JOC Notes

Peroxovanadium-Catalyzed Oxidative Esterification of Aldehydes†

Rangam Gopinath, Balaka Barkakaty, Bandana Talukdar, and Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology, Guwahati-781 039, India

patel@iitg.ernet.in

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Abstract: The peroxovanadium species generated from V_2O_5 and hydrogen peroxide, which is liberated from peroxy salts such as sodium perborate (SPB) or sodium percarbonate (SPC), transform aldehydes directly into esters in an alcoholic medium. Monoesters of diols have been achieved directly in one pot from aldehydes. High catalytic turnover number combined with inexpensive, easily available reagents and innocuous side products from the reaction make it a suitable alternative for the synthesis of esters from aldehydes.

The direct transformation of aldehydes to esters under mild conditions is a useful transformation in organic synthesis.[1] It is often required to transform aldehydes directly into esters during various stages in the synthesis of different natural products.[2] A comprehensive list of reagents for one-step transformation of an aldehyde in the presence of an alcohol into an ester has been compiled by Larock.[1a] Recently, such transformations have been achieved with peroxo species generated by the reaction of hydrogen peroxide with vanadium(V)[3,4] and with methyltrioxorhenium(VII) (MTO) in the presence of cocatalysts such as chloride or bromide ions.[5] Although several methods have been reported for the direct preparation of aldehydes to esters, those methods usually require a large amount of reagents, extremes of temperature, lengthy reaction times, inert atmosphere, photochemical conditions, poisonous and polluting reagents, mediators or cocatalyst, or hydrogen acceptors. Some of these reagents are also unsatisfactory for the specific oxidation of aldehydes containing deactivated, hindered, and double-bond-containing substrates, resulting in overoxidation and undesirable products, proceeding nonselectively, and giving poor to mediocre yields.

In today's context, one of the challenging issues for chemists is to pursue green chemical transformations.[6] Because of the amount of toxic wastes and byproducts arising from chemical processes and due to environmental protection laws, chemists have been compelled to develop cost-effective and environmentally friendly catalytic routes that minimize the hazardous waste. Our persistent interest in developing new selective oxidation procedures[3,4,7] has prompted us to use peroxy salts such as sodium perborate (SPB) and sodium percarbonate (SPC), which are inexpensive, readily available, safe, easy to handle, and convenient sources of active hydrogen peroxide especially for large-scale reactions.[8] Concentrated hydrogen peroxide is not readily available and is, furthermore, more risky to handle. Consequently, the ability of peroxy salts to release hydrogen peroxide in an aqueous or in an organic medium has made them useful latent reagents in organic synthesis.[8]

As a test substrate for the oxidative transformation of aldehydes to esters, 4-methoxybenzaldehyde **10** was chosen to optimize the reaction conditions. The addition sequence of different components and the ratios of substrate, catalyst, peroxy salt (SPB/SPC), and mineral acid such as 70% $HClO_4$ were varied in order to achieve higher product conversion. Both for SPB and SPC the optimum stoichiometry was 3.5 equiv per equivalent of aldehyde, although H_2O_2 contents in both the peroxy salts are different, 1 per molecule for the former and 1.5 per molecule for the latter. Both SPB and SPC have often been employed for the same purpose; unfortunately, the corresponding reports are separate and comparisons are lacking, but wherever available, SPB is used in higher proportions compared to SPC.[8d] A higher concentration of acid was also required for the efficient release of hydrogen peroxide from SPC because of SPC is slightly more alkaline compared to SPB.[9] The oxidation was carried out by adding 70% $HClO_4$ over a period of time to a mixture containing aldehyde, catalyst (V_2O_5), peroxy salt, and alcohol. During this process, H_2O_2 is slowly released from the peroxy salts, thereby forming the active oxidizing peroxovanadium species for the oxidative transformation. The peroxy salts help maintain the catalytic activity owing to their lower water content. The pH of the medium progressively decreased from ca. 10.68 at the beginning of the reaction to ca. 0.10 after the complete addition of the mineral acid and remained almost constant for SPB-mediated reactions, and the change was

† Dedicated to Prof. Dr. Fritz Eckstein on the occasion of his 70th birthday.

