JOM 23268

Convenient method for the preparation of catecholborane and promotion of the formation of alkenyl catecholborane using BH_3 complexes

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(Received September 23, 1992)

Abstract

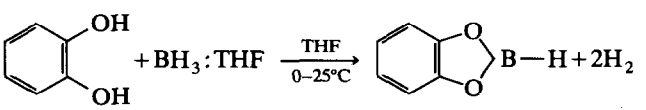
Catecholborane is prepared in benzene by passing B_2H_6, generated from $I_2/NaBH_4$, through a suspension of catechol at 25°C. The reagent prepared in this way is used for hydroboration-oxidation of representative alkenes and alkynes at 80°C. Hydroboration of 1-alkynes followed by iodination with I_2/NaOH gives the corresponding *trans*-1-alkenyl iodides in 70–72% yield. The alkenyl catecholboranes can be prepared at 25°C by performing the reaction in the presence of 10 mole% of $H_3B:N(C_2H_5)_2Ph$ or H_3B:THF. The reaction is believed to go through hydroboration of the alkynes by borane followed by exchange with catecholborane. Studies of the preparation of dialkylphenoxyboranes and alkenyldiphenoxyboranes through hydroboration of 1-decene and 1-decyne by use of $H_3B:N(C_2H_5)_2Ph$ and phenol are also reported.

1. Introduction

A number of partially alkylated boranes (R_2BH, RBH_2 *etc.*) have been shown to have advantages in selective hydroborations over simple BH_3 complexes [1]. However, the side products obtained in the oxidation of alkylboranes may pose problems in the isolation of products. The use of partially substituted, non-alkylated, hydroborating agents such as haloboranes (XBH_2 and X_2BH) [2] and catecholborane [3] are more advantageous since the side products (*e.g.* catechol) can be readily separated from the hydroboration products. In addition, in recent years catecholborane has been shown to be useful in several synthetic applications. For example, the combination of catecholborane and a transition metal catalyst such as $ClRh(PPh_3)_3$ is useful in selective hydroborations [4]. Asymmetric hydroboration has been achieved using catecholborane and a chiral cationic rhodium complex [5]. A combination of Corey's oxazaborolidine catalyst and catecholborane is useful in the asymmetric reduction of certain ketones [6]. We describe below a convenient method for the preparation of catecholborane in benzene and the promotion of the formation of alkenyl catecholboranes in the presence of $H_3B:N(C_2H_5)_2Ph$ complex [7], and also report the hydroboration properties of a combination of phenol and $H_3B:N(C_2H_5)_2Ph$.

2. Results and discussion

The catecholborane was prepared by reaction of catechol with BH_3:THF at 0–25°C [8]. Removal of the solvent under reduced pressure and distillation of the residue gives catecholborane in 70–80% yield.



(1)

However, catecholborane must be handled carefully because it is moisture sensitive, and we decided to seek a convenient *in situ* method for its preparation. It appeared that distillation is necessary in the method involving use of borane in THF since some polymeric aryloxyboranes could also be formed and we thought bubbling an of excess B_2H_6 through a suspension of catechol in a hydrocarbon solvent would give catecholborane.

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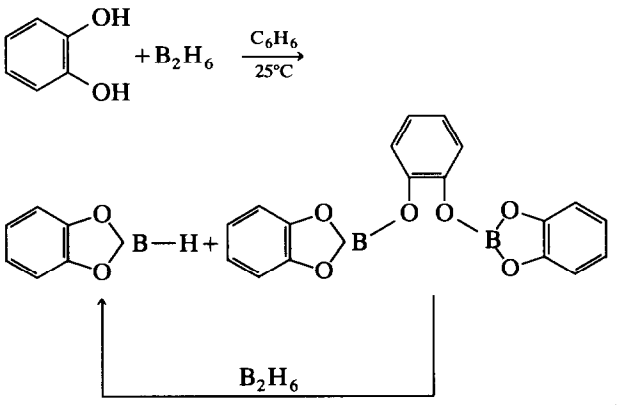
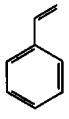
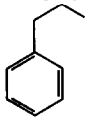
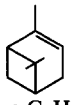
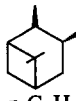
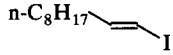
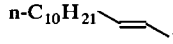


(2)

We found that the IR spectrum of a solution of catecholborane in benzene, prepared by passage of B_2H_6 (generated from $NaBH_4/I_2$ in diglyme) exhibits a single >B–H absorption at 2680 cm^{-1}, similar to that reported for catecholborane [9]. Hydroboration of alkenes and alkynes can be achieved with this reagent by carrying out the reaction at 80°C for 12 h (Table 1).

