Organic Process Research & Development **2001**, *5*, 152–157

Oxidation of Dibenzyl Ethers by Dilute Nitric Acid

S. R. Joshi, S. B. Sawant,* and J. B. Joshi

Department of Chemical Technology, University of Mumbai, Matunga, Mumbai - 400 019, India

Abstract:

A simple process for the manufacture of benzaldehyde (BzH) by oxidation of dibenzyl ether (DBE) has been reported in this paper. Two-phase reaction between dibenzyl ether and aqueous dilute nitric acid in the presence of catalytic amount of sodium nitrite has been investigated. Effect of stirring speed, concentration of nitric acid in the aqueous phase, mole ratio of reactants, sodium nitrite concentration, and reaction temperature on the conversion of DBE and yield of BzH has been investigated. 80% yield of BzH with 95% conversion of DBE has been reported. Oxidation of bis(chlorobenzyl) ethers to corresponding aldehydes is difficult compared to oxidation of DBE under otherwise identical conditions. Initial concentration of sodium nitrite does not affect the overall progress of the reaction.

1. Introduction

Benzyl alcohol (BnOH) is manufactured industrially by hydrolysis of benzyl chloride (BnCl) with sodium carbonate. This process gives 10−12% dibenzyl ether (DBE) as an unavoidable byproduct.[1] Thus substantial quantity of dibenzyl ether is available as the byproduct. It is possible to convert this DBE to benzaldehyde (BzH) which is a value added product. When 1 mmol DBE was stirred with chromatographic silica gel in CCl_4 under refluxing conditions, in an atmosphere of NO_2, 1.94 mmol BzH was obtained.[2] Sodium nitrate in the presence of sodium nitrite seed is reported to be efficient catalyst for oxidation of dibenzyl ether by oxygen in aqueous perchloric acid solution to give benzaldehyde.[3] DBE when passed over Al_2O_3 at 340 °C and a space velocity of 0.23 hr^{-1} gave 35% BzH.[4] DBE (100 g) when treated with HNO_3 (390 g, 15%) under refluxing conditions, gave BzH (46.5−57 g) after final workup.[5] Dilute nitric acid, is also an industrial byproduct and inexpensive oxidizing agent which can be used for oxidation of DBE. Oxidation of DBE to BzH with dilute nitric acid becomes economically viable route for manufacture of BzH as both the raw materials are industrial byproducts. Detailed information regarding yields of BzH, and other possible byproducts viz. BnOH and benzoic acid (BzOH) with respect to different operating parameters is not available in the published literature. Hence two-phase reaction between dibenzyl ether and aqueous dilute nitric acid in the presence of catalytic amount of sodium nitrite was taken up for investigation. All of the experiments were performed in the absence of any organic solvent. This increases output per batch and reduces a step of separation of the solvent from the product. Effect of stirring speed, concentration of nitric acid in aqueous phase, mole ratio of reactants, sodium nitrite concentration, and temperature on the conversion of DBE and yield of BzH was investigated in the present work. The main focus of the study was to develop a simple and commercially viable process for the manufacture of benzaldehyde from inexpensive raw material. Oxidation of chloro-substituted dibenzyl ethers was also investigated.

2. Experimental Section

2.1. Method. All the experiments were carried out in a batch manner. A borosilicate glass reactor of 75 mm i.d., 400 mL capacity, provided with a pitch-blade turbine down flow impeller (25 mm diameter), and baffles were used. Reaction temperature was maintained by using a constant-temperature bath.

A predetermined quantity of dibenzyl ether was added to the reactor placed in the constant-temperature bath. A measured quantity of sodium nitrite was then added, followed by addition of the aqueous nitric acid preheated to the required temperature and then the run was started. Small quantities of samples were withdrawn at predetermined time intervals. The sample was divided into two parts. The first part was analysed by gas chromatography to estimate the amount of benzaldehyde and benzyl alcohol formed and dibenzyl ether consumed. The second part of the sample was analysed by TLC using a Dessagga applicator and scanner to determine the amount of benzoic acid (BzOH) formed.

2.2. Analysis. The gas chromatographic analysis was done using a 2 m 10% OV-17 column. Nitrogen was the carrier gas and the detector was FID. The other parameters were as follows:

injection temperature: 350 °C
detector temperature: 350 °C
nitrogen flow rate: 30 mL/min
temperature programming: 110 °C for 5 min, 110 to 265 °C at the rate of 25 °C/min, temperature 265 °C for 2 min.