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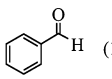
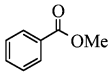
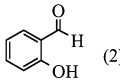
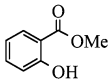
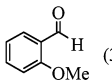
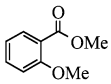
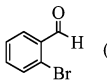
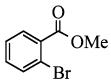
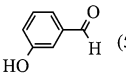
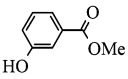
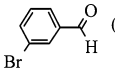
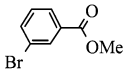
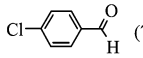
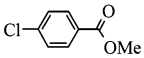
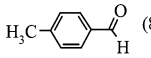
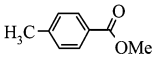
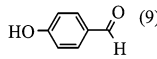
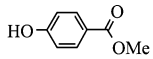
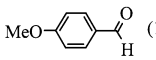
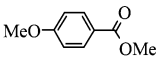
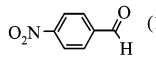
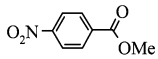
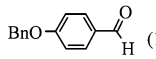
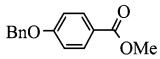
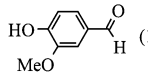
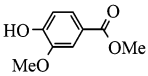
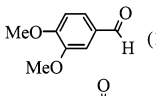
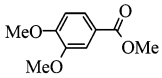
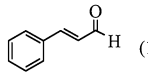
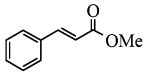
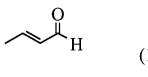
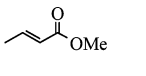
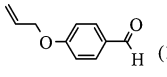
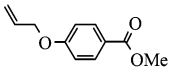
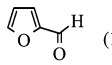
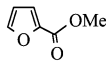
TABLE 1. Oxidative Esterification[a] of Aldehydes to Corresponding Methyl Esters

Substrate	Product	time/h	(yield %)[b]
		SPB	SPC
 (1)	 (1a)	0.3 (97)	0.3 (98)
 (2)	 (2a)	1.5 (94)	1.0 (96)
 (3)	 (3a)	2.0 (96)	1.3 (96)
 (4)	 (4a)	2.0 (96)	1.3 (96)
 (5)	 (5a)	1.3 (95[c,d])	1.3 (96[c,d])
 (6)	 (6a)	0.75 (98)	1.3 (98)
 (7)	 (7a)	2.0 (97)	1.0 (97)
 (8)	 (8a)	0.75 (98)	0.75 (98)
 (9)	 (9a)	2.0 (95)	1.0 (98)
 (10)	 (10a)	1.3 (90)	0.3 (92)
 (11)	 (11a)	1.0 (90[c,d])	1.0 (95[c,d])
 (12)	 (12a)	3.3 (85)	1.0 (95)
 (13)	 (13a)	2.3 (90)	2.0 (94)
 (14)	 (14a)	3.3 (80)	0.45 (97)
 (15)	 (15a)	3.3 (80[c,e])	0.3 (97[c,e])
 (16)	 (16a)	1.0 (80[c,e])	1.0 (90[c,e])
 (17)	 (17a)	3.5 (45)	3.0 (50)
 (18)	 (18a)	1.0 (85)	0.35 (95)

[a] Reactions were monitored by TLC and GC. [b] Isolated yield. [c] The reaction was performed by method B. [d] The reaction was performed at room temperature. [e] The reaction was performed at reflux. All the products are reported in the literature and confirmed by comparison with IR and ^{1}H NMR of the authentic sample.

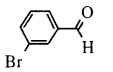
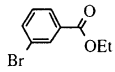
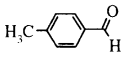
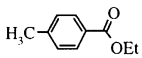
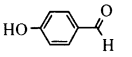
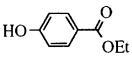
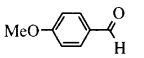
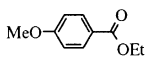
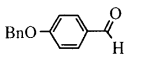
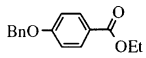
from ca. 12.7 to ca. 1.0 when SPC was used as the oxidant. In either case, no oxidation was observed without V_2O_5 or combination of V_2O_5 and peroxy salts, unless acid was added to the medium. Other mineral acids such as H_2SO_4, HCl, and HBr worked equally well. However, it is surprising to note that the reaction failed when acetic acid was used instead of perchloric acid. This observation is in contrast to the MTO-catalyzed reactions where only acetic acid is used to activate the catalyst.[5] This could be because the activation of V_2O_5 requires low pH and sodium borate/acetate formed by the reaction of SPB and SPC with acetic acid might buffer the medium to a relatively higher pH. In acidic solution ($[H^+] > 0.01$ M), vanadium(V) exists as VO_2^+. Addition of hydrogen peroxide to VO_2^+ can give the red oxoperoxo $VO(O_2)^+$ and yellow diperoxo $VO(O_2)_2^-$ species. These peroxo species are stable under acidic medium and unstable in neutral and basic medium.[10a]

