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Efficient Catalytic Synthesis of primary Carbamates using Preyssler heteropolyacid catalyst, $H_{14}[NaP_5W_{30}O_{110}]$ under solvent-free and in Green conditions

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Abstract

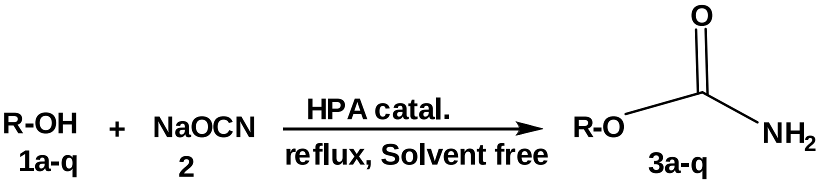
We wish to report synthesis carbamates using Preyssler heteropolyacid, in absence of solvent and at room temperature, in green conditions.This synthesis was in mild conditions, ecofrienly and environmentally friendly, clean and with a easy work-up.

Key Words: Heteropolyacid, catalyst, Preyssler, Solvent-free, carbamates, isocyanic acid

Heteropolyacids (HPA) have witnessed rapid growth in the last decade as solid acid catalyst. Polyoxometalates have been chosen as catalyst because of their easy availability and extreme stability in solution as well as in solid state. HPAs have several advantages that make them economically and environmentally attractive. They are good acid catalysts in homogeneous medium. They catalyze a wide variety of reactions in homogeneous phase offering strong option for efficient and cleaner processing compared to conventional mineral acids [1]. Until now, most of the research concerning catalytic properties of HPAs has been carried out using, Keggin structure and its derivatives as defect, mixed addenda, supported, etc. In the recent years, the interest in other HPAs, has been growing in the literature. As a part of a research project to develop environmentally friendly catalysts, we have recently applied the Preyssler HPA catalyst to various reactions [2]. However, the capability of this catalyst still has been largely overlooked [3]. In our opinion, advantages such as: high hydrolytic stability (pH 0–12), which demonstrates its functionality over a wide range of pH, high thermal stability and having a large number of acidic protons (14) along with exclusive structure for Preyssler's anion are outstanding and make it a good candidate for further studying. This polyanion consists of a cyclic assembly of five PW_6O_{22} units; each derived from the Keggin anion, $[PW_{12}O_{40}]^{3-}$, by the removal of two sets of three corner shared WO_6 octahedra [4]. In this paper we present a liquid phase alkylation of phenol with 1-octene over Preyssler heteropolyacid catalyst, $H_{14}[NaP_5W_{30}O_{110}]$, and compare the catalytic performance of this catalyst with other heteropolyacids such as $H_5[PMo_{10}V_2O_{40}]$, $H_6[PMo_9V_3O_{40}]$ and Wells–Dawson, $H_6[P_2W_{18}O_{62}]$. The influence of process variables such as reactant molar ratio, reaction time and catalyst type on the reaction have also been investigated. Carbamates (urethanes) are compounds of growing interest because of their applications in the agrochemicals industry[5] as herbicides, fungicides and pesticides, in the pharmaceuticals industry[5] as drug intermediates and in the polymer industry[5] in the synthesis of polyurethane and peptides. In addition, among the various amine-protecting groups, carbamates are commonly used due to their chemical stability towards acids, bases and hydrogenation [6]. The most widely utilized method for the synthesis of carbamates uses highly toxic phosgene as a reagent in organic solvents, which is also toxic and flammable[7]. Therefore, the conventional method involves environmental and safety problems. These procedures seem to be efficient, pose environmental and operational concerns since highly harmful and corrosive reagents are used. Efforts have been continuously made for the replacement of the phosgene with carbon dioxide and organic carbonates[8]. However these methods cannot produce *N*-unsubstituted (primary) carbamates. Synthesis of *N*-unsubstituted carbamates **1** from alcohols has been also accomplished by several-pot reaction methods such as; trichloroacetyl isocyanate[9]. Chloroformates (starting from toxic phosgene), [10] chlorosulfonyl isocyanate[11] and cyanogen chloride [12]. Loev and coworkers reported the synthesis of *N*-unsubstituted carbamates from alcohols by treatment with sodium cyanate and trifluoroacetic acid in certain organic solvents such as benzene, methylene chloride and carbon tetrachloride without any spectral data such as IR and NMR [13]. These solvents are toxic and are not eco-friendly. In addition, trifluoroacetic acid is very expensive. From the standpoint of 'green chemistry', significant efforts have been made to find an alternative to organic solvents. A very attractive substitute for these solvents is a solvent–free reaction (industrially important due to reduced pollution, low cost, and simplicity in process and handling) [14]. Grindstone Chemistry is a branch of green chemistry for solvent-free chemical reactions which can be probably conducted in high yield by just grinding solid/solid, solid/liquid, or even liquid/liquid together [15]. In attempts to synthesize primary carbamates from phenols and alcohols under solvent–free conditions, we have recently reported a method for the conversion of compounds containing hydroxyl group to primary carbamates at room temperature in the absence of solvent using heteropolyacid as well as spectra data such as IR, NMR and their dynamic NMR [16]. Since this acid is relatively toxic and corrosive, we were interested in developing methods for the synthesis of carbamates utilizing solid acids such as heteropolyacids as they are industrially important due to their potential at replacing conventional acid/base catalysts .

