# Catalysis of chlorosilane on the ring-expansion of cyclic acetals bearing a carbene precursor. Lewis acid–base effect on the oxonium ylide intermediate

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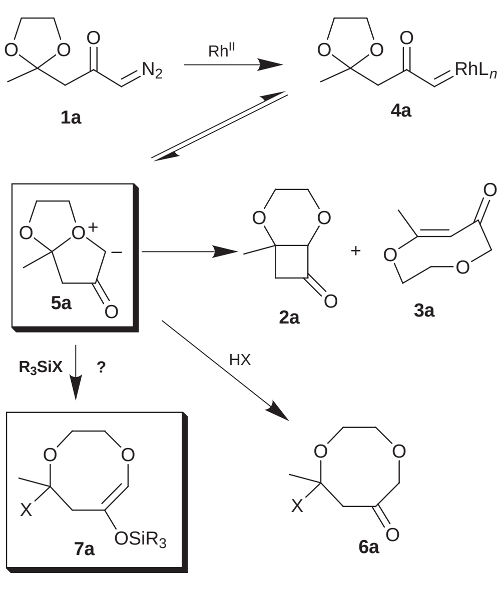
**Rhodium catalyzed (1–0.1 mol%) decomposition of 2-(3-diazo-2-oxopropyl)-2-methyldioxolane 1a or 2-(3-diazo-1-methyl-2-oxopropyl)-2-methyldioxolane 1b in the presence of a catalytic amount of TMSCl (10 mol%), yielded 4,7-dioxocane 3a (91%) or 3b (49%), whereas similar reaction in the absence of TMSCl caused 1,2-rearrangement to give bicyclobutanones 2a or 2b, respectively; Lewis acid-base catalysis by TMSCl of the ring-expansion of a bicyclooxonium ylide intermediate is revealed.**

It is well known that metal carbene complexes (or carbenoids) react with oxygen, nitrogen or sulfur compounds to form onium ylides and some are utilized for synthetic purposes.[1] Among them, ethereal oxonium ylides, the most short-lived species,[2] have been investigated recently. Nevertheless, they are so short-lived that their application to synthesis is limited to a few examples, *e.g.* [1,2]- and [2,3]-sigmatropic rearrangement.[3,4]

Johnson reported that a metal carbene complex generated from diazo ketone **1a** and $Rh_2(OAc)_4$ yielded [1,2]-rearrangement product **2a** as the major product (68%) and ring-expansion product **3a** in a minor amount (16%) (Scheme 1).[5] Recently, we reported that a protic nucleophile (*e.g.* MeOH, AcOH) protonates the ylide intermediate to form a bicyclic oxonium ion, suppressing the 1,2-rearrangement and facilitating three-carbon ring-expansion reactions.[6,7] In analogy to the ylide trapping method, we anticipated that a silyl cation may trap the ylide to form a silyl-substituted oxonium ion, ending up with a similar ring-expansion reaction. We report here the first evidence for Lewis acid–base catalysis by chlorosilanes of the oxonium ylides that is exerted in the three-carbon ring-expansion reaction.

In advance of the use of transition metal catalysts, we examined the stability of diazo ketone **1a** in the presence of various silyl reagents, because **1a** was suspected of decomposing in the presence of these species in the absence of the metal catalyst.[8] It was found that diazoketone **1a** decomposed only in the presence of TMSOTf.



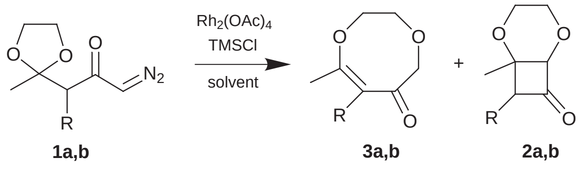
**Scheme 1**

The reaction of **1a** in the presence of $Rh_2(OAc)_4$ and various silyl reagents was performed as follows: the diazo ketone was slowly added to a solution of $Rh_2(OAc)_4$ (1 mol%) and the silyl reagent (1.0 equiv., initial concentration 0.1 mol $dm^{-3}$) at ambient temperature. After complete consumption of **1a**, the reaction was quenched with $Et_3N$ and products were isolated by silica gel flash chromatography.

