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Reactions on (R) and (S)-1,1,2-Triphenyl-1,2-Ethandiols Induced by Aminium Salts and Protic Acids. Solvent Effect.

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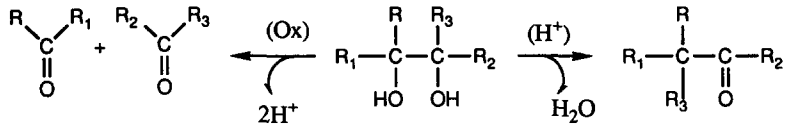
Abstract: (R) and (S) 1,1,2-triphenyl-1,2-ethandiols (**1a**) and (**1b**), upon treatment of their dichloromethane solutions with catalytic amounts of aminium salt cation radicals afforded mixtures of the corresponding pinacolones (Ph_3CCHO, 90 %) (**2**), ($Ph_2CHCOPh$, 10%) (**3**), whereas similar reactions, carried out in acetonitrile, led to consistent amounts of both pinacolones, together with benzophenone (**4**), benzaldehyde (**5**) (minor amounts), and new products (30 %), fully characterized as (R) and (S) 4,4,5-triphenyl-2-methyloxazolines (**7a,b**). The formation of these latter was selectively inhibited in the aminium salt induced reactions, modified by 2,6-di-*tert*-butylpyridine (**DBP**).

Introduction

The difficulties in distinguishing cation-radical catalysis from Brønsted-acid catalysis, *under aminium salt initiation* , widely debated in the recent literature,[1a-e] stem from the fact that aminium salts, such as *tris*-(4-bromophenyl) aminium hexachloroantimonate $(4\text{-}BrC_6H_4)_3\ N^{+\bullet}\ SbCl_6^-$ [E^{red}= 1.16 V. *vs* SCE] (**A**) and *tris*-(2,4-dibromophenyl) aminium hexachloroantimonate $(2,4\text{-}Br_2C_6H_3)_3\ N^{+\bullet}\ SbCl_6^-$ [E^{red}= 1.66 V. *vs* SCE] (**B**), behave not only as one-electron oxidizing agents, but also as an indirect source of protic acid. Thus, reaction products, accountable for by cation radical intermediates, often are also compatible with carbocations forming in protic acid catalyzed processes.

In this context, aromatic vicinal diols (electron-rich compounds) are suitable substrates better to distinguish a cation-radical mechanism from a protic acid catalyzed reaction. In fact, photo-induced electron-transfer reactions on aromatic *vic*-diols led, through an oxidative C-C bond cleavage of cation-radical intermediates, to simple carbonyl compounds,[2a-e] whereas the well known dehydration and migration process, catalyzed by protic acids, afforded mixtures of pinacolones,[3] see scheme 1.

Scheme 1



Ox= sens/hυ; one-electron oxidizing agents

Rearrangement *vs* oxidation of several aromatic *vic*-diols with different one-electron oxidizing agents has been the topic of several conflicting papers from various international groups[4a-g]. In the work of Arce de Sanabia and Carrion,[4c] a catalytic amount of nitrosonium tetrafluoroborate (**$NOBF_4$**) was found to cause a quantitative rearrangement of benzopinacol to 1,1,1-triphenyl acetophenone in acetonitrile at -5 °C, and consistent chemical and electrochemical proofs, accounting for a chain cation radical mechanism, were given. On the contrary, in the work of Shine and Han[4d], a significant molar excess of thianthrene cation radical (**$Th^{+\bullet}$ ClO_4^-** or **BF_4^-**) *vs* benzopinacol caused its quantitative oxidation to benzophenone, provided a sufficient amount of an organic base (2,6-di-*tert*-butyl-4-methylpyridine, **DTBPM**) was present to prevent the presumed acid-catalyzed rearrangement. Seemingly, Penn and *co-workers* [4e-g], by using iron(III) trisphenanthroline complexes **[Fe(III)L_3 $(PF_6)_3$]** [E^{red}= 1.09 V. vs SCE], or 2,3-dichloro-5,6-dicyanobenzoquinone (**DDQ**) [E^{red}= 0.52 V. *vs* SCE] and 2,6-di-*tert*-butylpyridine [E^{ox} = 1.82 V. vs. SCE] (**DBP**) observed facile electron-transfer processes on similar substrates, with oxidation potentials higher than 1.85 V. *vs* SCE, followed by a fast cleavage of the C-C bonds.

