

Nickel-catalysed Alkylative Alkenation of Orthothioesters with Grignard Reagents; a Convenient Procedure for introducing the Isopropenyl Group. Synthesis of Substituted 1,3-(Bis-trimethylsilyl)propenes

Yih-Ling Tzeng, Tien-Yau Luh,* and Jim-Min Fang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

Nickel-catalysed coupling of orthothioesters with MeMgI furnishes a general method for introducing the isopropenyl group; the application of this reaction to the synthesis of 1,3-(bis-trimethylsilyl)propenes is presented.

The use of nickel-catalysed coupling reactions of organo-sulphur compounds with Grignard reagents has been extensive.^{1,2} We recently uncovered several useful transformations concerning dithioacetal functionality.^{3–5} To illustrate this, dithioacetals can couple with Grignard reagents in the presence of a catalytic amount of NiCl₂(PPh₃)₂ to give the corresponding alkenes.³ Allyl, vinyl, as well as butadienyl silanes are synthesized in good to excellent yields.³ In these reactions, one of the carbon–sulphur bonds is replaced by a carbon–carbon bond and the other carbon–sulphur bond undergoes elimination to yield alkenes. Orthothioesters commonly serve as latent ester groups,⁶ other synthetic usage of this functionality being rare.⁷ This function has three carbon–sulphur bonds. We felt that the exploitation of the nickel-catalysed coupling reactions of orthothioesters with Grignard reagents would afford a convenient entry to the isopropenyl groups. We describe here an unprecedented application of orthothioesters in synthesis.

In a typical procedure, orthothioester (**1**), readily obtained from the reaction of the anion of dithiane with dimethyldisulphide according to the literature procedure,⁶ was mixed with five equivalents of MeMgI in the presence of NiCl₂(PPh₃)₂ (5 mol%) in benzene–ether, tetrahydrofuran (THF)–ether, or benzene alone and the mixture was heated under reflux overnight to give, after usual work-up and chromatographic separation, the coupling product (**2**).[†] Excess amount of the Grignard reagent was essential to achieve completion of the reaction. The results are summarized in Table 1. Orthothioesters, having different substituents on the aryl group, gave (**2**) in good to excellent yields. It is noted that the aryl ether linkage has been known to react under similar conditions.⁸ However, substrates containing such functionality remained intact throughout this study.

Although the actual mode of the reaction has not been established, the reaction may proceed *via* a similar pathway to that suggested for dithioacetals. The two carbon–sulphur bonds in (**1**) may first be replaced by two carbon–carbon bonds and the remaining carbon–sulphur bond may further proceed *via* oxidative addition with a Ni⁰ species to afford (**3**) which will then undergo β-elimination giving the isopropenyl group.

The extension of this reaction to the synthesis of silyl-substituted alkenes has been carried out. When the silyl-substituted Grignard reagent is employed, it may provide an extremely facile synthesis of (**4**) having both allyl and vinyl silane functionalities. These products may serve as a dianion synthon (**5**) which could be useful in synthesis.^{9,10} However, (**4**) can generally only be obtained *via* a multistep synthesis requiring starting materials which are not readily accessible.¹¹ Thus, treatment of orthothioester with five equivalents of Me₃SiCH₂MgCl and NiCl₂(PPh₃)₂ (5 mol%) in refluxing benzene followed by usual work-up and flash column chromatography[‡] afforded (**4**) in satisfactory yields.[†] The (*E*)- and (*Z*)-isomers of (**4**) were separated easily by preparative GLC using 10% SE30 as the stationary phase. The results are outlined in Table 1. The stereochemical assignments were based on the NMR data. The vinylic Me₃Si group of the (*E*)-isomers absorbed at higher field (δ -0.18 to -0.09), whilst that of the (*Z*)-isomers emerged at lower field (δ 0.12–0.21). With the exception of (**4a**), the alkenic proton for the (*Z*)-isomers appeared at lower field (δ 5.41–5.64) than those for the (*E*)-isomers (δ 5.26–5.44). These assignments have been confirmed by NOE experiments.

Compounds (**4**) were highly reactive and protonolysis

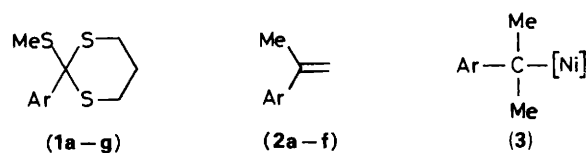
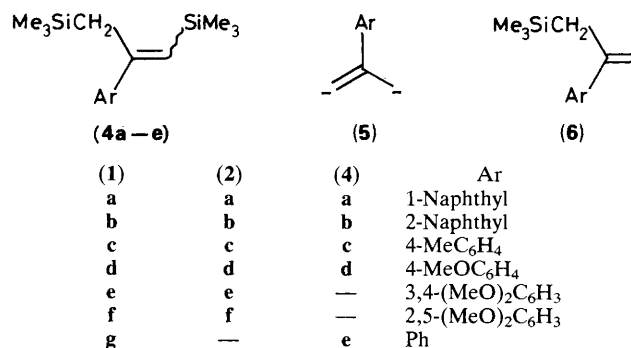


Table 1. Reactions of orthothioesters with the Grignard reagent in the presence of a catalytic amount of NiCl₂(PPh₃)₂

Substrate	Grignard reagent	Con- ditions ^a	Product	% Yield	<i>E</i> : <i>Z</i>
(1a)	MeMgI	A	(2a)	83	
(1b)	MeMgI	A	(2b)	73	
(1c)	MeMgI	A	(2c)	91	
(1d)	MeMgI	A	(2d)	86	
(1e)	MeMgI	B	(2e)	69	
(1f)	MeMgI	B	(2f)	69	
(1a)	Me ₃ SiCH ₂ MgCl	A	(4a)	79	1:3
(1b)	Me ₃ SiCH ₂ MgCl	C	(4b)	69	1:1
(1c)	Me ₃ SiCH ₂ MgCl	B	(4c)	68	1.2:2.3
(1d)	Me ₃ SiCH ₂ MgCl	A	(4d)	48	1:1
(1g)	Me ₃ SiCH ₂ MgCl	C	(4e)	72	1.9:3.6

^a A: in refluxing ether–benzene. B: in ether–THF at room temperature. C: in refluxing benzene.



[†] All new compounds gave satisfactory spectroscopic data (¹H and ¹³C NMR, and MS) and accurate mass measurement.

[‡] Desilylation can be avoided by using flash column chromatography for the purification of (**4**).

occurred readily upon prolonged contact of (4) with silica gel leading to a significant amount of allylsilanes (6).‡

In conclusion, we have demonstrated a simple procedure for introducing isopropenyl groups and a new facile synthetic methodology for the preparation of (4). The applications of (4) as the dianion synthon will be reported in due course.¹⁰

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