

Facile and Efficient Pinacol Rearrangement Using Tungstophosphoric Acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) under Solvent-free Conditions

M. Yahyae, E. Kianmehr,* C. Foroutan-nejad, and S. Beheshti

*School of Chemistry, College of Science, University of Tehran, Tehran, Iran. *E-mail: kianmehr@khayam.ut.ac.ir*

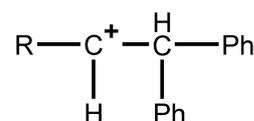
Received May 22, 2006

Key Words : Pinacol rearrangement, Tungstophosphoric acid, Tungstosilicic acid, Solvent-free

The pinacol-pinacolone rearrangement is a typical 1,2-rearrangement reaction of vicinal diols under acidic conditions^{1,2} which has been known since 1960.³ This rearrangement involving a dehydration and skeletal rearrangement is one of the earliest documented Wagner-Meerwein rearrangements in carbocation chemistry and has been used as a key step in organic synthesis.^{4,5} The intermediate cations are usually generated under Lewis or Bronsted acid conditions which often result in regioisomeric mixtures of ketones and aldehydes when unsymmetrical diols are used. Regioselectivity is determined by stability of the primary formed carbocation as well as migratory aptitude of the diol substituents which in turn are predicted by stereoelectronic factors. Because of the influence of these factors, it has not been possible to determine an unambiguous migratory order for substituents in the pinacol rearrangement. However, some general trends are discernible. Various studies on the relative migratory aptitudes in the pinacol rearrangement have been conducted.^{6,7} In general, the relative migratory tendency of aryl > alkenyl > hydride > alkyl is observed.

Organic reactions are found to occur efficiently under solvent-free conditions and many examples have been reported so far.⁸⁻²⁷ Heteropoly acids are the object of research for a long time. Much work has been done and there are several commercial processes utilizing heteropoly compounds.²⁸ In this work we report the usage of heteropoly acids such as tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) as solid acid for pinacol rearrangement. It is a commercially available and cheap crystalline compound. Also, it is easy to handle and in comparison to the results obtained by carrying out the reaction using other acids,²⁹ the reaction using tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) proceeds more efficiently under much milder conditions during a shorter reaction time. When a mixture of 1 : 3 molar ratio of diol and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ are ground at room temperature the products of rearrangement are obtained in high yield. Similar results are obtained by tungstosilicic acid but the conversion percents are lower and leads to formation of some byproducts.

Heteropoly acids as solid acids in Pinacol rearrangement affects the migratory aptitude of groups as well as conversions and facility of the reaction process.³⁰ As the results of Table 1 show the aryl anions migrate more easily than hydride does. Diol **1** led to aldehyde **1a**, exclusively, which results from para-methoxyphenyl migration and the product of hydride migration was not obtained under the reaction



4c

Scheme 1

condition. Diol **4** led to rearrangement products, aldehyde **4a** and ketone **4b**, which are obtained in ratio of 1:2.1 by para-methoxyphenyl and phenyl migrations, respectively. As it can be seen again no hydride migration is observed under the reaction condition. In the case of **4** because of the greater resonance stabilization of the carbonium ion (**4c**, Scheme 1), caused by methoxy group, gives mainly the thermodynamically controlled product **4b**.

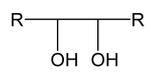
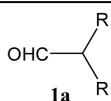
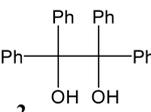
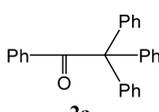
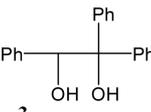
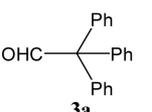
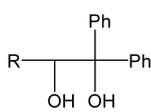
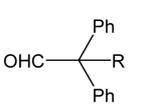
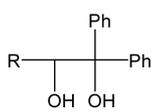
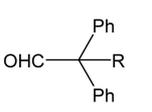
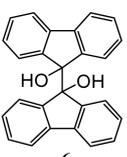
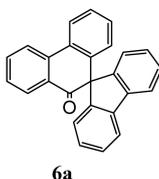
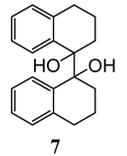
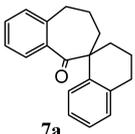
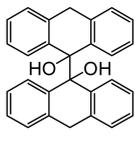
Therefore, the reaction of **4** is accelerated because of the greater stability of the carbocationic intermediate. Pinacol **5** is rearranged to aldehyde **5a** and ketone **5b** in the ratio of 1:0.5 which are obtained by paramethylphenyl and phenyl migrations, respectively. In the case of **5** the carbocation adjacent to the two phenyl groups is more stable and the reaction led to thermodynamically controlled product **5a**. Diol **3** led to aldehyde **3a** and ketone **3b** in the ratio of 1:0.37. Aldehyde **3a** is obtained by phenyl migration and ketone **3b** may be obtained by phenyl and/or hydride migration. However, we have no evidence to show that if phenyl or hydride migration has occurred to produce ketone **3b** but if we compare this reaction with entries **4** and **5**, we may anticipate that the ketone is obtained by phenyl migration and the reaction is thermodynamically controlled. The same trend was observed for rearrangement of **6** which led to **6a** in 95% yield. Anthrapinacol **8** gave bianthryl as a dehydration product under the reaction condition.

In summary we have shown that pinacol rearrangement is easily carried out by tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) under solvent-free conditions. Aryl groups migrate more easily than hydride does and the reaction is thermodynamically controlled.

Experimental Section

General procedure. A mixture of pinacol compound (200 mg, 1.0 eq) and tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) (3.0 eq) was thoroughly ground in an agate mortar for a few minutes.