For TLC analysis precoated silica gel plates (Merck) were used. 0.2 mL portion of the sample was diluted to 10 mL with methanol. Known quantities of diluted sample and authentic sample of BzOH was applied in form of 5 mm bands by using applicator (Dessagga). The plates were developed in a solvent system consisting of benzene and

* To whom correspondence should be addressed. E-mail: sbs@udct.ernet.in. Fax: 91-22-414 5614. Telephone: 91-22-414 5616.

(1) *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; VCH Verlagsgesellschaft mbH: Weinheim, 1985; Vol. A4.
(2) Nishiguchi, T.; Hiroaki O. *J. Chem. Soc., Chem. Commun.* **1990**, *22*, 1607.
(3) Levina, A. B.; Trusov, S. R. *Latv. Kim. Z.* **1991**, *6*, 686. (Russ.) [*Chem. Abstr*. **1992**, *116*, 193511n].
(4) Alfred R.; Helmut S.; Gisela R. *J. Prakt. Chem.* **1962**, *15*, 139.
(5) Bagdonov, K. A.; Antonova, V. A. *Masloboino-Zhirovaya Prom.* **1961**, *27*(2), 32 [*Chem. Abstr*. **1961**, *55*, 15395f].

 10.1021/op000085o CCC: $20.00
Published on Web 01/27/2001

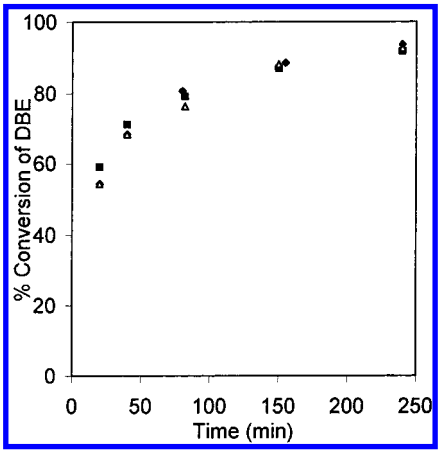

Figure 1. **Effect of speed of stirring on the progress of reaction at 90 °C. ◆: DBE = 0.15 mol; HNO_3 = 3.18 M, 59 mL; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm. ■: DBE = 0.15 mol; HNO_3 = 3.18 M, 59 mL; $NaNO_2$ = 1 g; speed of stirring =1500 rpm. □: DBE = 1.05 mol; HNO_3 = 3.18 M, 413 mL; $NaNO_2$ = 7 g; speed of stirring = 1500 rpm.**

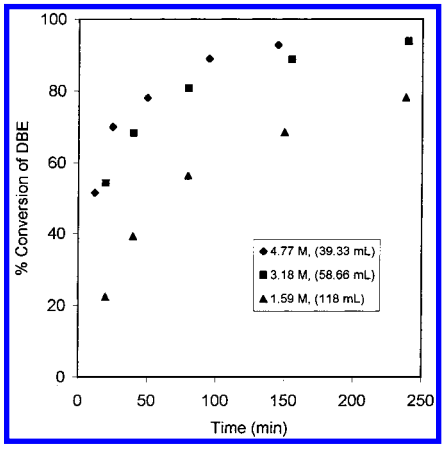

Figure 2. **Effect of HNO_3 concentration on the conversion of DBE at constant mole ratio of the reactants. DBE = 0.15 mol; HNO_3 = 0.1875 mol; temperature = 90 °C; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm.**

methanol (5:1 by volume). The developed plates were analysed by using densitometer (Dessagga).

3. Results and Discussion

The conversion of DBE (%) and yield of BzH (%) were determined by using following formulae:

$$\text{conversion of DBE (\%)} = \frac{\text{moles of DBE consumed}}{\text{moles of DBE charged}} \times 100$$

$$\text{yield of BzH (\%)} = \frac{\text{moles of DBE consumed for the formation of BzH}}{\text{moles of DBE consumed}} \times 100$$

The effect of the following variables on the conversion of substrate was studied: (1) speed of stirring, (2) HNO_3 concentration, (3) mole ratio of reactants, (4) $NaNO_2$ loading, (5) temperature, (6) different substrates.

3.1. Effect of Speed of Stirring. A chemical reaction involving two phases is regarded as mass transfer-controlled when the rate of mass transfer across the interface is slower compared to the rate of chemical reaction, while the same is kinetically controlled when the rate of mass transfer across the interface is fast but the rate of chemical reaction is slow. At the low stirring speed, the requirement for sufficiently rapid mass transfer of the reacting species is not met, and mass transfer controlled kinetics is observed. As we increase the speed of stirring, the rate of mass transfer across the interface increases and becomes faster than the chemical reaction rate. Thus, at higher stirring speeds, the reaction goes from being mass transfer-controlled to kinetically controlled.