Results and Discussion

In order to improve the synthesis of Primary carbamates, Primary carbamates **3a-q** were prepared in high yields and in high purity from reaction of either alcohol or phenol **2** with sodium cyanate 3 in the presence of heteropolyacid catalyst at room temperature (Scheme 1).



Scheme1

We used of preyssler heteropolyacid catalyst $H_{14}[NaP_5W_{30}O_{110}]$ in synthesis of primary carbamates and obtained good and high yield in short times and solvent free (Table 1).

Table 1. The yields of carbamates (3a-q) using Preyssler heteropolyacid,$H_{14}[NaP_5W_{30}O_{110}]$

Entry	R	Compound	[a]Yield (%)	Mp/°C Found
1	α-naphthyl	Naphthalen-1-yl carbamate (3n)q	84	178-180
2	β-naphthyl	Naphthalen-2-yl carbamate (3o)p	91	157-158
3	C_6H_5	Phenyl carbamate (3j)o	98	141-143
4	4-$CH_3C_6H_4$	4-Methylphenyl carbamate (3k)n	67	134-136
5	3-$CH_3C_6H_4$	3-Methylphenyl Carbamate(3q)m	88	137-139
6	2-$CH_3C_6H_4$	2-Methylphenyl Carbamate(3p)l	82	132-135
7	2-$C(CH_3)_3$-4-$CH_3C_6H_4$	2-*tert*-Butyl-4-Methylphenyl carbamate (3m)k	95	143-144
8	$C_6H_5CH_2$	Benzyl Carbamate(3g)j	86	87-89
9	4-BrC_6H_4	4-Bromophenyl carbamate (3l)i	65	139-142
10	$CH_2=CHCH_2$	Allyl carbamate (3i)h	71	19-21
11	$(CH_3)_3C$	*tert*-Buthyl carbamate(3f)g	78	106-108
12	$(CH_3)_2CHOCH_2CH_2$	Ethylene glycol monoisopropyl ether carbamate (3h)f	59	57-59
13	C_6H_{11}	Cyclohexyl carbamate (3d)e	58	108-110
14	$CH_3CH_2CH_2CH_2$	1-Buthyl carbamate (3d)	61	53-55
15	$CH_3CH_2CH_2$	1-Propyl carbamate (3c)	62	58-59
16	CH_3CH_2	Ethyl carbamate (3b)	60	46-48
17	(-)-Menthyl	Menthyl carbamate (3a)	79	166-168

[a] isolated yields.

