

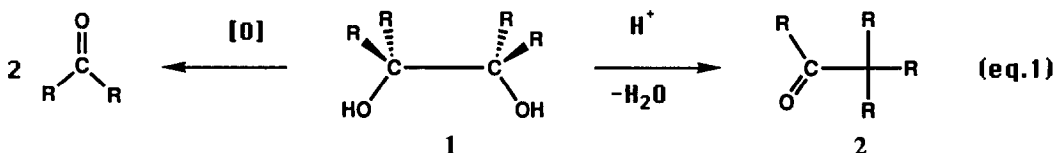
RADICAL CATION CATALYZED PINACOL-PINACOLONE REARRANGEMENT

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Summary: When electron-rich benzopinacols are electrooxidized or treated with catalytic amounts of NOBF_4 the corresponding pinacolones are obtained in quantitative yields. Control experiments rule out the possibility of adventitious acid intervening in the reaction and a radical-cation chain electron-transfer mechanism is proposed.

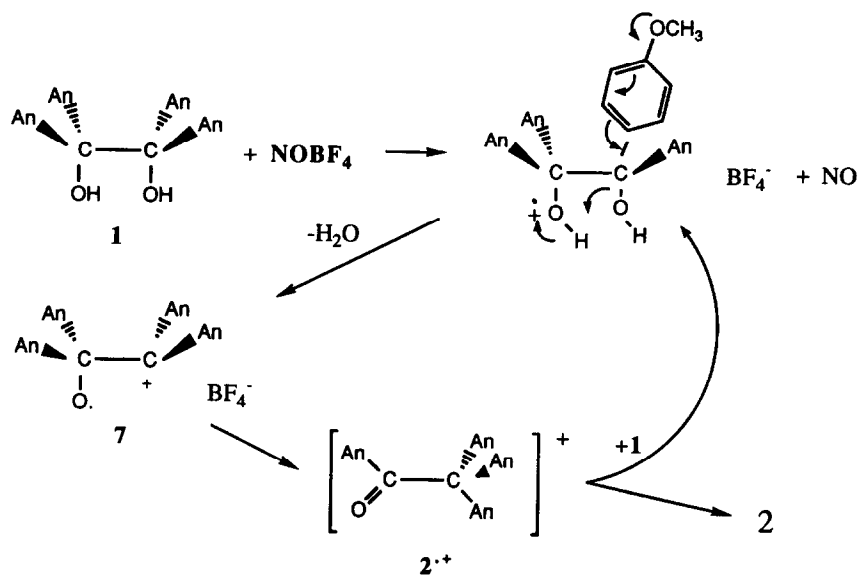
The pinacol-pinacolone acid-catalyzed rearrangement is one of the best studied rearrangements in the literature.¹ When a properly substituted *vic*-diol is exposed to acid, a 1,2-shift occurs to give an aldehyde or ketone with concomitant loss of a water molecule as shown in equation 1. However, when *vic*-diols are subjected to a wide variety of oxidative conditions, the reaction proceeds by bond cleavage to afford the corresponding carbonyl derivatives.² Various *vic*-diols have also been shown to undergo oxidative cleavage under photosensitized electron transfer (PET) conditions.³



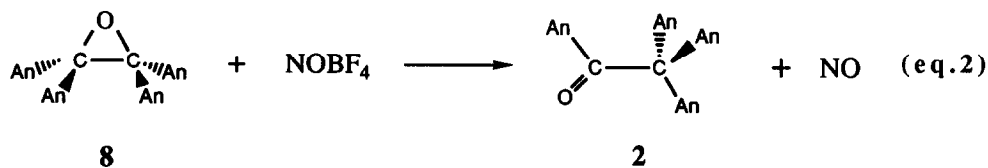
We have found that when NOBF_4 (20 mol %) in dry acetonitrile is added to a solution of tetra-*p*-anisylethylene glycol (1a) at -5°C , under nitrogen, the only product isolated in quantitative yield is pinacolone 2a. NOBF_4 has been effectively used in one-electron oxidations, and being a very weak electrophile leaves no doubt that it acts as an outer-sphere oxidant.⁴ Nevertheless, recent cases in the literature where one-electron oxidants have been used, have dealt with the possibility that these oxidants generate adventitious acid under the reaction conditions.⁵ To thoroughly

