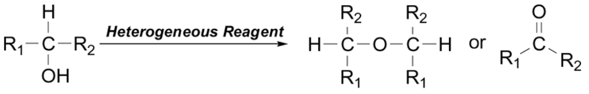
*Synthetic Communications*®, 41: 1544–1553, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.487982

# HIGHLY EFFICIENT ETHERIFICATION AND OXIDATION OF AROMATIC ALCOHOLS USING SUPPORTED AND UNSUPPORTED PHOSPHORUS PENTOXIDE AS A HETEROGENEOUS REAGENT

**Ardeshir Khazaei,[1] Mohammad Navid Soltani Rad,[2] Maryam Kiani Borazjani,[1] Shahnaz Saednia,[1] Mohammad Kiani Borazjani,[1] Maryam Golbaghi,[1] and Somayeh Behrouz[2]**
[1]*Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran*
[2]*Department of Chemistry, Faculty of Basic Sciences, Shiraz University of Technology, Shiraz, Iran*

## GRAPHICAL ABSTRACT



**$R_1$, $R_2$=aryl, H**
***Heterogeneous Reagent:$P_2O_5$ or $P_2O_5/SiO_2$ or $P_2O_5/Al_2O_3$***

**Abstract** *A highly efficient procedure for etherification and oxidation of aromatic alcohol is described using unsupported and supported $P_2O_5$ on alumina and/or silica gel. The silica gel and alumina proved to be the most suitable support among the supports examined in our experiments. It was illustrated that the etherification and oxidative performance in reactions depend largely upon variables including reaction temperature, the nature of the $P_2O_5$ used (supported or unsupported $P_2O_5$), and whether solvent-free conditions are applied. It was shown that $P_2O_5$ not only can convert the aromatic alcohols into corresponding ethers and/or aldehyde and ketone but also can convert aromatic ethers into aldehyde or ketone via oxidative cleavage. Finally, quantum mechanical calculations were performed to rationalized these events, and it was indicated that aldehyde and ketone are more favorable products on the basis of the heat of formation ($\Delta H_f$).*

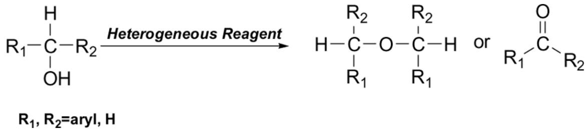
**Keywords** Alumina; aromatic alcohol; etherification; oxidation; $P_2O_5$; silica gel

## INTRODUCTION

The preparation of ethers is an important reaction in organic synthesis. A wide variety of procedures have been established for etherification during recent decades.[1]

Received February 16, 2010.

Address correspondence to Ardeshir Khazaei, Faculty of Chemistry, Bu-Ali Sina University, P.O. Box 651783868, Hamedan, Iran. E-mail: khazaei_1326@yahoo.com or Mohammad Navid Soltani Rad, Department of Chemistry, Faculty of Basic Sciences, Shiraz University of Technology, Shiraz 71555-313, Iran. E-mail: soltani@sutech.ac.ir, nsoltanirad@gmail.com



Scheme 1. Heterogeneous reagent: $P_2O_5$ or $P_2O_5/SiO_2$ or $P_2O_5/Al_2O_3$.

The most commonly used protocol is the Williamson ether synthesis,[2] which requires the initial transformation of alcohols into their corresponding halides or tosylates followed by their displacement with highly basic alkoxides or phenoxides. However, the strongly basic conditions used in the Williamson ether synthesis can damage complex molecules carrying base-sensitive functional groups. Thus, etherification by direct condensation of alcohols has been considered a useful alternative strategy that is conducted in the presence of catalytic amounts of organic or inorganic protic as well as Lewis acids.[3]