In this paper, with the aim to further substantiate that also pinacolones *might* arise from the primary pinacol cation-radical intermediates,[4a,b] we report herein the conclusions of a systematic study, carried out in methylene chloride or acetonitrile solutions of (R) and (S) enantiomers of 1,1,2-triphenyl-1,2-ethanediol (**1a**) and (**1b**) with catalytic amounts of the previous aminium salts **A**,**B**. Similar reactions have also been performed in the presence of organic bases, as well as with different protic acids as catalysts.

Results and Discussion

Typical experimental conditions were as it follows: different catalytic amounts of aminium salts **A**, or **B** (24 or 30 mg, 0.03 mmol, 5mol % ; 48 or 60 mg, 0.06 mmol, 10 mol %), were rapidly added to freshly distilled methylene chloride (15 ml) solutions of both enantiomers **1a** or **1b** (174 mg, 0.6 mmol, 100 mol %), under stirring at room temperature. The intensely blue or green colour of the solutions, depending on the aminium salt used, faded within a few minutes. Analyses of the reaction mixtures, monitored by TLC until completion, (starting materials decomposed on the GC column), and then by GC and GC/MS spectrometry, revealed the formation of two main reaction products, fully identified as triphenylacetaldehyde **2** (90 %) and benzhydrylphenyl ketone **3** (10 %), (runs 1-4), table 1. The ratio between these latter, notwithstanding the acidic reaction media, did not change within three days.

These experimental results were totally different from those reported in earlier literature, where **3** appeared the sole, or main reaction product, when either **1a** or **1b** were refluxed in the presence of various strong protic acids. [3]

To this regard, three different reactions (runs 5-7), carried out with 33 mol %, 100 mol %, and 300 mol % of methylene chloride solutions of perchloric acid *vs* 100 mol % of starting materials, respectively, afforded **3**, but through the preliminary formation of both pinacolones **2** and **3**. In addition to that, these latter reactions were apparently more efficient than those performed with other protic acids, such as sulphuric acid and *tri*-fluoroacetic acid. In fact, the reactions carried out with similar amounts of methylene chloride solutions of these latter acids, apparently inhibited after three days, analyzed after three weeks showed the total conversion of the starting materials into complex mixtures of **2** and **3** (main reaction products), minor amounts of benzophenone (**4**), benzaldehyde (**5**) and 1,1,2-triphenyl 1,2-ethane oxide (**6**).

To thoroughly rule out the claim that pinacolones must only arise from a protic acid-catalyzed process, we carried out several control experiments, whose results are still reported in the table, and depicted in the scheme 2