To investigate the effect of the speed of stirring, at 90 °C, 0.15 mol DBE was treated with 59 mL, 3.18 M aqueous nitric acid in the presence of 1 g of $NaNO_2$. The reaction was performed at stirring speeds of 1500 and 2500 rpm. Figure 1 shows the conversion of DBE with time. The results show that the reaction is not affected by stirring speed beyond 1500 rpm, and the reaction is kinetically controlled beyond 1500 rpm. All of the further experiments were performed at 2500 rpm to ensure that the effects of various operating parameters are evaluated when the reaction is kinetically controlled. If the experiments are performed under mass transfer controlled conditions, then the change in the reaction rate cannot be attributed to the variable under investigation alone.

Also to know if the method is scaleable we reacted 1.05 mol DBE with 413 mL, 3.18 M aqueous HNO_3 and 7 g of $NaNO_2$ at 90 °C. Figure 1 also shows the conversion profile of this experiment, which matches, well with reaction profiles of experiments at 2500 and 1500 rpm. The yields of benzaldehyde, benzyl alcohol, and benzoic acid were found to be same for all the three experiments given in the Figure 1.

3.2. Effect of Nitric Acid Concentration. To study the effect of concentration of nitric acid, 0.15 mol DBE was reacted with different concentrations of HNO_3 viz. 1.59 M, 3.18 M and 4.77 M. The amount of HNO_3 taken in each experiment was kept constant at 0.1875 mol by appropriately reducing the volume of aqueous phase as the concentration of HNO_3 increased. The experiments were performed at 90 °C and 2500 rpm; 1 g of $NaNO_2$ was added to the reaction mixture in each case. Figure 2 shows conversion of DBE versus time for each case. As can be seen from the figure, the rate of reaction increases as the concentration of the aqueous phase increases. Similar result has been reported by Levina et al.[6] However, the increase in the rate of reaction is not pronounced as concentration increases from 3.18 to 4.77 M. Figures 3−5 show variation of yield of BzH, BnOH, and BzOH with respect to conversion of DBE. The yield of BzH almost remains constant. The yield of BnOH goes on decreasing and that of BzOH increases with increasing conversion of DBE. During the oxidation of DBE, BnOH is formed and oxidised to BzH.[7] Benzoic acid is formed by oxidation of benzaldehyde. Therefore, with the progress of

(6) Levina, A. B.; Trusov, S. R. *Latv. Kim. Z.* **1991**, *6*, 695. (Russ.) [*Chem. Abstr*. **1992**, *116*, 193512p].
(7) Levina, A. B.; Trusov, S. R. *Kinet. Ketal*. **1991**, *32*(6), 1343 (Russ) [*Chem. Abstr*. **1992**, *116*, 83051e].

Table 1. **Material balance and consumption of HNO_3 for different parameters (DBE = 0.15mol, $NaNO_2$ = 1 g, temp = 90 °C)**

	DBE left in reaction mix. (mol)	BzH in reaction mix. (mol)	BnOH in reaction mix. (mol)	BzOH in reaction mix. (mol)	O_2 required (mol)	HNO_3 consumed (mol)
expt 1[a]	0.013	0.219	0.021	0.026	0.141	0.170
expt 2[b]	0.021	0.202	0.023	0.021	0.128	0.165
expt 3[c]	0.036	0.187	0.022	0.013	0.111	0.132
expt 4[d]	0.003	0.233	0.006	0.043	0.162	0.237

[a] Expt 1: HNO_3 = 4.77 M, 39 mL (0.1875 mol); batch time = 140 min. [b] Expt 2: HNO_3 = 3.18 M, 59 mL (0.1875 mol); batch time = 150 min. [c] Expt 3: HNO_3 = 1.59 M, 118 mL (0.1875 mol); batch time = 210 min. [d] Expt 4: HNO_3 = 4.77 M, 79 mL (0.377 mol); batch time = 85 min.

