Pinacol-Type Rearrangement Reactions of 2-Phenyl-3-silyloxyoxetanes: The Influence of the Lewis Acid on the Regioselectivity

Thorsten Bach* and Frank Eilers

Fachbereich Chemie der Philipps-Universität Marburg, D-35032 Marburg, Germany

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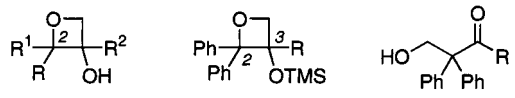
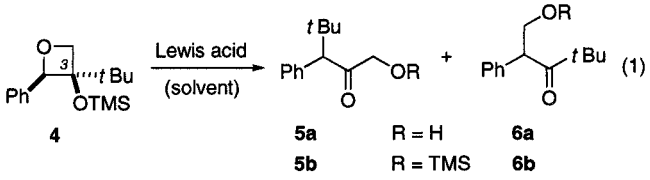
Oxetanols of the general structure **1** (R, R^1, R^2 = alkyl) undergo acid-catalyzed rearrangement reactions in the course of which a hydroxymethyl group migrates to the carbon atom C-2 in a pinacol-type 1,2-shift.[1,2] 2,2-Diphenyl-3-[(trimethylsilyl)oxy]oxetanes **2** similarly undergo hydroxymethyl group migrations to yield the corresponding rearrangement products **3** upon treatment with a Lewis acid (BF_3 or $TiCl_4$) in CH_2Cl_2.[3,4]



1 **2** **3**

Recently, we observed that 2-phenyl-3-[(trimethylsilyl)-oxy]oxetanes related to **2** exhibit migratory aptitudes different from **1** and **2**. It was found that the 1,2-migration of the R group at C-3 is preferred as compared to the hydroxymethyl shift (3:1 ratio).[5] In view of the potential use of the Lewis acid catalyzed rearrangement of 3-silyloxyoxetanes for kinetic resolution experiments[6] with chiral Lewis acids, we have studied the regioselectivity of these rearrangements more closely. To this end, the oxetane **4**, which is readily available by the photocycloaddition of benzaldehyde and 3,3-dimethyl-2-[(trimethylsilyl)oxy]-1-butene,[7] was treated with various Lewis acids in three different solvents, i.e., in a polar, coordinating solvent (diethyl ether), in a polar, noncoordinating solvent (CH_2Cl_2), and in a nonpolar solvent (toluene). The structure of the products so obtained are depicted in eq 1 and their relative ratios are summarized



4 **5a** R = H **6a**
5b R = TMS **6b**

in Table 1. The table does not include all the experiments we have conducted. A full list of data is contained in the Supporting Information.

In all runs the reaction mixture was quenched with water and the aqueous layer was extracted with CH_2Cl_2. The four possible products as depicted in eq 1 were detected by ^1H NMR spectroscopy, and their relative ratio was determined by integration. To ascertain their identity they were purified by chromatography and fully characterized (see Experimental Section). Silyl ether **5b** proved to be extremely moisture sensitive and decomposed even on silica gel. It is therefore possible that this compound was not detected after workup, although it had been present in the reaction mixture in some instances. Generally, these reactions proceeded fastest in CH_2Cl_2 as the solvent and slowest in ether, as exemplified by the $ZnCl_2$-promoted reactions (entries 1−3). Whereas there was no reaction in ether, the rearrangement occurred in toluene, but it was incomplete after 18 h. It was complete in CH_2Cl_2 after the same period of time. Similar trends were observed with other Lewis acids, e.g. $TiCl_4$ (entries 5−7) and $AlMe_3$ (entry 12), in the case of which only the reaction in CH_2Cl_2 went to completion. With almost all Lewis acids except $TiCl_4$ and $AlMe_3$ compounds **6** prevailed as products over **5**. If compounds **6** were the major products, the highest selectivity was often observed in toluene as the solvent. This tendency can be observed for $ZnCl_2$ (entries 1−3) and $AlMeCl_2$ (entries 9−11) from Table 1 and it also held true for $SnCl_4$ (entry 4) and $AlCl_3$ (entry 8), for which only the most selective reactions were included in the table. In addition, the solvent toluene often favored preferential formation of the silylated product **6b** (entries 3 and 11). In terms of regioselectivity, the best results were recorded either by employing $TiCl_4$ in ether, which resulted in the exclusive formation of **5a** (entry 5), or by employing $AlMeCl_2$ in toluene (entry 11), which promoted the

