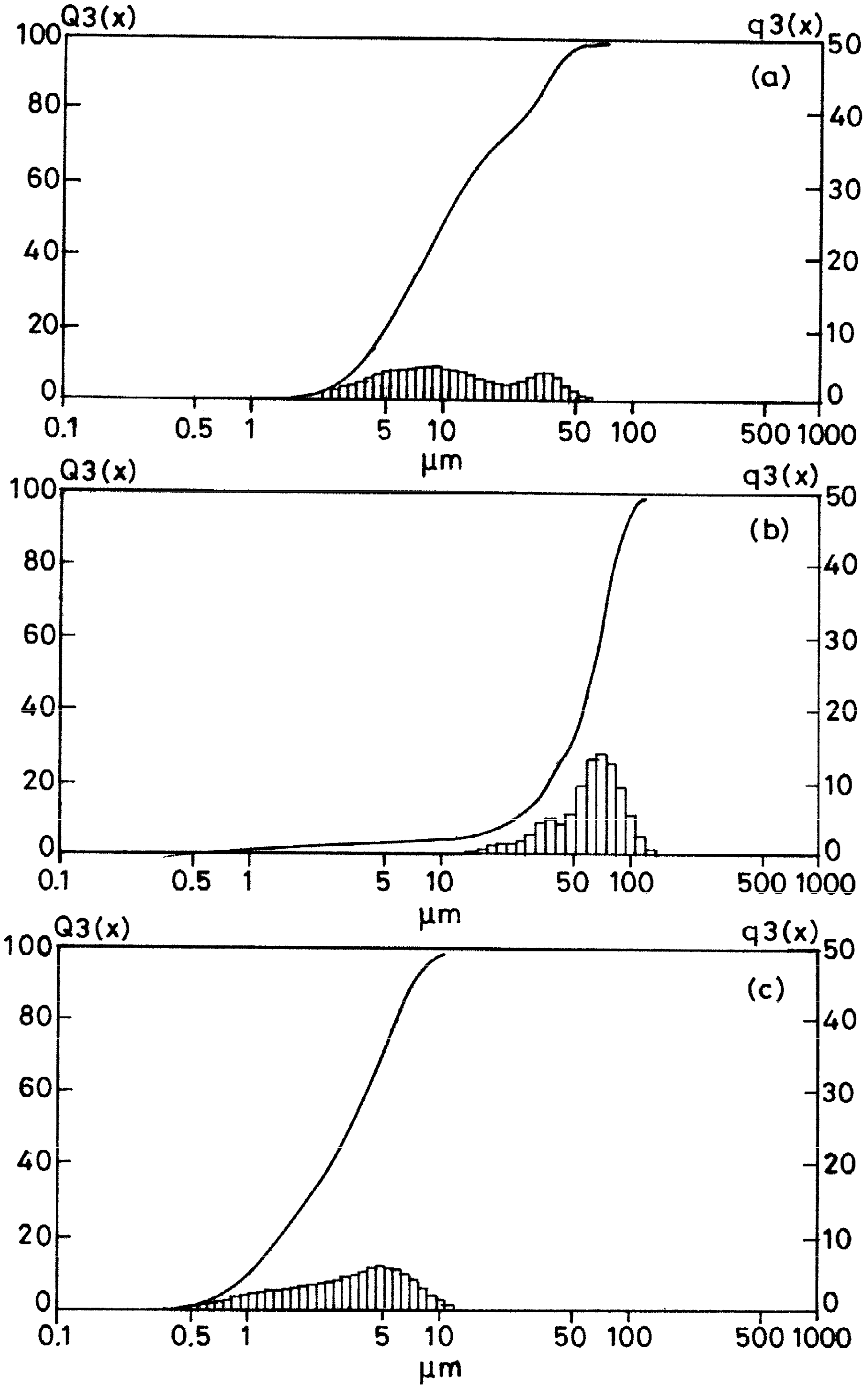
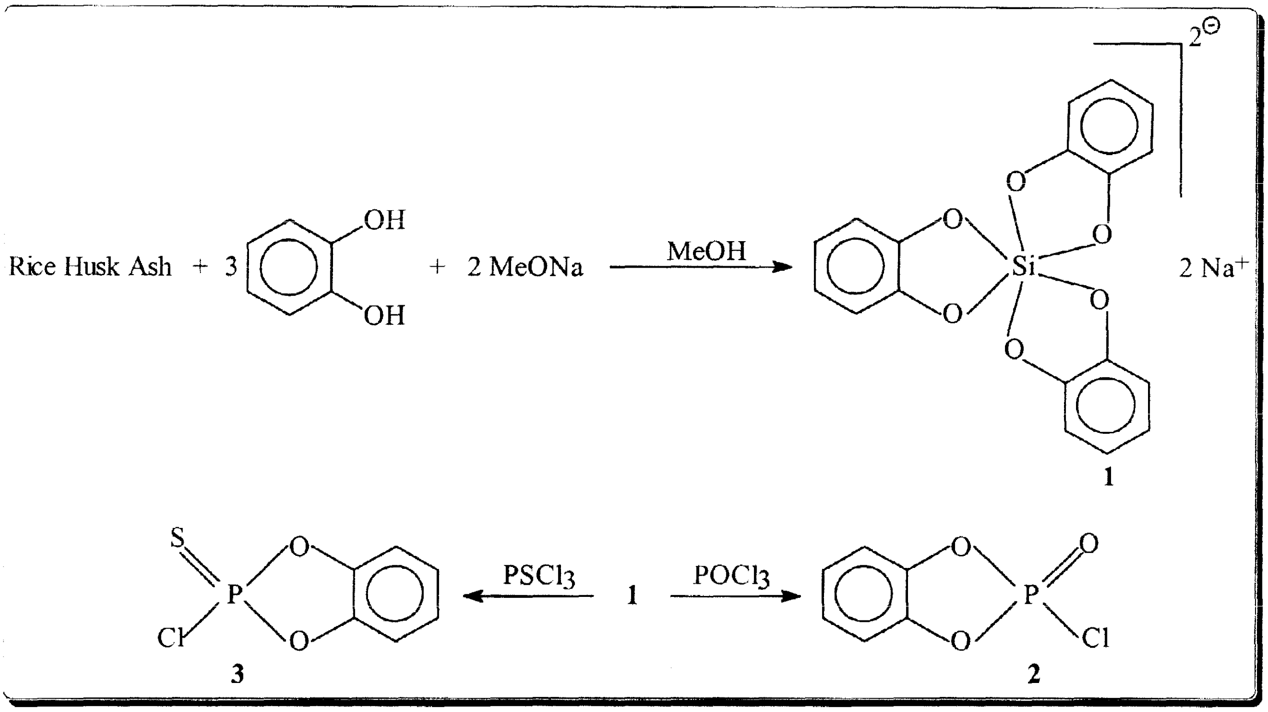


