

SYNLETT Spotlight 133

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Resin-Supported Sulfonic Acid

Compiled by Pranjal Gogoi

Pranjal Gogoi was born in Sivasagar, Assam (India) in 1978. He completed his B.Sc. with honors in chemistry in 1998 from Dibrugarh University and M.Sc. (2000) degree in chemistry from Gauhati University, Guwahati, India. He is currently working as a Junior Research Fellow for his Ph.D. in organic chemistry under the supervision of Dr. Dilip Konwar in Synthetic Organic Chemistry Division, RRL, Jorhat, India. His research interests are Lewis and Brønsted acid mediated organic synthesis.

Synthetic Organic Chemistry Division, Regional Research Laboratory (CSIR), Jorhat-785006, Assam, India
E-mail: gogoipranj@yahoo.co.uk

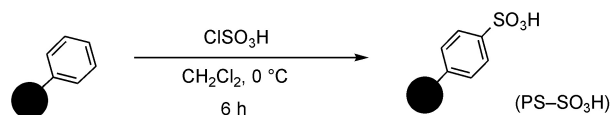


Introduction

There has been a plethora of polymer-supported syntheses since Merrifield began peptide synthesis on the solid phase.¹ Solid-phase organic synthesis (SPOS) has become a very efficient method for production of combinatorial libraries.² Resinsulfonic acid is one of the important functional polymer, which is already developed in organic synthesis.³ Resinsulfonic acids are particularly useful for the removal of basic compounds such as primary, secondary and tertiary amines. On the other hand, they are used as a separator and/or electrolyte in membrane-separated chlor-alkali cells and other electrochemical processes, solid polymer electrolyte fuel cells and batteries.^{3a} The use of resinsulfonic acids in organic synthesis was serendipitous. Generally, they are used as Brønsted acid in organic synthesis. Compared to conventional Brønsted acids, they have advantages of recyclability, operational simplicity and they can often be used in just catalytic amounts. Of late, resinsulfonic acids such as sulfonated polystyrenes (Dowex-50, Amberlite IR-112, Permutit-Q) and Nafion-H are commercially available.

Preparation

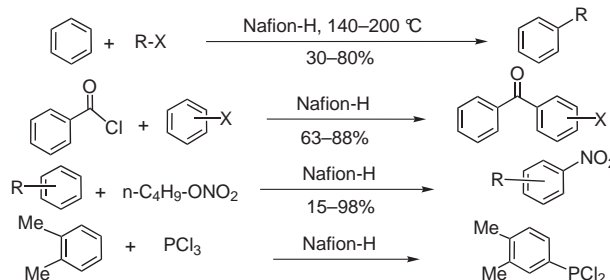
Nafion resins were first synthesized by Du Pont chemists.⁴ A variety of perfluorinated polymer sulfonic acids have been reported with their synthetic methods in the literature.^{3a} In the case of sulfonated polystyrenes, the sulfonic acid group introduced into the polystyrenes in a simple way. To a suspension of polystyrene in dichloromethane, chlorosulfonic acid is slowly added at 0 °C, and stirred for six hours followed by acetic acid treatment to give sulfonated polystyrenes. The amount of sulfonic acid can be estimated and its amount depends on the amount of chlorosulfonic acid used.⁵



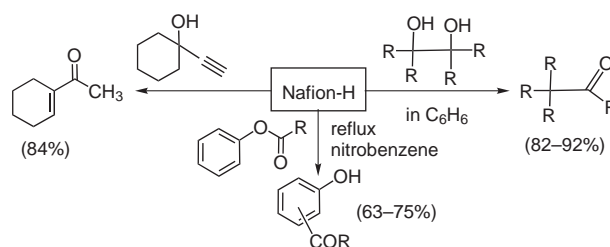
Scheme 1 Preparation of sulfonated polystyrenes

Abstracts

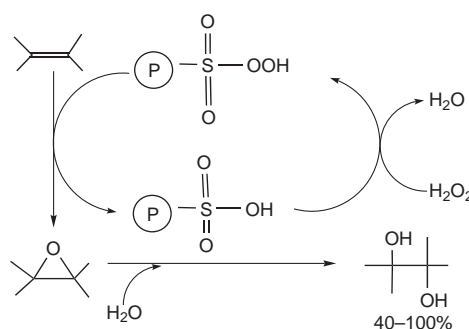
(A) Nafion-H catalyzes various electrophilic reactions, such as alkylation^{6a} (alkylation with olefins, alcohols, alkyl halides, alkyl esters), acylation^{6b} (acylation with aroyl chlorides and anhydrides), nitration of alkyl benzenes and other aromatics with butyl nitrate,^{6c} sulfonation,^{6d} isomerization,^{6e} phosphorylation^{6f} and polymerization.^{6g}



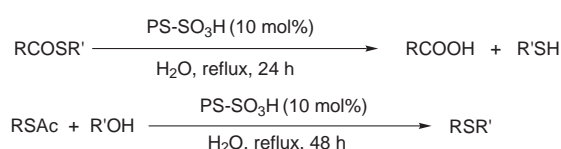
(B) Nafion-H has been reported to catalyze various rearrangement reactions, such as pinacol-pinacolone rearrangement,^{7a} Fries rearrangement,^{7b} Rupe rearrangement^{7c} of alkynyl tertiary alcohols and gas phase rearrangement of allyl alcohols to the corresponding aldehydes.^{7d}



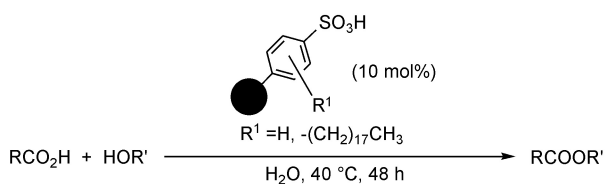
(C) Sato and co-workers⁸ have used resin-supported sulfonic acid in the presence of hydrogen peroxide for the catalytic dihydroxylation of alkenes under organic-solvent-free condition. Nafion SAC-13 showed almost the same catalytic activity as Nafion 50. The ion-exchange resin, amberlyst 15 (polystyrene-supported sulfonic acid) also proved to be a good catalyst for this transformation. Interestingly, the catalytic activity for dihydroxylation of olefins, resin-supported sulfonic acids is much higher than that of homogeneous acid catalysts, such as $\text{CF}_3\text{SO}_3\text{H}$, H_2SO_4 and $\text{C}_6\text{H}_5\text{SO}_3\text{H}$.



