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Triphase Catalysis. Backbone Structure-Activity Relationships[1]

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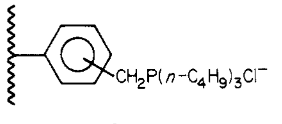
A series of cross-linked polystyrene resins has been synthesized bearing pendant methylenetri-*n*-butylphosphonium chloride groups. Matrix porosity, cross-link density, and percent ring substitution have each been systematically varied, and the resulting polymers evaluated as triphase catalysts for chloride ion displacement on *n*-decyl methanesulfonate. Efficiency data show that (1) macroporous polymers do not exhibit significantly greater activity than comparable microporous analogues, (2) increased cross-link density reduces catalyst efficiency for both macroporous and microporous polymers, (3) reduced percent ring substitution leads to higher efficiency in microporous and some macroporous resins, but lower efficiency in other macroporous polymers, and (4) operationally, many of these polystyrene-based catalysts display reasonably high efficiency.

Introduction

Recent efforts aimed at developing new and more active triphase catalysts have focused primarily on the chemical nature of the catalytic site.[2] Very little attention has been given thus far to the structure of the polymer support. We have reported a detailed kinetic study of the triphase catalytic displacement of chloride ion on *n*-decyl methanesulfonate employing microporous resins 1-4 (eq 1) and have concluded that both matrix diffusion and chemical reaction contribute to the observed kinetics and that analogous macroporous polymers might offer improved efficiency.[3-5] A similar conclusion has been reached in related work reported by Molinari et al. for the triphase displacement by iodide on *n*-octyl bromide.[6]

$$n\text{-}C_{10}H_{21}OSO_2CH_3(org) + NaCl(aq) \xrightarrow[\text{catalyst}]{\text{solid phase}} n\text{-}C_{10}H_{21}Cl(org) + CH_3SO_3^-Na\ (aq) \quad (1)$$



functionalized microporous
polystyrene-1% divinylbenzene
1, percent ring substitution (prs) = 4; 200-400 mesh
2, prs = 17; 200-400 mesh
3, prs = 52; 200-400 mesh
4, prs = 52; 20-50 mesh

In the present study we have examined the efficacy of over 40 closely related phosphonium-based polystyrene copolymers as triphase catalysts for reaction 1, where resin porosity, cross-link density, and percent ring substitution have been systematically varied. This work has been carried out for the dual purpose of (1) establishing whether or not macroporous copolymers do, in fact, improve catalytic efficiency and (2) identifying useful empirical relationships between cross-link density, percent ring substitution, and resin activity.

Results and Discussion

Catalyst Synthesis. Three general classes of cross-linked polystyrene have been chosen for this investigation: (1) microporous, (2) macroporous (low surface area), and (3) macroporous (high surface area) resins. Scheme I summarizes the specific methods of synthesis used. Suspension copolymerization of styrene, divinylbenzene, and vinylbenzyl chloride (60/40 meta/para) in the absence of an organic solvent yields polystyrene in the microporous form. When an inert solvent is used as a diluent, cross-linked polystyrene is obtained in a macroporous state.[7] Since these polymerizations go to completion and since the reactivity ratios of styrene and vinylbenzyl chloride are 0.72 and 1.08, respectively, an approximately random distribution of the chloromethylene groups must be present throughout these beads.[8] By use of procedures described in the Experimental Section, macroporous forms of chloromethylated polystyrene were prepared, having cross-link densities of 2, 5, 10, and 20%; microporous copolymers were prepared by using 1, 2, 5, 10, or 20% divinylbenzene. All chloromethylated polymers were converted into triphase catalysts by quaternization with tri-*n*-butylphosphine. Synthetic macroporous resins required less stringent conditions to bring about complete quaternization than microporous analogues, reflecting greater accessibility to the pendant chloromethylene groups (see Experimental Section.)[9] Surface areas measured for all of the synthetic macroporous catalysts were very low (<1 $m^2\ g^{-1}$; BET, nitrogen adsorption). Scanning electron microscope (SEM) examination of the surface and the interior (fractured bead) of a synthetic macroporous catalyst (10% divinylbenzene, 45% ring substitution) revealed the presence of large pores having an average diameter of ca. 3 μm (Figures 1 and 2). While micrographs recorded for 20% cross-linked synthetic macroporous catalysts showed similar porosity, neither this nor the more common microsphere-agglomerate pore structure were discernable for resins having 2 and 5% divinylbenzene.[10,11] Our classification of the latter as macroporous polymers is based solely on their method of preparation. A second type of macroporous catalyst has been prepared by chloro-