Table 1. Rearrangement of Pinacols to the corresponding products. All the reactions were carried out at room temperature

Entry	Pinacol	Product (s) ^a	Time (min)	Yield (%)
1	 1 , R= <i>p</i> -MeOC ₆ H ₄	 1a	10	93
2	 2	 2a	10	91
3	 3	 3a	10	69,26
4	 4 , R= <i>p</i> -MeOC ₆ H ₄	 4a	10	31,66
5	 5 , R= <i>p</i> -MeC ₆ H ₄	 5a	10	58,29
6	 6	 6a	5	95
7	 7	 7a	10	69
8	 8	 8a	5	91

^aAll the products are known compounds and characterized by physical and spectral analysis.

The reaction mixture was worked up by adding H₂SO₄ (2 N) and extracting by dichloromethane. The organic layer was dried over Na₂SO₄ and solvent was removed in vacuo. The resulting products were purified by column chromatography on silicagel (Merck, 100-200 mesh, ethylacetate-hexane, 1 : 9) to afford pure products. Starting materials (Pinacols) were prepared by Toda³¹ and Khurana³² methods.

Acknowledgement. Financial support of the research council of Tehran University is kindly appreciated.

References

- Mayo, P. *Rearrangement in Ground and Excited States*; Academic Press: New York, 1980; Vol. 1.
- Isaacs, N. S. *Reaction Intermediates in Organic Chemistry*; Wiley: New York, 1974.
- Berson, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4655.
- Pettit, G. R.; Lippert, J. W., III; Herald, D. L. *J. Org. Chem.* **2000**, *65*, 7438.
- Gasparski, P. M.; Herrinton, P. M.; Overman, L. E.; Wolfe, J. P. *Tetrahedron Lett.* **2000**, *41*, 9431.
- Tiffen, M.; Orekhoff, A. *Bull. Soc. Chim. Fr.* **1924**, *35*, 1639.

7. House, H. O.; Grubbs, E. J. *J. Am. Chem. Soc.* **1959**, *81*, 4733.
 8. Herreras, C. I.; Zhang, T. Y.; Li, C. J. *Tetrahedron Lett.* **2006**, *47*, 13.
 9. Jia, C. S.; Zhang, Z.; Tu, S. J.; Wang, G. W. *Org. Biomol. Chem.* **2006**, *4*, 104.
 10. Placzek, A. T.; Donelson, J. L.; Trivedi, R.; Gibbs, R. A.; De, S. K. *Tetrahedron Lett.* **2005**, *46*, 9029.
 11. Petersson, A. E. V.; Gustafsson, L. M.; Nordblad, M.; Borjesson, P.; Mattiasson, B.; Adlercreutz, P. *Green Chem.* **2005**, *7*, 837.
 12. Bougrin, K.; Loupy, A.; Soufiaoui, M. *J. Photochem. Photobiol. Rev.* **2005**, *6*, 139.
 13. Shirini, F.; Zolfigol, M. A.; Mohammadpoor-Baltork, I.; Abedidni, M. *Bull. Korean Chem. Soc.* **2005**, *26*, 1833.
 14. Bandgar, B. P.; Patil, A. V. *Tetrahedron Lett.* **2005**, *46*, 7627.
 15. Guillot, R.; Loupy, A.; Meddour, A.; Pellet, M.; Petit, A. *Tetrahedron* **2005**, *61*, 101, 29.
 16. Lin, Q.; Zhang, Y. M.; Wei, T. B.; Wang, H. *J. Chem. Res. (S)* **2004**, 298.
 17. Kimmich, B. F. M.; Fagan, P. J.; Hauptman, E.; Marshall, W. J.; Bullock, R. M. *Organometallics* **2005**, *24*, 6220.
 18. Hajipour, A. R.; Bagheri, H. R.; Ruoho, A. E. *Bull. Korean Chem. Soc.* **2004**, *25*, 1238.
 19. Jeon, S. J.; Li, H. M.; Walsh, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 16416.
 20. Besra, R. C.; Rudrawar, S.; Chakraborti, A. K. *Tetrahedron Lett.* **2005**, *46*, 6213.
 21. Ballini, R.; Bosica, G.; Fiorini, D.; Palmieri, A. *Green Chem.* **2005**, *7*, 825.
 22. Taguchi, K.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **2005**, *46*, 4539.
 23. Shirini, F.; Zolfigol, M. A.; Mohammadi, K. *Bull. Korean Chem. Soc.* **2004**, *25*, 325.
 24. Zolfigol, M. A.; Mirjalili, B. F.; Bamoniri, A.; Karimi Zarchi, M. A. *Bull. Korean Chem. Soc.* **2004**, *25*, 1414.
 25. Shirini, F.; Zolfigol, M. A.; Khaleghi, M. *Bull. Korean Chem. Soc.* **2003**, *24*, 1021.
 26. Kidwai, M.; Rastogi, S.; Saxena, S. *Bull. Korean Chem. Soc.* **2003**, *24*, 1575.
 27. Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A. *Bull. Korean Chem. Soc.* **2001**, *45*, 546.
 28. Mizuno, T. N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113.
 29. Martinelli, M. J.; Khau, V. V.; Horcher, L. M. *J. Org. Chem.* **1993**, *58*, 5546.
 30. Rashidi-Ranjbar, P.; Kianmehr, E. *Molecules* **2001**, *6*, 442.
 31. Toda, F.; Tanaka, K.; Kishigama, S. *J. Org. Chem.* **1990**, *55*, 2981.
 32. Khurana, J. M.; Sehgal, A. *J. Chem. Soc., Chem. Commun.* **1994**, 571.
-