Phosphorus pentoxide (phosphoric anhydride) has many applications in various organic transformations that can be used as a dehydrating agent for the formation of anhydride from two molecules of an ordinary acid,[4] ketenimines from amides,[4] vinyl ethers from acetals,[4] nitriles from amides,[4] amides from oximes (Beckmann rearrangement),[5] phenolic esters from carboxylic acids,[6] and so on. Additionally, $P_2O_5$ can be used as an activator of DMSO in a Swern type of oxidation of alcohols, namely the Onodera reaction.[7]

$P_2O_5$ is an effective reagent for one-pot etherification of alcohols; however, to the best of our knowledge, there is no report for oxidation of aromatic alcohols via $P_2O_5$. Hence, in this context, we reported a mild and convenient procedure for one-pot etherification–oxidation of aromatic alcohols using supported and unsupported $P_2O_5$. $P_2O_5$ can be used as a both dehydrating and oxidizing agent for attaining benzhydryl ether, benzyl ether and aldehydes or ketones from corresponding aromatic alcohols at different reaction conditions (Scheme 1).

## RESULTS AND DISCUSSION

Initially, we decided to investigate the proper control reactions in the presence of different solid supports. To render these oxidations economically more viable and simpler, we studied the effect of supported $P_2O_5$ on $SiO_2$ and $Al_2O_3$. These mineral supports are nontoxic, widely available, inexpensive, and useful in straightforward workup procedures. Thus, the benzhydrol was used as a model compound, and the oxidative effect of various supported $P_2O_5$ was studied. The results are depicted in Table 1.

As data in Table 1 indicate, supported $P_2O_5$ on both $Al_2O_3$ and $SiO_2$ (Table 1, entries 1 and 2) afforded the best yields for benzophenone in shortest reaction times, whereas, other supported-$P_2O_5$ reagents were not efficient enough. Although ZnO (Table 1, entry 3) results in reasonable yields; however, technical problems were encountered, as it becomes pasty on mixing with $P_2O_5$. This drawback complicates the reaction as well as workup procedures. Therefore, $Al_2O_3$ and $SiO_2$ were the supports of choice in all our experiments. The impregnation of $P_2O_5$ on solid

**Table 1.** Reactivity trend of $P_2O_5$ (0.5 g, 35.2 mmol) on 0.5 g supports for the oxidation of benzhydrol (1 mmol) under solvent-free conditions

| Entry | Support | Time (min) | Temperature (°C) | Isolated yield (%) |
|---|---|---|---|---|
| 1 | $Al_2O_3$ | 120 | 90 | 97 |
| 2 | $SiO_2$ | 100 | 90 | 95 |
| 3 | $ZnO^a$ | 180 | 90 | 87 |
| 4 | $AlCl_3{}^a$ | 240 | 90 | 48 |
| 5 | $TiO_2$ | 240 | 90 | 59 |

[a] Tedious workup procedures.

supports is effective for oxidation, and we questioned the theory based on the premise that the oxidation rate enhancements are due to their impregnation on the solid supports.[4] In this case, we investigated the influence of various parameters on oxidation and etherification of benzhydrol. The results are indicated in Table 2.

As data in Table 2 indicate, the presence of $P_2O_5$ is critically essential because using support ($SiO_2$ and/or $Al_2O_3$) alone either at room temperature and/or higher temperature (90 °C) did not afford the any product after 12 h under solvent-free conditions (Table 2, entries 1–4). The reaction is achieved at room temperature in the absence of support in nonpolar *n*-hexane and in more polar diethylether (Table 2, entries 5 and 6). The benzhydryl ether was attained exclusively in both solvents; however, the reaction took longer and produced a lower yield with *n*-hexane. Changing

