CHEMISTRY LETTERS, pp. 81-84, 1992.

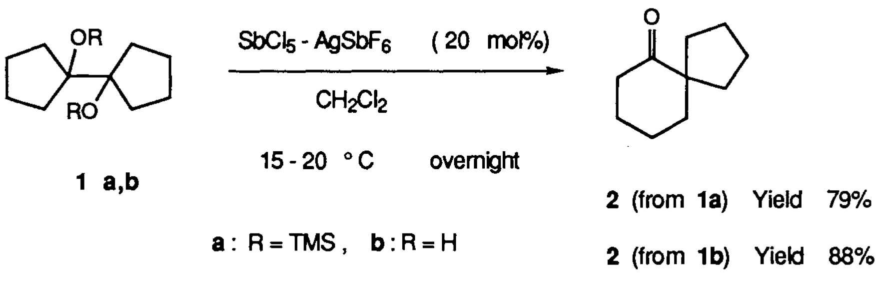
The Catalytic Pinacol Rearrangement of 1,2 - Diols Using an Antimony(V) Salt

Tsunehiro HARADA and Teruaki MUKAIYAMA
Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

In the presence of a catalytic amount of antimony(V) chloride or antimony(V) salt generated from antimony(V) chloride and silver hexafluoroantimonate, the pinacol rearrangement of several 1,2 - diols or their trimethylsilyl ethers proceeds smoothly to give the corresponding ketones in good yields.

The pinacol rearrangement is the skeletal rearrangement of 1,2 - diols in the presence of strong protic acids or Lewis acids, and is a valuable method for the preparation of aldehydes and ketones including interesting and unusual ones. The most common acid for the pinacol rearrangement is concentrated H_2SO_4, sometimes $HClO_4$ or $BF_3{\bullet}OEt_2$, and at least an equimolar amount of the acid is required$^{1)}$ and relatively little work has been reported on the pinacol rearrangement promoted by a catalytic amount of the acid. In the course of our continuous investigations$^{2)}$ to explore useful catalytic reactions by utilizing the antimony(V) salt **7**, easily prepared in situ from $SbCl_5$ and $AgSbF_6$, we have now found that the salt also promotes the pinacol rearrangement of 1,2 - diols or their trimethylsilyl ethers to afford the corresponding ketones in good yields.

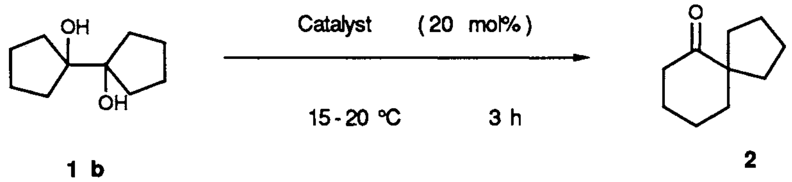
In the first place, the pinacol rearrangement of [Bicyclopentyl - 1,1' - diyl - bis(oxy)]bis[trimethylsilane] (**1a**)$^{3)}$ was tried in CH_2Cl_2 at 15 - 20 °C in the presence of a catalytic amount of **7** which was effective in the catalytic Beckmann rearrangement$^{4)}$ of the ketoxime trimethylsilyl ether. The reaction proceeded smoothly to afford spiro[4, 5]decane - 6 - one (**2**) in good yield (Scheme 1). The rearrangement of 1 , 2 - Diol **1b** as a substrate was also promoted by the same salt to give the corresponding ketone in good yield.



Scheme 1 .

Next, in order to optimize the reaction conditions, several Lewis acids and solvents were examined by taking the above mentioned reaction of **1b** as a model. The best result was obtained when the reaction was carried out in CH_2Cl_2 in the presence of the antimony(V) salt prepared in situ from $SbCl_5$ and $AgSbF_6$. It is noted that $SbCl_5$ itself also exhibits a rather good catalytic activity (Table 1).

