Pinacol-Pinacolone Rearrangement Promoted by Polyphosphoric Acid Trimethylsilyl Ester (PPSE)

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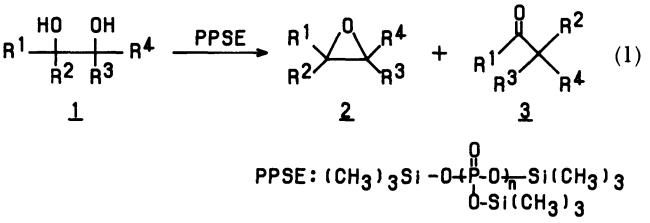
Synopsis. Pinacols afforded the corresponding pinacolones in high yields in the presence of the polyphosphoric acid trimethylsilyl ester (PPSE) at a temperature above 80 °C. Tetraphenylethylene oxide, in addition to benzopinacolone, was obtained in the reaction of benzopinacol under milder conditions. The solvent effect suggested that the rearrangement proceeded via the carbonium-ion intermediate.

Pinacol–pinacolone rearrangement has been known as an acid-catalyzed rearrangement which involves the carbonium-ion intermediate.[1] Strong acids, such as sulfuric acid,[2] iodine–acetic acid,[3] and trifluoroborane,[4] have been used as catalysts. We have previously investigated the reactivity of the polyphosphoric acid trimethylsilyl ester (PPSE), which is readily soluble in aprotic solvents. Because PPSE has the characteristics of both a Lewis acid and a dehydrating agent, it has been successfully applied to the Pummerer rearrangement of sulfoxides,[5] to the synthesis of dithioacetals from carbonyl compounds and thiols,[6] and to the synthesis of amidines from carboxylic acids and amines.[7] In this article, we describe the pinacol–pinacolone rearrangement promoted by PPSE.



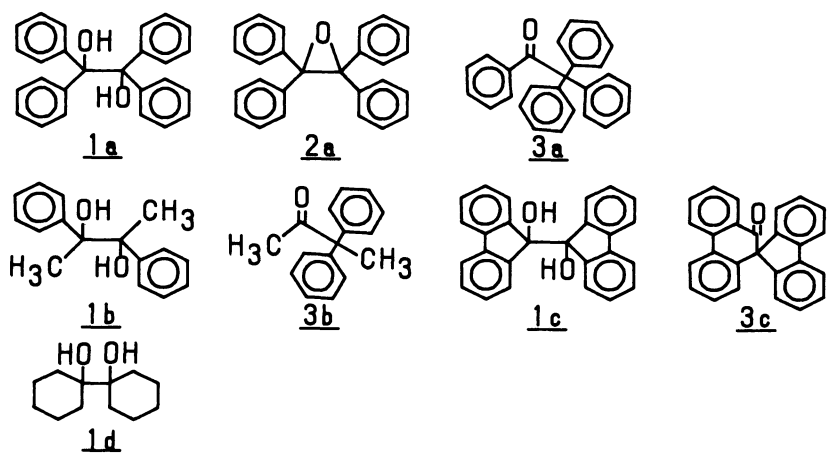
Results and Discussion

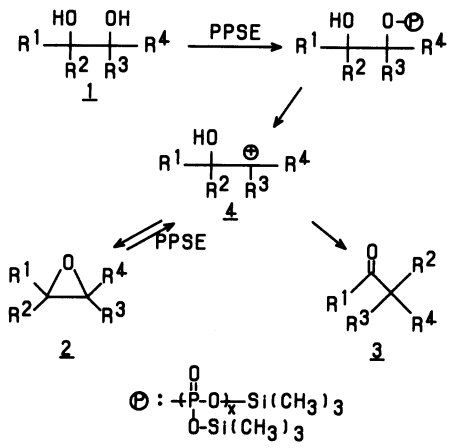
The results of the pinacol–pinacolone rearrangement are summarized in Table 1. Benzopinacol (**1a**) afforded both tetraphenylethylene oxide (**2a**) and benzopinacolone (**3a**) in a ratio depending markedly on the reaction conditions as shown in Entries 1—3. The use of an excess amount of PPSE or a higher reaction temperature (150 °C) afforded **3a** in a high yield. These results suggested that epoxide **2a** was an intermediate of the final rearrangement product **3a**. In fact, **2a** was completely converted into **3a** by treatment with an equimolar amount of PPSE in dichloroethane at 150 °C for 2 h. The acceleration effect of a polar solvent, tetrahydrothiophene 1,1-dioxide, sug-

Table 1. Pinacol–Pinacolone Rearrangement Using PPSE

Entry	Pinacol	Equivalent of PPSE	Solvent	Reaction temp/°C	Reaction time/h	Yield/%[a]	
						2	3
1	**1a**	1.0	$(CH_2Cl)_2$	80	2	61	26
2	**1a**	4.0	$(CH_2Cl)_2$	80	2	27	60
3	**1a**	1.0	$(CH_2Cl)_2$	150	2	0	97
4	**1a**	1.0	$(CH_2)_4SO_2$	80	2	0	95
5	**1b**	4.0	—	150	2	0	73
6	**1c**	1.0	$(CH_2Cl)_2$	150	2	0	88
7	**1c**	1.0	$(CH_2)_4SO_2$	80	2	0	95

a) Isolated yield.





Scheme 1.

gested that the rearrangement proceeded via an ionic intermediate (Entries 4 and 7). In the reaction of pinacols **1b** and **1c**, the corresponding epoxides **2** were not obtained, and the reactions afforded only pinacolones **3b** and **3c**, respectively, in high yields. The reaction of aliphatic pinacol **1d** and PPSE afforded an unknown mixture whose IR spectrum indicated that it did not include either alcohols or carbonyl functions. The formation of olefins with the elimination of water was a possible reaction from the NMR spectrum, but it did not succeed in isolating the olefinic products.

As shown in Scheme 1, the present reaction should involve the paths of the phosphorylation of a pinacol and the formation of the carbonium ion **4** by the elimination of the silylated phosphoric acid. There are two possible paths starting from **4**. One is the direct formation of pinacolone **3**, and the other is the formation of epoxide **2**. Epoxide **2** is also rearranged in the presence of PPSE via the carbonium ion **4**.

The details of the reaction mechanism will be reported in the near future. The pinacol–pinacolone rearrangement promoted by PPSE should have a wide range of application in organic synthesis, because the reaction proceeds under more neutral and milder conditions than usual acid-catalyzed rearrangements.

Experimental

A typical procedure was as follows: PPSE (20.00 mmol) was prepared in 10 ml of 1,2-dichloroethane as has been described in a previous paper.[7] To this solution, 1.830 g (5.00 mmol) of benzopinacol (**1a**) was added, and the mixture was stirred at 80 °C for 5 h. The resulting solution was poured into 100 ml of a 1 M aqueous sodium hydroxide solution (1 M=1 mol dm^{-3}) and then extracted with dichloromethane. Benzopinacolone (**3a**) (1.046 g, 60%), and tetraphenylethylene oxide (**2a**) (0.471 g, 27%), were obtained by the column chromatography (Silica gel, dichloromethane/hexane=1/2) of the crude product.

3a: mp 179—180 °C (lit, 180—181 °C);[8] IR (KBr plate) ν/cm^{-1}=1680, 1590, 1490.

2a: mp 206—207 °C (lit, 205—206 °C);[8] IR (KBr plate) ν/cm^{-1}=1590, 1480, 895.

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