**Table 2.** Optimization of temperature and solvent-free and solvent-assisted conditions on etherification and oxidation of benzhydrol (1 mmol) with supported and unsupported $P_2O_5$

| Entry | Reagent | Temperature (°C) | Condition | Time (min) | Mixture color | Product | Isolated yield (%) [Ref.] |
|---|---|---|---|---|---|---|---|
| 1 | $SiO_2$ | rt | Solvent free | 720 | White | — | NR[b] |
| 2 | $Al_2O_3$ | rt | Solvent free | 720 | White | — | NR[b] |
| 3 | $SiO_2$ | 90 | Solvent free | 720 | White | — | NR[b] |
| 4 | $Al_2O_3$ | 90 | Solvent free | 720 | White | — | NR[b] |
| 5 | $P_2O_5$ (0.05 g) | rt | *n*-Hexane[a] | 210 | Orange | Benzhydryl ether | 75[8,9] |
| 6 | $P_2O_5$ (0.15 g) | rt | Diethylether[a] | 180 | Orange | Benzhydryl ether | 95[8,9] |
| 7 | $P_2O_5$ (0.05 g) | 60 | Solvent free | 17 | Orange | Benzhydryl ether | 98[8,9] |
| 8 | $P_2O_5$ (0.5 g) | 90 | Solvent free | 180 | Orange-Brown | Benzhydryl ether (20%) + Benzophenone (80%) | — |
| 9 | $P_2O_5$ (0.5 g)/ $SiO_2$ | 90 | Solvent free | 100 | Orange-Brown | Benzophenone | 95 |
| 10 | $P_2O_5$ (0.5 g)/ $Al_2O_3$ | 90 | Solvent free | 120 | Orange-Brown | Benzophenone | 97 |

[a] Anhydrous solvent.
[b] No reaction after 12 h.

the reaction conditions into solvent-free status using unsupported $P_2O_5$ at 60 °C afforded the benzhydryl ether in less reaction time and excellent yield (Table 2, entry 7). Interestingly, when similar reaction conditions were used at increased temperature up to 90 °C, a mixture of products consisting of benzophenone and benzhydryl ether were simultaneously obtained in 80% and 20% yields respectively. Surprisingly, using the silica- or alumina-supported $P_2O_5$ at 90 °C afforded the benzophenone exclusively in excellent yields (Table 2, entries 9 and 10).

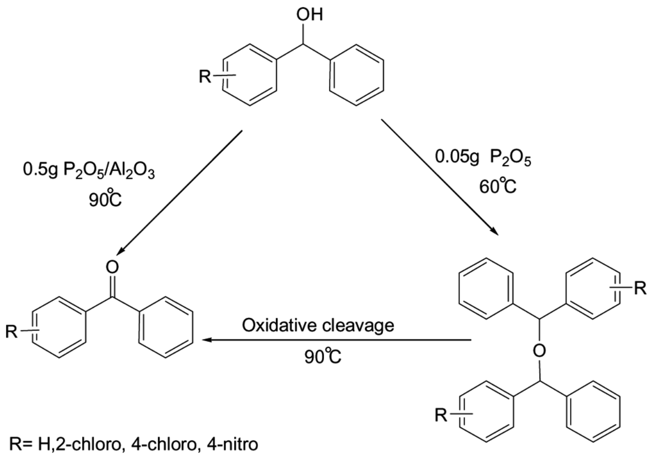
The schematic detail of the reaction is shown in Scheme 2.

To realize the versatility as well as generality of this method, we extended the optimized conditions for other benzhydrol derivatives to study the products in these derivatives. Thus, the effects of unsupported $P_2O_5$, $P_2O_5$-$Al_2O_3$, and $P_2O_5$-$SiO_2$ were investigated on 2- and 4-chlorobenzhydrol as well as 4-nitrobenzhydrol. The results are shown in Table 3.

As shown in Table 3, in general the same results were attained as in Table 2 with the exception that 4-nitrobenzhydrol merely afforded the corresponding ether at 60 °C in the presence of supported and unsupported $P_2O_5$ (Table 3, entries 7–9) while increment the temperature up to 90 °C changed the product into 4-nitrobenzophenone (Table 3, entries 10 and 11).

Encouraged by the results obtained for benzhydrol and its derivatives, we decided to study the effect of supported and unsupported $P_2O_5$ on etherification and potential oxidation of benzyl alcohols. Hence, we employed the same conditions as for benzhydrol. The results are presented in Table 4.