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[1] Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446).

[2] For a review of triphase catalysis, see: Regen, S. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421.

[3] Regen, S. L.; Besse, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 4059.

[4] Kun, K. A.; Kunin, R. *J. Polym. Sci., Part A* **1968**, *16*, 2689. Kunin, R.; Meitzner, E.; Bortnick, N. *J. Am. Chem. Soc.* **1962**, *84*, 305.

[5] Reinicker, R. A.; Gates, B. C. *AIChE J.* **1974**, *20*, 933. Wesley, R. B.; Gates, B. C. *J. Catal.* **1974**, *34*, 288. Gates, B. C.; Rodriquez, W. *Ibid.* **1973**, *31*, 27.

[6] Molinari, H.; Montanari, F.; Quici, S.; Tundo, P. *J. Am. Chem. Soc.* **1979**, *101*, 3920.

[7] Barret, J. H.; Heights, C. U.S. Patent 3843566, 1974.

[8] Technical Data Bulletin on Vinylbenzyl Chloride, Dow Chemical Co., Midland, MI.

[9] In this paper we refer to all macroporous polymers which have been synthesized in our laboratories as *synthetic* polymers, to distinguish them from XAD-2 and XAD-4 derived catalysts.

[10] Kun, K. A.; Kunin, R. *J. Polym. Sci., Part C* **1967**, *16*, 1457.

[11] The SEM of 2 and 5% cross-linked synthetic macroporous catalysts showed a closer resemblance to analogous microporous-type polymers.

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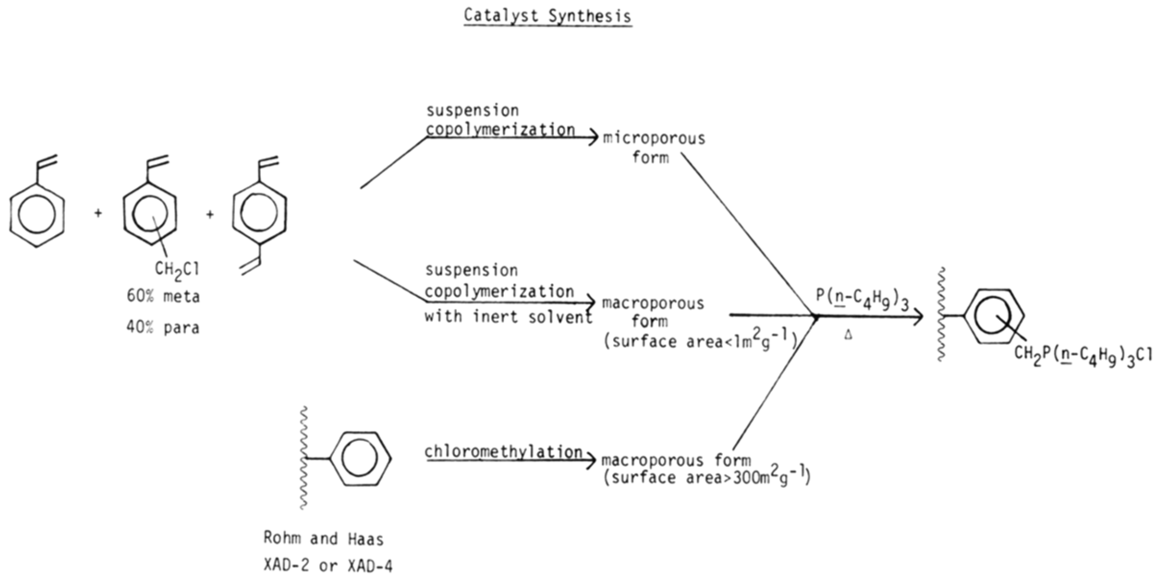
Scheme I



