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BIS(BROMOMAGNESIO)TRIMETHYLSILYLMETHANE

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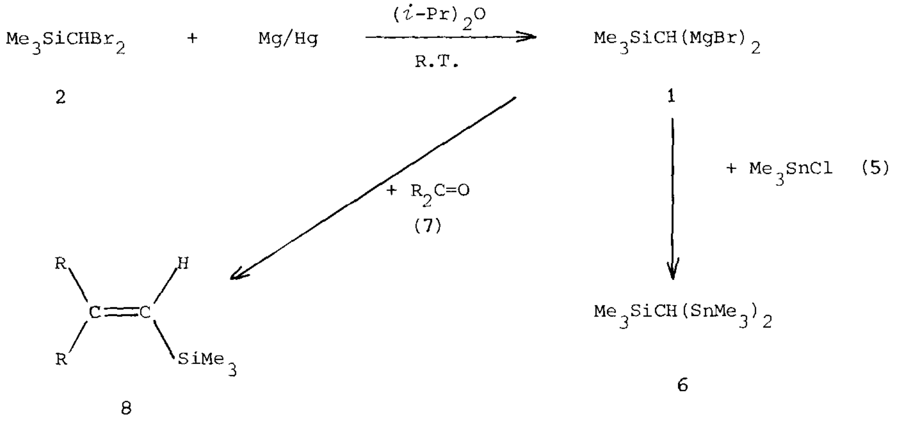
Abstract: The reaction of $Me_3SiCHBr_2$ with magnesium amalgam in diisopropyl ether furnished the di-Grignard reagent $Me_3SiCH(MgBr)_2$ in 70% yield. Derivatization with Me_3SnCl gave $Me_3SiCH(SnMe_3)_2$ (6,94%). Wittig type reaction occurred readily with benzophenone (80%), but the yield was low with cyclohexanone (13%).

We were interested in bis(bromomagnesio)trimethylsilylmethane (**1**) for two reasons. In the first place, its direct synthesis from dibromomethyltrimethylsilane (2) (Scheme 1) has not been achieved so far; **1** has only been prepared in a roundabout way via its dizinc analogue $Me_3SiCH(ZnBr)_2$ (3)[1]. If, however, **1** could be easily obtained from **2**, it is expected to be an attractive synthon comparable or even superior to the unsubstituted methylene-di-Grignard reagent $CH_2(MgBr)_2$ (**4**). Reaction with main group or transition metal halides would furnish substituted 1,3-dimetallacyclobutanes[2] or the derived metallaalkenes[3]; Wittig type reaction with ketones[4] would furnish vinylsilanes which possess considerable potential in organic synthesis[5].

Scheme 1



Making use of the demonstrated[2b] superior properties of diisopropyl ether for the preparation of **4**, we succeeded in the direct preparation of **1** from **2**. In a typical experiment, **2**[6] (2.3 g, 9.3 mmol) and magnesium amalgam (prepared from 2.7 g (112 mmol) magnesium and 20 ml mercury) were stirred in 180 ml diisopropyl ether for one night. A blackish grey precipitate formed; it was washed several times by decanting the solution and redistilling the diisopropyl ether. Finally, 150 ml diethyl ether were added to the precipitate; a clear solution formed immediately which, according to titration with HCl and EDTA, contained 70% **1**[7].

Compound **1** was chemically characterized by reaction with chlorotrimethylstannane (**5**) in THF to give **6** (a new compound[8]; 94% yield). The reaction of **1** with ketones was satifactory only in the case of the non-enolizable benzophenone (**7a**) where 1,1-diphenyl-2-trimethylsilylethene (**8a**)[9] was obtained in 80% yield; with cyclohexanone (**7b**), the Wittig type product **8b**[1] was formed in only 13% yield, the aldol condensation dimer of **7b** being the main product. Nevertheless, this result differs from the statement[1] that both **3** and **1** do not react at all with carbonyl compounds, and thus throws some doubt on the claim that **1** has really been obtained from **3**. On the other hand, the known reduced reactivity of 1,1-di-Grignard reagents in comparison to mono-Grignards is obvious. Relative to **4**, **1** is even less reactive; this must be due to the anion-stabilizing effect of the trimethylsilyl group, and possibly to steric hindrance.

References and Notes

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7. When diethyl ether/benzene was used as a reaction medium[4], the yield of **1** was 10%; 10% Me_3SiCH_2MgBr was also present; J.W. Bruin, unpublished results.
8. **6**: ^1H-NMR ($CDCl_3$; $CHCl_3$ at δ 7.27 ppm as internal standard) δ = 0.12 (s, $^2J(^{119}SnH)$ = 52.2 Hz, 9H, $SnCH_3$), 0.04 (s, $^3J(SnH)$ = 6.2 Hz, 9H, $SiCH_3$), -0.67 ppm (s, 1H, CH). ^{13}C-NMR ($CDCl_3$ at δ = 77.0 ppm as internal standard) δ = 3.28 (q, $^1J(CH)$ = 119.0 Hz, $^1J(SiC)$ = 50.3 Hz, $^3J(SnC)$ = 16.6 Hz, $SiCH_3$), -5.95 (q, $^1J(CH)$ = 127.8 Hz, $^1J(^{119}SnC)$ = 325.8 Hz, $^1J(^{117}SnC)$ = 311.3 Hz, $^3J(SnC)$ = 9.8 Hz, $SnCH_3$), -8.65 (d, $^1J(CH)$ = 113.2 Hz, $^1J(^{119}SnC)$ = 184.5 Hz, $^1J(^{117}SnC)$ = 176.4 Hz, $^1J(SiC)$ = 43.7 Hz, CH). Mass spectrum m/z (rel. intensity)(all peaks had the expected isotope patterns) 400(100)$[M-Me]^+$, 251(13) $[M-SnMe_3]^+$, 165(30)$[Me_3Sn]^+$, 73(71)$[Me_3Si]^+$. HRMS: $[M-15]^+$ $C_9H_{25}{}^{28}Si^{120}Sn_2$ calcd. 400.9769; found 400.9788.
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