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Synthesis of Olefins by the Reaction of β-((Trimethylsilyl)oxy)alkyl Iodides with Zinc

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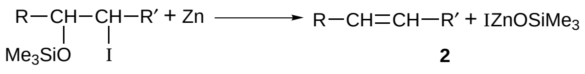
Summary: The synthesis of olefins, $RCH{=}CH_2$*, from β-((trimethylsilyl)oxy)alkyl iodide,* $RCHXCH_2Y$ *(*$R = PhOCH_2$*,* $C_{10}H_{21}$*,* $C_8F_{17}CH_2$*; X, Y = OSiMe*$_3$*, I or I, OSiMe*$_3$*), by treatment of zinc metal was studied. A telechelic derivative,* $Me_3SiOCH_2CHICH_2C_6F_{12}CH_2CHICH_2OSiMe_3$*, and a cyclic derivative, 1-iodo-2-((trimethylsilyl)oxy)cyclododecane, gave the corresponding olefins* $CH_2{=}CHCH_2C_6F_{12}CH_2CH{=}CH_2$ *and cyclododecene, respectively. A bromide,* $PhOCH_2CH(OSiMe_3)CH_2Br$*, also was transformed to* $PhOCH_2CH{=}CH_2$ *in high yield. The reaction was accelerated by pretreatment of the zinc surface with chlorotrimethylsilane.*

Introduction

The synthetic methods for the preparation of olefins by β-elimination with zinc metal, such as the dehalogenation of vicinal dihalides[2] and the elimination of alkoxy halogen from β-halo ethers[3] or acyloxy halogen from β-halo esters,[4] are well-known. However, the preparation of olefins via β-elimination of (trimethylsilyl)oxy and halogen with zinc was not reported. Recently, the transformation of oxiranes to β-((trimethylsilyl)oxy)alkyl iodides by ring opening with iodotrimethylsilane[5] has been developed. Furthermore, we have reported that the adduct formed from (trimethylsilyl)diethylamine and methyl iodide is useful for the ring opening of oxiranes[6] to β-((trimethylsilyl)oxy)alkyl iodides. Although the derivatization of the β-((trimethylsilyl)oxy)alkyl iodides thus prepared to allylic alcohols via dehydroiodination with DBU[5a] or DBN[5c] has been studied, the reaction pathway to olefin via β-elimination of (trimethylsilyl)oxy and iodide has not been developed as a useful synthetic method.[7] In this paper, we report the transformation of β-((trimethylsilyl)oxy)alkyl halides to the corresponding olefins via β-elimination with zinc dust.

Results and Discussion

The procedure is a simple one. To zinc dust (8 equiv) dispersed in THF is added the β-((trimethylsilyl)oxy)alkyl iodide **1** (1.0 equiv) at 60−70 °C. Upon completion of the reaction, the excess zinc dust was filtered and the filtrate was treated with dilute hydrochloric acid. The organic layer was extracted with ether or petroleum ether, dried and concentrated *in vacuo*. The residue was distilled under reduced pressure to give the olefin **2**.



$$\underset{\textbf{1}}{R{-}\underset{Me_3SiO}{CH}{-}\underset{I}{CH}{-}R'} + Zn \longrightarrow \underset{\textbf{2}}{R{-}CH{=}CH{-}R'} + IZnOSiMe_3$$

1

The preparations of several representative olefins were carried out in order to determine the scope and limitations of the reaction. The results are shown in Table 1. The elimination was accelerated by pretreating the zinc surface with a small amount of chlorotrimethylsilane.[8] The lower product yields in the case of fluorinated derivatives were due to the formation of polymeric byproducts.

The cyclic derivative 1-iodo-2-((trimethylsilyl)oxy)cyclododecane was converted to cyclododecene in 80% yield. The treatment of the telechelic iodide $Me_3SiOCH_2CHICH_2C_6F_{12}CH_2CHICH_2OSiMe_3$, prepared from $I(CF_2)_6I$ and $CH_2{=}CHCH_2OSiMe_3$, with zinc dust gave a diene, $CH_2{=}CHCH_2C_6F_{12}CH_2CH{=}CH_2$,[4a] in 54% yield based on $I(CF_2)_6I$. A bromide also was transformed to the corresponding olefin in high yield, although the reaction was slow. Treatment of 1-bromo-2-((trimethylsilyl)oxy)-3-phenoxypropane with zinc dust at reflux for 13 h gave allyl phenyl ether in 90% yield.