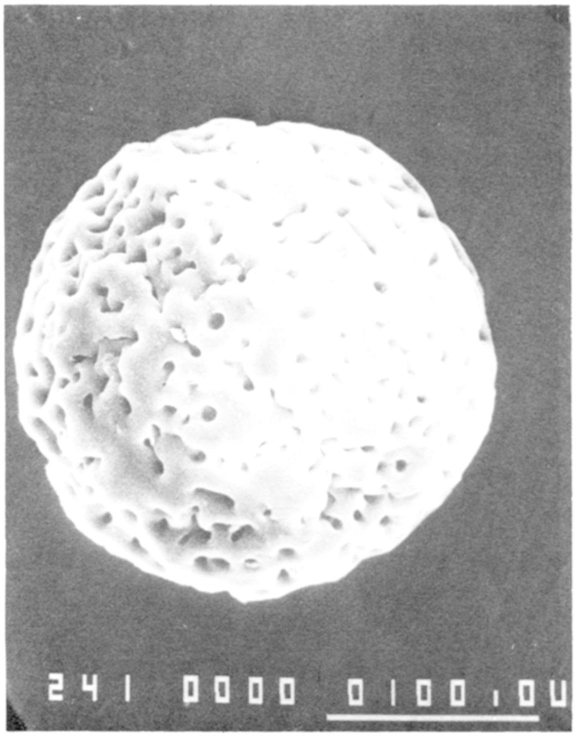


Figure 1. Electron micrograph of a synthetic macroporous catalyst (10% divinylbenzene; 45% ring substitution) showing the bead surface. Bar represents 100 μm.

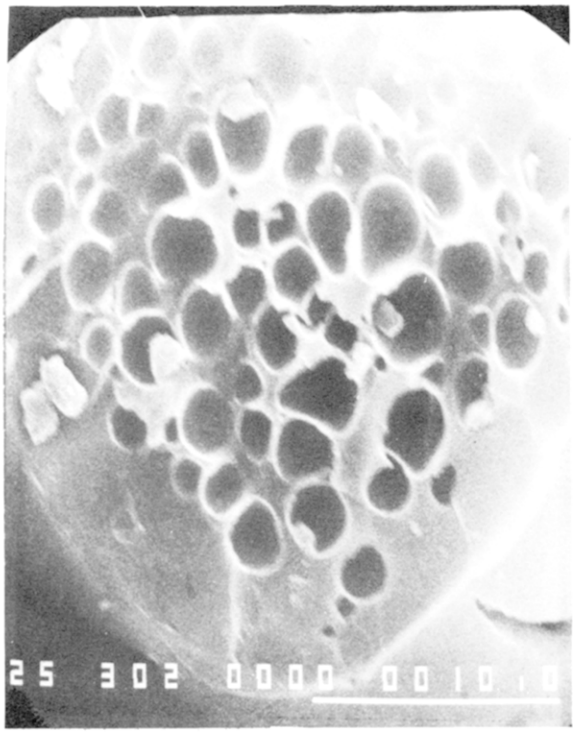


Figure 2. Electron micrograph of a synthetic macroporous catalyst (10% divinylbenzene; 45% ring substitution) showing the internal structure. Bar represents 10 μm.

methylating and quaternizing Rohm and Haas XAD-2 and XAD-4 resins. These commercial polymers are characterized by unusually high surface areas (330 and 725 m^2 g^{-1}, respectively), high cross-link densities (>50%), and small macropore diameters (90 and 40 Å, respectively). Because the chloromethylene groups are introduced after polymerization, their exact placement with regard to meta/para substitution and topography is poorly defined.