To arrive at an optimum stoichiometry, 4-methoxybenzaldehyde **10** (1 mmol) was allowed to react with 1, 2, and 3 equiv of SPB in the presence of V_2O_5 (0.04 mmol) and proportionate amount of perchloric acid, the yield of ester obtained was 32%, 64%, and 96%, respectively, thus proving the 1:3 ratio of the substrate and hydrogen peroxide as proposed earlier.[3] UV spectral analysis confirmed the intermediacy of the peroxovanadium(V) species with the appearance of the peak at $\lambda = 430$ nm. In our earlier paper, we have proposed a two-electron mechanism involving a hydride ion transfer in one of the steps. To ascertain the importance of the cleavage of the aldehydic C−H bond in the rate-determining step, the oxidation of the [^{2}H]benzaldehyde (PhCDO) was studied. The result showed no significant kinetic isotope effect ($K_H/K_D \approx 1$ at 273 K) indicating a different rate-determining step. The oxidation of benzaldehyde under the reaction conditions failed to induce the polymerization of methyl acrylate. Further, the addition of radical scavengers such as benzophenone has no effect on the reaction rate, ruling out the possibility of a free-radical mechanism. Thus, this reaction is expected to go via a two-electron mechanism as proposed earlier.[3] A catalytic turnover number of >500 was determined for both the methods.

Under these conditions, a wide range of aldehydes containing activated, deactivated, conjugated, and hindered aldehydes can all be oxidized to the corresponding methyl esters in good to excellent yields. As can be seen from Table 1, most of the substrates give excellent yields of the corresponding methyl esters. However, the deactivated substrate 4-nitrobenzaldehyde **11** gave a poor yield (35%) of the corresponding ester (**11a**), with the rest being the corresponding carboxylic acid. As an alternative approach, we decided to add SPB or SPC over a period of time to an acidic medium of aldehyde in methanol containing a catalytic amount of V_2O_5 at room temperature, which led to a better conversion as shown in Table 1. This is because of the controlled release of hydrogen peroxide and also in acidic medium the redox potential of the vanadium(V)−vanadium(IV) couple increases with acidity in the region from pH 1.5 to 2 M acid, thereby acting as a stronger oxidant for the deactivated substrate **11**.[10d] It may be mentioned here that esterification of a deactivated substrate such as 4-nitrobenzaldehyde **11** is

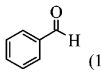
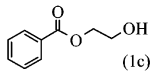
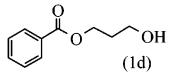
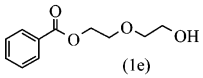
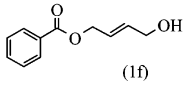
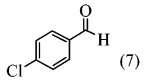
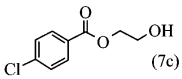
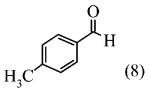
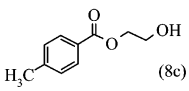
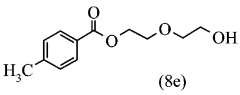
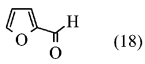
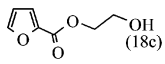
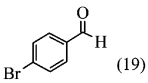
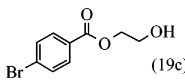
(10) (a) Butler, A.; Clague, M. J.; Meister, G. E. *Chem. Rev.* **1994**, *94*, 625−638. (b) Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1988**, *53*, 1165−1169. (c) Hubert, M.; Lucien, S.; Eric, D.; Michele, P.; Jean, F.; Raymond, W. *J. Am. Chem. Soc.* **1983**, *105*, 3101−3110. (d) Freeman, F. In *Organic Synthesis by Oxidation with Metal Compounds*; Mijs W. J., De Jonge, C. H. R. I., Eds.; Plenum Press: New York, 1986; Chapter 1, p 1.

