

Facile and Fast Pinacol Rearrangement by AlCl_3 in the Solid State

Parviz Rashidi-Ranjbar* and Ebrahim Kianmehr

Department of Chemistry Tehran University, Box 14155-6455, Tehran, Iran. Tel. (+98)-021-6113301, Fax (+98)-021-6405141.

* Author to whom correspondence should be addressed; e-mail Ranjbar@khayam.ut.ac.ir

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Abstract: A facile and efficient synthetic procedure for effecting the pinacol rearrangement catalyzed by AlCl_3 in the absence of solvent is developed. The rearrangement product is obtained at room temperature in a few minutes and in almost quantitative yield. Benzylic pinacols rearrange under these conditions, while aliphatic pinacols do not react.

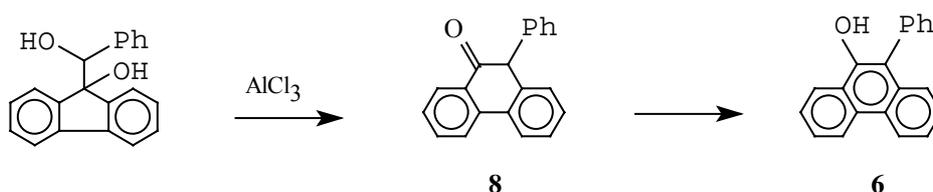
Keywords: Pinacol rearrangement, Solid state reactions, AlCl_3 , Lewis acid

Introduction

Organic reactions are found to occur efficiently in the solid state and many examples have been reported so far [1-5]. The pinacol rearrangement is usually carried out under drastic conditions, like heating in H_2SO_4 . Toda found that the reaction proceeds faster and more selectively in the solid state by using organic acids like $\text{CCl}_3\text{CO}_2\text{H}$ and p-TsOH [6]. It is possible to use a strong Lewis acid for the pinacol rearrangement and to the best of our knowledge, there has been no report on pinacol rearrangement by using a Lewis acid like AlCl_3 . This reagent has previously been used for Friedel-Crafts alkylation and acylation in the solid state [7] and also in Beckman rearrangements [8] under similar conditions. The novel utility of aluminium chloride as an efficient reagent for pinacol rearrangement is reported in this paper.

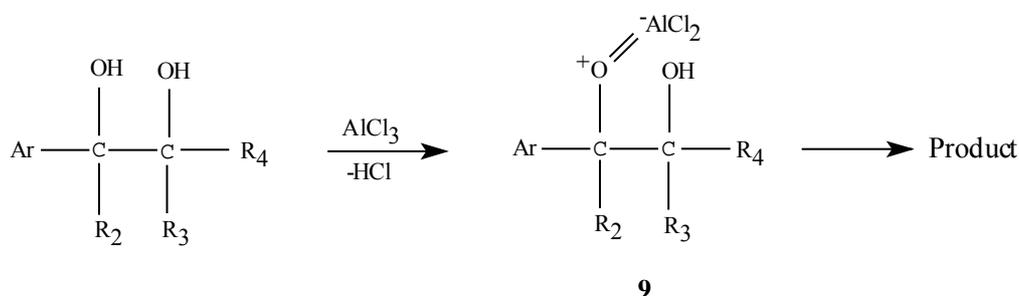
Results and Discussion

Benzylic pinacols react with AlCl_3 to give the corresponding rearrangement product in almost quantitative yield after only a few minutes. The reaction is easily carried out in an agate mortar and the reaction conditions and the subsequent workup are simple and quick. The pinacol compound is mixed with AlCl_3 in a ratio of 1:3 respectively and is then thoroughly ground at room temperature. A fast reaction happens, HCl evolves and a colored mass is immediately obtained. Workup of the reaction mixture by adding dilute H_2SO_4 and extracting with chloroform affords the rearrangement product in good yield. By adopting the above method, benzylic pinacol compounds have been rearranged to the corresponding pinacolones and it is found that the method is much better than all the methods known so far for its simplicity and high conversion. The list of substrates that have been rearranged by this method is given in Table 1. For anthrapinacol, entry 7, the only product detected was bianthryl which shows that this procedure can be used in systems that aromatize by dehydration. For tetralone pinacol, entry 5, the product of rearrangement was obtained in fairly good yield compared to the procedures described previously [9]. In series of compounds **2-6** it was found that the selectivity is affected by AlCl_3 and for entry 6 the rearranged product, **8**, undergoes keto-enol tautomerization to give 10-phenyl-9-phenanthrol, **6** (Scheme 1).