Kinetic Features. The experimental procedure used for carrying out and monitoring reaction 1 has been described in detail previously.[3] All systems reported in this work obeyed clean pseudo-first-order kinetics and the material balance and reproducibility of the observed rate constants, k_{obsd}, were good. The only product detected was 1-chlorodecane. In all experiments 0.010 g of resin was suspended at an aqueous–organic phase boundary having an approximate liquid–liquid interfacial area of 4.2 cm^2 (unstirred). All reactions were conducted as vigorously stirred (1500 rpm) processes.

Catalyst Efficiency. In order to put the activity of these triphase catalysts into perspective, we have compared them to a soluble catalyst ($C_6H_5CH_2P(n\text{-}C_4H_9)_3Cl$) used in a related phase-transfer-catalyzed process.[12] Because the percent of polymer-bound phosphonium sites involved in the catalysis is unknown, we are limited to an *operational* comparison between the triphase and phase-transfer

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(12) For general discussions of phase-transfer catalysis, see: Starks, C. M.; Liotta, C. "Phase-Transfer Catalysis"; Academic Press: New York, 1978; Weber, W. P.; Gokel, G. W. "Phase-Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977; Dehmlow, E. V. *Angew. Chem., Int. Ed. Eng.* **1977**, *16*, 493; Brandstrom, A. *Adv. Phys. Org. Chem.* **1977**, *15*, 267.

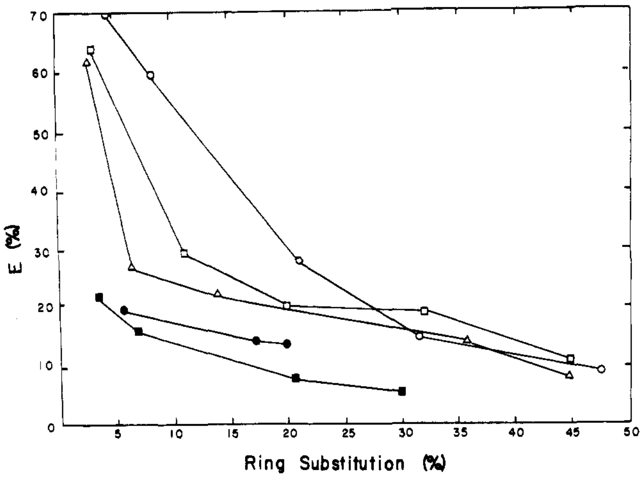

Figure 3. Plot of catalyst efficiency, E, as a function of percent ring substitution for 1% (○), 2% (□), 5% (△), 10% (●), and 20% (■) cross-linked microporous phosphonium-based polystyrene catalysts. All reactions were carried out at 1500 rpm.

systems. For this purpose, we now define an efficiency parameter, E, as shown in eq 2, where both the triphase

$$E = \frac{k_{\mathrm{obsd}}^{90\,^{\circ}\mathrm{C}}(\mathrm{TC})/\text{mol of resin-bound phosphonium groups}}{k_{\mathrm{obsd}}^{90\,^{\circ}\mathrm{C}}(\mathrm{PTC})/\text{mol of phosphonium salt}} \times 100 \quad (2)$$

catalysis (TC) and phase-transfer catalysis (PTC) reactions are carried out by using the same initial concentration of reactants and volumes of organic and aqueous phases.

