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Estimation of Bulkiness of a Highly Sterically Demanding 2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl Group

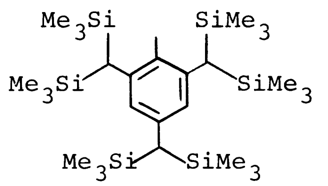
Renji OKAZAKI,* Masafumi UNNO, and Naoki INAMOTO
Department of Chemistry, Faculty of Science, The University
of Tokyo, Hongo, Tokyo 113

In two different types of reactions the title group behaves as a bulkier group than 2,4,6-tri-t-butylphenyl which has often been used for kinetic stabilization of highly reactive compounds.

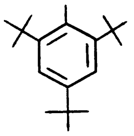
Recently we have reported the synthesis of 1,3,5-tris[bis(trimethylsilyl)-methyl]benzene derivatives and the use of 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl group (denoted as Tb) for kinetic stabilization of N-thiosulfinyl group (-N=S=S).$^{1)}$ Although 2,4,6-tri-t-butylphenyl group (denoted as Ar) has often been used as a protective group for highly reactive compounds$^{2)}$ a more sterically demanding group is needed when one wants to protect more reactive species. We now wish to report experimental evidence that Tb behaves as a bulkier group than Ar, thus establishing Tb as an easily available and useful group for kinetic stabilization.$^{3)}$

It has been demonstrated in these laboratories that kinetic vs thermodynamic enolate formation from benzyl methyl ketone can be used as a measure of the steric bulkiness of hindered bases.$^{5)}$ That is, the ratio of the enolate derived from methyl proton abstraction to that from benzyl proton abstraction (M/B) increases with the bulkiness of bases used. For example, the use of lithium diisopropyl-amide, mesityllithium, lithium 2,2,6,6-tetramethylpiperidide, and 2,4,6-tri-t-butylphenyllithium (ArLi) results in the M/B (at -50 °C) of 30/70, 32/68, 34/66, and 74/26, thus indicating that ArLi is a very bulky base. When TbLi$^{1)}$ was used instead of ArLi in this system, the M/B (at -50 °C) was 83/17. This result suggests that TbLi is a more hindered base than ArLi and hence Tb is a bulkier group than Ar.

A second experiment which shows that Tb is bulkier than Ar is the reactions of $TbSiF_3$ (**1**)$^{6)}$ with organometallics, the results of which are listed in Table 1 along with those for $ArSiF_3$ (**2**) reported by Nakadaira et al.$^{7)}$ Table 1 clearly



≡ **Tb**



≡ **Ar**

Table 1. Reactions of $TbSiF_3$ (1) and $ArSiF_3$(2)

Reagent	1		2	
	Conditions	Product9)	Conditions	Product9)
MeLi	r.t., 2 h	$TbSiFMe_2$	r.t., 1 h	$ArSiF_2Me$
EtMgBr	60 °C, 1 d	$TbSiF_2Et$	r.t., 8 h	$ArSiF_2Et$
t-BuLi	r.t., 1 d	No reaction	r.t., 3 h	$ArSiF_2Bu^t$
Mesityllithium	r.t., 1 d	No reaction	r.t., 1 d	$ArSiF_2Mes$

indicates that the reactions of 1 need more vigorous conditions than 2. Thus, the reaction of 2 with 1 equiv. of MeLi reportedly proceeds at room temperature within 1 h, while the reaction of 1 under identical conditions does not give any product and a large excess of MeLi and a longer reaction time are required for the reaction to occur, the product being dimethyl compound $TbSiFMe_2$.8) The reactions of EtMgBr with 1 and 2 both gave monoethylated products, but the reaction with 1 required much more vigorous conditions. The reactions with t-BuLi and mesityllithium with 2 gave the corresponding monosubstituted products, whereas no reaction took place when 1 was reacted under similar or more vigorous conditions.

In summary, we have shown in two reactions that Tb behaves as a bulkier group than Ar which has successfully been used for kinetic stabilization of reactive functional groups. This finding suggests that Tb is a new useful group for the synthesis of highly reactive species such as multiple bond compounds of heavier typical elements which have received much attention in recent years. Work along this line is now in progress.

References

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3) We have demonstrated1) that Tb-N=S=S is thermally more stable than Ar-N=S=S, but the estimation of the relative bulkiness of Tb and Ar is difficult in this case because Ar-N=S=S is equilibrated in solution with its cyclized form and the thermolysis proceeds mainly via the cyclized form which is a major component in the equilibrium.4)
4) Y. Inagaki, R. Okazaki, and N. Inamoto, Bull. Chem. Soc. Jpn., 52, 2002 (1979).
5) M. Yoshifuji, T. Nakamura, and N. Inamoto, Tetrahedron Lett., 28, 6325 (1987).
6) 1 was synthesized by the reaction of TbLi with SiF_4; mp 120-121°C, ^1H NMR 0.029(s, 36H), 0.049(s, 18H), 1.39(s, 1H), 1.78(s, 2H), 6.39(s, 2H); ^{19}F NMR -122.3; HRMS 636.2867, calcd for $C_{27}H_{59}F_3Si_7$ 636.2949.
7) Y. Nakadaira, K. Oharu, and H. Sakurai, J. Organomet. Chem., 309, 247 (1980).
8) No monomethylated product was formed. The reason for the sole formation of the dimethylated product is not clear at present.
9) The structure was established by spectroscopic and analytical data.

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