The regio and stereoselectivities observed in the hydroboration of representative alkenes are same as those for hydroboration with catecholborane prepared by use of BH_3:THF [3]. Hydroboration of 1-decyne and 1-dodecyne followed by oxidation with NaOAc/H_2O_2 gives the corresponding aldehydes in 90–91% yields (Table 1). The alkenyl catecholborane intermediates can also be readily converted into the corresponding *trans*-1-iodoalkenes by treatment with an excess of NaOH and I_2 (Table 1).

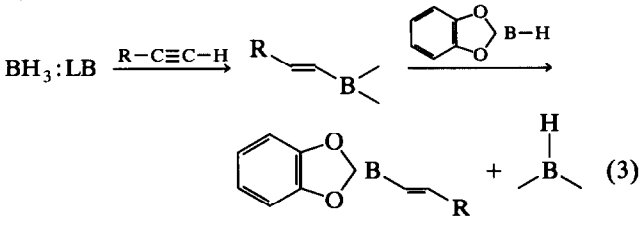
TABLE 1. Hydroboration of representative alkenes and alkynes with catecholborane prepared in benzene

Entry No.	Substrate [a]	Product	Yield (%) [e]
1	$n\text{-}C_8H_{17}\text{-}CH{=}CH_2$	$n\text{-}C_8H_{17}\text{-}CH_2CH_2OH$	88 [b]
2			80 [b]
3			85 [b]
4	$n\text{-}C_8H_{17}\text{-}C{\equiv}CH$	$n\text{-}C_8H_{17}\text{-}CH_2\text{-}CHO$	90 [c]
5	$n\text{-}C_{10}H_{21}\text{-}C{\equiv}CH$	$n\text{-}C_{10}H_{21}\text{-}CH_2\text{-}CHO$	91 [c]
6	$n\text{-}C_8H_{17}\text{-}C{\equiv}CH$		70 [d]
7	$n\text{-}C_{10}H_{21}\text{-}C{\equiv}CH$		72 [d]

[a] Reactions were carried on for 12 h at 80°C under N_2 with catecholborane (10.5 mmol) and the substrate (10 mmol) in benzene (40 ml). [b] Oxidation was carried out with 1M $NaOH/H_2O_2$. [c] Oxidation was carried out with 3M $NaOAc/H_2O_2$. [d] Iodination was carried out with 3M NaOH and I_2. [e] Yields are of products isolated by column chromatography on silica gel. The products were identified from spectral data (IR, ^1H and ^{13}C NMR) by comparison with data for authentic samples.

Unfortunately, catecholborane does not hydroborate alkenes and alkynes at 25°C. In recent years there have been several reports of the catalysis of catecholborane hydroborations at 25°C by using transition metal complexes. For example, alkyl catecholboranes can be prepared from alkenes and catecholborane at ambient temperature in the presence of the Wilkinson catalyst $ClRh(PPh_3)_3$ [4a] or related reagents [5b].

In continuation of our studies on development of new hydroborating agents [10], we thought it of interest to seek suitable catalysts for catecholborane hydroboration. In 1971 it was reported that triaryloxyboranes undergo exchange with trialkylboranes in the presence of a catalytic amount of BH_3:THF at 100°C to give the corresponding alkylaryloxyborane derivatives $(ArO)_2$-BR [11]. We thought that since such exchanges probably go through intermediates such as $(ArO)_2BH$ and/or R_2BH species, it was likely that hydroboration and exchange of the alkenyl/alkyl group with a diaryloxyborane such as catecholborane might be brought about by use of the route shown in eqn. (3):



(3)

We therefore examined the reaction of catecholborane with 1-decene (16 mmol) at 25°C for 24 h in the presence of N,N-diethylaniline-borane complex (1 mmol). Only 7.5% of 1-decanol was isolated after oxidation of the resulting organoborane and this could have come from hydroboration of 1-decene with the N,N-diethylaniline-borane complex. Evidently transfer of alkyl group from alkylborane to catecholborane does not take place in this case. However, when the alkene in the above experiment was replaced by an alkyne (16 mmol), the corresponding alkanal was obtained in 65–81% yields after oxidation with $NaOAc/H_2O_2$ (Table 2). These results indicate that alkenylboranes are formed in the reaction.