Table 1. Rearrangement Reactions of Oxetane 4 upon Treatment with Lewis Acids in Various Solvents

entry	Lewis acid	solvent	time,[a] h	temp, °C	product ratio (**5a**:**5b**):(**6a**:**6b**)
1	$ZnCl_2$	ether	18	reflux	−[b]
2	$ZnCl_2$	CH_2Cl_2	18	reflux	(43:0):(57:0)
3	$ZnCl_2$	toluene	18[c]	reflux	(11:0):(58:31)
4	$SnCl_4$	toluene	12	25	(29:0):(71:0)
5	$TiCl_4$	ether	2.5	25	(100:0):(0:0)
6	$TiCl_4$	CH_2Cl_2	0.1	−78	(74:0):(26:0)
7	$TiCl_4$	toluene	0.1	−78	(80:0):(20:0)
8	$AlCl_3$	toluene	18	25	(21:0):(79:0)
9	$AlMeCl_2$[d]	ether	20[e]	25	(11:0):(49:40)
10	$AlMeCl_2$[d]	CH_2Cl_2	20[f]	25	(28:0):(42:30)
11	$AlMeCl_2$[d]	toluene	20	25	(9:0):(17:74)
12	$AlMe_3$[g]	CH_2Cl_2	20	25	(50:6):(18:26)

[a] Time required for complete conversion at the designated temperature. [b] No reaction occurred. [c] 90% conversion. [d] A 1 M solution in hexane was used. [e] 35% conversion. [f] 60% conversion. [g] A 2 M solution in heptane was used.

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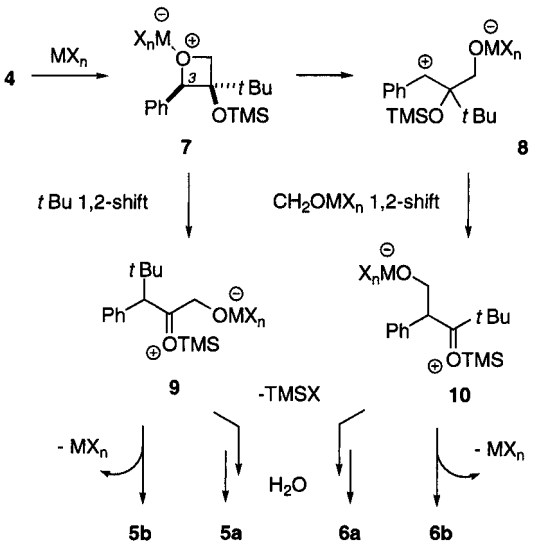
Scheme 1

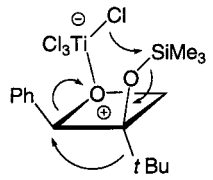


formation of products **6a** and **6b**. In preparative runs on a 1 mmol scale, the latter reaction yielded 73% of aldol **6a** after acidic workup and the former reaction yielded 70% of α-hydroxy ketone **5a**.

A proposed mechanism for the reaction is shown in Scheme 1 although it is certainly not possible to trace down every single experimental observation to a mechanistic key step. It postulates two competitive pathways responsible for the formation of compounds **5** and **6** (Scheme 1).