Figures 3 and 4 summarize catalyst efficiencies for all of the polymers tested. From these data it is clear that (1) increased cross-link density reduces catalyst efficiency for both macroporous and microporous polymers, (2) reduced percent ring substitution leads to higher efficiency in microporous and synthetic macroporous catalysts, but lower efficiency for XAD-2 and XAD-4 derived catalysts, and (3) macroporous polymers do not show significantly greater activity than comparable microporous analogues. The fact that high efficiency requires a low cross-link density is not surprising. This is a likely consequence of matrix diffusion contributing to the observed kinetics (matrix diffusion becomes less important as the cross-link density decreases). Similarly, the higher efficiency associated with low percent ring substitution in microporous and synthetic macroporous polymers can be accounted for in terms of reduced steric congestion throughout the lattice resulting in an increased rate of matrix diffusion. What is surprising, however, is the fact that XAD-2 and XAD-4 based catalysts, having high surface areas, exhibit very low efficiencies which increase as the percent ring substitution increases.

From a synthetic standpoint, these results demonstrate that high triphase catalytic efficiency is possible by using microporous copolymers. Moreover, macroporous analogues do not appear to offer any kinetic advantage. They also show that optimum use of the catalytic site is made when low cross-link densities and low percent ring substitutions are employed. While more effort will be required to sort out the physical and chemical basis of triphase catalysis, these results should prove to be of considerable value in the design of new triphase catalysts for organic synthesis.

Expermental Section

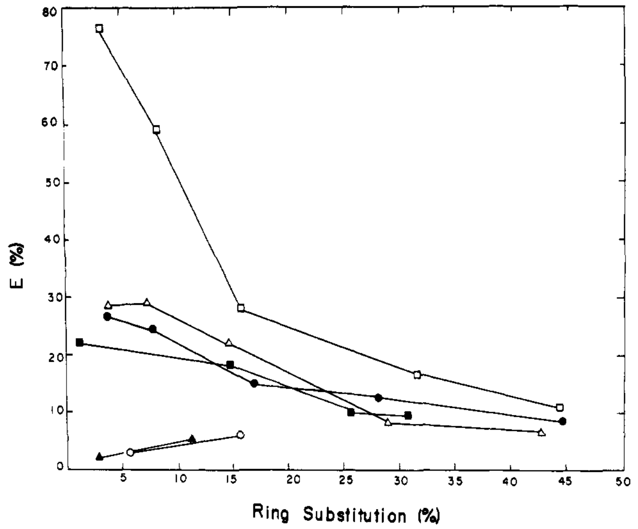

Figure 4. Plot of catalyst efficiency, E, as a function of percent ring substitution for 2% (□), 5% (△), 10% (●), 20% (■), XAD-2 (▲), and XAD-4 (○) cross-linked macroporous phosphonium-based polystyrene catalysts. All reactions were carried out at 1500 rpm.

General Methods. Unless stated otherwise, all reagents were obtained commercially and used without further purification. *n*-Decyl methanesulfonate was prepared by using established procedures.[13] Tri-*n*-butylphosphine (Aldrich Chemical Co.) was distilled under nitrogen prior to use. Toluene was purified by distillation from sodium benzophenone ketyl under nitrogen. Pyridine (Aldrich Chemical Co., gold label) was used as obtained; 4-methyl-2-pentanol was distilled over CaH_2. Deionized water was distilled from $KMnO_4/Ba(OH)_2$. Styrene (Aldrich Chemical Co.), divinylbenzene (Polysciences, Inc., 60% active), and vinylbenzyl chloride (Dow Chemical Co., 60/40 meta/para) were distilled under reduced pressure. Gelatin (Polysciences, Inc.) and polyvinylpyrrolidone (Aldrich Chemical Co.) were used as obtained. Amberlite XAD-2 and XAD-4 macroporous resins were a gift from the Rohm and Haas Company. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830 A flame-ionization instrument (2 ft × 0.125 in. UCW-982 on Chromosorb W column at 160 °C). Stirring speeds were determined with the use of a Cole–Parmer strobette stroboscope tachometer. The temperature of the oil bath used for kinetic experiments was controlled (±0.5 °C) with the aid of a THERM-O-WATCH electronic controller Model L6-1000 (I^2R Co., Cheltenhan, PA.) attached to a thermometer. Chloride ion analysis was determined by a modified Volhard titration using established procedures.[14]

Polymerization Reactions. General procedures for the preparation of cross-linked chloromethylated polymers are described below.