We studied the etherification and oxidation of 4-chlorobenzyl alcohol via supported and unsupported $P_2O_5$ as a control reaction. As can be seen in Table 4, various conditions were employed for etherification and oxidation of 4-chlorobenzyl alcohol. Using unsupported $P_2O_5$ either at room temperature or 90 °C afforded the corresponding ether in good yields (Table 4, entries 1 and 2). Furthermore, using anhydrous diethylether as a solvent at room temperature also afforded the good yield of ether, but the reaction time was long (Table 4, entry 3). Using



**Scheme 2.** Conversion of benzhydrol to benzhydryl ether and benzophenone using $P_2O_5$ under solvent-free conditions.

**Table 3.** Etherification and oxidation of benzhydrols (1 mmol) with supported and unsupported $P_2O_5$ under solvent-free condition

| Entry | Reagent | Alcohol | Temperature (°C) | Mixture color | Time (min) | Product | Isolated yield (%) [Ref.] |
|---|---|---|---|---|---|---|---|
| 1 | $P_2O_5$ (0.07 g) | 2-Cholorobenzhydrol | 60 | Yellow-orange | 15 | Ether | 93[8] |
| 2 | $P_2O_5$ (0.5 g)/ $SiO_2$ | 2-Cholorobenzhydrol | 90 | Yellow-orange | 15 | Ketone | 87 |
| 3 | $P_2O_5$ (0.5 g)/ $Al_2O_3$ | 2-Cholorobenzhydrol | 90 | Yellow-orange | 20 | Ketone | 88 |
| 4 | $P_2O_5$ (0.07 g) | 4-Cholorobenzhydrol | 60 | Brown | 15 | Ether | 95[8] |
| 5 | $P_2O_5$ (0.5 g)/ $SiO_2$ | 4-Cholorobenzhydrol | 90 | Brown | 15 | Ketone | 90 |
| 6 | $P_2O_5$ (0.5 g)/ $Al_2O_3$ | 4-Cholorobenzhydrol | 90 | Brown | 20 | Ketone | 93 |
| 7 | $P_2O_5$ (0.07 g) | 4-Nitrobenzhydrol | 60 | Brown | 20 | Ether | 90[8] |
| 8 | $P_2O_5$ (0.5 g)/ $SiO_2$ | 4-Nitrobenzhydrol | 60 | Brown | 15 | Ether | 88[8] |
| 9 | $P_2O_5$ (0.5 g)/ $Al_2O_3$ | 4-Nitrobenzhydrol | 60 | Brown | 20 | Ether | 90[8] |
| 10 | $P_2O_5$ (0.5 g)/ $SiO_2$ | 4-Nitrobenzhydrol | 90 | Brown | 15 | Ketone | 90 |
| 11 | $P_2O_5$ (0.5 g)/ $Al_2O_3$ | 4-Nitrobenzhydrol | 90 | Brown | 20 | Ketone | 92 |

**Table 4.** Effect of temperature, solvent, and supported and unsupported $P_2O_5$ on conversion of 4-cholorobenzylalcohol (1 mmol) into corresponding ether and aldehyde