The Lewis acid (depicted by the general structure MX_n) activates the oxetane by complexation to the Lewis-basic oxetane oxygen atom, yielding onium ion **7**. The *tert*-butyl migration can occur directly from this intermediate to yield rearrangement product **9**. Alternatively, the oxetane ring can open to benzylic carbenium ion **8**, which rearranges to intermediate **10** via a hydroxymethyl 1,2-shift. The rearrangement of **8** to **9** is less likely based on previous experiments[2,3] with oxetanes **1** and **2** (vide supra), in which carbenium ions related to **8** were the intermediates and in which the hydroxymethyl and not the alkyl migration dominated. In turn, **7** cannot be considered a viable precursor for rearrangement product **10**, as this hydroxymethyl migration would have to occur in a disfavored $[_\sigma2_s + _\sigma2_s]$-process (vide infra). As the oxetane competes with other Lewis bases for the Lewis acid, it is clear why the reaction proceeded with the lowest reaction rate in ether as solvent. CH_2Cl_2 is suited to stabilize ions and zwitterions better than toluene and is consequently the solvent in which the rearrangement proceeded most readily. The ratio of silylated to desilylated products is determined by the competition of silyl migration (**9** → **5b**, **10** → **6b**) with silyl cleavage (**9** → **5a**, **10** → **6a**). The dissociation of X^- is facilitated in CH_2Cl_2 and it leads to desilylation upon attack at the TMS group. On the contrary, the intramolecular silyl migration can proceed via a tight five- or six-membered transition state which should be favored in toluene. Indeed, the highest amounts of silylated products were formed in toluene. The process of silyl migration to afford products **5b** or **6b** is not only mechanistically interesting but it is also mandatory for a successful catalytic cycle. Only if the Lewis acid MX_n is regenerated can it activate another oxetane molecule for the rearrangement. So far, $AlMeCl_2$ was the only Lewis acid which allowed for a catalytic process to occur. In a preparative run in which $AlMeCl_2$ was employed in substoichiometric quantities (0.5 equiv) relative to oxetane **4**, the silylated product **6b** was isolated in 40% yield together with 31% of the desilylated aldol **6a**.

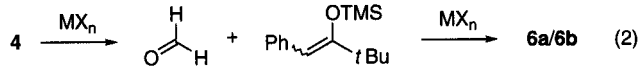
Concerning the regioselectivity of the reaction, the pathway followed in most cases (entries 2−4, 8−11 in the table) is the route **7** → **8** → **10**. This observation might be associated with the fact that the nucleophilicity of the *tert*-butyl group in **7** is not high enough to account for a successful competition of step **7** → **9** vs **7** → **8**. An increased nucleophilicity would be expected if the TMS group in **7** is either activated by an anion or replaced by a metal. Accordingly, the high tendency of $TiCl_4$ to effect the desilylation of silyl ethers rapidly even at low temperature[8] might be the clue to its different reaction mode. If desilylation of the oxetanol proceeds before the oxetane oxygen is activated for the migration or if $TiCl_4$ is capable of providing a chloride ion intramolecularly, as depicted in formula **11**,[9] the *tert*-butyl migration should be favored.



11

Ether should be the best solvent for this process, as oxetane activation is retarded in this solvent due to competing complexation of ether with the Lewis acid. $AlMe_3$, on the other hand, might lead to a significant degree of *tert*-butyl migration because its Lewis acidity is relatively low[10] and the ring opening **7** → **8** may be slower than the migration **7** → **9**.

We briefly looked into another possible pathway for the formation of compounds **6a** and **6b** by rearrangement of oxetane **4**. The $AlMeCl_2$-catalyzed process **4** → **6** can either proceed via the free carbenium ion **8** by an intramolecular 1,2-shift as discussed above or it could be due to a complete separation of formaldehyde from oxetane **4** in a retro-[2 + 2] fashion and a subsequent intermolecular Mukaiyama aldol reaction (eq 2).



