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A FACILE SYNTHESIS OF SYMMETRICAL 1,1-DISUBSTITUTED ETHYLENES

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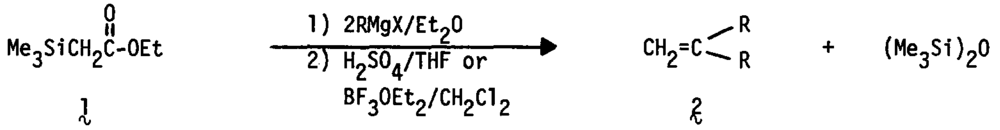
SUMMARY: The reaction of ethyl trimethylsilylacetate with two equivalents of a Grignard reagent in ether followed by treatment with acid gives 1,1-disubstituted ethylenes in excellent yield.

The use of β-hydroxysilanes in the formation of olefins has been a useful reaction in organic chemistry since the first report of dehydroxysilylation by Peterson.[2] Since that time numerous entries into β-hydroxysilanes, and therefore olefins, have been reported.[3] Surprisingly, the reaction of α-silylated esters with Grignard reagents has not been exploited in this regard.[4]

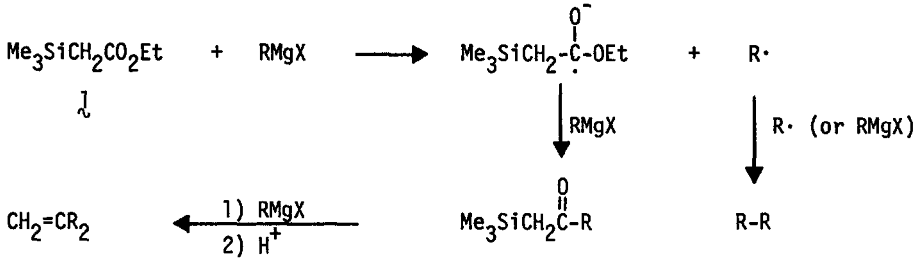
We wish to report herein on the reaction of ethyl trimethylsilylacetate,[5] **1**, with Grignard reagents to give, after acid treatment, the expected 1,1-disubstituted ethylenes, **2**,[6] (eq. 1). The results are shown in Table I.



$$Me_3SiCH_2\overset{O}{\overset{\|}{C}}\text{-OEt} \xrightarrow[2)\ H_2SO_4/THF\ \text{or}\ BF_3OEt_2/CH_2Cl_2]{1)\ 2RMgX/Et_2O} CH_2{=}C\begin{smallmatrix}R\\R\end{smallmatrix} + (Me_3Si)_2O \qquad (1)$$

1 **2**

Our initial attempts to carry out the reaction with benzylmagnesium chloride, phenylmagnesium bromide or n-pentylmagnesium bromide gave essentially two products which were **2** and the dimer, R-R, of the Grignard reagent employed. The amount of dimer ranged from 20-60% depending on the reaction conditions. Higher yields of the dimer were obtained when concentrations greater than ca. 0.25<u>M</u> were used, when the ether solvent was replaced by THF and when HMPA was added as a cosolvent with ether. Appropriate control experiments were carried out in an attempt to locate the source of the dimer formation. For example, preparation of benzylmagnesium chloride followed by refluxing in ether and workup gave toluene and 3 percent of the dimer 1,2-diphenylethane. Furthermore, preparation of phenylmagnesium bromide followed by treatment with ethyl acetate and an acidic workup gave 1,1-diphenylethylene (88%) and biphenyl (3%). We, therefore, attribute the formation of the dimer to a single electron transfer process[7] producing the anion radical, 3, which could be stabilized by the β-silyl group,[8] thus favoring the coupling reaction (eq. 2). The fate of all of the ester, 1, is not known at this time, although hexamethyldisiloxane is produced in nearly quantitative yield.