| Entry | Reagent | Temperature (°C) | Condition | Time (min) | Mixture color | Product | Isolated yield (%) [Ref.] |
|---|---|---|---|---|---|---|---|
| 1 | $P_2O_5$ (0.5 g) | 90 | Solvent free | 15 | Grey | Ether | 70[10] |
| 2 | $P_2O_5$ (0.5 g) | rt | Solvent free | 35 | Grey | Ether | 70[10] |
| 3 | $P_2O_5$ (0.5 g) | rt | Diethylether$^a$ | 60 | Grey | Ether | 75[10] |
| 4 | $P_2O_5$ (0.5 g)/ $SiO_2$ | 60 | Solvent free | 40 | Grey | Ether | 87[10] |
| 5 | $P_2O_5$ (0.5 g)/ $Al_2O_3$ | 60 | Solvent free | 50 | Grey | Ether | 88[10] |
| 6 | $P_2O_5$ (0.5 g)/ $SiO_2$ | rt | Diethylether$^a$ | 270 | Grey | Ether (65%) + aldehyde (35%) | — |
| 7 | $P_2O_5$ (0.5 g)/ $Al_2O_3$ | rt | Diethylether$^a$ | 300 | Grey | Ether (65%) + aldehyde (35%) | — |
| 8 | $P_2O_5$ (0.5 g)/ $SiO_2$ | 120 | Solvent free | 50 | Grey | Aldehyde | 88 |
| 9 | $P_2O_5$ (0.5 g)/$Al_2O_3$ | 120 | Solvent free | 65 | Grey | Aldehyde | 88 |

$^a$Anhydrous Solvent.

Table 5. Effect of temperature, and solvent and supported $P_2O_5$ on conversion of 4-nitrobenzylalcohol (1 mmol) into 4-nitrobenzyaldehyde

| Entry | Reagent | Temperature (°C) | Condition | Time (min) | Mixture color | Product | Isolated yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | $P_2O_5$ | 60 | Solvent free | 240 | Yellow | — | NR[a] |
| 2 | $P_2O_5$ (0.5 g)/$SiO_2$ | 60 | Solvent free | 240 | Yellow | — | NR[a] |
| 3 | $P_2O_5$ (0.5 g)/$Al_2O_3$ | 60 | Solvent free | 250 | Yellow | — | NR[a] |
| 4 | $P_2O_5$ (0.5 g)/$SiO_2$ | rt | Dry diethylether | 270 | Brown | Aldehyde | 20 |
| 5 | $P_2O_5$ (0.5 g)/$Al_2O_3$ | rt | Dry diethylether | 290 | Brown | Aldehyde | 30 |
| 6 | $P_2O_5$ (0.5 g)/$SiO_2$ | 120 | Solvent free | 60 | Brown | Aldehyde | 94 |
| 7 | $P_2O_5$ (0.5 g)/$Al_2O_3$ | 120 | Solvent free | 65 | Brown | Aldehyde | 92 |

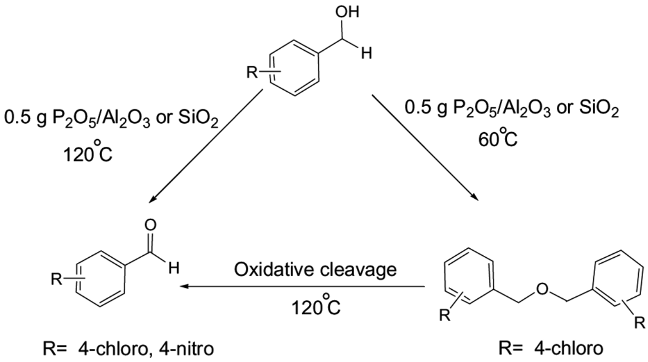
[a] No Reaction.

$P_2O_5$-$Al_2O_3$ and/or $P_2O_5$-$SiO_2$ merely provided the ether in excellent yields at 60 °C (Table 4, entries 4 and 5) while using these supports in anhydrous $Et_2O$ at room temperature led to a mixture of corresponding ether and aldehyde in 65% and 35% yields respectively (Table 4, entries 6 and 7). However, the increment in temperature up to 120 °C shifted the product into 4-chlorobenzaldehyde in excellent yields (Table 4, entries 8 and 9).

The optimized reaction conditions were also applied for the conversion of 4-nitrobenzylalcohol into products (Table 5); however, all of our attempts for synthesis of corresponding ether failed (Table 5, entries 1–3). Nevertheless, using silica- or alumina-supported $P_2O_5$ and increasing the temperature up to 120 °C remarkably enhanced the formation of 4-nitrobenzaldehyde from 4-nitrobenzylalcohols (Table 5, entries 6 and 7). Additionally, using silica- or alumina-supported $P_2O_5$ in anhydrous $Et_2O$ at room temperature exclusively provided 4-nitrobenzaldehyde in low yields (Table 5, entries 4 and 5).