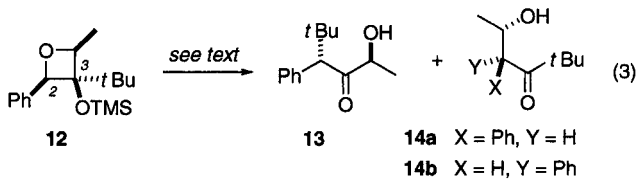
In agreement with previous crossover experiments,[3] we found no indication to support the latter notion. In competition reactions with acetaldehyde there was no hint for the incorporation of this substrate into the product, i.e., for the formation of a 1-hydroxyethyl-substituted ketone. Consequently, it appears reasonable to assume a carbenium ion as an intermediate in the $AlMeCl_2$-catalyzed reaction which is intramolecularly attacked in a pinacol-type rearrangement. This picture

(8) Some recent examples: (a) Jenal, A.; Zahra, J.-P.; Santelli, M. *Tetrahedron Lett.* **1983**, *24*, 1395. (b) Castedo, L.; Granja, J.; Maestro, M. A.; Mourino, A. *Tetrahedron Lett.* **1987**, *28*, 4589. (c) Crossley, M. J.; Hambley, T. W.; Stamford, A. W. *Aust. J. Chem.* **1990**, *43*, 1827. (d) Yamamoto, Y.; Abe, H.; Nishi, S.; Yamada, J.-i. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3253.

(9) We very much thank a referee for pointing out this possibility to us.

(10) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

is further supported by the fact that the rearrangement reaction of oxetane **12**[11] (eq 3) proceeded nonstereospe-



12 **13** **14a** X = Ph, Y = H
14b X = H, Y = Ph

cifically in the presence of $AlMeCl_2$. As expected, a 1-hydroxyethyl shift occurred predominantly and the reaction products **14a** and **14b** were isolated (66% yield). Their ratio was slightly dependent on the reaction temperature and varied between 70/30 and 80/20 in favor of **14b**. The assignment of the relative configuration was based on the $^3J_{HH}$ coupling constants of the protons C*H*OH and C*H*Ph and on the ^{13}C NMR data. In general, intramolecularly hydrogen-bonded *syn*-aldols are known to exhibit smaller $^3J_{HH}$ values than the *anti*-aldols.[12] Also, the ^{13}C NMR signals of carbinol and methine carbon atoms are shifted upfield in *syn*-aldols relative to *anti*-aldols.[13]

Contrary to the result obtained with $AlMe_2Cl$ and in agreement with our previous arguments, aldol-type products were observed in the $TiCl_4$-induced rearrangement of compound **12** only to a small extent. If the reaction was conducted at −78 °C, the aldols **14a** and **14b** were isolated in a ratio of 95/5 (17% yield). The major product was an α-hydroxyketone (47% yield), which was tentatively assigned the depicted configuration **13** based on the assumption that an inversion at the former C-2 carbon atom of oxetane **12** has occurred. The structure of compound **12** in the crystal[14] shows an anticlinal arrangement of the C-2/O and the *t*-Bu/C-3 bond (dihedral angle = 122.9°) which should facilitate a backside attack of the migrating group, as was postulated for the analogous migration **7** → **9**.

Further studies regarding the course of 1,2-rearrangements of 3-oxetanols and their derivatives are currently underway in our laboratories.

Experimental Section

General. For general remarks, see ref 15. Solvents (P = pentane, TBME = *tert*-butyl methyl ether) used for chromatography were distilled prior to use. The oxetanes **4** and **13** were prepared as described previously.[7,11] ^{13}C NMR multiplicities were obtained by DEPT experiments.

General Procedure for Lewis Acid Catalyzed Rearrangements. A solution of 1.0 mmol of oxetane was dissolved in 5 mL of the corresponding solvent and the mixture was cooled to −78 °C. Lewis acid (3.0 mmol) was slowly added to the vigorously stirred solution. After the addition was complete the mixture was warmed to the temperature indicated in Table 1. The reaction was quenched with 5 mL of water and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution (5 mL) and with brine (10 mL). After drying over $MgSO_4$ and filtration, the solvent was removed and the residue was analyzed by GLC and ^1H NMR spectroscopy (see Table 1). In preparative runs, 10 mL of 2 N aqueous HCl was used to quench the reaction mixture. The purification of the individual substances was conducted by chromatography, as indicated below.