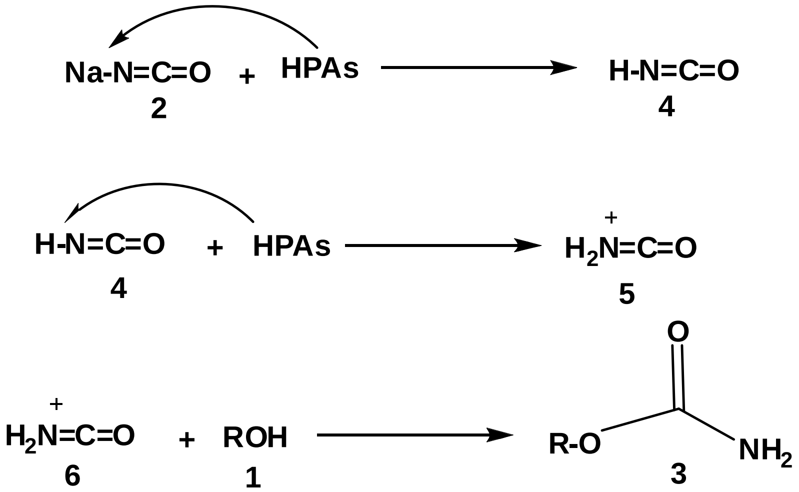
In this research, reported catalytic activities other heteropolyacids and catalysts (Table 2). We tested Wells-Dawson heteropolyacid, H_2SO_4, HY-Zeolit, H_3PO_4, $H_3[PW_{12}O_{40}]$, $H_4[PMo_{11}VO_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$, and compared the their results each other and the yield of Preyssler higher than H_2SO_4, HY-Zeolit, H_3PO_4 and other heteropolyacids, of course Wells-Dawson heteropolyacid, $H_5[PMo_{10}V_2O_{40}]$ showed good yields (Table 2), and the results of heteropolyacids were better and the yield more than mineral acids and HY-Zeolit (Table 2).

Table 2. The yields of using Phenyl carbamate (**3j**) using various catalysts

Entry	Catalyst	[a]Yield (%)
1	$H_6[P_2W_{18}O_{62}]$	92
2	$H_5[PMo_{10}V_2O_{40}]$	81
3	$H_4[PMo_{11}VO_{40}]$	77
4	$H_3[PW_{12}O_{40}]$	85
5	H_2SO_4	67
6	H_3PO_4	52
7	HY-Zeolit	68

[a]isolated yield.

As indicated in Table 1 some substrates with various structures were used to synthesis of primary carbamates **3a-q** purely and cleanly through this easy procedure. Primary, secondary, tertiary, allylic, benzylic alcohols and phenols showed a easy conversion to the corresponding carbamates. The crude product, in most cases, was completely pure and did not require to be purified or worked up anymore. The activation energy is provided from friction of available molecules in solid phase (alcohols **1a-h**, sodium cyanate and heteropolyacid). Since the activation energy is low for alcohols **1a-h** then their carbamates formation is very easy. However activation energy of phenols (**1a-h**)is higher than alcohols **1i-q**. The low nucleophilicity of the phenol oxygen is a reason of this difference. Phenols which carried electron-withdrawing substituents (CN, COOR and CHO) did not react successfully in our experimental conditions. These substituents very probably reduce the nucleophilicity of the phenol oxygen, so they fail to attack intermediate **4** and 5 (Scheme 2). This might have caused low yield (65%) of compound 3**i** (entry 9). Moreover, we found that the reaction conditions could tolerate such moieties as *O*-*i*-propyl (**3h**, entry 12) which often undergoes cleavage in strongly acidic media. By comparing the IR and physical properties of the products with those of authentic samples,23,25,32-36 carbamates **3a-q** were easily identified. The reaction of sodium cyanate **2** with an acid (Preyssler heteropolyacid (HPAs)) to produce isocyanic acid **5** could be the first step. Second step, for the generation of the intermediate **6**, the proton of Preyssler heteropolyacid (HPAs) is added to isocyanic acid **4** that the proton is perfectly added to nitrogen rather than oxygen. Finally, carbamate **1** is likely to be formed when either alcohol or phenol **1** attack to the carbon of the intermediate **6** (Scheme 2).



Scheme 2.

Conclusion

In conclusion, used of Preyssler heteropolyacid catalyst and solvent free at room temperature in short reaction times, with high yields and purity, without involvement of toxic solvents, expensive starting materials, formation of any undesirable side products. This conditions were green, environmentally friendly, ecofriendly, easy work-up. Also, this method does not require purification or separation techniques (column chromatography).

