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Cleavage of Si–Ar bond *vs* Si–Me bond: a remarkable counterion effect on reactivity†

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Formation of distinctly different products from the same alkoxide intermediate indicates a strong dependence of reaction pathways on counterions.

We have previously described[1] that nucleophile-assisted Ar–Si bond cleavage is particularly facile when the arene ring is complexed with a $Cr(CO)_3$ fragment (Chart 1). Stability of the aryl anion intermediate anchored on $Cr(CO)_3$ moiety is believed to facilitate such desilylation. This reaction provides a very useful method for introducing electron-withdrawing substituents on the arene ring by an *ipso* substitution of the $SiMe_3$ group. The facility of Si–Ar bond cleavage is evident also in a recently reported observation[2] of facile Brook rearrangement[3] (1,4:*C*-to-*O*) of the alkoxide resulting from addition of methyllithium to *o*-$SiMe_3$–benzaldehyde–$Cr(CO)_3$ complex (Chart 1).

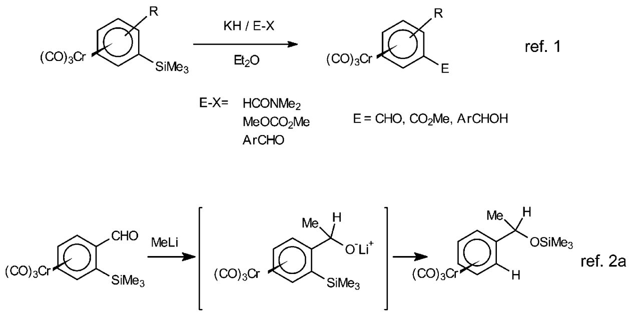
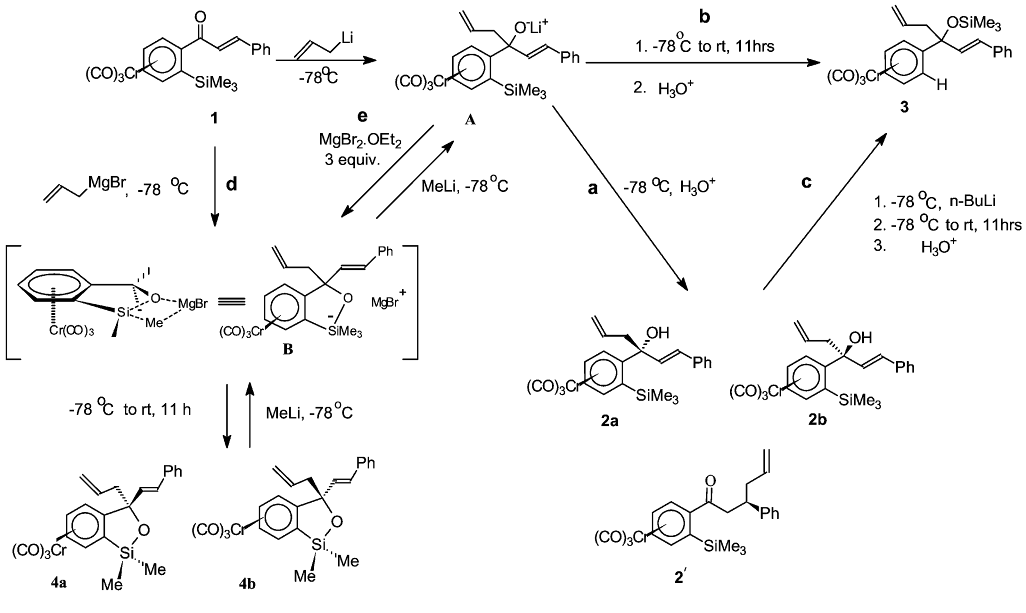


Chart 1

The present paper describes a dramatic departure from this seemingly simple picture. We report that a change of the counterion of the alkoxide intermediate (*e.g.* replacing lithium with magnesium) leads to an unexpected but decisive alteration of reaction course.