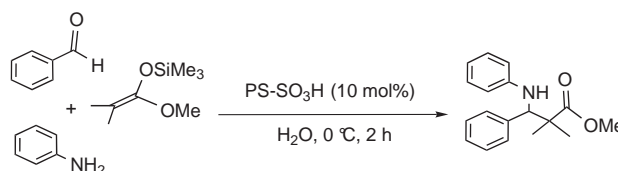
(D) Polystyrene-supported sulfonic acid can hydrolyze thioesters to corresponding acids in pure water.⁹ This catalyst is much superior to other Brønsted acid catalysts, including a surfactant-type Brønsted acid. Transprotection of thiols from thioesters to benzylic thioethers has also been realized in water using this catalytic system.



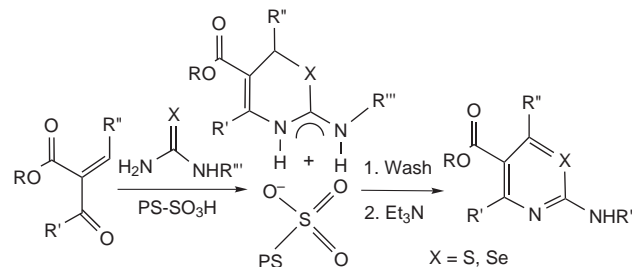
(E) Kobayashi and co-worker reported the dehydrative esterification of carboxylic acids with alcohols in water using hydrophobic polystyrene-supported sulfonic acids.⁵ The presence of hydrophobic nature and alkyl chains of the polystyrene-supported sulfonic acid play important roles for that transformation. Nafion-H can also be used for the synthesis of esters, ethers, acetals and thioacetals.^{3a}



(F) Three-component Mannich-type reaction can be performed using hydrophobic polymer-supported sulfonic acid catalyst in water.¹⁰ The hydrophobic PS-SO₃H was more efficient in comparison with the commercially available polymer-supported catalyst (Dowex 50W-X2) for this transformation. Ketene silyl acetal, silicon enolates, aldehyde/ketones and phosphates are used as the third component in this reaction.



(G) The polymer-supported sulfonic acid reagent act as a mediator for the synthesis of functionalized 1,3-thiazines and also binds them in situ as ion pairs. The nonbasic by-products and excess reagents can be removed by filtration and treatment with triethylamine.¹¹



References

- (1) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.
- (2) Nicolaou, K. C.; Hanks, R.; Hartwig, W. *Handbook of Combinatorial Chemistry*; Wiley-VCH: Weinheim, **2002**.
- (3) (a) Olah, G. A.; Iyer, P. S.; Surya, Prakash, G. K. *Synthesis* **1986**, 513; and references cited therein. (b) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557. (c) Hodge, S.; Sherrington, D. C. *Polymer-Supported Reactions in Organic Synthesis*; Wiley: London, **1980**.
- (4) (a) England, D. C. US Patent 2852554, **1958**; *Chem. Abstr.* **1959**, *53*, 2253. (b) Conolly, D. J.; Gresham, W. F. US Patent 3282875, **1966**.
- (5) Manabe, K.; Kobayashi, S. *Adv. Synth. Catal.* **2002**, *344*, 270.
- (6) (a) Olah, G. A.; Meidar, D. *Nouv. J. Chim.* **1979**, *3*, 269. (b) Olah, G. A.; Malhotra, R.; Narang, S. C.; Olah, J. A. *Synthesis* **1978**, 672. (c) Olah, G. A.; Narang, S. C. *Synthesis* **1978**, 690. (d) Vaughan, R. J. US Patent 4308215, **1981**; *Chem. Abstr.* **1982**, *96*, 87450. (e) Olah, G. A.; Meidar, D.; Olah, J. A. *Nouv. J. Chim.* **1979**, *3*, 275. (f) Cozens, R.; Hogan, P. J.; Lalkham, M. J. European Patent 24128, **1981**; *Chem. Abstr.* **1981**, *95*, 150884. (g) Hasegawa, H.; Higashimura, T. *Polym. J.* **1979**, *11*, 737; and references cited therein.
- (7) (a) Olah, G. A.; Meidar, D. *Synthesis* **1978**, 358. (b) Olah, G. A.; Arvanaghi, M.; Krishnamurthy, V. V. *J. Org. Chem.* **1983**, *48*, 3359. (c) Olah, G. A.; Fung, A. P. *Synthesis* **1981**, 473. (d) Olah, G. A.; Meidar, D.; Liang, G. *J. Org. Chem.* **1978**, *43*, 3890.
- (8) Usui, Y.; Sato, K.; Tamaka, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 5623.
- (9) Limura, S.; Manabe, K.; Kobayashi, S. *Org. Lett.* **2003**, *5*, 101.
- (10) Limura, S.; Nobutou, D.; Manabe, K.; Kobayashi, S. *Chem. Commun.* **2003**, 1644.
- (11) Strohmeier, G. A.; Kappe, C. O. *Angew. Chem. Int. Ed.* **2004**, *43*, 621.