The schematic detail of the reaction is shown in Scheme 3.

The reusability of both reagents on oxidation of benzhydrol into benzophenone was studied at 90 °C under solvent-free conditions for five successive runs. In



**Scheme 3.** Conversion of benzyl alcohol to benzyl ether and benzaldehyde using $P_2O_5$ under solvent-free conditions.

each run, the reaction was stopped after 120 min, cooled, and suspended in anhydrous $CH_2Cl_2$, the suspension was then filtered, and the reagent was washed with anhydrous $CH_2Cl_2$ (2 × 50 mL). The reagents allowed to be dried in vacuum oven (50 °C, 15 min) and immediately were used for the subsequent run. The results are depicted in Table 6. As Table 6 indicates, because of the strongly hygroscopic nature of both reagents, their reactivity remarkably decreased after the first run. This is due to the ready conversion of $P_2O_5$ into phosphoric acids upon absorption of water from reactants and the environment.

One of the interesting events that we observed in our experiments is the oxidative cleavage of benzhydryl as well as benzyl ether derivatives into their corresponding ketones and aldehydes accordingly (Schemes 2 and 3).

As is shown in Scheme 2, the benzohydol derivatives were primarily converted to their corresponding benzhydryl ethers using unsupported $P_2O_5$ at 60 °C under solvent-free condition. However, elevating the reaction temperature up to 90 °C readily converted the benzhydrol ethers into benzophenone derivatives.

In the same circumstance, as Scheme 3 indicates, supported $P_2O_5$ at 60 °C converted the benzyl alcohols into benzyl ethers; nevertheless, the increase in temperature up to 120 °C converted the benzyl ethers to corresponding benzaldehydes.

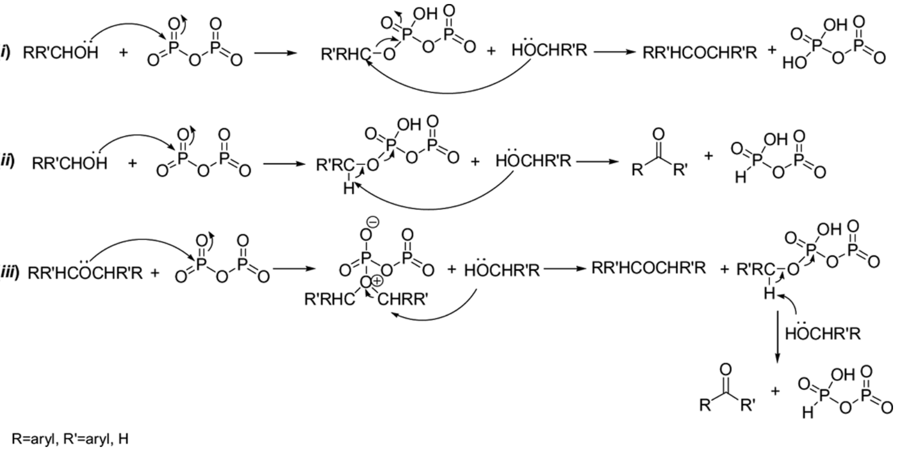
Which potential factors influence oxidative cleavage of aromatic ethers is an interesting question. We thought that the atmospheric oxygen may be responsible for such an oxidative cleavage. Therefore, we conducted the reaction under inert argon or nitrogen atmosphere, but surprisingly we witnessed again the oxidative cleavage of aromatic ethers into aldehydes or ketones. Interestingly, using $P_2O_5$ either in supported or unsupported form has no effect on oxidative cleavage of aromatic ether to aldehyde and ketone at higher temperature. Thus, we supposed that $P_2O_5$ could be the reason. Water abstraction via $P_2O_5$ can occur from a single alcohol or double alcohols, which results in aldehyde or ketone and also ether accordingly. As matter of fact, $P_2O_5$ played three different roles as a powerful dehydrating agent in our experiment. A tentative mechanism showing the three functions of $P_2O_5$ in our study is presented in Scheme 4.

