

CONJUGATE ADDITION OF ALLYLSILANES TO α,β -ENONES.

OBTENTION OF CYCLOBUTYL DERIVATIVES

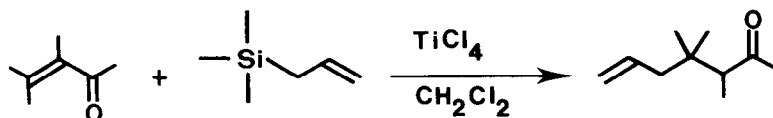
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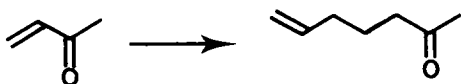
Summary : By conjugate addition of allylsilanes to α,β -enones, cyclobutyl derivatives are formed.

1,4-Addition reactions of organo-metallic compounds to α,β -unsaturated carbonyl compounds constitute one of the fundamental processes in organic synthesis.

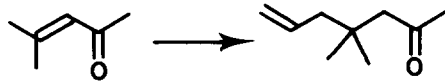
Recently, it has been demonstrated that allyl transfer reactions take place very smoothly from allylsilanes to α,β -enones to give δ,ϵ -enones (1).



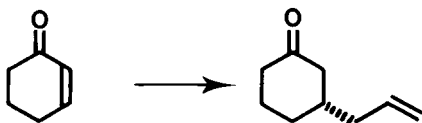
In continuation of our research on new annulation techniques (2), we next turned to the exploitation of this reaction. Several systems were examined; as was expected, we observed excellent to fairly good yields depending on the structure of enone. The sole minor product is generally the starting material (with methylvinylketone, we obtain higher boiling fractions) (3).



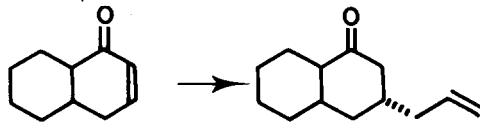
40 % yield
(+ higher boiling fraction (1))



50 % yield (1)
(45 % starting material recovery)



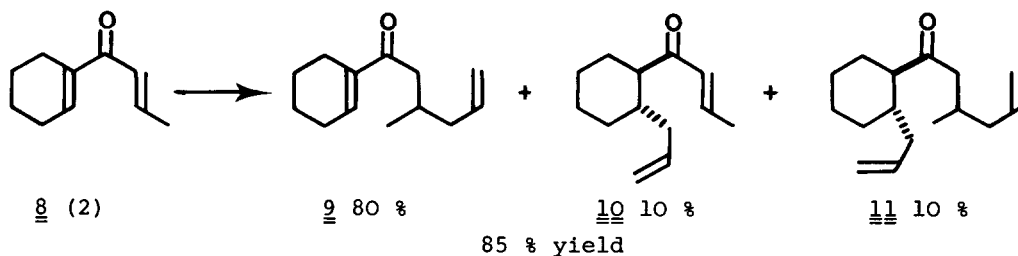
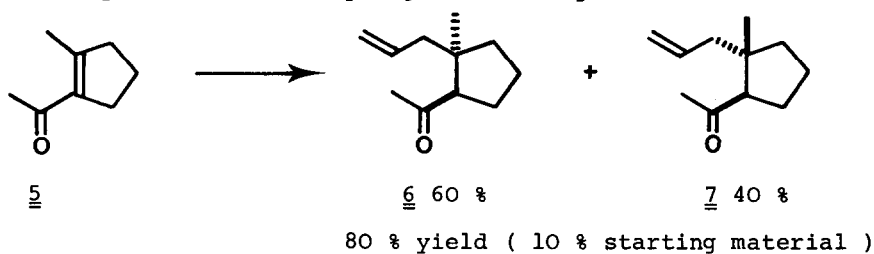
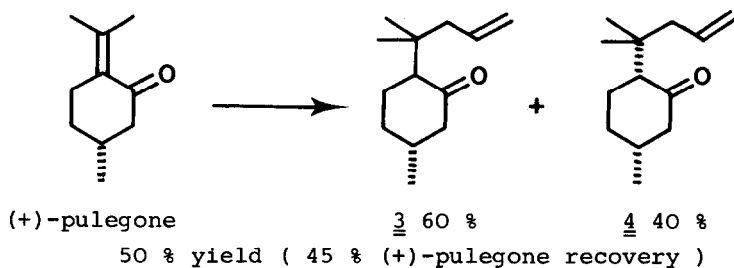
quantitative yield (1)



