Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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A. D. Sagar [a] , M. T. Thorat [a] , M. M. Salunkhe [a] , R. S. Seiukar [b] & P. P. Wadgaonkar [b]

[a] Department of Chemistry, Shivaji University, Kolhapur, 416 004, India

[b] Division of Polymer Chemistry, National Chemical Laboratary, Pune, 411 008, India

Published online: 23 Sep 2006.

To cite this article: A. D. Sagar , M. T. Thorat , M. M. Salunkhe , R. S. Seiukar & P. P. Wadgaonkar (1994) Polymer Supported Reagents: An Efficient and Simple Method for the Synthesis of Triaryl Phosphates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 24:14, 2029-2033, DOI: 10.1080/00397919408010211

To link to this article: http://dx.doi.org/10.1080/00397919408010211

SYNTHETIC COMMUNICATIONS, 24(14), 2029-2033 (1994)

POLYMER SUPPORTED REAGENTS:AN EFFICIANT AND SIMPLE METHOD FOR THE SYNTHESIS OF TRIARYL PHOSPHATES

A.D.Sagar, M.T.Thorat and M.M.Salunkhe*
Department of Chemistry, Shivaji University
Kolhapur-416 004 [India]

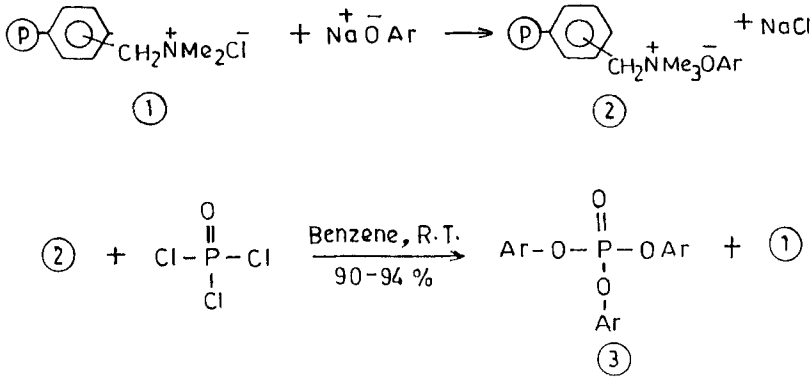
R.S.Seiukar and P.P.Wadgaonkar
Division of Polymer Chemistry,
National Chemical Laboratary,
Pune-411 008 [India]

ABSTRACT

The reaction of phosphoryl chloride with insoluble polymer-supported phenoxide ion reagents in benzene at room temperature, produced triaryl phosphates in excellent yields. The isolation of pure products by simple filtration and evaporation is an important feature of this method.

INTRODUCTION

Triaryl phosphates are of considerable interest because of their utility as plasticizers, flame retardants, lubricating oil additives and hydraulic fluids.[1] They are conventionally synthesized by reacting the hydroxyaryl compound with phosphoryl chloride either at elevated temperatures [160-250^{0}C] in the presence of a Lewis acid catalyst[2] or at room temperature using a phase-transfer catalyst.[3,4] The former method has a number of disadvantages,like 1] Liberation of hydrogen chloride gas which gives rise to corrosion problems, 2] Formation of

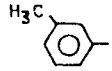
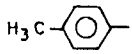
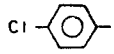
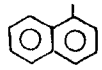
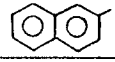


Scheme

by-products at the high temperature employed, and 3] Discoloration of the product due to the elavated temperatures used and hence distillation at low pressures [<1 mm Hg] to obtain a product of the desired purity. The phase-transfer catalyzed method works well at room temperature, however, it involves tedious reaction work-up.[4]

The applications of polymer-supported reagents in organic synthesis has received considerable attraction.[5,6] We wish to report herein an efficient and simple method for the synthesis of triaryl phosphates using insoluble polymer-supported phenoxide ions as reagents. The method involves aryloxylation of phosphoryl chloride with phenoxides supported on Amberlyst A-26, a strong anion exchange resin containing quaternary ammonium groups [1]. The treatment of an aqueous solution of the sodium salt of a phenol with Amberlyst A-26 forms the polymer-supported phenoxide ion reagent [2]. Triaryl phosphates were synthesized by reacting slightly more than three molar equivalents of the dried reagent [2] with one molar equivalent of phosphoryl chloride in benzene at room temperature.