The first reaction (i) expresses the route by which the etherification is achieved via dehydration using $P_2O_5$. The second reaction (ii) is the oxidative route, which can occur via the dehydration from single alcohol, and the third reaction (iii) is a potential oxidative route for cleavage of the aromatic ether into aldehyde or ketone. To rationalize the oxidative cleavage of aromatic ether into aldehyde and ketone, we employed the semi-empirical mechanical quantum calculations. The semi-empirical

**Table 6.** Reactivity study of recycled $P_2O_5$-$SiO_2$ and $P_2O_5$-$Al_2O_3$ on conversion of benzhydrol into benzophenone under solvent-free condition after 120 min

| Run | Temperature (°C) | Yield (%)[a] ($P_2O_5$-$SiO_2$) | Yield (%)[a] ($P_2O_5$-$Al_2O_3$) |
|---|---|---|---|
| 1 | 90 | 95 | 97 |
| 2 | 90 | 62 | 53 |
| 3 | 90 | 48 | 35 |
| 4 | 90 | 31 | 26 |
| 5 | 90 | 22 | 15 |

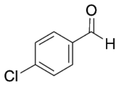
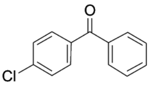
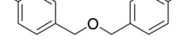
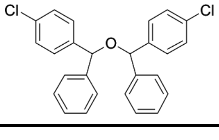
[a] Isolated yield.



Scheme 4. A tentative mechanism showing the three functions of $P_2O_5$.

Austin model 1 (AM1) and parameterized model 3 (PM3) calculations were run on MOPAC in CS Chem 3D Ultra 8 (2004 Cambridge Soft) and Hyperchem (Hypercube Inc., version 7). The heat of formation or $\Delta H_f$ is a criterion to estimate the stability of molecules in comparison with a molecule. The molecule that has a lower $\Delta H_f$ value has more stability in comparison with related molecules and thus thermodynamically is more prone to be produced. Therefore, $\Delta H_f$ values were calculated for 4-chloro benzaldehyde, 4-chlorobenzophenone, 4-chlorobenzylether, and 4-chlorobenzhydryl ether using both PM3 and AM1 semi-empirical calculations. The results are depicted in Table 7.

**Table 7.** Comparison of $\Delta H_f$ values attained from PM3 and AM1 calculations for oxidative–etherification products of 4-chlorobenzaldehyde and 4-chlorobenzhydrol

| | | Heat of formation ($\Delta H_f$) (Kcal/mol) | |
|---|---|---|---|
| Entry | Structure | PM3 | AM1 |
| 1 |  | −17.27 | −15.81 |
| 2 |  | 10.62 | 13.33 |
| 3 |  | −1.17 | −8.86 |
| 4 |  | 59.27 | 56.20 |

As shown in Table 7, both aldehyde and ketone (Table 7, entries 1 and 2) have lower $\Delta H_f$ values in comparison with their corresponding ethers, and these results indicate that there should be a greater tendency for formation of aldehyde and ketone rather than their corresponding ethers. As the results in Tables 2–5 also indicate, formation of corresponding ethers was observed predominantly in the early stages of reaction while increasing the temperature and prolonging the reaction time shifted the products to aldehydes and ketones. It seems that formation of ethers is controlled by kinetic factors while synthesis of aldehydes and/or ketones is controlled by thermodynamic factors. Furthermore, it is rationalized as well that the conjugation via carbonyl bond in aldehyde and ketone can be considered as a driving force for synthesis of aldehyde and ketone at higher temperature using supported and unsupported $P_2O_5$. Additionally, it is observed that benzhydrol ether derivatives are more prone to oxidative cleavage via $P_2O_5$ rather than benzyl ethers. Both experimental observations and calculations (Table 7, entries 3 and 4) confirmed this fact.

