

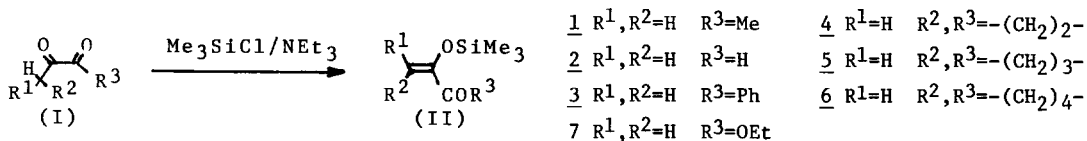
CATALYZED CYCLOADDITION REACTIONS OF α -SILYLOXY- α,β -UNSATURATED KETONE AND ALDEHYDE

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Summary: The reactions of α -silyloxy- α,β -unsaturated ketone and aldehyde with diene afforded [4+2] and [4+3] cycloadducts respectively in the presence of a catalyst.

Oxygen-substituted olefins are good candidates for the Diels-Alder reaction to furnish the functionalized cyclic compounds. Along this line, the growth of organosilicon chemistry allowed the remarkable development of dienol silyl ethers as 4π -components.² In contrast, little attention has been paid to enol silyl ethers as 2π -components; among them 3-(trimethylsilyl)oxy-3-buten-2-one (1) was hitherto known to react with the limited class of dienes.³ We wish to report here the divergent cycloaddition reactivity of α -silyloxy- α,β -unsaturated carbonyl compounds (II) in the presence of a catalyst. The starting unsaturated silanes were prepared by the usual silylations of the corresponding α -keto carbonyl compounds (I) with trimethylsilyl chloride and triethylamine in pentane or in acetonitrile.⁴

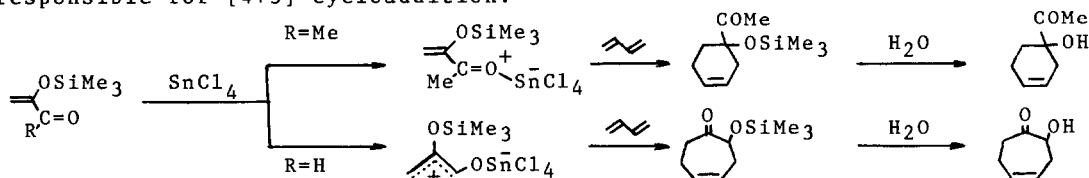


As a typical example, we have first chosen the reaction of the known reagent (1) with isoprene: As might be expected, no appreciable reaction took place without a catalyst. However, SnCl₄ or Et₃O⁺ BF₄⁻ catalyzed the reaction to give the [4+2] adduct in 45% yield at -78°C or in 65% yield at room temperature (entry 2). To the best of our knowledge this onium salt is not preceded as a catalyst for the Diels-Alder reaction. Nevertheless our examination indicated it effective; methyl vinyl ketone and isoprene reacted at room temperature within 1 hr under this catalysis to give 1-methyl-4-acetylcyclohexene (8) in 72% yield. The product structure was unequivocally determined by the independent synthesis of 10 by oxidation of 8 with *t*-BuOK and O₂.⁵ The reactions of 1 with other dienes proceeded smoothly to give the expected products. The [4+2] cycloadduct was also obtained from isoprene and 3. Interestingly, enol silyl ethers

derived from cyclic α -diketones (5 and 6) underwent the similar [4+2] cycloaddition reactions to give the bridgehead-hydroxylated bicyclic compounds; unfortunately five-membered 4 was unsuccessful because of the concomitant decomposition of the reagent under the employed conditions. The *cis*-fusion in 15 was confirmed by the spectral comparison of the hydrogenated product of 15 with known *cis*-9-hydroxy-1-decalone.⁶

The chemical behavior of silyl enol ether of pyruvaldehyde (2) is in good contrast: In this case SnCl_4 catalyzed the reaction of 2 with butadiene at -78°C better than the onium salt, but the product was found to be not [4+2] but [4+3] cycloadduct arising from the allyl cation type of reaction.⁷ The assigned seven-membered ring structure was affirmed by the identity of the hydrogenated product of 18 with the authentic sample.⁸ Similarly, the reactions of 2 with cyclopentadiene and furan afforded bicyclo[3.2.1]octanes 19 and 20 respectively; the latter formed only one isomer with a hydroxyl group *exo*-substituted. These results are summarized in Table 1.

