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A FACILE METHOD FOR THE PINACOL REARRANGEMENT OF PHENYLETHANEDIOL DERIVATIVES BY THE USE OF 2-CHLOROPYRIMIDINIUM SALT

Teruaki MUKAIYAMA, Yoshiaki ECHIGO, and Manzo SHIONO
Department of Chemistry, Faculty of Science
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

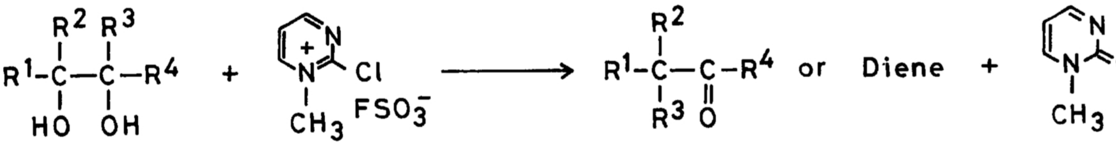
The pinacol rearrangement proceeds under mild conditions by treating phenylethanediol derivatives with 2-chloropyrimidinium salt to give the corresponding aldehyde or ketones in good yields.

In the course of our synthetic investigation utilizing the onium salts of azaaromatics[1], it was found that phenylethanediol derivatives are rearranged to aldehyde or ketones in good yields under mild conditions by the use of 2-chloropyrimidinium salt.

Concerning the pinacol rearrangement, there have numerous publications[2] appeared, but, in most cases, such strong acids as sulfuric acid, formic acid, p-toluenesulfonic acid, and phosphoric acid are used as reagents for the rearrangement.

The present method is represented by the following procedure for the rearrangement of 1,2-diphenyl-1,2-propanediol using 2-chloro-1-methylpyrimidinium fluorosulfate (I): To a mixture of I (1.2 mmol, 273 mg) and 1,2-diphenyl-1,2-propanediol (1.0 mmol, 228 mg) was added dry dimethoxyethane (8 ml) under an argon atmosphere and the mixture was stirred for half an hour at 0°C to give a white suspension. Then, it was refluxed for additional half an hour. The resulting mixture was treated with water and then extracted with ether. The extracts were washed with water and condensed under reduced pressure to give crude 1,1-diphenylacetone, which was purified by thin layer chromatography on silica gel, (184 mg, 88% yield).

In a similar manner, phenylethanediol derivatives were rearranged to the corresponding aldehyde or ketones in good yields as shown in the Table.

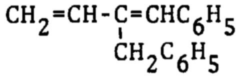


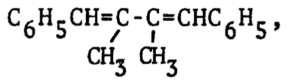
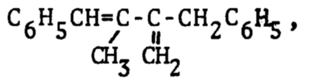
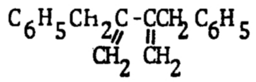
(I)

On the other hand, ethanediol derivatives having no benzylic hydroxyl group are mainly dehydrated to dienes, though these ethanediol derivatives are generally altogether rearranged to ketones under acidic conditions usually employed. Further, in the case of the pinacol rearrangement of trisubstituted ethanediol derivatives, the present reaction proceeds through the elimination of secondary hydroxyl group, in contrast with the results of losing tertiary hydroxyl group under usual acidic conditions.[3]

Table. The Reaction of Ethanediol Derivatives with I

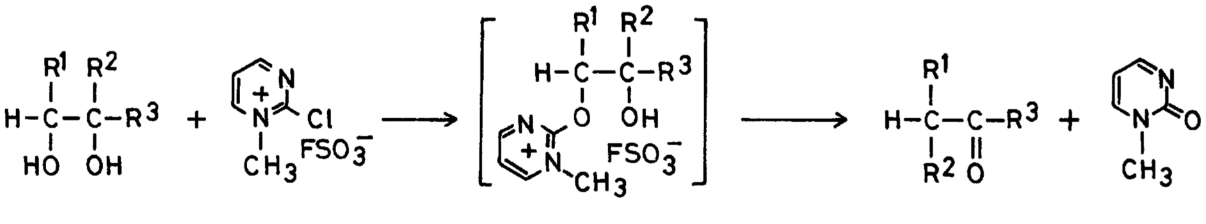
R^1	R^2	R^3	R^4	Yield (%)*	
				Ketone	Diene
C_6H_5	H	C_6H_5	H	54	-
C_6H_5	H	C_6H_5	CH_3	88	-
C_6H_5	H	C_6H_5	C_2H_5	73	-
C_6H_5	H	C_6H_5	C_6H_5	82	-
C_6H_5	H	$C_6H_5CH_2$	$C_6H_5CH_2$	60	-
CH_3	H	$C_6H_5CH_2$	$C_6H_5CH_2$	-	63¹⁾
CH_3	$C_6H_5CH_2$	CH_3	$C_6H_5CH_2$	-	90²⁾

1)  $CH_2=CH-\underset{CH_2C_6H_5}{C}=CHC_6H_5$

2) Mixture of  $C_6H_5CH=\underset{CH_3}{C}-\underset{CH_3}{C}=CHC_6H_5$,  $C_6H_5CH=\underset{CH_3}{C}-\underset{CH_2}{\overset{}{C}}-CH_2C_6H_5$, and  $C_6H_5CH_2\underset{CH_2}{C}-\underset{CH_2}{C}CH_2C_6H_5$

* All compounds exhibited ir and nmr spectrum data in accordance with assigned structures.

The peculiarity of this reaction may be explained by assuming that 2-chloropyrimidinium salt reacts predominantly with less hindered hydroxyl group of diols to form 2-hydroxyethoxypyrimidinium salts(II), which in turn are immediately converted to the corresponding ketones accompanied with the elimination of 1-methylpyrimidin-2-one.


(I) (II)

It is noted that 2-chloro-1-methylpyrimidinium fluorosulfate is a useful reagent for the promotion of the pinacol rearrangement to ketones or aldehyde with the elimination of benzylic secondary hydroxyl group from phenylethanediol derivatives.

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References

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3) M.M. Tiffeneau and A. Orekhoff, Bull. Soc. Chim. France, 33, 195 (1923).

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