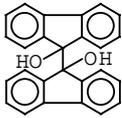
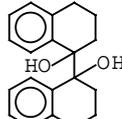
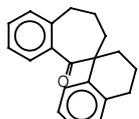
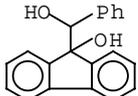
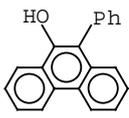
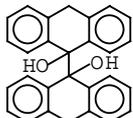
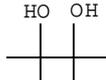
Scheme 1

Entry 8 shows that for rearrangement under these conditions, the existence of an aryl group adjacent to carbon which bears the OH group is necessary. The reaction is expected to proceed via the formation of an aluminium adduct **9** which is formed by reaction of aluminium chloride with the OH group followed by liberation of HCl gas. In the second step the rearrangement takes place by the migration of alkyl, aryl or hydride groups (Scheme 2).



Scheme 2

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

Entry	Pinacol	product		Time (min)	Yield
1			1	1	98
2	$\text{Ph}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}}-\text{Ph}$	$\text{Ph}-\underset{\text{O}}{\text{C}}-\text{CH}_2-\text{Ph}$	2	2	87
3	$\text{Ph}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{C}}(\text{Ph})-\text{Ph}$	$\text{Ph}-\underset{\text{O}}{\text{C}}-\underset{\text{Ph}}{\text{CH}}-\text{Ph}$	3	2	71
4	$\text{X}-\text{C}_6\text{H}_4-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{C}}(\text{Ph})-\text{Ph}$ X=OCH ₃	$\text{Ph}-\underset{\text{O}}{\text{C}}-\underset{\text{Ph}}{\text{CH}}-\text{C}_6\text{H}_4-\text{X}$	4	2	94
5			5	2	55
6			6	2	84
7			7	1	92
8		no reaction			

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Experimental

General

Solvents and reagents for the preparation of starting materials were used as received from Aldrich. ^1H - and ^{13}C -NMR spectra were recorded on Varian Unity Plus instruments (500 and 200 MHz). FT-IR spectra was obtained using a Shimadzu 4300 spectrophotometer.

General synthetic procedure

A mixture of the appropriate pinacol compound and anhydrous aluminium chloride (Aldrich, 99.99 %) was thoroughly ground in an agate mortar for a few minutes under an efficient hood. Hydrogen chloride is evolved violently. The reaction mixture was worked up by adding H_2SO_4 (2N) and extracting with chloroform. The organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo* to give the products. Pinacol starting materials were prepared by the methods of Toda [10] and Khurana [11].

Spectral Data

Compound 1, ^1H -NMR (500 MHz, CDCl_3) δ : 6.61(dd, $J=7.8$ and 1.3 Hz, 1H), 7.03(d, $J=7.6$ Hz, 2H), 7.06(dt, $J=7.7$ and 1.2 Hz, 1H), 7.16 (dt, $J=7.5$ and 1.1 Hz, 2H), 7.34(dd, $J=8.4$ and 1.4 Hz, 1H), 7.37(dt, $J=7.5$ and 1.0 Hz, 2H), 7.43(dt, $J=7.6$ and 1.0 Hz, 1H), 7.79(d, $J=7.6$ Hz, 2H), 7.8(m, 1H), 7.98(dd, $J=7.7$ and 1.5 Hz, 1H), 8.08(dd, $J=8.2$ and 1.0 Hz, 1H), 8.18(dd, $J=8.1$ and 0.3 Hz, 1H); ^{13}C -NMR (125 MHz, CDCl_3) δ : 68.68, 120.51, 123.17, 124.06, 124.70, 127.899, 127.984, 128.076, 128.258, 128.278, 128.529, 129.175, 130.09, 130.50, 134.81, 138.10, 139.32, 141.60, 147.08, 197.12, HRMS calcd for $\text{C}_{26}\text{H}_{16}\text{O}$ 344.12012, found 344.12163.