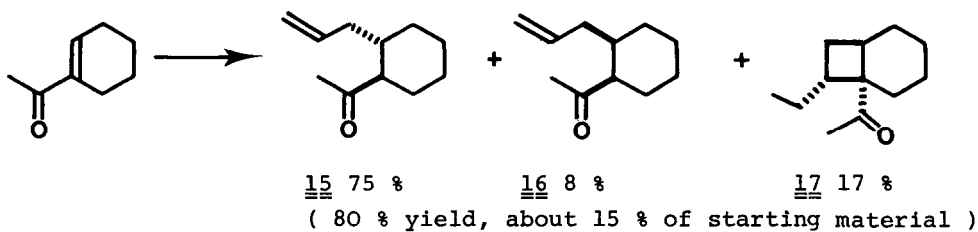
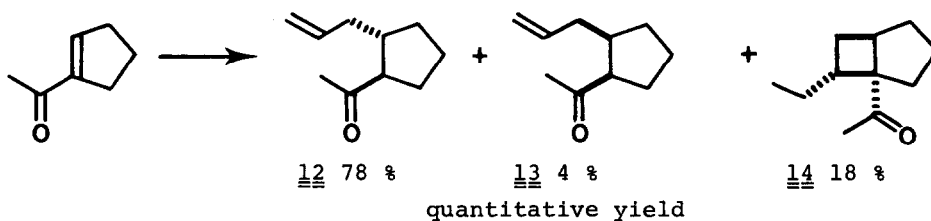
1 (2)

2

quantitative yield.



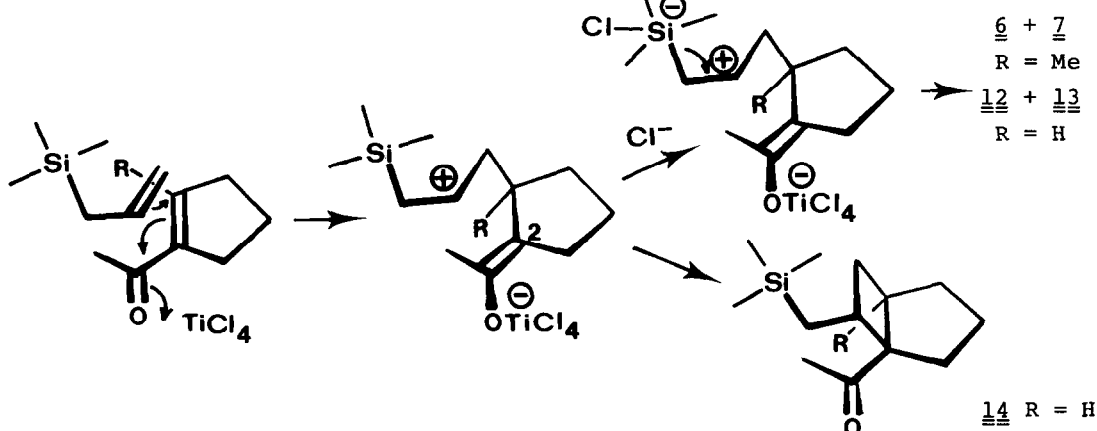
However, with acetylcyclopentene or cyclohexene, we have identified a minor product as the cyclobutyl derivative 14 or 17.



The structures 14 and 17 were supported by the full range of spectral data (4)

Possibly, the transition state for the allylic transfer has relatively high carbenium ion character and can benefit from the well known ability of silicon to stabilise a β -carbenium ion (5).