Choice of the silyl reagent was important. With TMSCN, the reaction did not take place, presumably because it poisoned the Rh catalyst. With TMSCl or TESCl, the expected ring-expansion product **3a** was obtained as the major product (80 or 44%, respectively). In both cases, minor products were [1,2]-rearrangement product **2a** and non-rearrangement product 2-(3-chloro-2-oxopropyl)-2-methyldioxolane.[9] In contrast, TBDMSCl (entry 4) did not give **3a**, probably because the chlorosilane was not reactive enough to capture the oxonium ylide. Again, TMSOAc gave **3a** although in low yield. Consequently, TMSCl was chosen as the most appropriate reagent, with which we examined the choice of solvent. Among those examined, benzene was the best for the production of **3** ($CH_2Cl_2$, 80%; benzene, 91%; THF, 68%).

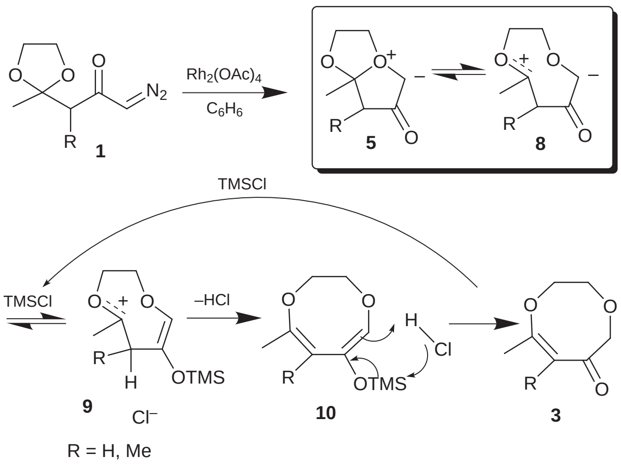
Ring-expansion product **3a** seems likely to be formed by the elimination–hydrolysis of silyl ether **7** in the work-up procedure.[10] However, searching for this intermediate **7** by $^1H$ NMR in the reaction mixture (benzene-$d_6$,) was unsuccessful. Therefore, we assumed that the chlorosilane is acting as a catalyst[11]

**Table 1** Effect of stoichiometry and concentration of TMSCl in the ring-expansion reaction



| Entry[a] | Substrate | TMSCl Equiv. | TMSCl Init. conc./mol $dm^{-3}$ | Addition time/min | Products (%) |
|---|---|---|---|---|---|
| 1 | **1a** | — | — | — | **3a** (16), **2a** (68)[b] |
| 2 | **1a** | 1.0 | 0.10 | 10 | **3a** (91) |
| 3 | **1a** | 0.5 | 0.05 | 10 | **3a** (40), **2a** (20) |
| 4 | **1a** | 0.1 | 0.01 | 10 | **3a** (33), **2a** (37) |
| 5 | **1a** | 0.1 | 0.10 | 10 | **3a** (38), **2a** (12) |
| 6 | **1a** | 0.1 | 0.10 | 120 | **3a** (77) |
| 7 | **1b** | — | — | 120 | **2b** (58)[b] |
| 8 | **1b** | 0.1 | 0.10 | 120 | **3b** (27), **2b** (41) |
| 9 | **1b** | 0.5 | 0.50 | 120 | **3b** (42), **2b** (21) |
| 10 | **1b** | 1.0 | 1.00 | 120 | **3b** (49), **2b** (10) |

[a] The amount of catalyst $Rh_2(OAc)_4$ was 1 mol% relative to **1** for entries 1–5, 0.1 mol% for entries 6–10. [b] Ref. 5.



**Scheme 2**

and investigated the stoichiometric effect of TMSCl (Table 1, entries 2–6). It is clear that, as the molar amount of TMSCl *vs.* **1a** decreases, the yield of [1,2]-rearrangement product **2a** increases (entries 2–4). However, even with a decreased amount of chlorosilane (0.1 equiv.), the catalytic role of TMSCl can be exerted effectively under the following conditions: (1) the initial concentration of TMSCl is kept at a relatively high level, *e.g.* 0.1 mol dm$^{-3}$ (entries 2, 5, 6); (2) the amount of $Rh_2(OAc)_4$ is as low as 0.1 mol% (entry 6); (3) the diazo ketone is added as slowly as possible (entry 6). Under such conditions, the oxonium ylide is formed in very low concentration and, although very short-lived, it can react effectively with the large excess of TMSCl.