rule out this possibility we carried out several control experiments, as suggested recently by Bauld.⁶ In the first of these experiments, glycol **1a** was subjected to the same reaction conditions but substituting the NOBF₄ for an equimolar amount of a protic acid.⁷ Under these conditions, 100% unreacted glycol **1a** was recovered. Furthermore, when the reaction of glycol **1a** with 20 mol % NOBF₄ was carried out in the presence of an excess (32 mol %) of 2,6-di-*tert*-butyl pyridine, the isomerization proceeded to the same extent to give **2a**.⁸ The same series of experiments have been carried out with tetra-*p*-dimethylaminophenyl ethylene glycol **1b** affording also rearrangement product **2b** quantitatively under similar conditions. NOBF₄ did not promote the rearrangement of benzopinacol or electron-deficient tetra-*p*-chlorophenyl ethylene glycol, evidencing that the nitrosonium ion itself does not act as an acid catalyst or generates acid under these conditions.

Our results contrast sharply with those of benzopinacols under PET conditions. In those cases the reaction proceeds by oxidative cleavage to afford the corresponding ketones.³ Under those conditions a radical anion is generated in the process and is proposed to exist as a caged ion pair with the radical cation. Several mechanistic possibilities for the oxidative cleavage have been proposed, all actively involving the radical anion. Das and co-workers generated pinacols radical cations on irradiation of 1,4-naphthalenedicarbonitrile (NDN) which fragmented to afford the corresponding ketones.^{3c} The proposed mechanism involves back electron transfer from the radical anion before leading to fragmentation. Albin and Mella, on the other hand, invoke a deprotonation of the pinacol radical cation by the radical anion in the solvent cage.^{3b} A similar mechanism has been postulated by Whitten and coworkers for the observed fragmentation of 1,2-aminoalcohols and diols under PET conditions.^{3d} In our case, no nucleophilic radical anion is present since the species generated is gaseous NO which is a poor nucleophile and has low tendency for back electron transfer. Our observations can best be accounted as the thermal reaction of the benzopinacols radical cations which, in the absence of efficient electron donors or nucleophiles, rearrange generating the corresponding pinacolones by means of an electron transfer mechanism as described in the Scheme.



The oxidation potentials of both glycol **1a** and pinacolone **2a** were obtained by CV in acetonitrile (0.1M LiClO₄ vs Ag/Ag⁺) and found to be 1.32 and 1.46 V, respectively. These data is in agreement with our mechanism that favors **2** having a higher oxidation potential than **1** for the propagation of the chain. The intervention of intermediate **7** is further supported by the fact that tetra-*p*-anisylethylene oxide (**8**) also rearranges to **2** with catalytic amounts of NOBF₄ (equation 2). Similar observations with opoxides radical cations have also been described by other investigators.⁹



Electrooxidation experiments using **1a** and **1b** also afford pinacolones **2a** and **2b** respectively in quantitative yields.¹⁰ When the electrooxidations are carried out in presence of 2,6-di-*tert*-butyl pyridine the same products **2a** and **2b** are obtained in the same yields respectively ruling out the possibility that adventitious acid might be responsible for the rearrangement under these conditions.

ACKNOWLEDGMENTS: We are very grateful for the financial assistance of the National Science Foundation and the University of Puerto Rico.

References and Notes

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6. Reynolds, D. W.; Lorentz, K. T.; Chiou, H.; Bellville, D. J.; Pabon, R. A. and Bauld, N. L. *J. Am. Chem. Soc.* **1987**, 109, 4960 .
7. H₂SO₄ was used as the protic acid avoiding the use of trifluoroacetic acid which has been shown to act as an oxidant in the presence of O₂ (see ref. 5c).
8. Under these conditions di-*tert*-butylpyridine completely suppresses the acid-catalyzed rearrangement of benzopinacol to benzopinacolone (see ref. 2d).
9. A similar mechanism for the radical-cation rearrangement of epoxides have been proposed by (a) Delaunay, J.; Lebouc, A.; Tallec, A. and Simonet, J. *J. Chem. Soc., Chem. Comm.* **1982**, 387; (b) Lopez L. and Troisi L., *Tetrahedron Lett.*, **1989**, 30, 3097 and references therein.
10. The electrooxidation of a 0.005 M solution of **1a**, for example, was carried out at a controlled potential of 1.7 V vs Ag/Ag⁺, in dry acetonitrile as solvent and 0.1M in LiClO₄. In this case 0.12 mol of e⁻ were consumed per mole of **1a**.

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