## CONCLUSIONS

In summary, a highly efficient procedure has been established for etherification and oxidation of aromatic alcohols using supported or unsupported $P_2O_5$ under solvent-free conditions. It was shown that the reaction trends toward etherification and oxidation of aromatic alcohols are dependent upon various factors including temperature, support, and solvent or solvent-free conditions. Furthermore, semiempirical quantum mechanical calculations have been achieved that confirmed the propensity of reaction toward the synthesis aldehydes and ketones as oxidative products.

## EXPERIMENTAL

All products were characterized by comparison of their physical and spectral data (mp, $^1H$ NMR, and IR) with those of authentic samples.

### Preparation of Supported $P_2O_5$ on Alumina or Silica Gel [50% (W/W)]

$P_2O_5$ (5 g, 35 mmol) was added to anhydrous alumina (5 g, 50 mmol) (neutral, 0.063–0.200 mm) or anhydrous silica gel (5 g, 83 mmol) (0.040–0.063 mm), which was previously dried and kept at 120 °C for 24 h in vacuum oven, and mixed. The obtained white solid was corked and stored at room temperature in vacuum-desiccator flask for subsequent use.

### General Procedure for Etherification or Oxidation of Aromatic Alcohols Using Supported $P_2O_5$ on Alumina or Silica Gel

Supported $P_2O_5$ on alumina or silica gel (0.67 g, 50%w/w) was added to an aromatic alcohol (2 mmol). The mixture was kept at an appropriate temperature (see Tables 2–5). When thin-layer chromatography (TLC) monitoring indicated no further progress in reaction, then the reaction was stopped, cooled, and diluted with anhydrous $Et_2O$ (100 mL). The $Et_2O$ solution was dried on anhydrous $Na_2SO_4$ and filtered, and the filterate was evaporated to give an almost pure product.

## ACKNOWLEDGMENT

The authors acknowledge to Bu-Ali Sina University Research Council and Center of Excellence in Development of Chemical Methods (CEDCM) for support of this work.

## REFERENCES

1. March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: Singapore, 2005.
2. Smith, K. (Ed). *Solid Supports and Catalysts in Organic Synthesis*; Prentice Hall: New York, 1992.
3. Clark, K. J. H. (Ed). *Catalysis of Organic Supported Inorganic Reagents*; VCH: New York, 1994; p. 38.
4. March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985; p. 904.
5. Eaton, C. L. Phosphorus pentoxide–methanesulfonic acid: Convenient alternative to polyphosphoric acid. *J. Org. Chem.* **1973**, *38*, 4071.
6. Eshghi, H.; Rafei, M.; Karimi, M. H. $P_2O_5/SiO_2$ as an efficient reagent for esterification of phenols in dry media. *Synth. Commun.* **2001**, *31*, 771.
7. Tidwell, T. T. Dimethyl sulfoxide–phosphorus pentoxide. In *Encyclopedia of Reagents for Organic Synthesis*; L. Paquette, (Ed.), John Wiley & Sons: New York, 2004.
8. Toda, F.; Takumi, H.; Akehi, M. Efficient solid-state reactions of alcohols: Dehydration, rearrangement, and substitution. *J. Chem. Soc., Chem. Commun.* **1990**, 1270.
9. Namboodiri, V. V.; Polshettiwar, V.; Varma, R. S. Expeditious oxidation of alcohols to carbonyl compounds using iron(III) nitrate. *Tetrahedron Lett.* **2007**, *48*, 8839.
10. Firouzabadi, H.; Iranpoor, N.; Jafari, A. A. Facile preparation of symmetrical and unsymmetrical ethers from their corresponding alcohols catalyzed by aluminumdodecatangstophosphate ($AlPW_{12}O_{40}$), as a versatile and a highly water-tolerant Lewis acid. *J. Mol. Catal. A, Chem.* **2005**, *227*, 97.