We found that catecholborane in benzene does not hydroborate alkynes at 25°C within 24 h. The reaction of 1-decyne with H_3B:$N(C_2H_5)_2Ph$ complex followed by oxidation with $NaOAc/H_2O_2$ gives 1-decanol; presumably hydroboration leading to the *gem*-dibora derivative takes place in this case. The absence of alcoholic products derived from *gem*-dibora compounds in the experiments with catecholborane and N,N-diethylaniline-BH_3 indicates that the alkenyl

TABLE 2. Hydroboration of alkynes with catecholborane in the presence of the $H_3B:N(C_2H_5)_2Ph$ complex

Sl. No.	Substrate [a]	Product	Yield (%) [d]
1.	$n\text{-}C_6H_{13}\text{-}C{\equiv}CH$	$n\text{-}C_6H_{13}\text{-}CH_2\text{-}CHO$	65 [b]
2.	$n\text{-}C_8H_{17}\text{-}C{\equiv}CH$	$n\text{-}C_8H_{17}\text{-}CH_2\text{-}CHO$	76 [b]
3.	$n\text{-}C_{14}H_{29}\text{-}C{\equiv}CH$	$n\text{-}C_{14}H_{29}\text{-}CH_2\text{-}CHO$	81 [b]
4.	$H_3COOC\text{-}(CH_2)_8\text{-}C{\equiv}CH$	$H_3COOC\text{-}(CH_2)_8\text{-}CH_2\text{-}CHO$	68 [b]
5.	$C_8H_{17}\text{-}C{\equiv}CH$	$n\text{-}C_8H_{17}$ 	65 [c]
6.	$n\text{-}C_{14}H_{29}\text{-}C{\equiv}CH$	$n\text{-}C_{14}H_{29}$ 	67 [c]

[a] Reactions were carried out under nitrogen using catecholborane (10 mmol) and the substrate (16 mmol) in the presence of N,N-diethylaniline-borane complex (1 mmol). [b] Products obtained after oxidation with 3M $NaOAc/H_2O_2$. [c] Products obtained after iodination with 3M NaOH and I_2. [d] Yields are of isolated and purified products calculated on the basis of catechol utilized. The products were identified from spectral data (IR, ^1H and ^{13}C NMR) by comparison with data for authentic samples.

transfer reaction to give the alkenyl catecholborane is faster than the formation of *gem*-dibora compounds. Similar results were obtained with the reagent prepared by passing an excess of B_2H_6 through a mixture of N,N-diethylaniline (1 mmol) and catechol (10 mmol) in benzene at 25°C.

The stability of the ester group under these conditions is noteworthy, since catecholborane reduces esters to alcohols at 65°C [12]. In order to examine whether alkynes could be selectively hydroborated in the presence of alkenes we employed a mixture of 1-decyne (16 mmol) and 1-decene (16 mmol) in a reaction with catecholborane (10 mmol) and N,N-diethylaniline-BH_3 (1 mmol), but only 4.5 mmol of 1-decanal was formed along with 2 mmol of 1-decanol. The decanol probably comes from the hydroboration of 1-decene by BH_3-N,N-diethylaniline. An equivalent of catecholborane remained unchanged even after 24 h. This retardation of the reaction is not unexpected, since formation of trialkylborane would remove the 'BH_3' species.