In continuation of our on-going investigations with arene–tricarbonylchromium complexes,[4] we carried out addition of allyllithium to an acyclic enone **1** (Scheme 1).[5] When the reaction was carried out at −78 °C and the reaction mixture was quenched immediately after complete consumption of starting material (15–30 min), the carbinol **2a** was isolated in 39% yield as a diastereomerically pure product[6] (path *a*, Scheme 1). Unexpectedly, a conjugate addition product **2′** was also obtained from the same reaction mixture in 47% yield as a pure diastereomer. Clean conversion of **2a** to **3** in presence of BuLi (path *c*, Scheme 1) established that the conjugate addition product **2′** was not formed by an anionic oxy-Cope rearrangement of the intermediate alkoxide during allyllithium addition to **1**; rather, it resulted from a competitive parallel reaction. When the reaction was allowed to warm up to room temperature after the addition of allyllithium and stirred for several hours, complex **3** resulting from a Brook rearrangement was obtained instead of carbinol **2a** in 40% yield (path *b*, Scheme 1) along with some **2′** (45%).

On the other hand, reaction of allylmagnesium bromide and complex **1** at −78 °C for 20 min showed poor diaster-



Scheme 1

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† Electronic supplementary information (ESI) available: spectroscopic data and experimental section. See http://www.rsc.org/suppdata/cc/b2/b205373j/

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eoselectivity and afforded isomeric carbinols **2a** and **2b** (as 1 : 1 mixture) in excellent yield (96%). When the reaction mixture of allylmagnesium bromide and complex **1** was allowed to slowly attain room temperature over several hours, isomeric five-membered heterocycles (**4a** and **4b**) were the only isolable products[7] (path *d*, Scheme 1). Two distinct three-proton singlets corresponding to the two Si–Me groups at 0.50 and 0.66 ppm are the diagnostic proton NMR features for isomer **4a**. For **4b** these peaks appear at 0.45 and 0.68 ppm. Fortuitously, they could be readily separated by fractional crystallization and the structure of isomer **4a** was confirmed by crystal structure determination[8] (Fig. 1). No Brook product was obtained in this reaction.

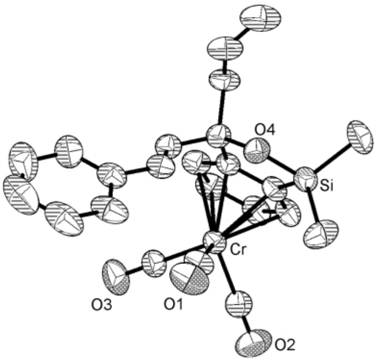

Fig. 1 ORTEP diagram of **4a**. Atoms are drawn at 50% probability.

That the heterocyclic product **4** was indeed formed by a pathway dictated by magnesium counterion was readily ascertained by treatment of lithium alkoxide **A** with a three-fold excess of MgBr$_2$–Et$_2$O prior to warming up, which yielded **4a** instead of **2a** or **3** as the product (path *e*, Scheme 1). Also, addition of one equivalent of benzophenone in the reaction mixture *after* allylmagnesium bromide had completely consumed substrate **1** but *before* warming up, afforded diphenyl methyl carbinol in 74% yield (yield of **4** was 82%), thereby accounting for the methyl group that departed from silicon as a nucleophile.

Based on the above observations, we propose that the reaction proceeds *via* the common alkoxide intermediate **A**, which can exist in equilibrium with a cyclic intermediate **B** featuring a pentacoordinated silicon[9] (Scheme 1). At low temperature the equilibrium favors **A**. When lithium is the counterion, and the temperature is raised, Ar–Si bond cleaves to produce an aryl anionic species stabilized by tricarbonylchromium complexation, with concomitant formation of O–Si bond, affording the Brook product. It could occur in a stepwise manner or by a concerted, intramolecular, S$_N$*i* type displacement[10] at silicon by the alkoxide. The driving force behind preferential rupture of a Si–Me bond mediated by magnesium counterion, on the other hand, appears much less obvious at this point.[11] The intermediate **B** seems significant only when the counterion is magnesium and temperature is raised from −78 °C. Formation of intermediate **B** is certainly facilitated[12] by *gem*-disubstitution at the chiral center (*cf.* Thorpe-Ingold effect). One is prompted to invoke an analogy from the literature[13] to suggest a four-centered transition state for facile expulsion of MeMgBr to complete—simultaneously—the heterocycle formation. Addition of methyllithium to **4** reverses the steps of heterocyclization to provide the lithium alkoxide **A**, eventually preferring Brook rearrangement as the kinetically favored pathway at warmer temperatures.