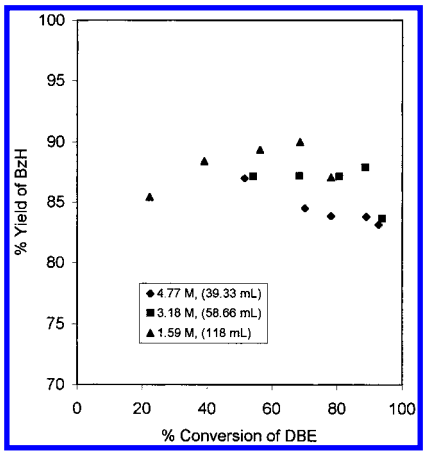

Figure 3. **Effect of HNO_3 concentration on the yield of BzH at constant mole ratio of the reactants. DBE = 0.15 mol; HNO_3 = 0.1875 mol; temperature = 90 °C; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm.**

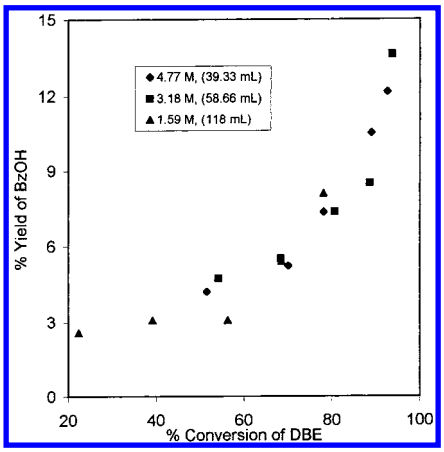

Figure 5. **Effect of HNO_3 concentration on the yield of BzOH at constant mole ratio of the reactants. DBE = 0.15 mol; HNO_3 = 0.1875 mol; temperature = 90 °C; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm.**

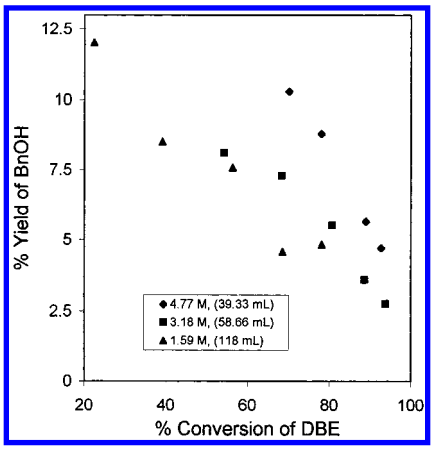

Figure 4. **Effect of HNO_3 concentration on the yield of BnOH at constant mole ratio of the reactants. DBE = 0.15 mol; HNO_3 = 0.1875 mol; temperature = 90 °C; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm.**

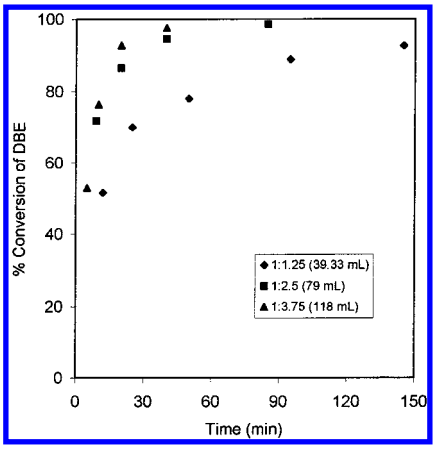

Figure 6. **Effect of mole ratio of reactants on the conversion of DBE. DBE = 0.15 mol; HNO_3 = 4.77 M; $NaNO_2$ = 1 g; temperature = 90 °C; speed of stirring = 2500 rpm.**

the reaction the yield of BnOH decreases and that of BzOH increases. Presence of BnOH in the final product may not be a serious problem as it can be recovered from the reaction mixture by fractional distillation and is a value-added product.

Material balance and consumption of nitric acid for different parameters has been presented in Table 1. Nitric acid concentration in case of experiment 3 is 0.5 M which indicates even at low nitric acid concentrations the reaction takes place.

3.3. Effect of Mole Ratio of the Reactants. DBE (0.15 mol, 28.6 mL) was treated with 4.77 M HNO_3 at 90 °C in the presence of 1 g of $NaNO_2$. The speed of stirring was 2500 rpm in each case. The volume of aqueous phase varied (viz. 39.33 mL, 79 mL, 118 mL) with change in the mole ratio of the reactants. Figure 6 shows conversion versus time plots for this set of the experiments. As DBE to HNO_3 mole ratio changes from 1:1.25 to 1:2.5 there is increase in the rate of consumption of DBE, but when mole ratio changes from 1:2.5 to 1:3.75, there is marginal increase in the rate of the reaction. At higher mole ratios, concentration of unreacted HNO_3 in the aqueous phase is higher, and as seen from Figure 6, this higher concentration increases the conversion of DBE under otherwise identical conditions.