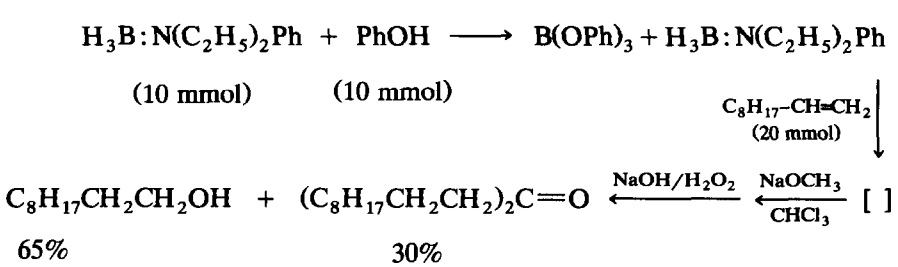
In a search for further confirmation of the formation of alkenylborane derivatives under the conditions applied, we also performed the iodination reaction with $NaOH/I_2$. The alkenyl boronic acid was isolated free from catechol by distilling off the benzene after hydrolysis. The crude alkenyl boronic acid was iodinated with $NaOH/I_2$ by a published procedure [13], and the corresponding isomerically pure *trans*-alkenyl iodides were obtained in 65–67% yield (Table 2, entries 6 and 7).

In order to ascertain whether other partially substituted aryloxyboranes could be prepared by passing B_2H_6 through a suspension of the corresponding phenol we carried out experiments with phenol and 1,1'-binaphthol. In these cases, the solution IR spectra showed no –OH or $\rangle BH$ absorptions indicating that the aryloxy boranes formed did not contain $\rangle BH$ bonds. This is not surprising since alkoxy and aryloxy boranes containing $\rangle BH$ bonds are generally unstable decomposing readily to diborane and aryloxyboranes [3].

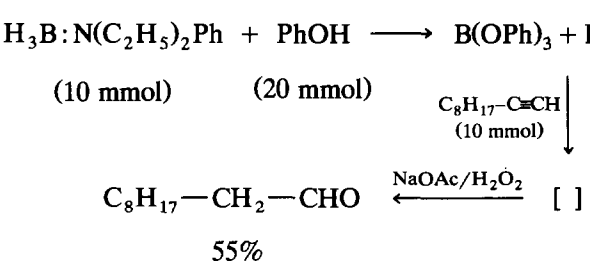
$$6(RO)_2BH \rightleftharpoons B_2H_6 + 4(RO)_3B$$

However, it was of interest to find out whether dialkylmonophenoxyborane can be prepared by use of the reagent prepared by adding an appropriate amount of phenol to $H_3B:N(C_2H_5)_2Ph$ in benzene. We carried out several experiments in order to examine this possibility, with the results shown in Scheme 1, in which [ ] denotes unspecified intermediates.

Evidently, the reaction does not give dialkylboron



Scheme 1.



Scheme 2.

species clearly, as indicated by the formation of dialkylketone in only low yields after the reaction with $NaOCH_3/CHCl_3$ followed by oxidation [10b].

To find out whether alkenyl phenoxyborane could be prepared from phenol in a similar way, we used appropriate amounts of PhOH, $H_3B:N(C_2H_5)_2Ph$ and 1-decyne with the result shown in Scheme 2.
In this case, the yield of the aldehyde was only 55%, and 32% of alkyne was recovered. No 1-decanol was isolated, indicating that the *gem*-dibora derivative is not formed. However, the yield of the aldehyde is lower than in the experiments with catecholborane.

Since the appearance of our preliminary account [7], it has been reported that hydroboration with catecholborane is promoted by $LiBH_4$ in THF [14] and that $Li(C_2H_5)_3BH$ promotes hydroboration of alkenes with dialkoxyboranes [15]. These developments, along with our results, made available a pool of reagents for the synthesis of alkyl and alkenylboranes that have been shown to be useful synthetic intermediates.

3. Experimental details

Benzene distilled over benzophenone-sodium was used in all the experiments. Infrared spectra were recorded on a Perkin-Elmer IR spectrometer 1310 with polystyrene as reference. NMR spectra were recorded on a Jeol-FX-100 spectrometer in deuterated chloroform with tetramethylsilane as internal standard. For TLC, plates coated with silica gel were used with hexane/ethyl acetate or hexane/chloroform mixtures as eluent and spots were developed in an iodine chamber. For column chromatography chromatographic silica gel (100–200 mesh) was used.

3.1. Preparation of catecholborane

Catechol (1.10 g, 10 mmol) was placed in an oven-dried 2-necked flask bearing a side-arm septum admitting a bubbler. Dry benzene (40 ml) was introduced through a cannula. Diborane generated by slow addition of iodine (6.4 g, 25 mmol) in diglyme to sodium-borohydride (2 g, 50 mmol) in diglyme was passed slowly through the suspension during 3–4 h at 25°C. The outlet was connected to an acetone trap to destroy the excess of diborane. A clear benzene solution of catecholborane was obtained. The IR spectrum of the resulting solution showed a $\rangle$BH absorption at 2680 cm^{-1} [9].