Figure: (a) PSD of TLC Silicagel (b) PSD of RHA-1
(c) PSD of RHA-2

and there was no indication of formation of **1**. This underscores the importance of particle size distribution on the reactivity of the insoluble reactant in the heterogeneous reaction. In accordance with a recent report[3] **1** reacts with $POCl_3$ and $PSCl_3$ to afford the catechol containing phosphate 2 and thiophosphate 3 (scheme).



Scheme

In conclusion we have shown that rice husk, a waste product, can successfully be converted into a useful value added organo silicon compound by a straightforward and simple synthetic strategy. Apart from the novelty of the silicon source this strategy also may be useful in addressing the problem of minimising the waste thrown in the environment.

Acknowledgements: VC and SN thank Department of Science and Technology, India for financial support.

References:

1. Chuit, C.; Corriu, R.J.P.; Reye, C.; Young, J.C. *Chem.Rev.* **1993**, 93, 1371-48.
2. Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R.J.P.; Reye, C. *Organometallics* **1988**, 7, 1165-1171.

3. Kingston, J.V.; Sudheendra Rao, M.N. *Tetrahedron Letters* **1997**, 38, 4841-4844.
4. a) Kirk-Othemer Encyclopedia of Chemical Technology, 3rd Ed., Vol 20, 750-880 (Wiley-Interscience, New York, 1979). b) Rochow, E.G. Silicon and Silicones. Springer-Verlag, Heidelberg, Germany, 1987.
5. Laine, R.M.; Blohowiak, K.Y.; Robinson, T.R.; Hope, M.L.; Nardi, P.; Kampf, J.; Uhm, J. *Nature* **1991**, 353, 642-44.
6. Hoppe, M.L.; Laine, R.M.; Kampf, J.; Gordon, M.S.; Burggraf, L.W. *Angew.Chem.Int.Ed.Engl.* **1993**, 32, 287-289.
7. Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R.J.P.; Reye, C. *Angew.Chem.Int.Ed.Engl.* **1986**, 25, 474-476.
8. Rawtari, A.V., Rao, M.S., Gokhale, K.V.S.K. *Ind. Eng. Chem.Res.* **1989**, 28, 1411.
9. RHA-2 (0.7 g, 11.2 mmOl), catechol (7.5 g, 33.6 mmol) and sodium methoxide (1.1 g, 22.4 mmol) were heated together under reflux in methanol (100 ml) for 96h. Removal of solvent afforded a residue, which was washed with ether. The residue was recrystallised from THF to afford colourless crystals of **1**, which was identified by FAB Mass, ^{13}C and ^{29}Si NMR.