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PREPARATION OF 3-METHOXY-1-TRIMETHYLSILYL-1,3-DIENES USING A ONE-POT WITTIG-HORNER REACTION

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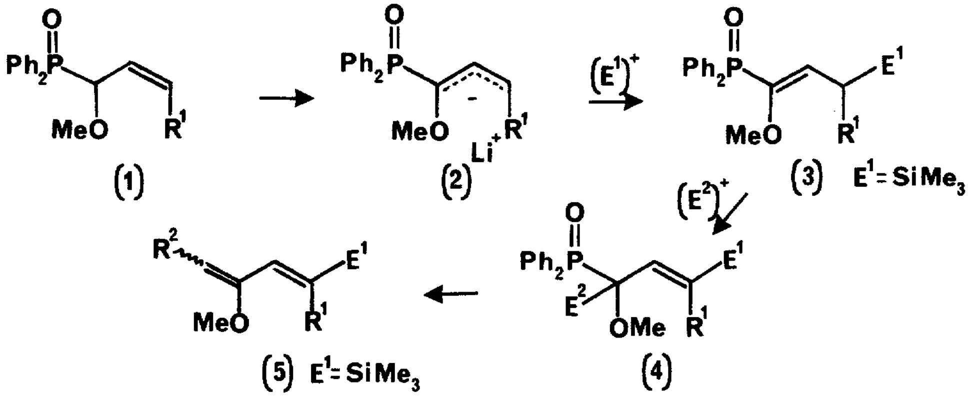
Abstract: 3-Methoxy-1-trimethylsilyl-1,3-dienes, bearing a variety of substituents, have been conveniently prepared in a one-pot double quenching reaction of ylides derived from α-methoxyallyldiphenylphosphine oxides.

The presence of conjugated double bonds in conjunction with a silicon group in a vinylic position makes 1-silyl-1,3-dienes potentially useful intermediates for organic synthesis,[1] and consequently the synthesis of such compounds has received much attention from organic chemists. Literature methods for the preparation of 1-silylated 1,3-dienes, in the main, involve the Wittig reaction, or various elaborations,[2] of silylated α,β-unsaturated aldehydes, but other successful approaches include the hydroalumination of silylated 1,3-diynes,[3] the thermolysis of silylated sulpholenes[4], the transition metal-catalysed coupling of a vinyl halide with a silylated vinyl tin reagent,[5] or a trimethylvinylsilane with a vinyl halide in the presence of silver nitrate,[6] and the silylolefination of allylic dithioacetals[7]. However, only one isolated example of a 3-oxygenated 1-silyl-1,3-diene has appeared in this previous work. We now report a convenient one-pot synthesis of a series of substituted 3-methoxy-1-trimethylsilyl-1,3-dienes, based on two sequential quenching reactions of the anions of readily available α-methoxyallyldiphenylphosphine oxides (1).

Previously we have shown that the regioselectivity of the reaction of these phosphine oxide anions (2) with electrophilic species is dependent on the nature of the electrophilic species,[8] the substrate[9], and the metal counterion.[10] The generally high yields, regioselectivity and stereoselectivity observed in the quenching reactions of (2) studied to date, together with the significantly different conditions which have been found to lead to γ-or to α-attack of the allylic anion indicated to us that double quenching sequences should have great synthetic potential. In particular we envisaged that a sequence of γ-attack to give (3) followed by α-attack on the new anion (or ate complex)[10] of (3) would lead ultimately to the insertion of the methoxyallyl unit of the original phosphine oxide, see (4), between two electrophilic entities, see Scheme 1. If $E^2 = R^2CHO$, the sequence would then allow us to prepare a variety of methoxydienes (5).