(*RS*)-1-Hydroxy-4,4-dimethyl-3-phenyl-2-pentanone (5a).[5] Following the general procedure, 1.0 mmol of oxetane **4** (278 mg) and 3.0 mmol of $TiCl_4$ (570 mg, 330 μL) were allowed to react in 5 mL of ether at −78 °C for 10 min. Workup and subsequent flash chromatography (P/TBME/NEt_3 = 95/4/1) gave 145 mg (70%) of ketone **5a** as a colorless solid. R_f = 0.20 (P/TBME = 9/1); ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 3.11 (t, J = 4.7 Hz, 1 H), 3.49 (s, 1 H), 4.11 (dd, J = 19.0 Hz, J = 4.7 Hz, 1 H), 4.20 (dd, J = 19.0 Hz, J = 4.7 Hz, 1 H), 7.26−7.30 (m, 5 H). All other analytical data were in agreement with the literature values.[5]

(*RS*)-4,4-Dimethyl-3-phenyl-1-[(trimethylsilyl)oxy]-2-pentanone (5b). For comparison, this sensitive silyl ether was prepared from 0.66 mmol of compound **5a** (137 mg) by silylation with 1.3 mmol of TMSCl (140 mg, 165 μL) and 1.3 mmol of NEt_3 (130 mg, 180 μL) in 5 mL of CH_2Cl_2 at ambient temperature. The workup was conducted with pH 7 buffer. Purification with neutral alumina (P/TBME = 95/5) gave 172 mg (94%) of silyl ether **5b** as a colorless oil. R_f = 0.49 (P/TBME = 9/1); ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 0.99 (s, 9 H), 3.65 (s, 1 H), 4.08 (d, J = 18.0 Hz, 1 H), 4.17 (d, J = 18.0 Hz, 1 H), 7.25−7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −0.7 (q), 28.0 (q), 34.5 (s), 62.2 (d), 69.4 (t), 127.1 (d), 127.9 (d), 130.4 (d), 135.5 (s), 209.1 (s). Anal. Calcd for $C_{16}H_{26}O_2Si$ (278.5): C, 69.01; H, 9.41. Found: C, 68.80; H, 9.48.

(*RS*)-1-Hydroxy-4,4-dimethyl-2-phenyl-3-pentanone (6a).[5] Following the general procedure, 1.0 mmol of oxetane **4** (278 mg) and 3.0 mmol of $AlMeCl_2$ (3.0 mL of a 1 M solution in hexane) were allowed to react in 5 mL of toluene at room temperature for 2 h. Workup and subsequent flash chromatography (P/TBME/NEt_3 = 95/4/1 → 80/19/1) gave 150 mg (73%) of ketone **6a** as a colorless solid. In addition, 35 mg (17%) of ketone **5a** was obtained. R_f = 0.05 (P/TBME = 9/1); ^1H NMR ($CDCl_3$) δ 1.08 (s, 9 H), 1.94 (s, 1 H), 3.70 (dd, J = 11.0 Hz, J = 5.3 Hz, 1 H), 4.08 (dd, J = 11.0 Hz, J = 8.6 Hz, 1 H), 4.38 (dd, J = 8.6 Hz, J = 5.3 Hz, 1 H), 7.22−7.40 (m, 5 H). All other analytical data were in agreement with the literature values.[5]

(*RS*)-4,4-Dimethyl-2-phenyl-1-[(trimethylsilyl)oxy]-3-pentanone (6b). Following the general procedure, 1.0 mmol of oxetane **4** (278 mg) and 0.5 mmol of $AlMeCl_2$ (0.5 mL of a 1 M solution in hexane) were allowed to react in 5 mL of toluene at room temperature for 18 h. Workup and subsequent flash chromatography (P/TBME/NEt_3 = 98/1/1 → 85/14/1) gave 112 mg (40%) of ketone **6b** as a colorless oil. In addition, 64 mg (31%) of ketone **6a** and 42 mg (20%) of ketone **5a** were obtained. R_f = 0.65 (P/TBME = 9/1); ^1H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.09 (s, 9 H), 3.58 (dd, J = 9.4 Hz, J = 5.0 Hz, 1 H), 4.14 (t, J = 9.4 Hz, 1 H), 4.38 (dd, J = 9.4 Hz, J = 5.0 Hz, 1 H), 7.23−7.27 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −0.7 (q), 26.2 (q), 45.1 (s), 55.1 (d), 66.1 (t), 127.2 (d), 128.4 (d), 128.6 (d), 136.3 (s), 214.1 (s). Anal. Calcd for $C_{16}H_{26}O_2Si$ (278.5): C, 69.01; H, 9.41. Found: C, 69.04; H, 9.65.

