A Facile Synthesis of 1,5-Dienes and β,γ-Unsaturated Nitriles via Trityl Perchlorate-Catalyzed Allylation

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In the presence of a catalytic amount of trityl perchlorate, secondary and tertiary allyl ethers smoothly react with allylsilanes and silyl cyanide to give the corresponding 1,5-dienes and β,γ-unsaturated nitriles, respectively, in good yields.

In the previous paper,[1] we have reported the synthesis of γ,δ-unsaturated ketones from enol silyl ethers utilizing the effective activation of secondary and tertiary allyl methyl ethers by trityl perchlorate. Based on this characteristic property of trityl cation to activate allyl ethers, a study on cross-coupling reactions employing a variety of nucleophiles was continued and, in this communication, we wish to report a facile synthsis of 1,5-dienes and β,γ-unsaturated nitriles via trityl perchlorate-catalyzed reactions of allyl ethers with allylsilanes and silyl cyanide, respectively.

In the first place, allyl ethers (1a-1c) derived from (E)-4-phenyl-3-buten-2-ol were treated with allyltrimethylsilane (2) under various reaction conditions, and it was found that the desired allylation smoothly proceeds at -45 °C to give the corresponding 1,5-dienes(3, 4) in good yields (Table 1). In particular, 1,5-dienes were almost quantitatively obtained in the case of allyl tetrahydropyranyl(THP) ether (1c), which contains an unsymmetrical mixed acetal function in the molecule. According to the similar procedure, various 1,5-dienes were synthesized and the results are summarized in Table 2. The nucleophilic attack by allylsilanes takes place exclusively at the position γ to silicon atom (Entries 2, 6). The regiospecificity concerning allyl ethers was not observed suggesting that the present reaction proceeds via S_N1-type mechanism. The tertiary allyl ether was also rapidly coupled with 2 (Entry 9). Though, allyl THP ethers generally show a higher reactivity than allyl methyl ethers under the present reaction conditions, allyl methyl ether gave the best result in case of 2-methyl-2-propenylsilane, which is more nucleophilic than 2 (Entries 3, 4).

The typical experimental procedure is as follows: Under an argon atmosphere to a CH_2Cl_2 solution (1.5 ml) of trityl perchlorate (8 mg, 0.02 mmol) was added a CH_2Cl_2 solution (2.5 ml) of THP ether (1c, 80 mg, 0.27 mmol) and trimethyl(3-methyl-2-butenyl)silane (60 mg, 0.42 mmol) at -45 °C. After stirring at that temperature for 1.5 h, a few drops of pyridine were added in order to stop the reaction. The solvent was evaporated and the residue was purified by preparative
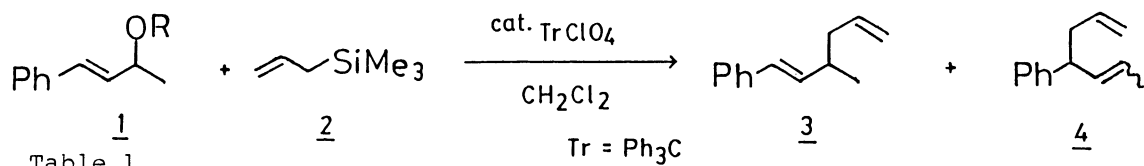
Table 1.

Entry	Allyl ether (1)		Temp /°C	Time	Yield / %	3 : 4
1	OMe PhCH=CHCHMe	1a	-78	1 d	43	a)
2	1a		-45	2 h	88	72 : 28
3	OCH$_2$OMe PhCH=CHCHMe	1b	-78	4 h	19	a)
4	1b		-45	2 h	76	77 : 23
5	1b		-23	2 h	76	72 : 28
6	OTHP PhCH=CHCHMe	1c	-78	1 d	25	76 : 24
7	1c		-45	2 h	99	72 : 28
8	1c		-23	2 h	98	69 : 31

a) The ratio was not determined.
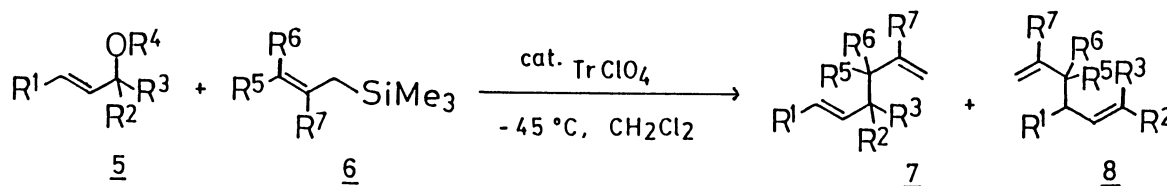
Table 2.   The Synthesis of 1,5-Dienes

Entry	Allyl ether (5)		Allylsilane (6)	Time	Yield/%[a]	7 : 8[b]
1	OTHP PhCH=CHCHMe	1c	CH$_2$=CHCH$_2$SiMe$_3$	2 h	99	72[c] : 28[d]
2	1c		Me$_2$C=CHCH$_2$SiMe$_3$	3 h	90	84[c] : 16[d]
3	1c		CH$_2$=CMeCH$_2$SiMe$_3$	1 h	50	~50[c] : 50[d]
4	OMe PhCH=CHCHMe	1a	CH$_2$=CMeCH$_2$SiMe$_3$	10 min	81	~50[c] : 50[d]
5	OTHP PhCH=CHCHPh	5a	CH$_2$=CHCH$_2$SiMe$_3$	3.5 h	92	–
6	5a		Me$_2$C=CHCH$_2$SiMe$_3$	1.5 h	94	–
7	5a		MeCH=CHCH$_2$SiMe$_3$	3 h	73[e]	–
8	OMe PhCH$_2$CH$_2$CHCH=CHMe		CH$_2$=CHCH$_2$SiMe$_3$	f)	96	21[c] : 79[d]
9	OTHP PhCH=CHCMe$_2$		CH$_2$=CHCH$_2$SiMe$_3$	30 min	89	17[c] : 83

a) All products gave satisfactory ^{1}H NMR and IR spectra. Yields are based on the allyl ethers. b) The ratio was determined by GLPC analysis and/or ^{1}H NMR spectra. c) Only E-isomer was observed by ^{1}H NMR. d) The geometry of the double bond was not determined. e) The diastereomers ratio is 59:41. The stereochemistry was not assigned. f) The reaction mixture was stirred at -45 °C for 3 h and then at -23 °C for 5 h.