Table 3. Spectra data for compounds (3a-o)

Entry	Compound	IR *V*maxcm^{-1} (KBr disk)	^{1}H NMR *δ* (ppm) Solvent ($CDCl_3$)
1	Naphthalen-1-yl carbamate (1n)	3430 (m), 3343 (vw), 3275 (w), 3200 (w), 3055 (vw), 2920 (vw), 1698 (vs), 1603 (s), 1360 (vs), 1254 (s), 1222 (s), 1150 (m), 1082 (s), 1041 (m), 1010 (m), 958 (m), 801 (s), 773 (vs), 582 (m), 553 (w)	6.10 (br, d, 2H), 7.20 (d, J = 7.5 Hz, 1H), 7.35-7.45 (m, 3H), 7.63 (d, J = 8.2 Hz, 1H), 7.78 (dd, J = 9.3 Hz, J = 2.1 Hz, 1H), 7.92 (dd, J = 8.8 Hz, J = 2.1 Hz, 1H)
2	Naphthalen-2-yl carbamate (1o)	3405 (m), 3038 (w), 3270 (w), 3197 (vw), 3055 (vw), 1697 (vs), 1610 (w), 1506 (w), 1388 (s), 1355 (s), 1239 (s), 1206 (s), 1155 (m), 987 (s), 895 (m), 858 (m), 821 (m), 775 (m), 758 (w), 734 (m), 543 (w), 474 (m)	6.25 (br, s, 2H), 7.20 (dd, J = 8.7 Hz, J = 2.1 Hz, 1H), 7.34-7.41 (m, 2H), 7.49 (d, J = 2.1 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.7 Hz, 2H)
3	Phenyl carbamate (1j)	3400 (m), 3300 (m), 3250 (m), 2950 (w), 1700 (vs), 1590 (w), 1490 (w), 1470 (vw), 1380 (m), 1300 (m), 1200 (m), 970 (w), 820 (w), 760 (w), 740 (w), 700 (w), 580 (vw), 500 (vw)	5.06 (br, s, 2H), 7.16 (d, J = 8.2 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 2H)
4	4-Methylphenyl carbamate (1k)	3410 (m), 3405 (m), 3200 (vw), 3265 (w), 2915 (w), 1700 (vs), 1613 (m), 1505 (m), 1361 (s), 1382 (s), 1217 (s), 1205 (s), 1163 (w), 1016 (w), 975 (w), 853 (w), 810 (w), 549 (w), 501 (w)	2.36 (s, 3H), 5.23 (br, s, 2H), 7.04 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H)
5	3-Methylphenyl Carbamate	3400 (m), 3310 (m), 3250 (m), 3180 (w), 1700 (s), 1600 (w), 1580 (w), 1480 (w), 1350 (m), 1240 (m), 1150 (m), 1080 (w), 1010 (w), 1000 (w), 970 (w), 910 (w), 800 (w), 750 (w), 700 (w), 680 (w), 550 (w)	2.38 (s, 3H), 5.12 (br, s, 2H), 6.96 (d, J = 8.1 Hz, 1H), 6.98 (s, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H)
6	2-Methylphenyl Carbamate	3400 (m), 3350 (w), 3300 (w), 2800 (vw), 1700 (s), 1610 (w), 1490 (w), 1360 (m), 1225 (m), 1180 (m), 1110 (m), 1040 (w), 970 (m), 780 (w), 750 (w), 720 (w), 600 (w)	2.24 (s, 3H), 5.11 (br, s, 2H), 7.07 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.21 (t, J = 6.3 Hz, 1H)
7	2-*tert*-Butyl-4-Methylphenyl carbamate (1m)	3450 (m), 3250 (m), 2950 (m), 1720 (vs), 1610 (m), 1570 (w), 1490 (m), 1480 (w), 1450 (m), 1360 (s), 1280 (w), 1200 (s), 980 (m), 840 (w), 790 (w), 770 (w), 730 (w), 670 (w), 590 (w)	1.39 (s, 9H), 2.36 (s, 3H), 5.30 (br, 2H), 6.97 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 7.19 (s, 1H)
8	Benzyl carbamate	3420 (s), 3326 (m), 3285 (m), 3200 (w), 3020 (w), 2940 (w), 1675 (vs), 1615 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1470 (w), 1440 (m), 1400 (s), 1335 (s), 1120 (w), 1085 (m), 1070 (s), 1025 (w), 910 (m), 880 (w), 780 (w), 730 (s), 693 (m), 620 (w), 570 (w)	4.8 (br, 2H), 5.10 (s, 2H), 7.30 (quasi s, 5H)
9	4-Bromophenyl carbamate (1l)	3400 (m), 3300 (m), 3250 (w), 3200 (w), 1700 (s), 1650 (w), 1610 (w), 1580 (w), 1560 (w), 1540 (w), 1480 (m), 1460 (w), 1380 (m), 1200 (m), 1060 (w), 1010 (w), 980 (w), 800 (w), 722 (w), 500 (m)	5.05 (br, s, 2H), 7.06 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H)
10	Allyl carbamate (1i)	3475 (s), 3350 (s), 3195 (m), 3085 (w), 2945 (w), 1713 (vs), 1647 (w), 1601 (s), 1574 (w), 1558 (w),1539 (w), 1518 (w), 1504 (w), 1486 (w), 1445 (w), 1397 (s), 1331 (s), 1286 (w), 1119 (m), 1062 (s), 995 (m), 931 (m), 783 (m)	4.49 (d, J = 5.5 Hz, 2H), 5.15 (d, J = 10.4 Hz, 1H), 5.25 (dd, J = 17.2 Hz, J = 1.1 Hz, 1H), 5.38 (br, 2H), 5.85 [o (ddt), J = 17.2 Hz, J = 10.6 Hz, J = 5.4 Hz, 1H)]