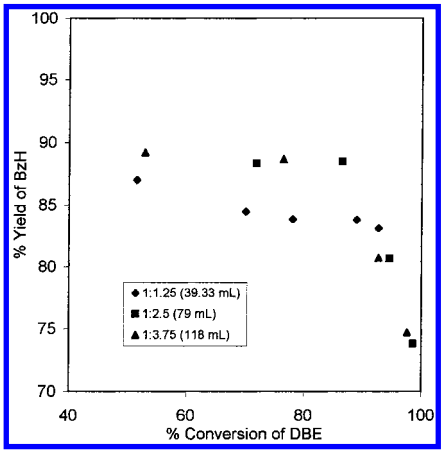

Figure 7. **Effect of mole ratio of reactants on the yield of BzH. DBE = 0.15 mol; HNO_3 = 4.77 M; $NaNO_2$ = 1 g; temperature = 90 °C; speed of stirring = 2500 rpm.**

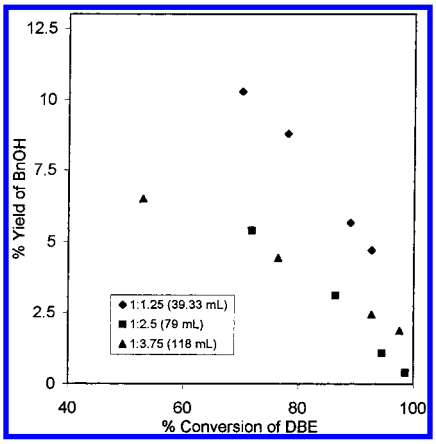

Figure 8. **Effect of mole ratio of reactants on the yield of BnOH. DBE = 0.15 mol; HNO_3 = 4.77 M; $NaNO_2$ = 1 g; temperature = 90 °C; speed of stirring = 2500 rpm.**

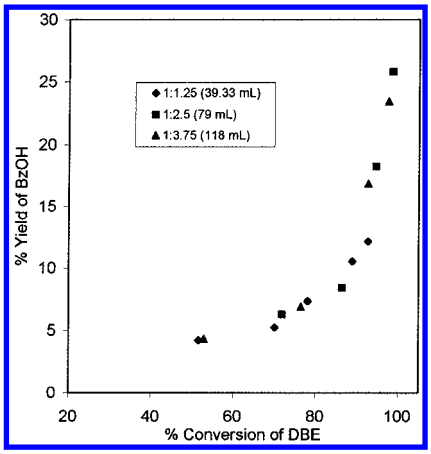

Figure 9. **Effect of mole ratio of reactants on the yield of BzOH. DBE = 0.15 mol; HNO_3 = 4.77 M; $NaNO_2$ = 1 g; temperature = 90 °C; speed of stirring = 2500 rpm.**

Figures 7−9 show variation of yield of BzH, BnOH, and BzOH, respectively, with respect to conversion of DBE. Figure 8 has again demonstrated that the yield of BnOH decreases as conversion of DBE increases. It is seen from Figures 7 and 9 that after about 90% conversion of DBE there is a rather sharp decrease in the yield of BzH and increase in the yield of BzOH particularly for mole ratios

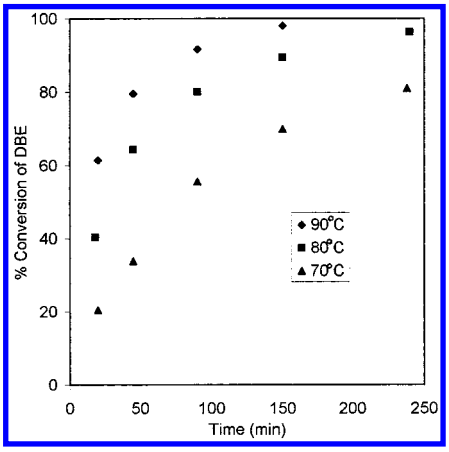

Figure 10. **Effect of temperature on the conversion of DBE. DBE = 0.15 mL; HNO_3 = 3.18 M, 79 mL; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm.**

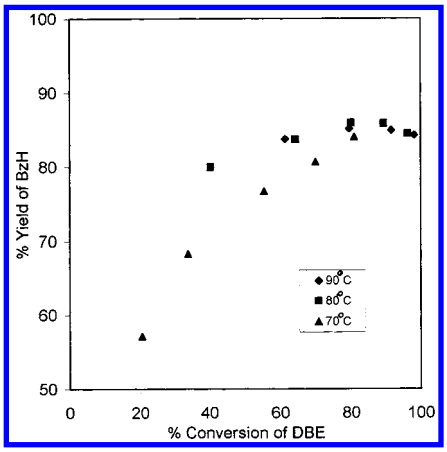

Figure 11. **Effect of temperature on the yield of BzH. DBE = 0.15 mL; HNO_3 = 3.18 M, 79 mL; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm.**

1:2.5 and 1:3.75. Even after 90% conversion of DBE, there is considerable amount of HNO_3 left in the aqueous phase, which is responsible for further oxidation of BzH to BzOH.