In this paper we exploit such a procedure for the synthesis of 3-methoxy-1-trimethylsilyl-1,3-dienes (5). α-Methoxyallyldiphenylphosphine oxides (1) were prepared in one step from chlorodiphenylphosphine and the dimethyl acetal of the appropriate α,β-unsaturated aldehyde. Preparative details and spectroscopic evidence for the structure assignments of these phosphine oxides have been presented elsewhere.[10,11] Anions (2) were readily available from these oxides on treatment with lithium diisopropylamide (THF, -70°C). Silylation of these anions with trimethylsilyl chloride proved to be efficient (> 80%) and regiospecific, the sole product being the α-methoxy-γ-trimethylsilyl vinylphosphine oxide (3). Coupling constants ($^3J_{PH}$ = 9-12 Hz) in the products (3) are indicative of a hydrogen atom cis to the phosphorus moiety,[12] hence the adducts were designated the E-isomers, thought to result from preferential co-ordination of lithium to the methoxy group. Subsequent treatment of these γ-silylated products (3) with lithium diisopropylamide (THF, 0°C) and quenching of the resulting anion with aldehydes, yielded 3-methoxy-1-trimethylsilyl-1,3-dienes (5) in good yields.

Scheme I

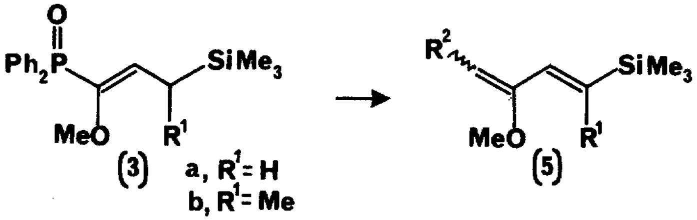


In view of the success of the double-quenching procedure described above it was anticipated that both operations could be carried out in one-pot. This proved to be practical and the same 3-methoxy-1-trimethylsilyl-1,3-dienes were obtained in higher yields (see Table 1) by treating the initially formed solution of the γ-silylated phosphine oxide at 0°C with 1 equivalent of n-BuLi, followed by 1 equivalent of the appropriate aldehyde after an interval of 10 minutes.

Where it is possible for (E)- and (Z)-geometry to exist at the 3-position of these dienes, both isomers were usually observed. The formation of two geometric isomers is quite standard in Wittig-Horner reactions leading to enol ethers,[13] and examination of ^{1}H chemical shifts for a series of methyl enol ethers[14] reveals a characteristic pattern, the vinyl proton of the (E)-isomer appearing downfield of the corresponding hydrogen atom of the (Z)-isomer, presumably as a result of deshielding by the adjacent methoxyl group. It was on this basis that we assigned the geometry at the 3,4-double bond in the products obtained in the present study.

Synthetic applications of these functionalised silylated dienes are currently under investigation. In particular we are exploiting the intramolecular Diels-Alder reactions of dienes (5d,e,m,n) for the preparation of tricycles which may be valuable intermediates for the synthesis of cannabinoids.

Table 1 3-Methoxy-1-trimethylsilyl-1,3-dienes (5) via Wittig-Horner Reactions



Silyl Phosphine Oxide	Aldehyde, R^2CHO R^2 =	1,3-diene[a] number	Yield %[b]	3E:3Z ratio[c]
(3a)	Ph	(5a)	52	2:3
	p-Tolyl	(5b)	50	1:2
	p-Anisyl	(5c)	54	1:2
	o-Allyloxyphenyl	(5d)	64	7:2
	o-Crotyloxyphenyl	(5e)	60	3:1
(3b)	H	(5f)	40	-
	Me	(5g)	38	1:1
	Me_2CH	(5h)	45	3:2
	$MeCH_2$	(5i)	38	1:2
	Ph	(5j)	60	5:4
	p-Tolyl	(5k)	57	1:1
	p-Anisyl	(5l)	56	3:2
	o-Allyloxyphenyl	(5m)	68	5:2
	o-Crotyloxyphenyl	(5n)	63	5:2
	2-Furyl	(5o)	45	3:4

a. The products were characterised by NMR, IR, mass spectra and chemical analysis.

b. Yields quoted are for the one-pot reaction; the other product in these one-pot reactions is silylated phosphine oxide (3) which can be recycled.

c. Estimated from the ratio of the integrals for the methoxy protons and/or the protons on the 4-position.

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