Scheme 2

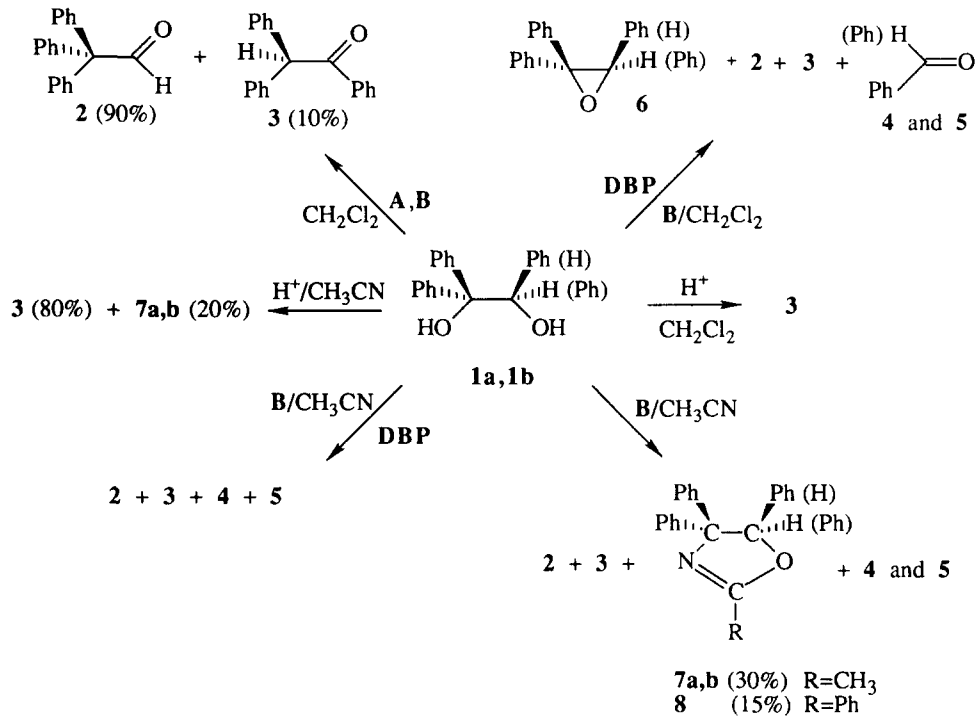


Table . **Reactions of (R) and (S) 1,1,2-triphenyl-1,2-ethanediols with aminium salts and protic acids.**

Run	Reagents[a] (mol%)		Base (mol %)	Solvent	Reaction products (mol %)				
1	**1a**	**A**(5)[b]		CH_2Cl_2	**2** (88)[d]	**3** (10)			
2	**1b**	**B**(5)[b,c]		"	" (90)[d]	" (10)			
3	**1b**	**A**(10)		"	" (92)	" (8)			
4	**1b**	**B**(10)[c]		"	" (91)	" (9)			
5	**1b**	$HClO_4$ (33)		"	" (8)	" (92)[e]			
6	**1b**	$HClO_4$ (100)		"	" (tr)	" (98)			
7	**1b**	$HClO_4$ (300)		"	" (tr)	" (98)			
8	**1b**	**B** (10)	**DBP** (5)	"	" (88)	" (10)	**4,5** (tr)		
9	**1b**	**B** (10)	**DBP** (10)	"	" (50)	" (25)	" (tr)	**6** (20)	
10	**1b**	**B** (10)	**DBP** (30)	"	" (20)	" (35)	" (25)	" (20)	
11	**1a**	**B** (10)	**DABCO** (10)		-	-	-	-	-
12	**1a**	**B** (10)	**DABCO** (5)	"	" (70)	" (30)[f]			
13	**1b**	**B** (30)		CH_3CN	" (30)	" (35)	" (5)		**7** (30)
14	**1a**	**B** (30)		"	" (30)	" (35)	" (5)		" (30)
15	**1b**	$HClO_4$		"		" (80)			" (20)
16	**1b**	H_2SO_4		"		" (70)			" (25)
17	**1b**	**B** (30)	**DBP** (30)	"	" (20)	" (25)	" (50)		
18	**1b**	**B** (30)	**DBP** (60)	"	" (15)	" (25)	" (60)		

[a] The reactions have been performed by using 100 mol % of starting materials **1a**, **1b** over the reagents. [b]The same reaction products have been obtained by performing the reactions 1-2 under nitrogen atmosphere. [c] The same reaction products reactionn have been obtained by performing the reactions 1-4 in the the presence of 2 mol equivalents of the corresponding triarylamines. [c] [d]Trace amounts of triphenylmethane and triphenyl carbinol were detected by GC/MS spectrometry. [e] These protic acid-induced reactions appeared more efficient than those performed in the same solvent with CF_3COOH and H_2SO_4 as catalysts. [f] Very low conversions of pinacols (<30%) were observed.

Catalytic amounts (10 mol %) of aminium salts **A** or **B** were rapidly added to methylene chloride solutions of **1a** or **1b** (100 mol %) in the presence of different and increasing amounts of **DBP** (0.03, 0.06, 0.18 mmol, 5, 10, 30 mol %). These reactions (runs 8-10), apparently slower than those unmodified, afforded mixtures of carbonyl compounds **4** and **5**, from oxidative C-C bond cleavage, pinacolones **2** and **3**, and the corresponding epoxide **6**. In particular, in the presence of the higher amount of **DBP** *vs* the aminium salt initiator, the conversion of starting materials into pinacolones was reduced and mainly replaced by oxidation to