TABLE 2. Oxidative Esterification[a] of Aldehydes to Corresponding Ethyl Esters

Substrate	Product	SPC	
		time / h	yield (%)[b]
 (1)	 (1b)	1.0	95
 (2)	 (2b)	4.5	89
 (3)	 (3b)	5.0	90
 (6)	 (6b)	3.0	92
 (8)	 (8b)	1.5	93
 (9)	 (9b)	3.0	95
 (10)	 (10b)	3.0	96
 (12)	 (12b)	5.5	88
 (18)	 (18b)	2.5	93

[a] Reactions were monitored by TLC and GC. [b] Isolated yield. All the products are reported in the literature and confirmed by comparison with IR and ^{1}H NMR of the authentic sample.

TABLE 3. Oxidative Monoesterification[a] of Diols with V_2O_5–H_2O_2

Substrate	Product[b]	SPC	
		time/h	yield (%)
 (1)	 (1c)	2.0	78
	 (1d)	2.0	75
	 (1e)	3.0	28
	 (1f)	2.0	75
 (7)	 (7c)	2.2	75
 (8)	 (8c)	1.4	82
	 (8e)	3.0	25
 (18)	 (18c)	3.0	72
 (19)	 (19c)	1.0	89

[a] Reactions were monitored by TLC and GC. [b] Isolated yield.

usually difficult and has been achieved under reflux conditions.[3] Slower reaction rates for the conjugated systems can be due to an unfavorable equilibrium in hemiacetal formation, due to disruption of conjugation. The compatibility of the methodology was demonstrated by the regioselective esterification of unsaturated aldehydes in good yield as shown in the case of aldehydes **15**, **16**, and **17**. Importantly, no other side products, viz. epoxide, were observed.

Other alcohols could be substituted for methanol to provide corresponding esters. With this end in view, the reaction was performed in the presence of ethyl alcohol using SPC as the source of hydrogen peroxide under identical conditions as described for methyl esters. Thus, various ethyl esters can be prepared efficiently and in good yields by the present methodology as shown in Table 2.

The success of this methodology was further demonstrated by oxidative esterification of benzaldehyde **1** with other alcohols such as 1-propanol and 1-butanol, which gave 88% and 83% of the corresponding esters[11] after 1 h. However, esters of branched alcohols such as 2-propanol and *tert*-butyl alcohol could not be obtained, which could be due to an unfavorable equilibrium in hemiacetal formation. Formation of benzyl ester was also not satisfactory by this methodology and gave a poor yield of benzyl benzoate (15%, 2 h).[11]

The novel aspect of the present methodology was applied to achieve the monoesterification of diols in a one-pot process since glycol monoesters have widespread applications as intermediates for sex pheromone of lepidoptera[12] and cross-linking agents for polyesters or as fungicides.[13] The major drawback in the preparation of these compounds from the diols is the simultaneous formation of diesters along with the monoesters making the separation procedure a tedious one.[14] Alternatively, they have been prepared by the oxidation of the cyclic acetals using a variety of oxidizing agents.[1a,15] These methods are not only two-step process involving acetalization followed by oxidation of cyclic acetals to hydroxy esters but also suffer from some disadvantages such as easy handling, longer reaction times, higher amounts of reagents/catalyst, etc. Interestingly, by applying this method, monoesters of diols can be directly obtained from aldehydes in good yields as reported in Table 3 using 1,2-ethanediol, 1,3-propanediol, di(ethylene glycol), and even diols containing a double bond. Thus, reaction of benzal-

(11) *The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra*; Aldrich Chemical Company, Inc.: Milwaukee, 1993; Ed. I.

(12) (a) Leznoff, C. C. *Acc. Chem. Res.* **1978**, *11*, 327−333. (b) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845. (c) Rossi, R. *Synthesis* **1977**, 817.

(13) Hosokawa, T.; Imada, Y.; Murahashi, S.-I. *J. Chem. Soc., Chem. Commun.* **1983**, 1245−1246.

(14) Babler, J. H.; Coghlan, M. J. *Tetrahedron Lett.* **1979**, 1971−1974.