3.2. Hydroboration of 1-decene with catecholborane

Catecholborane (10.5 mmol) was prepared as described above at 25°C and 1-decene (1.4 g, 10 mmol) was then added. The mixture was refluxed for 12 h then cooled to 10°C and quenched with H_2O (10 ml). THF (10 ml) was added and the organoborane was oxidised with 1 M $NaOH/H_2O_2$ [1]. The mixture was extracted with ether (3 × 10 ml), washed successively with dilute hydrochloric acid (5 ml, 3N), 1 M NaOH solution (3 × 20 ml), water and brine, then dried over anhydrous $MgSO_4$. The 1-decanol obtained was purified by column chromatography (n-hexane:ethyl acetate/95:5). Yield: 1.38 g, 88%. IR: 3350, 1060 cm^{-1}. ^{13}C NMR ($CDCl_3$): 62.5, 32.5, 31.9, 29.6, 29.3, 25.8, 22.6, 13.9.

3.3. Hydroboration-oxidation of 1-decyne with catecholborane

The procedure was as above. THF (10 ml) was added and the oxidation was carried out with 3 M $NaOAc/H_2O_2$. Work-up gave 1-decanal, which was purified by column chromatography on silica gel (n-hexane:ethyl acetate/95:5). Yield: 1.40 g, 90%. IR: 2700, 1720 cm^{-1}. ^{13}C NMR ($CDCl_3$): 202.8, 43.9, 31.9, 29.7, 29.4, 29.1, 22.7, 22.0, 14.0.

3.4. Hydroboration-iodination of 1-dodecyne with catecholborane

A solution of catecholborane (10.5 mmol) in benzene, prepared as above, was refluxed with 1-dodecyne (1.66 g, 10 mmol) for 12 h. The mixture was cooled to 0°C and ether (20 ml) was added followed by aqueous NaOH (3 M, 15 ml). After subsequent slow addition of a solution of iodine (3.8 g, 15 mmol) in ether (40 ml), the mixture was stirred for 3 h then shaken with ether (3 × 20 ml). The organic layer was washed three times with aqueous sodium thiosulphate to remove iodine then shaken successively with 1 M aqueous NaOH, water and brine, and dried over anhydrous $MgSO_4$.

The trans-1-dodecenyl iodide obtained was purified by column chromatography on silica gel with hexane as eluent. Yield 2.10 g, 72%. IR: 3100, 1620, 940, 720 cm^{-1}. ^{13}C NMR ($CDCl_3$): 146.7, 74.4, 36.1, 31.9, 29.5, 29.3, 29.1, 28.9, 28.4, 22.7, 14.1.

3.5. Reaction of methyl-10-undecynoate with catecholborane at 25°C in the presence of N,N-diethylaniline-borane complex

A solution of catecholborane (10 mmol) in dry benzene was prepared as described above. The N,N-diethylaniline-borane complex was prepared by passing B_2H_6 into a benzene solution of N,N-diethylaniline at 10°C [10c] and a volume of the solution containing 1 mmol of the complex was added to the catecholborane solution through a cannula under nitrogen and methyl-10-undecynoate (3.2 g, 16 mmol) was then added. The mixture was stirred at 25°C for 24 h, then quenched with H_2O (10 ml) and THF (10 ml) was added. The mixture was oxidized with 3 M $NaOAc/H_2O_2$ then extracted with ether (2 × 20 ml). The organic extract was washed successively with 3 M hydrochloric acid (10 ml), 1 M aqueous NaOH (3 × 20 ml), water, brine then dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the expected aldehyde, which was further purified by column chromatography (n-hexane : chloroform/60 : 40). Yield: 1.45 g, 68%, IR: 2700, 1740, 1720 cm^{-1}. ^{13}C NMR ($CDCl_3$): 201.5, 173.3, 50.9, 33.6, 28.8, 28.6, 28.4, 28.2, 24.5, 18.0.