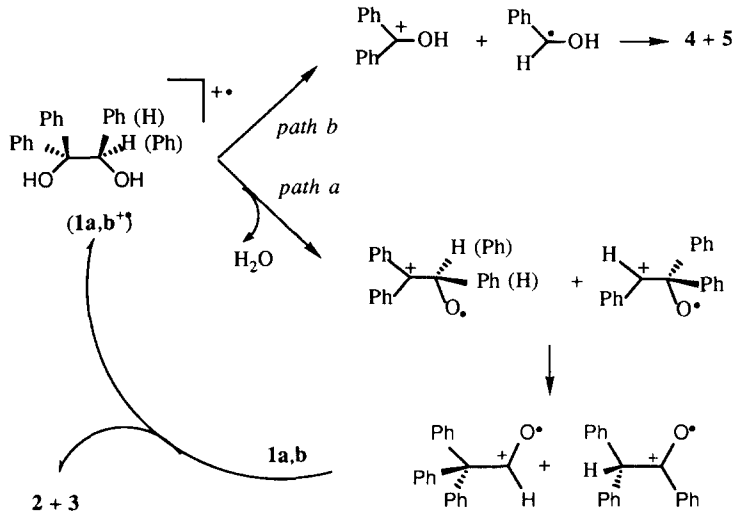
benzophenone and benzaldehyde. On the contrary, the reactions, modified by 1,4-diazabicyclo [2.2.2] octane (**DABCO**) (0.03-0.06 mmol, 5-10 mol %), appeared totally inhibited or simply retarded, depending on its relative amount *vs* the aminium salt employed (runs 11-12).

Some of the previous reactions have also been studied in acetonitrile as solvent. These reactions, (runs 13-14), apparently slower than those performed in methylene chloride solutions, required 30 mol % of the more powerful oxidizing aminium salt **B** and they afforded trace amounts of benzaldehyde and benzophenone together with pinacolones **2** (30 %), **3** (35 %), and consistent amounts of new reaction products (30 %). These latter **7a,b**, isolated by silica gel column chromatography, showed similar MS, IR, ^{1}H, ^{13}C-NMR spectroscopic data and opposite optical activities. The spectroscopic data are consistent with those of pure synthesized samples of 2-methyl-4,4,5-triphenyl-oxazolines, by following a known protocol, (runs 15, 16).[5a,b] Similar reactions, carried out in benzonitrile as solvent, afforded the corresponding 2,4,4,5-tetraphenyl-oxazoline **8** (15 %), equivalent amounts of **2** and **3** (35 %), and C-C oxidative bond cleavage carbonyl compounds, see scheme 2.

Unexpectedly, *however,* similar acetonitrile reactions, carried out in the presence of different amounts of **DBP** (30 and 60 mol %), afforded benzaldehyde **4** and benzophenone **5** (50-60 %) together with pinacolones **2** (15-20 %) and **3** (25 %), whereas no trace of the corresponding oxazolines **7a,b** was detected by TlC, GC chromatographies and GC/MS spectrometry, (runs 17, 18).

The complex of our experimental results can best be accounted for the thermal reactions of cation radical intermediates $(\mathbf{1a,b})^{+\bullet}$, which can either rearrange to pinacolones **2** and **3**, or subside a C-C bond cleavage leading to benzaldeyde **4** and benzophenone **5**, depending on the reaction conditions. The chain cation-radical mechanism (*path a*) involves a dehydration step, easily accounted for a deprotonation/protonation process on the cation radical intermediates, followed by phenyl migration, leading to carbonyl cation radicals. These latter are converted to pinacolones through an exothermic electron transfer process with the starting materials, scheme 3.

Scheme 3



Starting our discussion from the experimental results obtained in acetonitrile as solvent, at first sight, they could be better accounted for a protic acid catalyzed process than for a chain cation-radical mechanism. In fact, control reactions, carried out in acetonitrile solutions with perchloric or sulphuric acid as catalysts, at low temperature 0°C, led (runs 15, 16) to mixtures of **3** (75-80 %) and oxazolines **7a,b** (20-25 %). On the contrary, the total disappearance of oxazolines **7a,b** among the reaction products, when **DBP** modified aminium salt induced reactions are performed (runs 17, 18), strongly supports the hypothesis that **1a** and **1b** undergo a catalytic chain cation-radical rearrangement (*path a)*, as well as, an oxidative C-C bond cleavage (*path b)*, through a common pinacol cation-radical intermediate $(\mathbf{1a,b})^{+\bullet}$. Furthermore, the increasing amounts of benzaldehyde **4** and benzophenone **5** *vs* pinacolones, observed when 30 and 60 mol % of the sterically hindered base **DBP** was added to the reaction solutions (runs 10, 17, 18), coupled with the lower conversion of starting materials, might not be due to the suppression of the protic acid-catalyzed rearrangement, but to other mechanisms; *as for instance* , to the deprotonation of cation-radical intermediates, which would favour the oxidative pathway.