Table 1. Effect of Catalyst and Solvent



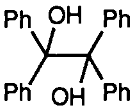
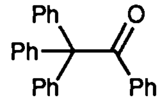
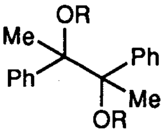
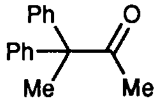
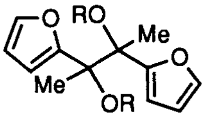
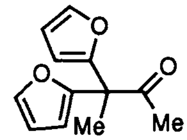
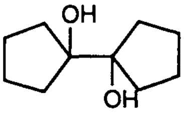
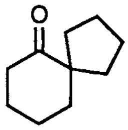
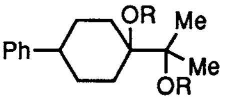
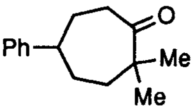
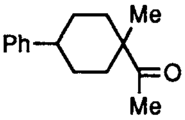
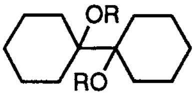
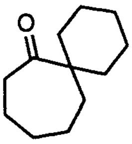
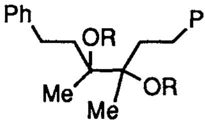
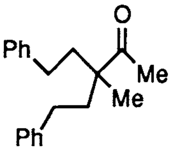
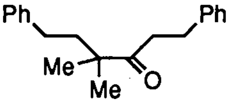
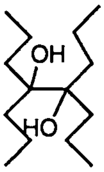
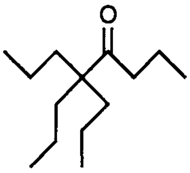
Entry	Catalyst	Solvent	Yield / %
1	$SbCl_5$	CH_2Cl_2	83
2	$SnCl_4$	CH_2Cl_2	56
3	$TiCl_4$	CH_2Cl_2	24
4	$BF_3 \cdot OEt_2$	CH_2Cl_2	62
5	$AlCl_3$	CH_2Cl_2	trace
6	$SbCl_5$ - $AgSbF_6$	CH_2Cl_2	88
7	$SbCl_5$ - $AgClO_4$	CH_2Cl_2	85
8	$SbCl_5$ - $AgBF_4$	CH_2Cl_2	79
9	$SbCl_5$ - AgOTf	CH_2Cl_2	76
10	$SbCl_5$ - $AgSbF_6$	EtCN	57
11	$SbCl_5$ - $AgSbF_6$	toluene	66

Several examples of the present pinacol rearrangement are demonstrated in Table 2. In all cases, the reaction proceeds smoothly to give the corresponding ketones in good to excellent yields. The results show that, in the case of the substrates having a labile migrating group, $SbCl_5$ itself is the best catalyst (Entries 1 - 3). While, for example, 1,2 - migration of simple alkyl chains, the combination of $SbCl_5$ and $AgSbF_6$ gave better results (Entries 5, 7, 8). In general, there is little difference in yields between 1,2 - diol and its trimethylsilyl ether (Entries 2, 5, 6, 7), however, in the case of the substrate having an acid sensitive group, trimethylsilyl ether of 1,2 - diol gave a better result (Entry 3).

In the case of trimethylsilyl ether of 1,2 - diol, the catalytic cycle of this rearrangement is postulated as shown in Scheme 2. The salt **7** activates a trimethylsilyloxy group of 1,2 - diol moiety, which is followed by rearrangement of R to form the intermediate cation stabilized by antimonate anion **9**. Then **9** reacts with initially formed tetrachloro(trimethylsilyloxy)antimony (**8**) to give the desired ketone **10** along with a regeneration of the catalyst **7** and TMS_2O.5) In the case of 1,2 - diol, since **7** is probably readily hydrolyzed with the produced H_2O to afford $SbCl_4(OH)$ and $HSbF_6$, the latter, extremely strong acid,6) may behave as the promoter of this rearrangement.

