Communications

Amination of Zirconocene Alkyl Chlorides with O-(Mesitylsulfonyl)hydroxylamine as a Method of Preparing Primary Amines

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Zirconocene alkyl chlorides, RZrCp₂Cl, readily available from alkenes by hydrozirconation with HZrCp₂Cl,¹ Schwartz's reagent, undergo a number of useful transformations with various electrophiles.² Interestingly, amination of RZrCp₂Cl with electrophilic aminating reagents has never been explored. This is puzzling since both polar organometallic reagents such as RMgX and RLi and nonpolar organometallics like R₃B and R₂Zn have been investigated with various levels of success.³ Since zirconium is relatively electropositive, 1.2-1.3, on the Pauling scale, and the Zr-C bond is polar, we reasoned that it should react with electrophilic aminating reagents to provide amines. As part of our ongoing interest in the chemistry or organozirconocenes,⁴ we have explored this point and in this paper we present the successful results of our efforts.

Of the various electrophilic aminating reagents available for reaction with RM, we decided to try the Oarylhydroxylamines. They are readily available from easily accessible starting materials in a number of highyielding steps.^{5,6} Some are reported to be especially stable.⁶ One reagent, o-(mesitylsulfonyl)hydroxylamine (MSH), has the additional attribute of being soluble in organic solvents. Our scheme of things, therefore, involved hydrozirconation of an alkene followed by reaction of the RZrCP₂Cl with MSH (Scheme 1).

This two-step procedure worked well for a variety of monosubstituted alkenes and alkylidenes. Results are summarized in Table 1. Styrene (Table 1, entry 9), however, gave two products in a 3:1 ratio, indicative that the hydrozirconation was not completely regioselective.⁷ Since it is well known that hydrozirconation of trisubstituted alkenes places zirconium on the least hindered carbon, that class of alkenes was not investigated.⁸ We

Table 1.	Preparation	of Primary	Amines	from	Alkenes ^a
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^a All reactions were carried out on a 1 mmol scale in 1 mL of THF in the ratio of alkenes:HZr(Cl)Cp₂:RONH₂, 1.2:1.0:1.2. ^b Isolated yield, based on HZr(Cl)Cp₂. ^c Characterized as the benzoyl amide derivative which was purified by preparative TLC. d Obtained as a 3:1 mixture as determined by ¹H NMR analysis.



also investigated the amination of an zirconocene allylic chloride (entry 8) to give an allylic amine.⁹ Reaction of the latter could either occur at the terminal carbon or proceed with allylic rearrangement.¹⁰ Examination of its ¹H NMR spectrum revealed two nonequivalent methyl groups on a double bond. Amination thus occurred at the terminal carbon, without allylic rearrangement, providing access to this important group of compounds.¹¹ The preparation of n-octylamine is typical.¹²

Some comments regarding the preparation and the handing of MSH should be adhered to. We have found that MSH is not stable for more than 1 day, even in recrystallized form and under argon in the cold. It should thus be prepared freshly and used almost immediately, certainly no longer than 12 h after its preparation. On the other hand, its immediate precursor, ethyl O-(mesi-

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⁽¹⁾ The preferred method of preparation is according to: Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. Tetrahedron Lett. 1987, 28, 3895.

<sup>Tetrahedron Lett. 1987, 28, 3895.
(2) (a) Negishi, E.; Takahashi, T. Synthesis 1988, 1. (b) Schwartz, J.; Arvanitis, G. M.; Smegel, J. A.; Meier, I. K.; Clift, S. M.; Van Engen, D. Pure Appl. Chem. 1988, 60, 65. (c) Negishi, E.; Takahashi, T. Aldrichim. Acta 1985, 18, 31. (d) Dzhemilev, U. M.; Vostrikova, O. S.; Ibragimov, A. G. Russ. Chem. Rev. 1986, 55, 66. (e) Cardin, D. J.; Lappert, M. F.; Raston, C. L. Chemistry of Organo-Zirconium and Hafnium Compounds; Ellis Harwood Limited: Chichester, 1986.
(2) (a) For an eucellert anxioux context of the rev. M. Chem. Part.</sup>

^{(3) (}a) For an excellent review, see: Erdik, E.; Ay, M. Chem. Rev. 1989, 89, 1947. (b) For a good source for general references, see: March, J. Advanced Organic Chemistry, 4th ed.; Wiley-Interscience Publications: New York, 1992; p 616.

