

REACTION OF ALLYLSILANE WITH α -NITRO OLEFIN
AND ITS DEVELOPMENT TO SYNTHESIS OF CYCLOPENTENONE

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Summary: Michael addition of allylsilane to α -nitro olefin in the presence of $AlCl_3$ proceeded smoothly at low temperature to give unsaturated nitronic acid, which was converted into the $\gamma\delta$ -enone using aqueous $Ti(III)$. Transformation of the enone into the 1,4-diketone followed by the intramolecular aldol condensation with the latter provided a convenient new synthesis of cyclopentenone.

Recently allylsilanes have been used significantly in organic synthesis owing to their stability and regioselectivity.¹ They react with various kinds of electrophiles: carbonyl compounds,² acetals,³ acid chlorides,⁴ epoxides,⁵ *etc.* They also react with $\alpha\beta$ -enones in conjugate fashion to give $\delta\epsilon$ -enones.⁶ We now wish to report the Michael addition of allylsilane 1 to α -nitro olefin 2 and its application to the synthesis of some cyclopentenones 6.

Various kinds of $\alpha\beta$ -disubstituted- α -nitro olefins 2 were prepared readily from the corresponding primary nitroalkanes and aldehydes directly or stepwise (condensation, acetylation, and elimination of acetic acid).⁷ They are well-known to be unstable especially in strong basic media, hence their use as the Michael acceptor would be rather preferable under the neutral or acidic conditions. Recently Yoshikoshi *et al.*⁸ reported the reaction of α -nitro olefin and silyl enol ether in the presence of Lewis acid.

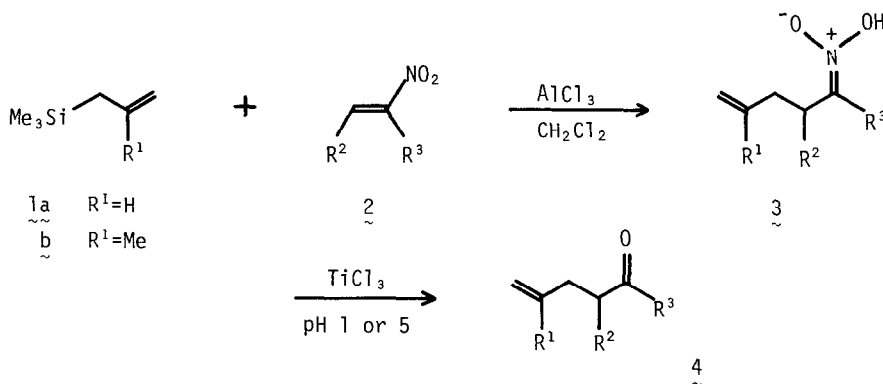
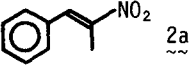
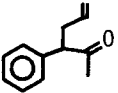
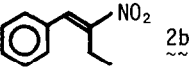
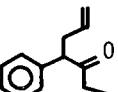
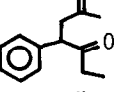
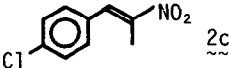
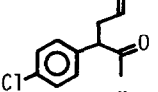
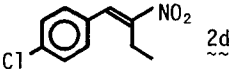
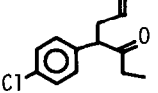
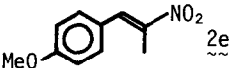
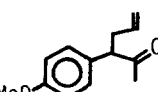
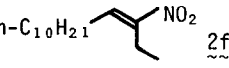
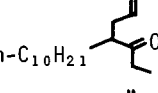
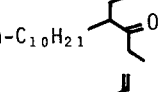
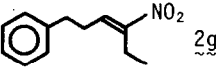
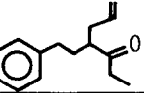


Table Michael Addition of Allylsilane 1 to α -Nitro Olefin 2 in the Presence of AlCl_3 and Successive Nef-type Reaction to $\gamma\delta$ -Enone 4

Michael addition ^a		Nef reaction		product	(% yield) ^d
allylsilane	α -nitro olefin ^b	method	reaction time (hr) ^c		
<u>1a</u>	 <u>2a</u>	B	24	 <u>4a</u>	(51)
<u>1a</u> ^e	 <u>2b</u>	B	15	 <u>4b</u>	(62)
<u>1b</u> ^f	<u>2b</u>	B	24	 <u>4b</u>	(62)
<u>1a</u> ^g	 <u>2c</u>	B	72	 <u>4c</u>	(55)
<u>1a</u>	 <u>2d</u>	A	24	 <u>4d</u>	(49)
<u>1a</u>	<u>2d</u>	B	48	<u>4d</u>	(55)
<u>1a</u>	 <u>2e</u>	A	48	 <u>4e</u>	(59) ^h
<u>1a</u>	<u>2e</u>	B	24	<u>4e</u>	(48) ^h
<u>1a</u>	 <u>2f</u>	A	18	 <u>4f</u>	(74)
<u>1b</u>	<u>2f</u>	A	60	 <u>4f</u>	(74)
<u>1a</u> ⁱ	 <u>2g</u>	A	24	 <u>4g</u>	(50)