Compound 2, ^1H -NMR (200 MHz, CDCl_3) δ : 4.30(s, 2H), 7.29-7.50(m, 8H), 8.03-8.08(m, 2H); ^{13}C -NMR (50 MHz, CDCl_3) δ : 45.22, 126.67, 128.38, 128.44, 129.29, 132.96, 134.36, 136.33, 197.36, HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{O}$ 196.08882, found 196.08696.

Compound 3, ^1H -NMR (200 MHz, CDCl_3) δ : 6.05(s, 1H), 7.22-7.51(m, 13H), 7.99-8.03(d, $J=7.5$ Hz, 2H); ^{13}C -NMR (50 MHz, CDCl_3) δ : 59.39, 127.14, 128.61, 128.71, 128.96, 129.13, 133.05, 136.75, 139.05, 198.178, HRMS calcd for $\text{C}_{20}\text{H}_{16}\text{O}$ 272.12012, found 272.12148.

Compound 4, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 3.75 (s, 3H), 5.97(s, 1H), 6.84 (m, 2H), 7.18-7.26(m, 5H), 7.29-7.32(m, 2H), 7.37-7.40(m, 2H), 7.48-7.50(m, 1H), 7.99-7.99(m, 2H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 55.17, 58.55, 126.99, 128.53, 128.62, 128.89, 129.00, 130.12, 131.11, 132.90, 136.87, 139.45, 158.66, 198.41, HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{O}_2$ 302.14191, found 302.13247.

Compound 5, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.70-2.08(m, 6H), 2.15-2.21(m, 1H), 2.27-2.33(m, 1H), 2.73-2.93(m, 4H), 6.97-7.01(m, 1H), 7.04-7.18(m, 4H), 7.30-7.37(m, 1H), 7.37-7.44(m, 2H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 19.17, 22.33, 29.44, 29.85, 32.31, 36.25, 52.82, 125.91, 126.16, 126.94, 127.70, 127.78, 128.45, 129.51, 131.09, 136.15, 137.17, 141.93, 142.47, 214.86, FTIR (1680 cm^{-1} , CO), HRMS calcd for $\text{C}_{20}\text{H}_{20}\text{O}$ 276.15142, found 276.15170.

Compound 6, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 5.45(s, OH), 7.24-7.44(m, 2H), 7.46-7.55(m, 4H), 7.59-7.72(m, 4H), 8.38(ddd, $J=8.2$, 1.5 and 0.5Hz, 1H), 8.66(ddd, $J=8.7$, 1.2 and 0.5Hz, 1H), 8.71(ddd, $J=8.7$, 1.2 and 0.5Hz, 1H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 117.25, 122.51, 122.57, 123.07, 123.99, 124.98, 125.36, 126.41, 126.63, 126.81, 127.22, 127.85, 128.63, 129.80, 131.03, 131.47, 132.47, 134.49, HRMS calcd for $\text{C}_{20}\text{H}_{14}\text{O}$ 270.10447, found 270.10628.

Compound 7, $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 7.06-7.14(m, 8H), 7.41(dd, $J=6.3$ and 1.2Hz, 2H), 7.43(dd, 6.3 and 1.2Hz, 2H), 8.13(d, 8.5Hz, 4H), 8.66(s, 2H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 125.24, 125.75, 126.78, 127.16, 128.47, 131.492, 131.570, 133.024, HRMS calcd for $\text{C}_{28}\text{H}_{18}$ 354.14085, found 354.13923.

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Sample Availability: Available from author.

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