(15) (a) Stork, G.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1987**, *109*, 1564−1565. (b) Sato, K.-I.; Igarashi, T.; Yanagisawa, Y.; Kawaichi; Hashitoma; Yoshimura, J. *Chem. Lett.* **1987**, *28*, 2835−2836. (c) Sviridov, A. F.; Ermolenko, M. S.; Yashunsky, D. V.; Borodkin, V. S.; Kochetkov, N. K. *Tetrahedron Lett.* **1987**, *28*, 3835−3838 and 3839−3842. (d) Hanessian, S.; Staub, et A. P. A. *Tetrahedron Lett.* **1973**, 3551−3554. (e) Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. *Synlett* **1999**, 777−779.

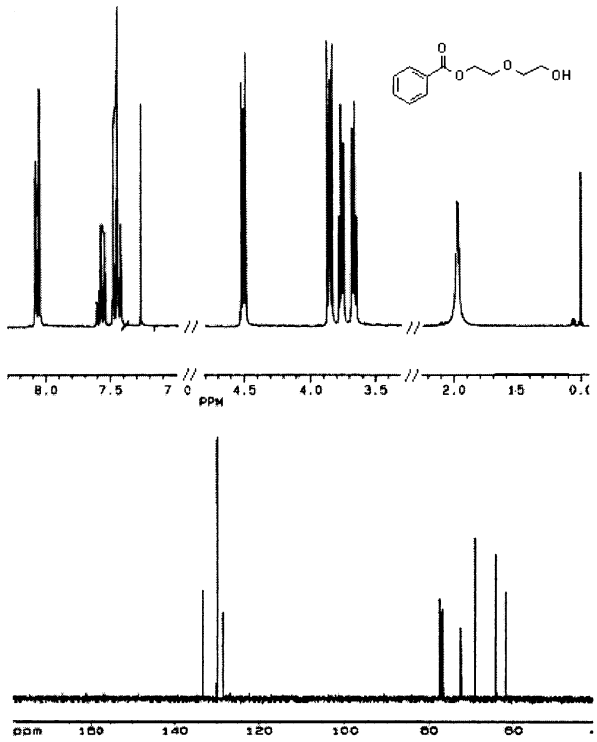


FIGURE 1. ^{1}H and ^{13}C NMR spectra of di(ethylene glycol) monobenzoate **1e**.

dehyde with di(ethylene glycol) resulted di(ethylene glycol) monobenzoate (28%, 3 h). The ^{1}H and ^{13}C NMR spectra of di(ethylene glycol) monobenzoate **1e** are shown in Figure 1. Formation of diesters was not observed by this method for any of the diols. To the best of our knowledge, this is the first successful monoesterification of diols in one pot directly from diols and aldehydes.

In conclusion, the method represents a simple, rapid way to oxidize a variety of aldehydes to a wide range of esters, including an efficient preparation of monoesters from diols. The simplicity and convenience of this oxidation procedure are appealing, the fact that the reaction proceeds in high yields, and in particular, its use in aqueous media hold promise as the basis for this process, which is environmentally safe, and economical. The high catalytic turnover number combined with inexpensive, easily available reagents and innocuous side products in the reaction makes it a suitable practical alternative.

Experimental Section

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60−120 mesh size) was used for column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). Gas liquid chromatography was performed using a crossed-linked methyl silicon gum capillary column (30 m × 0.32 mm × 0.25 μm) fitted with FID. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H (300 and 400 MHz) or $CDCl_3$ solvent as the internal standard for ^{13}C (75 and 100 MHz). The following esters derived from parent aldehydes have been reported in the literature: methyl esters[3,11] **1a**−**16a**, and **18a**; ethyl esters[11] **1b**−**3b**, **6b**, **8b**−**10b**, and **18b**; glycol monoesters[16] **1c**, **7c**, **8c**, and **18c**.