A. Macroporous Copolymers. Procedures similar to that described for the preparation of 10% cross-linked, 20% ring-substituted chloromethylated polystyrene in a macroporous form were followed for all of the macroporous copolymers synthesized. To a 300-mL wide-mouthed reaction flask equipped with a detachable lid and a Teflon-coated magnetic stirring bar (7/8 × 5/16 in. octagonal bar with pivot ring) were added 115 mL of water containing 0.11 g of polyvinylpyrrolidone, 0.8 g of 50% aqueous sodium hydroxide, 0.66 g of boric acid, and 0.25 g of gelatin dissolved in 2 mL of water. After the solution was stirred vigorously under nitrogen for 30 min at ambient temperature, a mixture of vinylbenzyl chloride (2.75 g, 18 mmol), styrene (7.5 g, 72 mmol), divinylbenzene (1.3 g, 10 mmol), and 6.2 g of 4-methyl-2-pentanol was added. Benzoyl peroxide (0.2 g) was then added and the flask immersed in an oil bath maintained at 80 °C. After the mixture was stirred for 10 h under a nitrogen atmosphere, the inert solvent was removed by steam distillation. The resin was filtered, extracted (Soxhlet) with toluene for 24 h, dried under reduced pressure [24 h, 100 °C (0.05 mm)], and screened with appropriate sieves, yielding 10.90 g of polymer. A broad distribution of spherical beads was obtained; only 100–200

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[13] Williams, H. R.; Mosher, H. S. *J. Am. Chem. Soc.* **1954**, *76*, 2984.

[14] Stewart, J. M.; Young, J. D. "Solid Phase Peptide Synthesis"; W. H. Freeman: San Francisco, CA, 1969; p 55.

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mesh were used for all kinetic work. Anal. Calcd for 20% ring substitution: Cl, 1.57 mmol/g. Found: Cl, 1.33 mmol/g.

B. Microporous Copolymers. Procedures used for the preparation of all microporous copolymers were similar to that described for the macroporous analogues, except that 4-methyl-2-pentanol was omitted.

Chloromethylation of XAD-2 and XAD-4 Resins. Procedures used for chloromethylating Rohm and Haas macroreticular resins were similar to those described for microporous polymers.[15] Prior to chloromethylation, these macroporous resins were extensively washed by using procedures described in the literature.[16]

Quaternization of Chloromethylated Copolymers with Tri-*n*-butylphosphine. Procedures similar to that used for the quaternization of macroporous chloromethylated polystyrene (10% divinylbenzene, 20% ring substitution) were followed for all macroporous copolymers. A 50-mL culture tube (Corning no. 9826, 25 × 150 mm) equipped with a Teflon-lined screw cap was charged with 1.0 g of macroporous copolymer (1.33 mmol of CH_2Cl) plus 10 mL of toluene. After the contents of the tube was purged with nitrogen for 5 min, tri-*n*-butylphosphine (2.69 g, 13.0 mmol) was added, and the tube was sealed, placed in an oil bath (90 °C) for 24 h, and then cooled to room temperature. The resin was filtered, extracted (Soxhlet) with toluene for 6 h, and dried under reduced pressure [6 h, 100 °C (0.05 mm)], yielding a polymer having a chloride ion content of 1.1 mmol/g (95% quaternization). Quaternization of the microporous polymers was carried out at 110 °C for 72 h (1 and 2% divinylbenzene), 120 h (5% divinylbenzene), or 168 h (10 and 20% divinylbenzene). Except for the 20% cross-linked microporous resins, where only 35–50% of the chloromethylene groups underwent displacement, the degree of quaternization was generally high (>80%). Chloromethylated XAD-2 and XAD-4 polymers required reaction times of 120 h at 90 °C to obtain fully quaternized resins.

Kinetic Methods. All kinetic experiments were performed at 90 °C using 50-mL culture tubes as reaction vessels and procedures identical with those previously described.[3] Stirring speeds of 1500 rpm were used in all cases.