In summary, the elimination of the (trimethylsilyl)oxy group and halide from β-((trimethylsilyl)oxy)alkyl halides by the action of zinc proceeded readily to give the olefin in good yield.

Experimental Section

General Remarks. Commercially available benzene and THF were dried using molecular sieves. Zinc dust was dried by azeotropic dehydration with benzene, followed by evaporation of benzene under reduced pressure, prior to use. β-((Trimethylsilyl)oxy)alkyl halides were prepared according to procedures described in the literature.[5,6] The olefinic products were characterized by comparison of spectral data with those of authentic samples. IR spectra were recorded on a JASCO

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Table 1. Derivatization of β-((Trimethylsilyl)oxy)alkyl Halide (1) to Olefin by Treatment with Zinc

β-((trimethylsilyl)oxy)alkyl iodide (**1**)	reacn procedure[a]	addition time (min)	subsequent reacn time (h)	products (yield (%))[b]
$PhOCH_2C(OSiMe_3)HCH_2I$	A	45	1	$PhOCH_2CH{=}CH_2$ (93)
$PhOCH_2C(OSiMe_3)HCH_2I$	B	45	0	$PhOCH_2CH{=}CH_2$ (91)
$C_{10}H_{21}C(OSiMe_3)HCH_2I$	A	60	2	$C_{10}H_{21}CH{=}CH_2$ (94)
$C_8F_{17}CH_2C(OSiMe_3)HCH_2I$	A	30	2	$C_8F_{17}CH_2CH{=}CH_2$ (76)
$C_8F_{17}CH_2C(OSiMe_3)HCH_2I$	B	30	0.5	$C_8F_{17}CH_2CH{=}CH_2$ (69)
$C_8F_{17}CH_2CHIC(OSiMe_3)H_2$	A	45	1	$C_8F_{17}CH_2CH{=}CH_2$ (58)
$C_8F_{17}CH_2CHIC(OSiMe_3)H_2$	B	45	0	$C_8F_{17}CH_2CH{=}CH_2$ (69)
$PhOCH_2C(OSiMe_3)HCH_2Br$	B	60	12	$PhOCH_2CH{=}CH_2$ (90)

[a] See the Experimental Section for details. [b] Isolated yield.

IR-810 spectrometer. ^1H NMR spectra were obtained using a JEOL JNM-PMX60Si spectrometer. GC−MS spectra were measured by a Shimadzu GC−MS QP-1000S and a JEOL JMS600H instrument.

Reaction of β-((Trimethylsilyl)oxy)alkyl Iodide with Zinc. Procedure A. In a four-necked flask, equipped with a mechanical stirrer, a condenser, a thermometer, and a dropping funnel, was placed zinc dust (39.0 g, 0.6 mol) and THF (100 mL), and the mixture was heated to reflux. With stirring, 1-iodo-2-((trimethylsilyl)oxy)-3-phenoxypropane (52.5 g, 0.15 mol) was added over a period of 45 min. After a 1 h reflux period, the reaction mixture was cooled and the excess zinc was filtered. The filtrate was treated with 5% hydrochloric acid (500 mL), and the separated organic layer was extracted with petroleum ether. After drying of the extracts over anhydrous sodium sulfate and concentration, the residue was fractionally distilled at reduced pressure to give 18.7 g (93%) of allyl phenyl ether, bp 68−69 °C/7 Torr.