(2*RS*,4*RS*)-2-Hydroxy-5,5-dimethyl-4-phenyl-3-hexanone (13). Following the general procedure, 1.0 mmol of oxetane **12** (293 mg) and 3.0 mmol of $TiCl_4$ (570 mg, 330 μL) were allowed to react in 5 mL of ether at −78 °C for 10 min. Workup and subsequent flash chromatography (P/TBME/NEt_3 = 95/4/1 → 85/14/1) gave 104 mg (47%) of ketone **13** as a colorless oil. R_f = 0.23 (P/TBME = 9/1); ^1H NMR ($CDCl_3$) δ 1.01 (s, 9 H), 1.38 (d, J = 7.1 Hz, 3 H), 3.42 (d, J = 5.5 Hz, 1 H), 3.74 (s, 1 H), 4.04 (dq, J = 7.1 Hz, J = 5.5 Hz, 1 H), 7.15−7.18 (m, 2 H), 7.26−7.31 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 20.1 (q), 28.1 (q), 34.4 (s), 63.0 (d), 71.7 (d), 127.5 (d), 128.3 (d), 130.3 (d), 134.7 (s), 212.5 (s). Anal. Calcd for $C_{14}H_{20}O_2$ (220.3): C, 76.33; H, 9.15. Found: C, 76.00; H, 9.15.

5-Hydroxy-2,2-dimethyl-4-phenyl-3-hexanone (14). Following the general procedure, 1.0 mmol of oxetane **12** (293 mg) and 3.0 mmol of $AlMeCl_2$ (3.0 mL of a 1 M solution in hexane) were allowed to react in 5 mL of toluene at −78 °C for 18 h. Workup and subsequent flash chromatography (P/TBME/NEt_3 = 95/4/1 → 85/14/1) gave 145 mg (66%) of the ketones **14a** and **14b** (**14a**/**14b** = 35/65) as a yellowish solid. The diastereoisomers were not separable. R_f = 0.12 (P/TBME = 9/1). Anal. Calcd for $C_{14}H_{20}O_2$ (220.3): C, 76.33; H, 9.15. Found: C, 75.93; H, 9.53.

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(15) Bach, T.; Schröder, J. *J. Org. Chem.* **1999**, *64*, 1265.

(4*RS*,5*RS*)-Diastereoisomer (**14a**): ^{1}H NMR ($CDCl_3$) δ 0.94 (d, J = 6.3 Hz, 3 H), 0.99 (s, 9 H), 2.50 (s, 1 H), 3.96 (d, J = 8.7 Hz, 1 H), 4.19−4.30 (m, 1 H), 7.15−7.26 (m, 5 H, arom. H); ^{13}C NMR ($CDCl_3$) δ 20.2 (q), 26.7 (q), 45.4 (s), 61.7 (d), 70.6 (d), 127.3 (d), 128.7 (d), 129.4 (d), 136.3 (s), 216.4 (s).

(4*RS*,5*SR*)-Diastereoisomer (**14b**): ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.05 (d, J = 6.2 Hz, 3 H), 2.44 (s, 1 H), 3.94 (d, J = 6.7 Hz, 1 H), 4.19 (virt. quintet, J = 6.4 Hz, 1 H), 7.15−7.26 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.7 (q), 26.5 (q), 45.4 (s), 59.5 (d), 69.7 (d), 127.5 (d), 128.7 (d), 129.4 (d), 135.1 (s), 216.4 (s).

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Supporting Information Available: A table of all data recorded and complete spectral data for compounds **5b**, **6b**, **13** and **14** (IR, NMR assignments, MS). This material is available free of charge via the Internet at http://pubs.acs.org.

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