$$\begin{tikzcd}
\underset{1}{Me_3SiCH_2CO_2Et} + RMgX \arrow[r] & Me_3SiCH_2\text{-}\overset{O^-}{\underset{\cdot}{C}}\text{-}OEt \arrow[d, "RMgX"] & + \; R\cdot \arrow[d, "R\cdot\ (\text{or } RMgX)"] \\
CH_2{=}CR_2 & Me_3SiCH_2\overset{O}{\overset{\|}{C}}\text{-}R \arrow[l, "1)\ RMgX", "2)\ H^+"'] & R\text{-}R
\end{tikzcd} \qquad (2)$$

The problem was finally resolved by using high purity magnesium turnings[9] to prepare the Grignard reagents, although concentrations less than ca. 0.25 M were still necessary. In this way only small amounts (<3-4%) of the dimer were found. It is particularly noteworthy that the new double bond is introduced regiospecifically. For example, benzylmagnesium chloride gives 1,1-dibenzylethylene and none of the corresponding styrene.

The reaction is not without some of the expected limitations. For example, sterically hindered Grignard reagents give several products and considerable amounts of starting material back. The bis-Grignard of 1,5-dibromopentane gave a mixture of at least six components, none of which predominated. In addition n-butyllithium and phenyllithium produced complex reaction mixtures.

Coupled with our recent report on the direct C-silylation of ester enolates[10] and the fact that α-silyl esters can be alkylated via their enolates[11] the reaction reported herein should be applicable to the synthesis of more highly substituted olefins.

The preparation of 1,1-dibenzylethylene is representative. A standard apparatus was flame dried under nitrogen and charged with 70 mL of a 0.25 M solution of benzylmagnesium chloride in ether (17.5 mmol). The solution was cooled to -78° (or to 0°) and 0.88 g (5.41 mmol) of 1 in 5 mL of ether added. The reaction was warmed to rt and stirred overnight, washed with 10% NH_4Cl and the ether layer concentrated under vacuum. The crude β-hydroxysilane was dissolved in 60 mL of THF and 1 mL of concentrated H_2SO_4 added followed by stirring for 15 h. The solution was washed with 10% $NaHCO_3$, the aqueous extracted with ether and the organic layer dried and concentrated. Kugelrohr distillation gave 1.19 g of product which was 94% pure by GC analysis.

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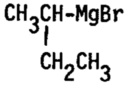
Table I: Formation of 1,1-Disubstituted Ethylenes From Ethyl Trimethylsilylacetate.

Entry	RMgX	Elimination conditions[a]	Product	% Yield[b]
1	PhMgBr	A	$CH_2{=}CPh_2$	82
2	$pMeOC_6H_4$	B	$CH_2{=}C(pMeOC_6H_4)_2$	73
3	$PhCH_2MgCl$	A	$CH_2{=}C(CH_2Ph)_2$	98
4	$CH_2{=}CHCH_2MgCl$	B	$CH_2{=}C(CH_2CH{=}CH_2)_2$	79
5	$^{n}C_3H_7MgBr$	B	$CH_2{=}C(^{n}C_3H_7)_2$	44
6	$^{n}C_5H_{11}MgBr$	A	$CH_2{=}C(^{n}C_5H_{11})_2$	78
7	$(CH_3)_2CHCH_2MgBr$	A		c
8	$^{c}C_5H_9MgBr$	A		c
9	 $CH_3\underset{\displaystyle CH_2CH_3}{\underset{\vert}{CH}}\text{-}MgBr$	A		c
10	$^{c}C_5H_{11}MgBr^{d}$	A		d
11	$(CH_3)_2CHCH_2MgBr^{e}$	B		e

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[a] A is with THF/H_2SO_4; B is with $BF_3OEt_2/CH_2Cl_2/2h/rt$.

[b] Isolated yields; all products were characterized by H-NMR, MS, IR spectral data and comparison of properties to literature data where possible.

[c] Starting ester recovered in reasonable (40-50%) yield

[d] In THF several products formed.

[e] Refluxing ether, several products formed.

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