⁽⁴⁾ Zheng, B.; Srebnik, M. J. Org. Chem. 1995, 60, 486 and references cited therein.

Houben, J.; Schmidt, E. *Chem. Ber.* **1913**, *46*, 3616.
 Tamura, Y.; Minamikawa, J.; Sumoto, K.; Fujii, S.; Ikeda, M. J.

⁽⁷⁾ Fandra, T., Minamikawa, S., Sunow, K., Fuji, S., Ikeda, M. S.
Org. Chem. 1973, 38, 1239.
(7) For a study of the regioselectivity of hydrozirconation in various systems, see: Annby, U.; Karlsson, S.; Gronowitz, S.; Hallberg, A.;
Alvhäll, J.; Svenson, R. Acta Chem. Scand. 1993, 47, 425.

⁽⁸⁾ Schwartz, J.; Labinger, J. A. Angew. Chem., Int. Ed. Engl. 1976, 15. 333.

⁽⁹⁾ For the synthesis of allylic amines using nucleophilic aminating reagents and MeZrCp₂Cl, see: Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (10) In a separate study we have determined that some electrophiles,

i.e., D₂O, react with allylic zirconocene chlorides with rearrangement. Zheng, B.; Srebnik, M. Unpublished results.

⁽¹¹⁾ Otsuka, S.; Tani, K. Synthesis 1991, 665.

tylsulfonyl)acetohydroxamate, is very stable and can be stored in the cold indefinitely. We also tried amination with O-(tolylsulfonyl)hydroxylamine. The yields with 1-octene were comparable to those obtained with MSH. But the overall yield of the preparation of the tolyl derivative is much lower than that of MSH, and it is even less stable. Other electrophilic aminating reagents were

(12) **Preparation of n-Octylamine.** A suspension of HZr(Cl)Cp₂ (258 mg, 1 mmol) in THF (1 mL) was stirred at ambient temperature under an atmosphere of argon. Distilled 1-octene (134 mg, 1.2 mmol) was added. After the cloudy reaction mixture turned a clear yellow, it was placed in an ice bath. A solution of MSH (220 mg, 1.2 mmol) in ether (1 mL) was added dropwise. After being stirred for 10 min, the reaction mixture was acidified with 1 M HCl (10 mL) and extracted with ether. The aqueous layer was then made alkaline with NaOH (0.5 g) and extracted with ether (2 \times 8 mL). The combined organic layer was dried over Na₂SO₄. Removal of solvent yielded 99 mg (77%) of *n*-octylamine.

(13) (a) Brown, H. C.; Heydkemp, W. R.; Breuer, E.; Murphy, W. S. J. Am. Chem. Soc. **1964**, 86, 3365. (b) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. Organic Synthesis via Boranes Wiley: New York, 1975. (c) This limitation, to a degree was overcome by the use of mixed RMe₂B reagents where R shows considerably better migratory aptitude than the methyl groups. But, of course, this requires the preparation of RMe₂B: Brown, H. C.; Kim, K. B.; Srebnik, M.; Singaram, B. Tetrahedron **1987**, 43, 4071. not investigated because of their instability, difficulty of synthesis, difficulty of drying, or low yields of amines obtained with their use.³

Finally, in the present methodology only the alkyl group of RZrCp₂Cl transfers, and thus it is more efficient than the reactions involving R_3B reagents where one group is lost¹³ or those involving R_2Zn reagents with monochloroamine or nitrogen trichloride where yields are low and mixtures are usually obtained.¹⁴

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Supplementary Material Available: General experimental procedures and ¹H NMR and ¹³C NMR spectra for compounds in Table 1 (22 pages).

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^{(14) (}a) Coleman, G. H.; Hermanson, J. L.; Johnson, H. L. J Am. Chem. Soc. 1937, 59, 1896. (b) Coleman, G. H.; Andersen, H. P.; Hermanson, J. L. J. Am. Chem. Soc. 1934, 56, 1381.