Actually, this hypothesis was originally advanced by Dinnocenzo and Schmittel in the aminium salt-induced *cis-trans* isomerization of aryl cyclopropane derivatives, [7] as well as by Albini [2b] and Witthen[2c] in the photoinduced electron-transfer reactions in acetonitrile solutions of aromatic *vic*-diols.

In these latter reports, the authors suggested that both acceptor anion-radical basicity and a drastically reduced C-C bond energy in the cation radical intermediates contributed to the low activation energy for fragmentation in the ion-radical pair. In addition to that, Albini claimed that sensitizers, like 1,4-naphthalene dicarbonitrile (**NDN**), are not sensitizers in the true sense, but reagents, favouring the deprotonation of the pinacol cation-radicals by the radical anion, directly in the solvent cage.

Shine[4d] and Penn's[4e] groups, *however*, in order to account for the efficient pinacol oxidation process, even with poorer one-electron oxidizing agents, as **DQQ**, pointed out on the short half-life and on the surprisingly low C-C bond dissociation energies of the corresponding pinacol cation-radicals. At the same time, they claimed that the only function of added organic bases was to prevent the protic-acid catalyzed process.
Thus, the likelihood that these intermediates could competitively have time to lose a molecule of water in the chain rearrangement process appeared questionable. However, as observed with several pinacol cation radicals, $(\mathbf{DQQ})^{-\bullet}$ anion radical, co-generated in the preliminary electron-transfer step, can act as the base for proton-transfer, as well as the electron acceptor in the ketyl oxidation to form 2,3-dichloro-5,6-dicyanohydroquinone.[2e]

In our case, *instead*, the preliminary electron-transfer steps between **1a** or **1b** and aminium salts **A** or **B** are not only less endoergonic than those observed with several other one electron oxidizing agents,[4c-g] but also they afford, as by products, *tris* (4-bromophenyl)amine and *tris*-(2,4-dibromophenyl)amine, non nucleophilic, weak bases, unable to deprotonate the cation radical intermediates. As a consequence, the cation radical intermediates might have time to lose a molecule of water. This has been confirmed carryng out aminium salts induced reactions on methylene chloride solutions of starting materials in the presence of a remarkable excess of these latter bases, see note at the bottom of the table.

Thus, given that pinacol-pinacolone rearrangements are: (a) exclusively intramolecular; (b) the course of the process usually depends on which hydroxyl group is most easily removed; (c) the migrating group is that which is better able to stabilize a positive charge; (d) the kinetically controlled ratio between pinacolones

depends to some extent on the solvent and acid employed; (e) the classic mechanistic probes (reactions carried out in the presence of non nucleophilic bases, such as 2,6-di-*tert*-butylpyridine **DBP** [E^{ox} = 1.82 V. *vs* SCE],[8] and 1,4-diazabicyclo [2.2.2] octane **DABCO**[E^{ox} = 0.64 V. *vs* SCE][9] do not appear conclusive, being the results strictly related to the nature, relative amount of the base employed and protocol followed[4d]; (f) the concentration of the protic acid developed under aminium salts initiation is, not only too low to catalyze the isomerization of pinacolones, but also to induce a protic acid rearrangement of pinacols, our experimental results seem to confirm the involvement of a preliminary electron-transfer reaction between **1a** or **1b** and aminium salts with formation of the corresponding amines and cation-radicals $\mathbf{1a}^{+\bullet}$ or $\mathbf{1b}^{+\bullet}$, which can undergo a rearrangement *via* a chain radical-cation mechanism (*path a*), as well as cleavage of C-C bond with formation of **4** and **5** (*path b*), depending on the reaction conditions, see table and schemes 2, 3.

In this context, given that the pK values of cation radicals $\mathbf{1a}^{+\bullet}$ and/or $\mathbf{1b}^{+\bullet}$ are much lower than those of the neutral starting materials,[10] proton loss from our intermediates, showing benzylic and hydroxylics hydrogens, might afford different radical intermediates, and then different reaction products might derive therefrom[10] in relation with the reaction conditions.

In conclusion, we believe that our mechanistic study contributes to shed more light on the factors which govern the rearrangement *vs* the oxidative process in cation radicals of *vic*-diols. However, the evaluation of pK values of cation-radical intermediates, together with the synthetic utility of chiral oxazoline ring system, well documented in the recent literature,[11,12] warrant further investigations on this intriguing topic.