TLC (silica gel) affording the corresponding 1,5-dienes (68 mg, 94 %); ^{1}H NMR 1.00 (s, 3H), 1.11 (s, 3H), 3.28 (d, J=9 Hz, 1H), 4.91 (dd, J=17 and 1.7 Hz, 1H), 5.02 (dd, J=10 and 1.7 Hz, 1H), 5.92 (dd, J=17 and 10 Hz, 1H), 6.37 (d, J=15 Hz, 1H), 6.57 (dd, J= 15 and 9 Hz); IR (neat) 1635, 1595, 740, 695 (cm^{-1}).

Several methods for the coupling of allyl groups have already appeared in literatures. However, they have the following limitations; the Wurtz-type reaction is restricted to homo-coupling;[2] reductive coupling reaction using titanium trichloride should be carried out at an elevated temperature in refluxing DME;[3] the TiCl$_4$-mediated reaction of allyl ethers with allylsilanes or allylstannanes requires an equimolar amount of the promoter and tertiary allyl ethers cannot successfully be employed.[4] Therefore, the present cross-coupling reaction provides a facile method for the preparation of 1,5-dienes.

Next, allyl ethers were allowed to react with silyl cyanide and the desired β,γ-unsaturated nitriles were obtained in good yields by the combination of allyl methyl ether and p-methoxyphenyldiphenylmethyl perchlorate as a promoter (Table 3). In other cases, the formation of some undesired products[5] was observed by TLC. The synthesis of various β,γ-unsaturated nitriles was shown in Table 4. α,β-Unsaturated nitriles, the products of double bond isomerization, were not detected in all cases.

The known methods for the cross coupling of allyl group and cyano group is restricted to primary allyl group.[6] In contrast, α-substituted β,γ-unsaturated nitriles can be readily prepared by the promotion of a catalytic amount of trityl salt according to the present reaction.
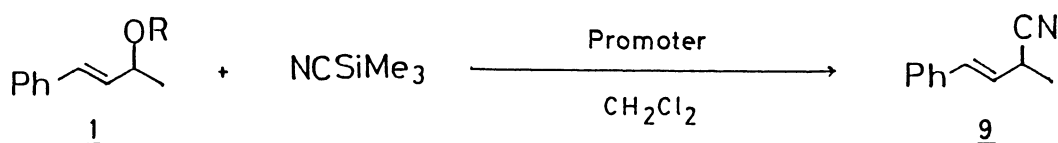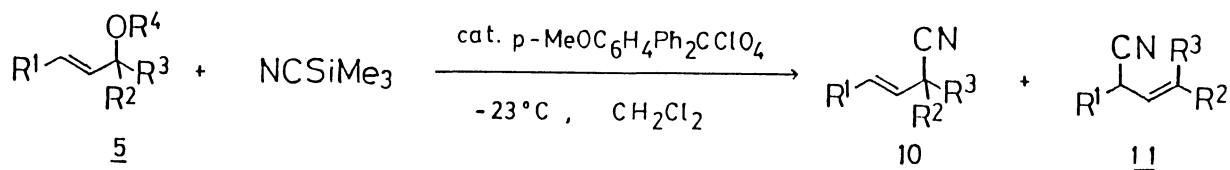
$$\text{Ph}\overset{\displaystyle OR}{\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown} \quad + \quad \text{NCSiMe}_3 \quad \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{Promoter}} \quad \text{Ph}\overset{\displaystyle CN}{\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown}$$

$\underline{1}$ $\underline{9}$

Table 3.

Entry	$\underline{1}$	Temp / °C	Time	Promoter	Yield / %
1	$\underline{1a}$	-45	1 d	TrClO$_4$	33
2	$\underline{1a}$	-23	1 h	TrClO$_4$	66
3	$\underline{1a}$	-23	40 min	p-MeOC$_6$H$_4$Ph$_2$CClO$_4$	77
4	$\underline{1b}$	-45	30 min	TrClO$_4$	53
5	$\underline{1c}$	-45	2 h	TrClO$_4$	52

Table 4. The Synthesis of β,γ-Unsaturated Nitriles[a]

Entry	5		Temp / °C	Time	Yield / %	10[b] : 11
1	PhCH=CHCHMe (OMe)	1a	-23	40 min	77	> 95 : 5
2	PhCH=CHCHPh (OMe)	5a	-23	1.5 h	65	-
3	PhCH=CHCMe₂ (OMe)		-45	3 h	98	88 : 12

a) The similar experimental procedure to that for the synthesis of 1,5-dienes was performed.   b) Only E-isomer was observed by ^{1}H NMR.

It should be noted that the reaction of secondary and tertiary allyl ethers with allylsilanes or silyl cyanide is effectively promoted by a catalytic amount of trityl salt to afford the corresponding cross-coupling products in good yields.

References

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5) The product formed by the substitution on the acetal carbon atom was isolated (27%) in case of Entry 5 (Table 3).

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