TABLE ; Triaryl phosphates [3] synthesized.

Product No.	Ar	Reaction time [min]	Yield [%]	M.P./ B.P. [°C]	Lit.
3a		60	94	49	49-51
3b		70	90	90	90-91
3c		65	92	259-262 *	258-263 *
3d		70	90	77	77
3e		65	93	37	37
3f		65	94	116	117
3g		65	90	148-149	149-150
3h		65	90	111	111

* = Boiling point

The reactions were complete within 60-70 minutes. The nucleophilicity of polymer-bound phenoxide ion is increased sufficiently to allow the reaction with phosphoryl chloride in a manner which is related to the principles of phase-transfer technique. The results of the synthesis of triaryl phosphates are given in the table. The products were isolated easily by simply filtering off the resin and removing the solvent under reduced pressure. It is worth emphasizing that triaryl phosphates synthesized by this method were formed in excellent yields [90-94%] and were essentially pure

[by TLC] in the crude state. All the triaryl phosphates were characterized by their IR and ^{1}H-NMR spectra. The spent polymer supported reagent could be regenerated by washing with dilute hydrochloric acid solution and reused.

In conclusion, the procedure described here appears to be a useful method for the synthesis of triaryl phosphates under mild conditions. The advantage of this method lies in its simplicity and also its avoidance of aqueous work-up and extraction steps.

EXPERIMENTAL

Polymer Supported Phenoxide Reagents [1]:-

Amberlyst A-26 chloride form [5g] packed in a column was washed by 0.25 N aqueous sodium salt of phenol [25 mmol of phenol dissolved in 0.25 N NaOH (100 ml)], until complete removal of the chloride ions. The resin was then successively washed with water [100 ml], ethanol [25 ml] and ether [25 ml]. Finally the resin was dried azeotropically with toluene.

The Capacity of the Polymer Supported Phenoxide:-

The exchange capacity was determined by passing aqueous 1 M NaCl [100 ml] through the resin [0.39] packed in a column and the amount of phenoxide anion in the eluent was estimated by titration against 0.01 N HCl using methyl orange as an indicator. The capacity was found to be in the range of 1.2-1.9 mmol/g of dry resin.

Triaryl Phosphates [3]: General Procedure:-

A mixture of phosphoryl chloride [76.75 mg,5 mmol], polymer supported phenoxide reagent [16.5 mmol] and dry benzene [30 ml] was stirred at room temperature. After completion of the reaction the resin was filtered off and washed with benzene.

The combined filtrate and washings were evaporated to a residue consisting of essentially pure, [TLC, IR and ^{1}H-NMR] triaryl phosphate [3].

ACKNOWLEDGEMENT :

A.D.Sagar gratefully acknowledges fianancial assistance from the University Grants Commission [New Delhi].

REFERENCES;

1. Cherbuliez, E. in "Organic Phosphorous Compounds" Vol.6. Kosolapoff, G.M. and Maler, L.[eds], Willey Interscience, New York, 1973, 454.
2. Faith, W.L., Keyes, D.B. and Clark, R.L."Industrial Chemicals" 4th Edn, Wiley-Interscience, New York, 1975, 849.
3. Krishnakumar, V.K. and Sharma, M.M., Synthesis, 1983, 558.
4. Krishnakumar, V.K., Synth. Commun., 1984, 14, 189.
5. Trost, B.M. and Hutchinson, C.R.[eds.] "Organic Synthesis Today and Tomorrow", Pergamon Press, New York, 1981, 19.
6. Laszlo, P. [ed] "Preparative Chemistry Using Supported Reagents", Academic Press, San Diego, 1987.
7. Akelah, A. and Moet, A.,"Functionalized Polymers and their Applications", 1st Edn, Chapman and Hall [eds], USA, 1990.

(Received in The Netherlands 17 December 1993)