Experimental

Melting points were taken on an electrothermal apparatus and are uncorrected. ^{1}H and ^{13}C-NMR spectra were recorded on a Varian XL-200 and on a Bruker AM-500 MHz instruments. IR, MS spectra were performed, respectively, on a Perkin-Elmer FT-1710 (KBr pellets), and on a Hewlett and Packard GC/Mass MSD 5970 instruments. Optical rotations were measured using a Perkin-Elmer 241 MC polarimeter. GC analyses were carried out on a Hewlett and Packard gas chromatograph, model 5750 B, on columns (1/4"x15 feet) packed with SP 2100 (5% on Supelcoport 100/120). Dichloromethane was purified by washing with sulphuric acid solution, distillation over calcium hydride and then stored in the dark under nitrogen atmosphere and over molecular sieves. Acetonitrile HPLC grade from Carlo Erba Co. has been used as received. Starting materials **1a,b** are pure commercial samples from Aldrich Co. 1,4-diazabicyclo[2,2,2]-octane **DABCO**, 2,6-di-*tert*-butylpyridine **DBP** are commercial samples from Aldrich Co. Aminium salts **A**, **B** have been synthesized by following the procedures reported in the refs. 13a,b.

Pinacol-Pinacolone rearrangement of diols 1a and 1b by aminium salts: general procedure:

Catalytic amounts of aminium salts **A** or **B** (41.8 or 50.8 mg, 0.06 mmol, 10 mol %) were rapidly added, under air atmosphere at room temperature, to a stirred solution of both enantiomers **1a** or **1b** (174 mg, 0.6 mmol, 100 mol %) in dry CH_2Cl_2 (10 ml). The intensely green or blue colour of the solutions, depending on the aminium salts used, faded within a few minutes. The progress of the reactions was monitored by TLC, GC

and GC/MS spectrometry until completion (1h). The reactions were quenched with $NaHCO_3$ solution (10 %) (3 ml), then dichoromethane (10 ml) was added. The organic layer was separated and dried over (Na_2SO_4). The solvent was removed in *vacuum* and the reaction products **2**, and **3**, isolated by column chromatography (silica gel, petroleum ether/ ethyl ether 10/1 as eluant), have been fully characterized by physical, spectral data, and by comparison with authentic synthesized samples:

2 ($C_{20}H_{16}O$): 146 mg (90 %) yield; m.p. 104-105°C (lit.[14] 104-105 °C); I.R (KBr):υ_{max}/cm^{-1}= 3058, 2724, 1685; MS: m/z (%): 243 (M^+- CHO, 100), 165 (56); ^1H NMR ($CDCl_3$): δ_H = 10.28 (s, 1H) and consistent aromatic resonances.

3 ($C_{20}H_{16}O$): 16 mg (10 %), m.p. 134-135 °C (lit.[14] 133-135 °C); I.R. (KBr):υ = 3065, 2978, 1683 cm^{-1}; MS m/z (%): 272 (M^+, 2), 167 (40), 105 (100), 77 (19); ^1H NMR ($CDCl_3$): δ_H 8.03-7.95 (m, 2H), 7.58-7.18 (m, 13 H), 6.06 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 199.82, 139.35, 137.05, 133.21, 129.30, 129.11, 128.97, 127.83, 59.43 ppm. Benzophenone, benzaldehyde, the oxirane **6**, triphenylmethane **4** and triphenylcarbinol **5** have been fully characterized by GC/MS spectrometry and comparison with the fragmentation patterns of authentic commercial and/or synthesized samples.The reactions modified by **DBP** or **DABCO** have been analyzed as above.

Pinacol-Pinacolone rearrangement of diols 1a and 1b by protic acids: general procedure:

Aliquots of dichloromethane solutions of protic acids ($HClO_4$, CF_3COOH and H_2SO_4) were rapidly added at room temperature, to stirred solutions of enantiomers **1a** or **1b** (174 mg, 0.6 mmol, 100 mol %) in dry CH_2Cl_2 (10 ml). The progress of the reactions, monitored by TLC, GC and GC/MS spectrometry, revealed that only the reactions induced by perchloric acid were efficient, leading to the formation of **3** as the sole or main reaction products. Working up the reaction mixtures, as usual, the solvent was then removed in vacuum, and the reaction product, isolated by column chromatography (silica gel, petroleum ether/ ethyl ether 10/1 as eluant), had been fully characterized by physical and spectral data. The reactions induced by CF_3COOH and H_2SO_4 led slowly to more complex mixtures of carbonyl compounds.