a) Reactions were performed as described in the text unless otherwise noted. b) Stereochemistry of the α -nitro olefins was deduced from their ^1H NMR spectra⁹; the signals of vinyl protons of 2a–2g appear at δ 8.08, 7.97, 8.0, 7.89, 8.08, 7.03, and 7.03 ppm. c) Reactions were carried out at room temperature. d) Yields after isolation by TLC. e) After stirring a mixture of 2b and AlCl_3 in dichloromethane at -20°C for 1hr, a solution of 1a in dichloromethane was added at -20°C . f) Reaction time: 1hr. g) 2 Molar equivalents of AlCl_3 were used. h) p-Methoxybenzaldehyde was obtained as a minor product. i) Reaction time: 3hr.

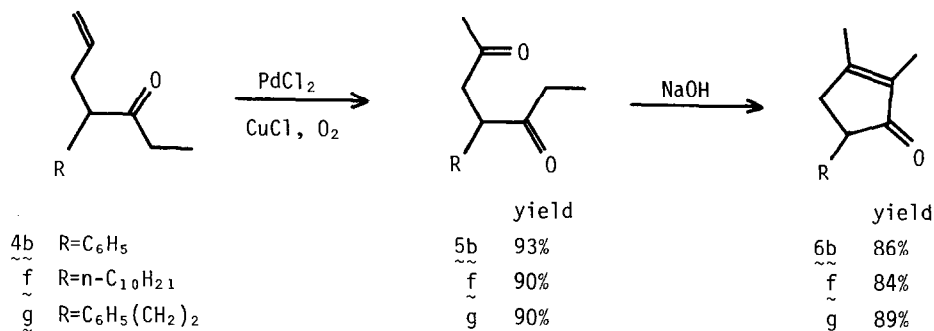
The reaction of allylsilane 1 with α -nitro olefin 2 was found to proceed smoothly in the presence of AlCl_3 to give unstable allylated nitronic acid 3 in good yield. A complex formation between α -nitro olefin 2 and the Lewis acid may have an important role in this reaction.

A typical procedure is as follows. To a stirred mixture of AlCl_3 (600 mg, 4.5 mmol) in dichloromethane (10 ml) was added dropwise a solution of 2-nitro-1-phenyl-1-propene (2a) (245 mg, 1.5 mmol) and allyltrimethylsilane (1a) (3 mmol) in dichloromethane (5 ml) over 5 min at -20°C in nitrogen. Immediately the solution yellowed, but the color disappeared after being stirred for 2hr at -20°C . After addition of water, the mixture was extracted with ether and the extract was treated as usual to give unsaturated nitronic acid 3 ($\text{R}^1=\text{H}$, $\text{R}^2=\text{Ph}$, $\text{R}^3=\text{Me}$) (300 mg) as a highly pure substance [^1H NMR (CDCl_3) δ 1.86 (3 H, s, $-\text{CH}_3$), 2.63 (2 H, t, $J = 8$ Hz, $-\text{CH}_2-$), 4.60 (1 H, t, $J = 8$ Hz, $-\dot{\text{C}}\text{H}-$), 4.86-5.30 (2 H, $=\text{CH}_2$), 5.40-6.20 (1 H, m, $-\text{CH}=\text{C}$), 7.25 (5 H, s, $-\text{C}_6\text{H}_5$), and ca 10 ppm (1 H, s, $-\text{OH}$, D_2O exchangeable signal)].

Generally nitronic acid has been known to have a very short half-life.¹⁰ In this allylation reaction, the decomposition of the product 3 was observed on TLC when the reaction temperature was raised to 0°C . Hence, acid 3 obtained was immediately subjected to the following transformation into ketone 4 without further purification.

There have been known many methods for Nef-type reaction including reductive and oxidative process. Nitronic acid 3 was converted into $\gamma\delta$ -enone 4 using aqueous titanium (III) chloride; Method A, $\text{TiCl}_3/\text{glyme}/\text{at pH } 1$; Method B, $\text{NaOMe}/\text{MeOH}/\text{TiCl}_3/\text{NH}_4\text{OAc}/\text{at pH } 5$.¹¹ The results are summarized in Table.

Nitronic acid 3 was usually formed in high yield. The moderate to good yields of $\gamma\delta$ -enones 4 in Table are attributable to the Nef-type reaction.



The terminal olefin of ketone 4 was easily converted into acetyl group by palladium catalyzed oxidation reaction¹² using palladium chloride/cuprous chloride/oxygen in dimethyl-

formamide to give 1,4-diketone 5 in excellent yield. The successive intramolecular aldol condensation of unsymmetrical 1,4-diketone 5 with 2% NaOH in 95% aqueous methanolic solution afforded selectively the 2,3-dimethylcyclopentenones 6 under kinetically controlled conditions following the recent work of McCurry, Jr., *et al.*¹³ The direction of this aldol condensation was found to be that expected from their report.

Reaction of allylstannane with α -nitro olefin also proceeds well and it will be the subject of a further publication.

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(Received in Japan 6 December 1980)