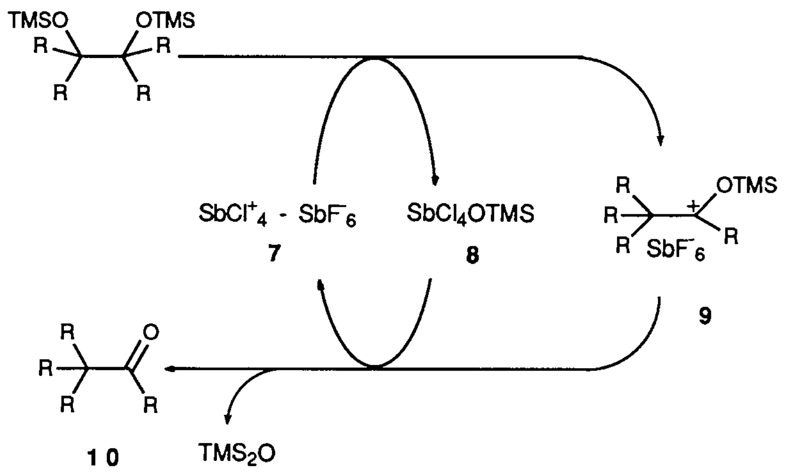
A typical experimental procedure for the pinacol rearrangement of benzopinacol is as follows; a 0.5 M solution of antimony(V) chloride (0.12 ml) in CH_2Cl_2 was added to a silver hexafluoroantimonate (20.6 mg, 0.06 mmol) solution in CH_2Cl_2 under ice cooling with the protection from the light. After stirring for 1h, a suspension of benzopinacol (110.0 mg, 0.3 mmol) in CH_2Cl_2 was added at -78 °C. The mixture was stirred for 1h at -78 °C and for 10 min at -23 °C. The reaction was quenched with phosphate buffer (pH 7). The organic layer was separated and dried over Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by preparative TLC to afford 103.6 mg (99%) of 2,2,2 - triphenylacetophenone, mp 182 - 183 °C.

Table 2. The Catalytic Pinacol Rearrangement of 1,2-Diols and Their Trimethylsilyl Ethers

Entry	Substrate[7]	Product	Method[a]	Temperature / °C	Time	Yield /%
1			A B	-23	10 min	99 96
2			A (R = H) B (R = TMS) B (R = H)	0	overnight	96 98 92
3			A (R = TMS) B (R = TMS) B (R = H)	-78	5 h	75 87 39
4			B	15-20	3 h	83
5		 **3**  **4**	A (R = TMS)	15-20	overnight	74[b]
			A (R = H) B (R = H)	15-20	5 h	80[c] 45[d]
6			B (R = TMS) B (R = H)	15-20	overnight	51 52
7		 **5**  **6**	A (R = TMS)	15-20	overnight	64[e]
			A (R = H) B (R = H)	15-20	3 h	63[f] 49[g]
8			A B	15-20	3 h	68 59

a) Method A: $SbCl_5$-$AgSbF_6$, B: $SbCl_5$.

b) **3**:**4** = 61:13. c) **3**:**4** = 69:11. d) **3**:**4** = 31:14. e) **5**:**6** = 46:18. f) **5**:**6** = 46:17. g) **5**:**6** = 39:10.



Scheme 2. The catalytic cycle.

References

1) C. A. Buehler and D. E. Pearson, "Survey of Organic Synthesis," Wiley-Interscience, New York (1970), p. 677; D. Dieterich, "Methoden der Organischen Chemie," Thieme, Stuttgart (1973), Vol. 7/2a, p. 927; B. P. Mundy and R. D. Otzenberger, *J. Chem. Educ.*, **48**, 431 (1971); M. Bartok and A. Molnar, "In Chemistry of Ethers, Crown Ethers, Hydroxyl Compounds and Their Sulfur Analogues," ed by S. Patai, New York (1980), p. 722, and references cited therein.
2) T. Mukaiyama, M. Katsurada, and T. Takashima, *Chem. Lett.*, **1991**, 985; T. Mukaiyama, T. Ohno, T. Nishimura, S. Suda, and S. Kobayashi, *ibid.*, **1991**, 1059, and references cited therein.
3) TMS ether **1a** was easily prepared in 92% yield by teatment of **1b** with TMSCl and imidazole in DMF.
4) T. Mukaiyama and T. Harada, *Chem. Lett.*, **1991**,1653; T. Harada, T. Ohno, S. Kobayashi, and T. Mukaiyama, *Synthesis*, in press.
5) TMSOTf (20 mol%) was not effective in the rearrangement of **1a** (9% yield).
6) Spirodecanone **2** was obtained in 67% yield by use of CF_3SO_3H (20 mol%), but not obtained by that of CF_3CO_2H (20 mol%).
7) T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, **1973**,1041; E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *J. Org. Chem.*, **41**, 260 (1976); J. P. Morizur and J. Wiemann, *Bull. Soc. Chim. Fr.*, **1964**, 1619.

(Received October 14, 1991)