Pinacol-Pinacolone rearrangement of diols 1a and 1b by aminium salts in acetonitrile

The required amount of aminium salt **B** (303 mg, 0.3 mmol, 30 mol %) was rapidly added at room temperature to a stirred solution of (S)-1,1,2-triphenyl-1,2-ethanediol **1a** $[\alpha]_D^{20}$ = -214, (c=1, C_2H_5OH) (290 mg, 1 mmol, 100 mol %) in acetonitrile (20ml). The intensely green colour of the solutions turned to dark brown within 3 hours. The progress of the reaction was monitored by TLC, GC and GC/MS spectrometry until completion (3-4 h). The reaction was then quenched with $NaHCO_3$ solution (10 %) (9 ml), added with water (20 ml), and extracted with diethyl ether (3x15 ml). The organic layer was separated and dried over Na_2SO_4. After removal of the solvent, the residue was adsorbed on silica gel and chromatographed as usual. The reaction products **2** and **3**, isolated as above, were fully characterized by physical, spectral data and by comparison with authentic synthesized samples. On the contrary, only a few fractions, containing the pure oxazoline **7a**, were collected. Better results were obnaited changing the protocol as it follows: after the colour of the aminium salt disappeared, the reaction mixture was quenched with water (20 ml), and extracted with diethyl ether (2x15 ml). The organic layer, dried over Na_2SO_4, was evaporated under vacuum, and the residue, adsorbed on silica gel, was chromatographed on a short silica gel column (10 cm) with petroleum

ether/diethyl ether (10/1 v/v) as eluant. The reaction products **2** and **3**, eluted after the amine, were characterized as above. The silica gel column chromatography was then eluted with dietyl ether/methanol 8/2, v/v, and the collected fractions, washed with $NaHCO_3$ (10 %) solution (2 x 10 ml) and then water (10 ml), were extracted with diethyl ether and dried over sodium sulphate (Na_2SO_4 dry). The solvent was removed in vacuum and the crude reaction product, (90 mg, 30 %),was further purified by a preparative TLC cromatography (diethylether/petroleumether 1/1 as eluant). This latter, $[\alpha]_D^{20}$ = -2.28, (c = 1, $CHCl_3$), was identified, as 2-methyl-4,4,5-triphenyl-oxazoline **7a** ($C_{22}H_{19}NO$), through the following spectral data: I.R (KBr):υ_{max}/cm^{-1}= 3346, 3061, 3033, 2927, 2851, 2257, 1677, 1600, 1494, 1448, 1385, 1299, 1258, 1211, 1180, 1157; MS: m/z (%): 313 (M^+, 1), 207 (100), 167 (12), 166 (79), 165 (81), 106 (1), 105 (4), 82 (5), 77 (5); ^1H NMR ($CDCl_3$): δ_H = 2.2 (s, 3H), 6.28 (s, 1H), 6.9-7.67 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$): δ_C = 164.3, 146.3, 141.6, 137.3, 128.5, 128, 127.8, 127.3, 127.2, 126.9, 126.4, 89.9 (d), 83.3, 14.2 (q) ppm. From the substrate (R)-1,1,2-triphenyl-1,2-ethandiol **1b** $[\alpha]_D^{20}$ = +210 (c=1, C_2H_5OH) was isolated the oxazoline **7b**, showing the same spectral data, but opposite optical rotation $[\alpha]_D^{20}$ =+ 2.1, (c = 1, $CHCl_3$). The same reaction product was obtained by following a known procedure (see refs. 5a,b) and by treatment of a pure synthesized sample of **6** with catalytic amounts of aminium salt **B** in acetonitrile as solvent. See also reference 6, 12, 13. Similar reactions, performed in benzonitrile as solvent, led to the corresponding 2,4,4,5-tetraphenyl-oxazoline **8,** fully characterized by GC/MS spectrometry; MS /m/z (%): 375 (M^+, 0), 269 (100), 167 (6), 166 (33), 165 (62), 106 (1), 105 (4), 82 (5), 77 (7). The reactions performed in the presence of **DBP** (30 and 60 mol %) afforded benzaldehyde and benzophenone together with pinacolones **2** and **3**, as reported in the table.

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