In summary, we presented here an interesting example of counterion dependence of reaction pathways involving arguably the same intermediate alkoxide. Two different counterions lead to two mutually exclusive products seemingly as a result of kinetic selection. These results once again raise important questions as to the exact role of counterions—the nature of ion-pair, solvation, structure and stability of pentacoordinated silicon intermediates, factors that precisely tune the energetics of different mechanistic possibilities. Our current endeavors strive to address some of these subtle yet significant issues, and explore the scope and generality of these observations to invent useful synthetic applications.

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Notes and references

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6 The stereochemical assignments in the present paper are based on close similarity of spectral data among the analogs of **2a** and **2′** and crystal structure of an analog of **2a** that have been recently reported: S. Sur, S. K. Mandal, S. Ganesh, V. G. Puranik and A. Sarkar, *Indian J. Chem., Sect. B*, 2001, **40**, 1063.

7 For examples of cyclization by reaction of oxygen nucleophile on a trimethylsilyl group, see: (*a*) Y. M. Hijji, P. F. Hudrlik and A. M. Hudrlik, *Chem Commun.*, 1998, 1213; (*b*) P. F. Hudrlik, Y. M. Abdallah and A. M. Hudrlik, *Tetrahedron Lett.*, 1992, **33**, 6747; (*c*) Y. Yamamoto, Y. Takeda and K. Akiba, *Tetrahedron Lett.*, 1989, **30**, 725; (*d*) W. Kirmse and F. Soellenboehmer, *J. Chem. Soc., Chem. Commun.*, 1989, 774; (*e*) K. Tamao, T. Nakajima, R. Sumiya, H. Arai, N. Higuchi and Y. Ito, *J. Am. Chem. Soc.*, 1986, **108**, 6090; (*f*) M. Uemura, T. Kobayashi, K. Isobe, T. Minami and Y. Hayashi, *J. Org. Chem.*, 1986, **51**, 2859; (*g*) H. Oda, M. Sato, Y. Morizawa, K. Oshima and H. Nozaki, *Tetrahedron.*, 1985, **41**(16), 3257.

8 (*a*) Needle like yellow single crystals were grown in a mixture of dichloromethane and pet ether. Data were collected on a *MACH-3* diffractometer using Mo-Kα radiation with fine focus tube. C$_{23}$H$_{22}$CrO$_4$Si, M = 442.50. Crystals belong to monoclinic, space group $P2_1/n$, a = 12.488(2), b = 9.1030(9), c = 20.682(3) Å, β = 107.16(1)°, V = 2246.4(5) Å^3, Z = 4, D_c = 1.308 Mg m^{-3}, μ(Mo-Kα) = 0.587 mm^{-1}, T = 293(2) K, 3546 unique [$I > 2\sigma(I)$], R_1 = 0.0341, wR_2 = 0.0811. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (SHELXTL)[8b] was used for structure solution and full matrix least squares refinement on F^2. CCDC 187534. See http://www.rsc.org/suppdata/cc/b2/b205373j/ for crystallographic files in .cif or other electonic format (*b*) G. M. Sheldrick, SHELX-97 program for crystal structure solution and refinement, University of Goettingen, Germany, 1997.

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10 E. W. Colvin, in *Silicon in Organic Synthesis*, Butterworths, 1981, p. 42.

11 We have found that tricarbonylchromium plays no role in this cyclization. Uncomplexed substrates also similarly cyclize in the presence of magnesium counterion (Suresh Kumar Tipparaju, unpublished results).

12 A *gem*-dimethyl substitution is equally effective. The lithium alkoxide derived from (CO)$_3$Cr-[o-TMS-C$_6$H$_4$-C(Me)$_2$OH] leads to Brook product, while magnesium alkoxide promotes cyclization (Suresh Kumar Tipparaju, unpublished results).

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