3.4. Effect of Temperature. As the temperature increases the rate of consumption of substrate increases. But with different energies of activations for different reactions, the change in the magnitude of the rate of reaction is not the same for all the reactions. The effect of temperature was mainly investigated to find out whether yield of BzH can be improved. DBE (0.15 mol) was treated with 79 mL of 3.18 M HNO_3 in the presence of 1 g of $NaNO_2$ at 2500 rpm. The results are presented in Figures 10−13. From Figure 10 it can be seen that increasing the temperature also increases the rate of reaction. Figures 12 and 13 also show that the yields of BnOH and BzOH do not change with temperature. Figure 11 shows the yield of BzH for different temperatures. In this set of experiments it is observed that yield of BzH remains practically constant even after 90% conversion of DBE. Figures 12 and 13 indicate that at higher conversions of DBE, the decrease in the yield BnOH corresponds to increase in the yield of BzOH indicating that rate of formation of BzH from BnOH almost equals the rate of oxidation of BzH to BzOH. Further independence of yields

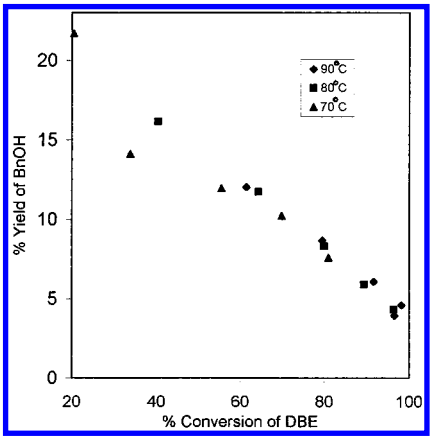

Figure 12. **Effect of temperature on the yield of BnOH. DBE = 0.15 mL; HNO_3 = 3.18 M, 79 mL; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm.**

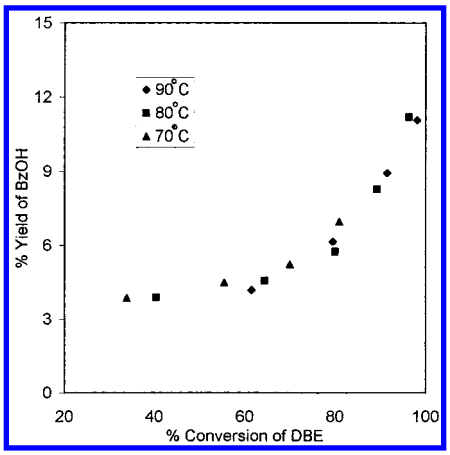

Figure 13. **Effect of temperature on the yield of BzOH. DBE = 0.15 mL; HNO_3 = 3.18 M, 79 mL; $NaNO_2$ = 1 g; speed of stirring = 2500 rpm.**

of all the products on temperature indicate identical activation energies for all the reactions.

3.5. Effect of Sodium Nitrite Concentration. When 0.15 mol DBE was treated with 118 mL, 1.59 M HNO_3 in the absence of $NaNO_2$ at 90 °C, the conversion of DBE was found to be less than 1.5% after 4 h. Previous experiments have shown that in the presence of sodium nitrite, substantial conversion (>80%) of DBE can be achieved. We decided to determine the effect of $NaNO_2$ concentration on the progress of reaction. 0.15 mol DBE was treated with 118 mL, 1.59 M HNO_3 at 90 °C at the stirring speed of 2500 rpm. Figure 14 shows conversion of DBE with time at sodium nitrite loading of 1, 0.5, and 0.1 g. As can be seen from the figure, the rate of consumption of DBE is independent of concentration of $NaNO_2$. Addition of $NaNO_2$ to HNO_3 produces nitrous acid, which is the species necessary for initiation of oxidation reaction.[8] Also it has been reported that nitrous acid formed simply acts an initiator and rate of oxidation is independent of its concentration.[8] The oxidation reaction does not proceed when urea is added to the reaction mixture which is a scavenger of nitrous acid.[8] Figures 15−17 show the effect of $NaNO_2$ concentration on the yield of BzH, BnOH, and BzOH, respectively. It may

(8) Ogata Y.; Sawaki Y.; Matsunaga F.; Tezuka H. *Tetrahedron* **1966**, *22*, 2655.