3.6. Preparation of 1-decenylcatecholborane in the presence of N,N-diethylaniline-borane complex at 25°C and iodination

A benzene solution of 1-decenylborane (10 mmol) was prepared as described above at 25°C and the solution treated with H_2O (10 ml). The benzene was removed under nitrogen at reduced pressure and the residue washed with water (2 × 10 ml) to give 1-decenyl boronic acid. This was dissolved in ether (30 ml) and the solution cooled to 0°C and aqueous NaOH (5 ml, 3 M) was added. A solution of iodine (1.5 g, 6 mmol) in ether (20 ml) was added at 0°C during 15 min, with stirring. The mixture was subsequently stirred for 3 h at 25°C and the excess of iodine was destroyed with aqueous sodium thiosulphate. The organic layer was separated and the aqueous layer extracted with ether (2 × 20 ml). The combined organic extract was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed and the product was purified by column chromatography on silica gel with hexane as eluent. Yield: 1.72 g, 65%. IR: 3100, 1620, 940, 720 cm^{-1}. ^{13}C NMR ($CDCl_3$): 146.8, 74.4, 36.1, 31.9, 29.4, 29.0, 28.5, 22.7, 14.1.

3.7. Hydroboration of 1-decene with $H_3B:N(C_2H_5)_2Ph$ in the presence of phenol followed by reaction with $NaOCH_3/CHCl_3$

Diborane, generated from $NaBH_4$ (25 mmol) and I_2 (12.5 mmol) at 10°C, was passed for 1 h through a solution of N,N-diethylaniline (1.49 g, 10 mmol) in dry benzene (40 ml) [10c]. A solution of phenol (0.94 g, 10 mmol) in benzene was added under nitrogen through a cannula and the mixture stirred for 8 h at 25°C. 1-Decene (2.8 g, 20 mmol) was injected and the mixture stirred for 24 h. MeOH (10 ml) was added to destroy any remaining hydride, followed by THF (10 ml) and $CHCl_3$ (10 ml). Sodium methoxide (2.16 g, 40 mmol) was added during 30 min, from a solid-addition funnel. The mixture was stirred for 1 h at 25°C and then at 50°C for 2 h and H_2O (10 ml) was added, followed by THF (10 ml). The mixture was oxidised with 1 M $NaOH/H_2O_2$ [1], the organic layer separated, and the aqueous layer was extracted with ether (2 × 20 ml). The combined organic layer was washed with 3N HCl (3 × 20 ml), 1 M aqueous NaOH (3 × 20 ml) and brine, and dried over anhydrous $MgSO_4$. Purification by column chromatography on silica gel (n-hexane : ethyl acetate/95 : 5) yielded n-didecylketone and 1-decanol. Yield (n-didecylketone): 0.93 g, 30%. IR: 2990, 2885, 1710 cm^{-1}. ^{13}C NMR ($CDCl_3$): 211.0, 42.9, 32.1, 29.4, 29.1, 23.8, 22.8, 14.1. Yield (1-decanol): 2.05 g, 65%. IR: 3350, 1060 cm^{-1}. ^{13}C NMR ($CDCl_3$): 62.5, 32.5, 31.9, 29.6, 29.3, 25.8, 22.6, 13.9.

3.8. Hydroboration-oxidation of 1-decyne with phenol and N,N-diethylaniline-borane

A solution of the N,N-diethylaniline-BH_3 complex (10 mmol) in benzene was prepared at 10°C as described above. A solution of phenol (1.88 g, 20 mmol) in benzene (40 ml) was added and the mixture stirred for 8 h at 25°C. 1-Decyne (1.38 g, 10 mmol) was then injected and the mixture stirred for 24 h. The reaction was quenched with water (10 ml), THF (10 ml) was added, and the mixture oxidised with 3 M $NaOAc/H_2O_2$. After workup, the expected aldehyde was isolated by column chromatography on silica gel (n-hexane : ethyl acetate/95 : 5). Yield: 0.86 g, 55%. IR: 2700, 1720 cm^{-1}. ^{13}C NMR ($CDCl_3$): 202.8, 43.9, 31.9, 29.7, 29.4, 29.1, 22.7, 22.0, 14.0. 1-Decyne (0.44 g, 3.2 mmol) was recovered.

Acknowledgments

This work was supported by CSIR (New Delhi). We are grateful to the UGC for support under the Special Assistance and COSIST Programmes. We also thank Mr. A.S. Bhanu Prasad for some preliminary experiments.

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