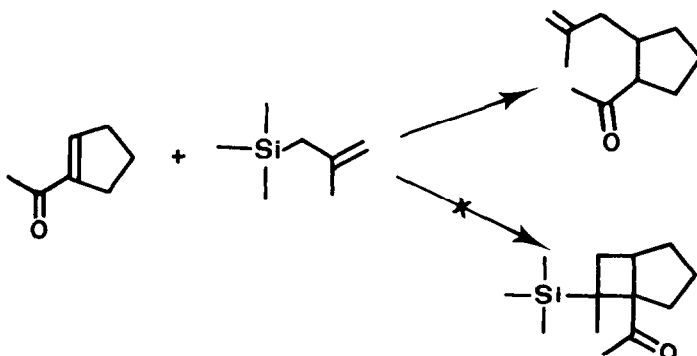
The cyclisation reaction presumably proceeds by nucleophilic attack by the C-2 atom of the enolate on the β -carbenium ion :



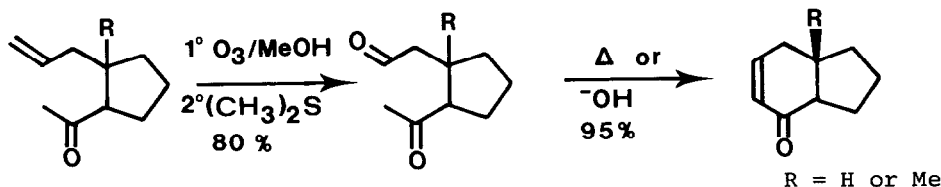
These structures 14 and 17 correspond to 4-Exo-Trig cyclisation (favoured and observed course (6))

When R = Me, we do not observe the cyclobutyl product formation. As the carbenium ion approaches closely to the C-2 atom of the enolate, the acetyl group moves down below the initial molecular plane. This observation suggests a steric hindrance between acetyl and methyl groups (R = Me) in the transition state (product development control).

Similarly, we do not observe cyclobutyl derivative from methylallyl-trimethylsilane :



As a demonstration of the synthetic utility of the conjugate addition of allylsilanes and as further proof of structure, δ,ϵ -enones 6 + 7, and 12 + 13 were converted to the known bicyclic ketones (2) :

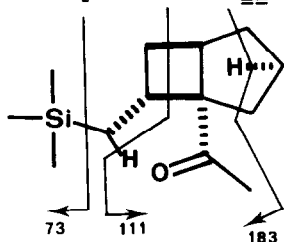


References and notes :

- (1) (a) A. HOSOMI and H. SAKURAI, *J. Amer. Chem. Soc.*, **99**, 1673 (1977)
 (b) T. YANAMI, M. MIYASHITA and A. YOSHIKOSHI, *J. Chem. Soc., Chem. Comm.* 525 (1979).
- (2) Z. BOUNKHALA, S. HACINI, R. PARDO and M. SANTELLI, *ibid.*, 263 (1979).
- (3) In a typical experiment, to a solution of TiCl_4 (10 mmol) in dry CH_2Cl_2 (10 ml) cooled at -20°C , was added the α,β -enone (10 mmol) in dry CH_2Cl_2 (5 ml). After stirring 5 min, the mixture was cooling to -78°C and allyltrimethylsilane (15 mmol) in dry CH_2Cl_2 (15 ml) was added. The mixture was kept at -78°C for 5 h and at -30°C for 5 h and was then hydrolysed.
- (4) ^{13}C nmr data (FT 80) (assignments confirmed by off-resonance decoupling):

	1	211.22	6	32.89		1	212.16	5	26.32
	2	69.02	7	28.03		2	58.17	6	24.93
	3	47.63	8	25.50		3	39.27	7	21.80
	4	39.53	9	24.71		4	37.31	8	-3.28
	5	36.93	10	-3.27			31.73		
							30.96		

Mass spectrum of 14 (70 eV) :



M^+/e : 224 (9.5 %), M^++1 : 1.9 % , M^++2 : 0.55 %
 209 ($M^+ - \text{CH}_3$) (9.5 %); 183 (52 %);
 134 (12.5 %); 111 (66 %); 92 (10 %); 79 (12 %);
 75 (35 %); 73 (100 %); 63 (12 %); 59 (24 %);
 45 (55 %); 43 (50 %); 41 (11 %).

- (5) C. EABORN, *J. Chem. Soc., Chem. Comm.*, 1255 (1972).
 E. EHLINGER and P. MAGNUS, *ibid.*, 421 (1979) and ref. therein.
- (6) J.E. BALDWIN, *ibid.*, 734 (1976).

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