General Procedure for Preparation of Esters. Method A. To an ice-cooled and stirred solution of aldehyde (5 mmol) in methanol (10 mL) were added vanadium pentoxide (0.2 mmol) and sodium perborate (SPB) or sodium percarbonate (SPC) (17.5 mmol). To this heterogeneous mixture was added 70% perchloric acid (21.5 mmol for SPB and 43 mmol for SPC) over a period of 1 h, and the progress of the reaction was monitored by TLC and GC. After completion of the reaction, the reaction mixture was concentrated in vacuo and the residue was redissolved in ethyl acetate (20 mL). The organic layer was first washed with 5% sodium bicarbonate solution (2 × 5 mL) (except in the case of phenolic benzaldehydes) and then with water (2 × 5 mL), dried over anhydrous sodium sulfate, and concentrated. Further purification was achieved by vacuum distillation or by passing through a short column of silica gel, and products were identified by comparison of their NMR, IR, GC, and GC co-injection with authentic samples prepared by known methods.

Method B. To an ice-cooled and stirred solution of aldehyde (5 mmol) in methanol (10 mL) were added vanadium pentoxide (0.2 mmol) and 70% perchloric acid (21.5 mmol for SPB and 43 mmol for SPC). To this heterogeneous mixture was added sodium perborate (SPB) or sodium percarbonate (SPC) (17.5 mmol) over a period of 1 h, and the progress of the reaction was monitored by TLC and GC. After completion of the reaction, further workup and purification were done as in method A.

4-Allyloxybenzoic acid methyl ester (17a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3H), 4.58 (m, 2H), 5.39 (m, 2H), 6.10 (m, 1H), 6.93 (d, 2H, J = 8.94 Hz), 7.98 (d, 2H, J = 8.94 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 162.3, 132.6, 131.5, 122.7, 118.0, 114.3, 68.8, 51.8.

4-Benzyloxybenzoic acid ethyl ester (12b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, 3H), 4.33 (q, 2H), 5.11 (s, 2H), 6.96 (d, 2H, J = 14.4 Hz), 7.31−7.53 (m, 5H), 7.99 (d, 2H, J = 14.8 Hz).

4-Bromobenzoic acid 2-hydroxyethyl ester (19c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.80 (brs, 1H), 3.94 (t, 2H), 4.44 (t, 2H), 7.56 (d, 2H, J = 8.49 Hz), 7.90 (d, 2H, J = 8.49 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 131.6, 131.1, 128.6, 128.2, 66.6, 60.9.

Benzoic acid 3-hydroxypropyl ester (1d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (m, 2H), 2.40 (brs, 1H), 3.78 (t, 2H), 4.50 (t, 2H), 7.40−7.60 (m, 3H), 8.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 133.0, 130.0, 129.6, 128.4, 61.8, 59.2, 31.9.

Benzoic acid 2-(2-hydroxyethoxy)ethyl ester/di(ethylene glycol) monobenzoate (1e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (brs, 1H), 3.66 (m, 2H), 3.75 (m, 2H), 3.86 (m, 2H), 4.53 (m, 2H), 7.40−7.62 (m, 3H), 8.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1, 130.0, 129.7, 128.4, 72.48, 69.28, 64.05, 61.79.

4-Methylbenzoic acid 2-(2-hydroxyethoxy)ethyl ester (8e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (brs, 1H), 2.41 (s, 3H), 3.66 (m, 2H), 3.76 (m, 2H), 3.84 (m, 2H), 4.48 (m, 2H), 7.24 (d, 2H, J = 8.05 Hz), 7.94 (d, 2H, J = 8.14 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 143.7, 129.7, 129.1, 127.3, 72.4, 69.3, 63.8, 61.7, 21.6.

Benzoic acid 4-hydroxybut-2-enyl ester (1f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.1 (brs, 1H), 4.33 (d, 2H, J = 6.52 Hz), 4.93 (d, 2H, J = 6.91 Hz), 5.74 (m, 1H), 5.89 (m, 1H), 7.30−7.60 (m, 3H), 8.08 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 133.4, 133.0, 130.0, 129.5, 128.3, 125.5, 60.6, 58.3.

Acknowledgment. B.K.P. acknowledges the support of this research from DST New Delhi SP/S1/G-28/98 and CSIR 01(1688)/00/EMR-II, and R.G. acknowledges the financial support to the Institute. Thanks are due to RSIC, Lucknow; IACS, Kolkata; IICT, Hyderabad; and IIT Kanpur for providing NMR spectra. We are thankful to all reviewers for their valuable comments and suggestions.

Supporting Information Available: NMR spectra for the following compounds: methyl ester of **17a**, monoesters of diols **1f**, and di(ethylene glycol) monoester of **8e**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0266902

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