On the other hand, the analogous reactions of 7 with butadiene and cyclopentadiene afforded neither [4+2] nor [4+3] cycloadduct under the same catalyzed conditions as above. We believe that the observed difference in reactivity may originate from the extent to which the catalyst coordinates with the carbonyl groups and thus polarizes them. While the complex formation of the catalyst with the ketones (1, 3, 5 and 6) brings about changes in their frontier orbitals due to partial contribution of allyl-cation-like nature,⁹ that with the aldehyde (2) leads to the formation of discrete fully opened allyl cation, which is responsible for [4+3] cycloaddition.



Consequently the present catalyzed cycloaddition reactions of α -silyloxy- α,β -unsaturated ketone and aldehyde provide a convenient method for the preparation of cyclic α -ketols. Further conversions of the obtained α -ketol are illustrated as follows: 1) NaIO_4 -oxidation¹⁰ of 10 to cyclohexenone (21), implying 1 as a ketene synthone. 2) Anionic cyclization of 10 with ethyl formate to spiro-furanone (22), according to the known procedure.¹¹

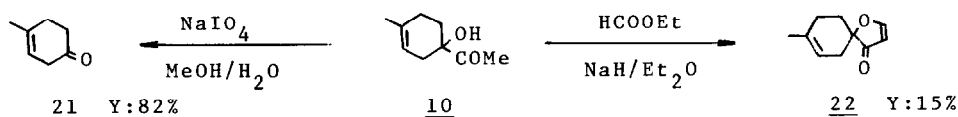

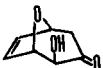


Table 1. Catalyzed Cycloaddition Reactions of 1 - 6 with Some Dienes.^a

entry	silane	diene	conditions ^b			product ^c yield	IR ^d cm ⁻¹	NMR ^e δ
			1.	2.	3.			
1	<u>1</u>		S [M]	-45 rt	7 12]	 <u>9</u> R=H Y:29% [Y:35%]	3500, 1710 1650, 750	5.66 (2H, m, CH=CH), 3.30 (1H, s, OH), 2.20 (3H, s, CH ₃ CO).
2	<u>1</u>	R=Me	S [M]	-78 rt	7 12]	 <u>10</u> R=Me Y:45% [Y:65%]	3500, 1715 1645, 760	5.25 (1H, m, CH=C), 3.28 (1H, s, OH), 2.20 (3H, s, CH ₃ CO), 1.70 (3H, br s, CH ₃ C=C). Mass spectrum (30 eV), m/e 154 (M ⁺), 136 (M ⁺ -H ₂ O).
3	<u>1</u>		M	rt	12	 <u>11</u> Y:72%	3500, 1710 1670	5.30 and 5.04 (each 1H, m, CH=C), 3.23 (1H, s, OH), 2.18 (3H, s, CH ₃ CO), 1.67 and 1.60 (each 3H, br s, CH ₃ C=C).
4	<u>1</u>	Ph-CH=CH-CH=CH-Ph	M	rt	12	 <u>12</u> Y:74%	3500, 1705 1655, 1600	7.13 (5H, br s, phenyl), 5.98 and 5.60 (each 1H, br AB q, J=12 Hz, CH=CH), 3.72 (1H, s, OH), 3.28 (1H, br s, CHPh), 1.37 (3H, s, CH ₃ CO).
5	<u>1</u>		M	0	6	 <u>13</u> Y:40%	3550, 1720	6.12 and 5.86 (each 1H, dd, J=3 and 5 Hz CH=CH), 3.38 (1H, s, OH), 1.16 (3H, s, CH ₃ CO).
6	<u>3</u>		M	rt	12	 <u>14</u> Y:80%	3500, 1670 1605	7.1-8.2 (5H, m, phenyl), 5.23 (1H, br s, CH=C), 3.52 (1H, s, OH), 1.67 (3H, br s, CH ₃ C=C).
7	<u>5</u>		M	rt	12	 <u>15</u> R=H Y:48%	3500, 1700	5.63 (2H, m, CH=CH), 3.86 (1H, s, OH).
8	<u>5</u>	R=Me	M	rt	12	 <u>16</u> R=Me Y:70%	3500, 1705	5.35 (1H, m, CH=C), 4.07 (1H, s, OH), 1.75 (3H, br s, CH ₃ C=C).
9	<u>6</u>		M	rt	12	 <u>17</u> Y:72%	3550, 1685	5.58 (2H, m, CH=CH), 3.78 (1H, s, OH).
10	<u>2</u>		S	-78	2/3	 <u>18</u> Y:32%	3500, 1710	5.85 (2H, m, CH=CH), 4.33 (1H, dd, J=5 and 11 Hz, CHOH), 3.83 (1H, s, OH). Mass spectrum (75 eV), m/e 126 (M ⁺), 108 (M ⁺ -H ₂ O)
11	<u>2</u>		S	-78	5	 <u>19</u> Y:72% (endo:exo=73:27)	3500, 1710 3450, 1700	5.98 (2H, m, CH=CH), 4.05 (1H, d, J=4 Hz, CHOH), 3.29 (1H, s, OH). 6.15 and 5.92 (each 1H, dd, J=3 and 6 Hz, CH=CH), 3.77 (1H, s, OH), 3.57 (1H, br s, CHOH).