11	*tert*-Buthyl carbamate	3415 (s), 3330 (w), 3250 (w), 3200 (w), 2970 (m), 2920 (w), 1675 (vs), 1600 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1473 (w), 1382 (m), 1360 (m), 1250 (w), 1167 (m), 1055 (m), 1025 (w), 845 (w), 785 (w), 560 (w)	1.34 (s, 9H), 4.40 (br, 2H)
12	Ethylene glycol monoisopropyl ether carbamate (1h)	3420 (vs), 3326 (s), 3285 (s), 3200 (s), 2970 (s), 2950 (m), 2900 (w), 2870 (w), 1718 (vs), 1612 (vs), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1467(m), 1455 (m), 1400 (s), 1368 (w), 1320 (vs), 1279 (w), 1240 (w), 1179 (w), 1146 (w), 1124 (s), 1100 (m), 1065 (vs), 1005 (s), 964 (m), 885 (w), 850 (w), 790 (w), 780 (w), 733 (w), 670 (w), 580 (m), 535 (m), 505 (w)	1.15 (d, J = 6.1Hz, 6H), 3.59 (h + t, 3H), 4.16 (t, J = 4.6 Hz, 2H), 5.19 (br, 2H)
13	Cyclohexyl carbamate (1d)	3418 (s), 3317 (m), 3275 (m), 3200 (m), 2945 (m), 2880 (w), 1680 (s), 1615 (m), 1600 (m), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1460 (w), 1440 (m), 1400 (w), 1360 (m), 1340 (m), 1310 (w), 1100 (w), 1050 (s), 1020 (w), 910 (w), 790 (w), 560 (w)	1.21-1.89 (m, 10H), 4.6 (m, 1H), 4.95 (br, 2H)
14	1-Buthyl carbamate (1e)	3415 (s), 3320 (s), 3265 (m), 3200 (w), 2960 (s), 2870 (w), 1680 (vs), 1610 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1455 (w), 1415 (m), 1360 (m), 1334 (s), 1125 (w), 1075 (s), 915 (w), 885 (w), 785 (w), 735 (w), 680 (w)	0.95 (t, J = 6.7 Hz, 3H), 1.23-1.80 (m, 4H), 4.12 (t, J = 6.7 Hz, 2H), 5.0 (br, 2H)
15	1-Propyl carbamate (1c)	3420 (s), 3326 (w), 3285 (m), 3200 (w), 2950 (m), 2890 (w), 1680 (vs), 1620 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1440 (w), 1425 (s), 1360 (s), 1300 (w), 1115 (w), 1060 (s), 917 (w)	0.90 (t, J = 7.0 Hz, 3H), 1.6 (sextet, J = 7.0 Hz, 2H), 4.00 (t, J = 7.0 Hz, 2H), 4.90 (br, 2H)
16	Ethyl carbamate (1b)	3420 (s), 3322 (m), 3278 (m), 3200 (m), 2987 (m), 2900 (w), 1688 (s), 1615 (m), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1420 (m), 1380 (m), 1330 (m), 1075 (m)	1.25 (t, J = 6.3 Hz, 3H), 4.16 (q, J = 6.3 Hz, 2H), 5.0 (br, 2H)
17	Menthyl carbamate (1a)	3415 (s), 3326 (w), 3285 (m), 3200 (w), 2950 (s), 2875 (w), 1675 (vs), 1610 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1455 (w), 1400 (s), 1370 (m), 1337 (w), 1319 (w), 1180 (w), 1100 (w), 1080 (w), 1060 (m), 1048 (s), 917 (w), 780 (w), 704 (w), 575 (m)	0.80 (d, J = 6.9 Hz, 3H), 0.86 (dd, J = 12.1 Hz, J = 3.2 Hz, 1H), 0.90 (d, J = 2.7 Hz, 3H), 0.91 (d, J = 2.1 Hz, 3H), 0.97 (q, J = 12.0 Hz, 2H), 1.06 (qd, J= 13.1 Hz, J = 3.3 Hz, 1H), 1.30 (tt, J = 11.6 Hz, J = 2.9 Hz, 1H), 1.44-1.52 (m, 1H), 1.65 -1.69 (m, 2H), 1.94 (hd, J = 6.9 Hz, J = 2.5 Hz, 1H), 2.06 (dt, J = 11.8 Hz, J = 4.64 Hz, 1H), 4.54 (td, J = 10.9 Hz, J = 4.4 Hz, 1H), 4.85 (br, 2H)