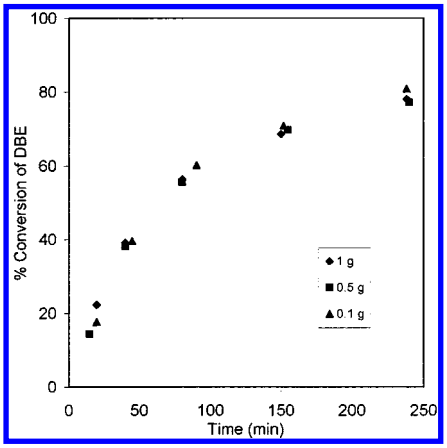

Figure 14. **Effect of $NaNO_2$ loading on the conversion of DBE. DBE = 0.15 mol; HNO_3 = 1.59 M, 118 mL; temperature = 90 °C; speed of stirring = 2500 rpm.**

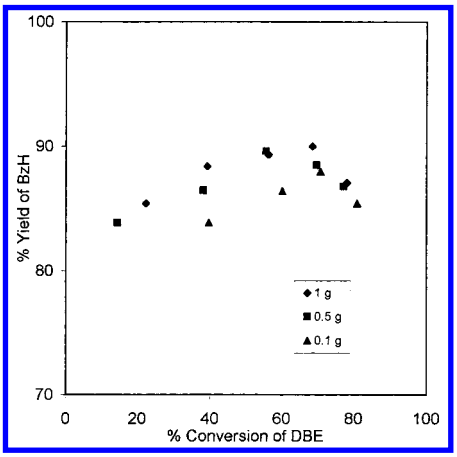

Figure 15. **Effect of $NaNO_2$ loading on the yield of BzH. DBE = 0.15 mol; HNO_3 = 1.59 M, 118 mL; temperature = 90 °C; speed of stirring = 2500 rpm.**

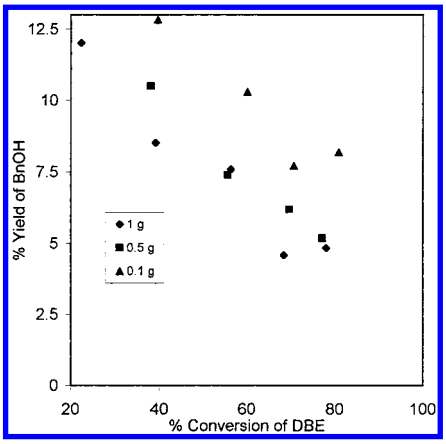

Figure 16. **Effect of $NaNO_2$ loading on the yield of BnOH. DBE = 0.15 mol; HNO_3 = 1.59 M, 118 mL; temperature = 90 °C; speed of stirring = 2500 rpm.**

be noted that for low sodium nitrite loading (0.1 g), although the conversion pattern is identical to that at higher concentrations, the yield of BnOH is higher, while yields of BzH and BzOH are somewhat lower.

3.6. Effect of Different Substrates. Symmetric chloro-substituted dibenzyl ethers were synthesized by the reaction of chlorobenzyl chlorides and corresponding chlorobenzyl

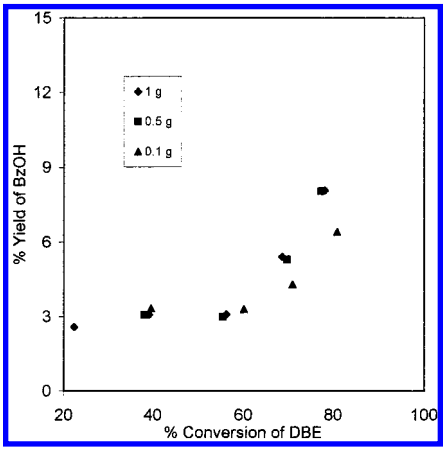

Figure 17. **Effect of $NaNO_2$ loading on the yield of BzOH. DBE = 0.15 mol; HNO_3 = 1.59 M, 118 mL; temperature = 90 °C; speed of stirring = 2500 rpm.**

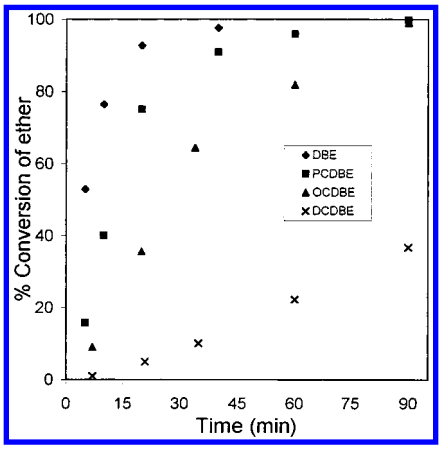

Figure 18. **Effect of different substrates on the conversion. Substrate = 0.15 mol; HNO_3 = 4.77 M, 118 mL; $NaNO_2$ = 1 g; temperature = 90 °C; speed of stirring = 2500 rpm.**