Table 1. continued

12	<u>2</u>		S	-78	1/6		3400, 1700	6.30 and 6.22 (each 1H, AB q, J=5.5 Hz, CH=CH), 5.10 and 5.02 (each 1H, br s, C ₁ -H and C ₂ -H), 4.37 (1H, br d, J=5 Hz, C ₅ -H), 3.60 (1H, s, OH), 2.92 (1H, dd, J=5 and 15 Hz, C ₄ -H), 2.42 (1H, dd, J=1 and 15 Hz, C ₄ -H).
						<u>20</u>	Y:43%	

^a Elemental analyses were found to be satisfactory. ^b Reaction conditions: 1. catalyst:S, SnCl₄; M, Et₃O⁺ BF₄⁻. 2. temperature in °C: rt, room temperature. 3. reaction time in hour.

^c In entry 2, 3, 4, 6 and 8, there are depicted the structures of the major product of the possible regioisomers. The NMR spectra of the product mixtures suggested more than 86% "para" selectivity (integration ratio of acetyl or olefinic signals. Eu(fod)₃ was employed if required). mp: 13, 79-80°C (lit.^{3b} mp 80-82°C). 15, 58-60°C. *endo*-19, 78-82°C. *exo*-19, 119-121°C. 20, 76-78°C. All others were obtained in oil. ^d Crystalline 13, 15, 19 and 20 were scanned in KBr disks and all others in neat. ^e Solvents used are CDCl₃ for 16 and 20, and CCl₄ for all others. In NMR spectra of 18, 19 and 20, coupling constants between C₁-H and C₂-H support *endo*- and *exo*-positions of the hydroxyl groups; H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Am. Chem. Soc.*, 94, 3940 (1972).

Typical Procedure. To a solution of unsaturated silane (1 mmol) and diene (1.5 mmol) in dry CH₂Cl₂ (3 ml) was added 1 eq. of catalyst in dry CH₂Cl₂ (1 ml) at the temperature designated in Table 1, and the reaction mixture was stirred for an appropriate time. After evaporation of the solvent the residue was treated with MeOH (10 ml) and 1N HCl (1 ml) for 30 min, and poured into ice-water containing NaHCO₃. After extraction with ether and evaporation of the solvent, purification on a silica gel column (CHCl₃) gave a product.

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