Some of these optimized conditions were also applied to methyl-substituted diazo ketone **1b** (Table 1, entries 7–10). In the absence of chlorosilane (entry 7), **2b** was formed as the sole product,[5] whereas the addition of TMSCl to the reaction mixture increased the formation of ring-expansion product **3b**. Increasing both the molar amount and initial concentration of TMSCl also improved the yield of **3b** (entries 8–10).

On the basis of the above-mentioned findings, we propose the mechanism depicted in Scheme 2. First, the treatment of diazo ketone **1** with the transition metal catalyst generates oxonium ylide **5** *via* its carbenoid **4**, both being in equilibrium[12] (see Scheme 1). Ylide **5** is in equilibrium with zwitterion **8**, which is trapped by the chlorosilane to form oxocarbenium ion **9** in preference to the [1,2]-rearrangement. Ion **9** undergoes deprotonation with counter ion $Cl^-$ to produce diene **10**, which results in the formation of final product **3**. Relatively low yields of **3b** in comparison with **3a** may be attributable to the steric effect encountered in the deprotonation of **9** where two methyl groups must adopt a (*Z*) disposition. The double bond structure of **3** has been described as *trans*.[5] If it is *trans*, the mechanism for the double bond formation from the ylide should be a concerted one, being inconsistent with a sequential profile of the present mechanism. Therefore, we measured the X-ray crystallographic structure of **3a** (mp 67 °C) to obtain a clear insight into the mechanism.† As shown in Fig. 1, the geometry of the enone is *cis*.

To summarize, $Rh_2(OAc)_4$ catalyzed decomposition of diazo ketones **1a** and **1b** in the presence of a catalytic amount of TMSCl yielded three-carbon ring-expansion products **3a** and **3b** in better yields than in the absence of the chlorosilane, while the catalyst role of TMSCL in this sequential reaction was verified.

This hitherto unknown catalysis by chlorosilanes in the control of ethereal oxonium ylides seems promising for its utilization with other onium ylides.

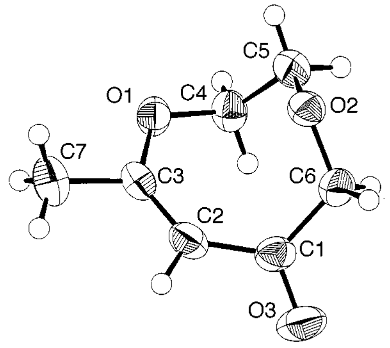


**Fig. 1** Molecular structure of **3**. Selected torsion angles (°): O(1)–C(3)–C(2)–C(1) 7.9(4), C(1)–C(2)–C(3)–C(7) −175.7(2).

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## Notes and references

† *Crystal data* for $C_7H_{10}O_3$ **3**: $M$ = 142.15, monoclinic, $a$ = 13.686(1), $b$ = 4.231(1), $c$ = 14.018(2) Å, $\beta$ = 117.924(3)° $U$ = 721.9(2) Å$^3$, $T$ = 296 K, space group $P2_1/a$ (no.14), $Z$ = 4, $\mu$(Mo-K) = 1.02 cm$^{-1}$, $D_c$ = 1.308 g cm$^{-3}$, 1431 unique reflections measured. The structure was solved using direct methods and refined by full-matrix least-squares to $R$ = 0.034 and $wR$ = 0.046 for 948 reflections with $I > 3\sigma(I)$. $\Sigma w(|F_o| - |F_c|)^2$ was minimized. Single crystals of $C_7H_{10}O_3$ **3a** were obtained by recrystallization from hexane–$Et_2O$ after purification by silica gel flash chromatography. CCDC 182/1283. See http://www.rsc.org/suppdata/cc/1999/1339/ for crystallographic data in .cif format.

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