Acknowledgment. We are grateful to Professor Keith Hall (University of Wisconsin, Milwaukee) for providing us with the use of his BET surface area apparatus and to the National Science Foundation for the purchase of a JEOL JSM-35 scanning electron microscope. We are also grateful to Mr. K. Ramasami and Mr. L. Wang for providing valuable technical assistance.

Registry No. Ethenylbenzene 1-(chloromethyl)-3-ethenylbenzene, 1-(chloromethyl)-4-ethenylbenzene 1,4-bisethenylbenzene copolymer tributylphosphine salt, 77080-45-6.

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(15) Feinberg, R. S.; Merrifield, R. B. *Tetrahedron* **1974**, 3209.
(16) Farrall, M. J.; Frichet, J. M. J. *J. Org. Chem.* **1976**, *41*, 3877.

Phosphite-Mediated in Situ Carboxyvinylation: A New General Acrylic Acid Synthesis[†]

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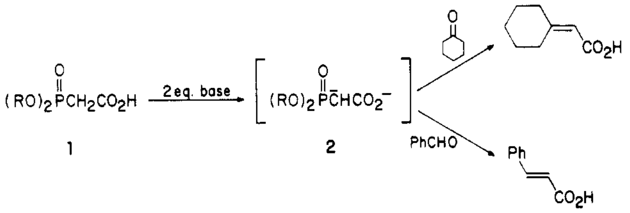
Sequential treatment of a 2-halo carboxylic acid with a dialkyl phosphite and an aldehyde or ketone in the presence of 3 equiv of sodium hydride in glyme constitutes a new general acrylic acid synthesis superior to conventional methods. An alkoxide-in-alcohol variant may be used with bromo- or chloroacetic acid and aryl aldehydes to produce cinnamic acids conveniently. The scope and other features of the synthesis are discussed.

The α,β-unsaturated carboxylic acid[1] moiety is a widely occuring structural subunit of many natural products and a versatile synthetic intermediate. In addition, many acrylic acids are of interest in their own right. Classical acrylic acid syntheses possess various shortcomings: the Perkin reaction succeeds only with aromatic aldehydes,[2] and the (Doebner) Knoevenagel reaction[3] suffers from unavailability of the requisite malonic acids, severe reaction conditions, long reaction times, and rapidly decreasing yields as the alkyl group of alkylmalonic acids becomes larger.[4]

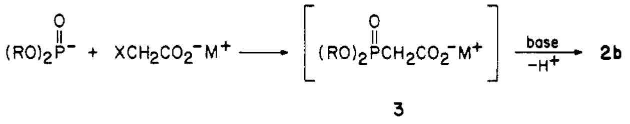
There are numerous acrylic ester syntheses, but these require an extra hydrolysis step to obtain the acrylic acid, and hydrolysis of α,β-unsaturated carboxylic esters can result in low yields.[5] Use of the Horner–Wadsworth–Emmons phosphonoacetate reagent, the most convenient route to acrylic esters,[6] is little used for the synthesis of α-substituted acrylates;[7] it necessitates preparation of the individual α-substituted phosphonoacetate reagents, and the product esters can isomerize to β,γ-unsaturated esters under the reaction conditions.[8]

Scheme I[a]



[a] a, R = $PhCH_2$;[9] b, R = C_2H_5.[10,11]

Scheme II



Along with Koppel and Kinnick[9] and Coutrot et al.,[10] we have carried out Horner–Wadsworth–Emmons-type

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[†] Contribution No. 2871 from the Central Research and Development Department, E. I. du Pont de Nemours and Co.

(1) For convenience, α,β-unsaturated carboxylic acids will hereafter be referred to generically as acrylic acids in this paper.
(2) Johnson, J. R. *Org. React.* **1942**, *1*, 210.
(3) Jones, G. *Org. React.* **1967**, *15*, 203.

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