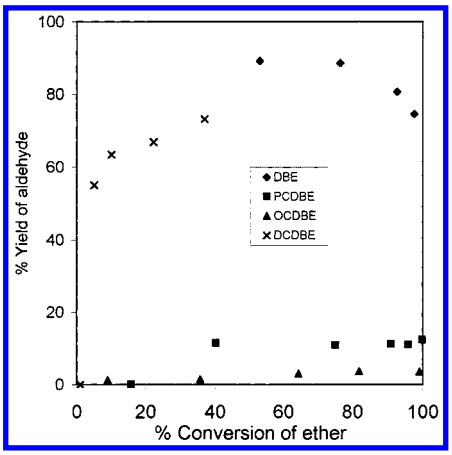

Figure 19. **Effect of different substrates on the yield of aldehyde. Substrate = 0.15mol; HNO_3 = 4.77 M, 118 mL; $NaNO_2$ = 1 g; temperature = 90 °C; speed of stirring = 2500 rpm.**

alcohols in the presence of concentrated NaOH and trialkylamine as the catalyst.[9] The ethers were purified by recrystallization. (4-clorobenzyl)$_2$O, (2-chlorobenzyl)$_2$O, and (2,4-dichlobenzyl)$_2$O are abbreviated as PCDBE and OCDBE, and DCDBE, respectively.

(9) Joshi S. R.; Sawant S. B. Forewarded for publication.

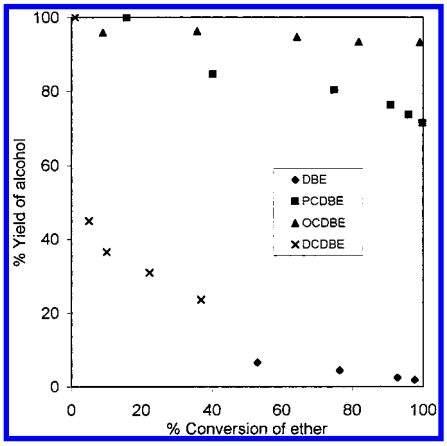

Figure 20. **Effect of different substrates on the yield of alcohols. Substrate = 0.15mol; HNO_3 = 4.77 M, 118 mL; $NaNO_2$ = 1 g; temperature = 90 °C; speed of stirring = 2500 rpm.**

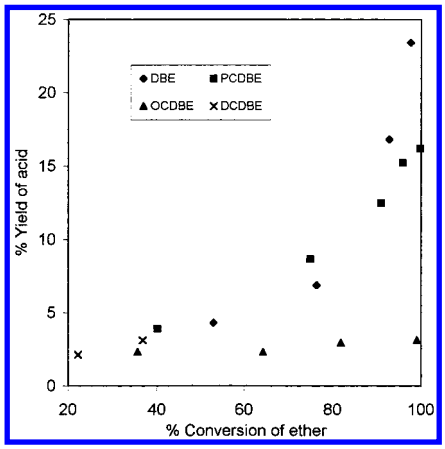

Figure 21. **Effect of different substrates on the yield of acid. Substrate = 0.15mol; HNO_3 = 4.77 M, 118 mL; $NaNO_2$ = 1 g; temperature = 90 °C; speed of stirring = 2500 rpm.**

To investigate the progress of reaction with different substrates, 0.15 mol of ethers, were treated with 118 mL, 4.77 M HNO_3 at 90 °C in the presence of 1 g of $NaNO_2$. Figure 18 shows conversions of different ethers with time. Figures 19−21 show yield of corresponding aldehydes, alcohols, and acids, respectively. It can be seen that in the case of PCDBE and OCDBE yield of corresponding alcohols is high. In case of DCDBE the overall reactivity towards oxidation is low.

4. Conclusions

(1) Successful synthesis of benzaldehyde from dibenzyl ether with nitric acid has been demonstrated. The reaction can be carried out even at low nitric acid concentration.

(2) As dibenzyl ether and dilute nitric acid are both byproducts, the current strategy is economically viable.

(3) Chloro-substituted dibenzyl ethers are rather difficult to oxidise to corresponding aldehydes with dilute nitric acid.

(4) Initial concentration of sodium nitrite does not affect the overall progress of the reaction.

(5) As the reaction can be carried out in the absence of any solvent, it enhances output per batch as well as eliminates the step of separation of solvent from the product.

Received for review July 31, 2000.
OP000085O