Procedure B. To a mixture of zinc dust (52.0 g, 0.80 mol) and THF (150 mL) in a four-necked flask was added chlorotrimethylsilane (0.65 g, 0.006 mol), and the contents were heated at reflux for 1 h. With stirring, 1-iodo-2-((trimethylsilyl)oxy)-3-phenoxypropane (70.0 g, 0.20 mol) was added over a period of 45 min. Subsequently, the reaction mixture was cooled and the excess zinc was filtered. The usual workup of the filtrate according to procedure A, followed by fractional distillation, gave 24.3 g (91%) of allyl phenyl ether.

Preparation of Cyclododecene. To a refluxing mixture of zinc dust (52.0 g, 0.80 mol) and THF (150 mL) was added 1-iodo-2-((trimethylsilyl)oxy)cyclododecane (76.4 g, 0.20 mol) over a period of 1 h with stirring. After a 1.5 h reflux period, the usual workup and fractional distillation gave 26.8 g (81%) of cyclododecene; bp 85−86 °C/3 Torr.

Preparation of 1-((Trimethylsilyl)oxy)-2-iodo-4,4,5,5,6,6,-7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane. In a four-necked flask, equipped as above, was placed α,α,α,α′,α′,α′-hexafluoro-*m*-xylene (50 mL) and 2,2′-azobis(isobutyronitrile) (1 g), and the mixture was heated at 70−80 °C. A mixture of 1-iodo-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane (546 g, 1.0 mol) and (allyloxy)trimethylsilane (143.0 g, 1.1 mol) then was added over a period of 3 h. After the addition, another 4 g of 2,2′-azobis(isobutyronitrile) was added in increments over a period of 13 h, keeping the temperature at 70−90 °C. The solvent was evaporated, and the residue was fractionally distilled under reduced pressure to give 456 g (80% yield based on 84% conversion) of 1-((trimethylsilyl)oxy)-2-iodo-4,4,5,5,-6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane: bp 98−99 °C/2 Torr; GC−MS 676 (M^+); ^1H NMR (δ, in CCl_4) 0.17 (s, 9H, $OSiMe_3$), 2.00−3.37 (m, 2H, $-CF_2CH_2-$), 3.43−3.93 (m, 2H, $-CH_2OSi$), 3.93−4.37 (m, 1H, $-CHI-$); IR (neat) 1250 (SiMe), 1100−1200 (CF), 850, 870 cm^{-1} (Me_3SiO-). HR-CIMS: found *m/z* 676.9726 ($(M + H)^+$), calcd for $C_{14}H_{15}F_{17}IOSi$ M 676.9665. Isotope abundance: found 676.9726 (100), 677.9745 (19.9), 678.9707 (5.7); calcd for $C_{14}H_{15}F_{17}IOSi$ 676.9665 (100), 677.9689 (21.0), 678.9666 (5.6).

Preparation of 4,4,5,5,6,6,7,7,8,8,9,9-Dodecafluoro-1,11-dodecadiene. The same procedure was used in the reaction of 1,6-diiodo-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexane (332 g, 0.6 mol) and (allyloxy)trimethylsilane (195 g, 1.5 mol) in the presence of AIBN. Finally, the reaction mixture was concentrated *in vacuo* and the precipitated materials were removed by filtration. The product was presumed to be 1,12-bis((trimethylsilyl)oxy)-2,11-diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane from the following spectral data: ^1H NMR (δ, in CCl_4) 0.16 (s, 9H, $OSiMe_3$), 2.00−3.30 (m, 2H, $-CF_2CH_2-$), 3.30−3.93 (m, 2H, $-CH_2OSi$), 3.93−4.37 (m, 1H, $-CHI-$); IR (neat) 1250 (SiMe), 1100−1200 (CF), 845, 870 cm^{-1} (Me_3SiO-). This crude product (475 g), without further purification, was treated with zinc dust (302 g, 4.6 mol, previously activated with 0.3 g of chlorotrimethylsilane) in THF (570 mL) at reflux for 1.5 h. The workup according to procedure A, followed by fractional distillation under reduced pressure, gave 123.5 g of 4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-1,11-dodecadiene (54% based on the starting diiodide, $I(CF_2)_6I$), bp 67−70 °C/4 Torr. The structure was confirmed by comparison of its IR and NMR spectra with those reported in the literature.[4a]

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