References

[1] I. V. Kozhevnikov, *Russ. Chem. Rev*. 56 (1987) 811.
[2] F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Jahangir, *Appl. Catal.* 302 (2006) 42.
[3] M. H. Alizadeh, S.P. Harmalker, Y. Jeannin, J. Martin-Frere, M.T.
Pope, *J. Am. Chem. Soc.* 107 (1985) 2662.
[4] C. Hu, Y. Zhang, L. Xu, G. Peng, *Appl. Catal. A: Gen.* 177 (1999)
237.
[4] A. Dibenedetto, M. Aresta, C. Fragale, M. Narracci, M. *Green Chemistry*, *4*(2002) 439.
[5] L. L. Martin, L. Davis, J. T. Klein, P. Nemoto, G. E. Olsen, G. M. Bores, F. Camacho, W. W. Petko, D. K. Rush, D. Selk, C. P. Smith, H. M. Vargas, J. T. Wilson, R. C. Effland, D. M. Fink, *Bioorg. Med. Chem. Lett.* 7(1997) 157.
[6] W. T. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis,* 2nd Edn.; Wiley: New York, 1991; pp 327 and 403.
[7] S. P. Gupte, A. B. Shivarkar and R. V. Chaudhari, *J. Chem. Soc. Chem. Commun.* (2001) 2620.
[8]M. Yoshida, N. Hara, S. Okuyama, *J. Chem. Soc., Chem. Commun*. 2000, 151.
[9] P. Kocovsky, *Tetrahedron Let.* 27(1986) 5521.
[10] S. Raucher, D. S. Jones, *Synth. Commun. 15*(1985) 1025.
[11] R. Graf, *Ber. 96*(1963) 56.
[12] R. Fuks, M. A. Hartemink, *Bull. Chim. Belg.* 82(1973) 23.
[13] B. Loev, M. F. Kormendy, *J. Org. Chem.* 28(1963) 3421.
[14] K. Tanaka, *Solvent-Free Organic Synthesis*; Wiley-VCH: Morlenbach, 2003.
[15] A. K. Bose, S. Pednekar, S. N. Ganguly, G. Chakraborty, M. S. Manhas, *Tetrahedron Lett.* 45(2004) 8351.
[16] A. R. Modarresi-Alam, M. Rostamizadeh, P. Najafi, *Turk. J. Chem.* 30(2006)269.