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LATENT ACETONYLATION OF α,β-ENONES WITH ALLYLTRIMETHYLSILANE OR 2-METHYL-2-PROPENYLTRIMETHYLSILANE: SYNTHESIS OF 1,5-DIKETONES AND ANNELATION TO FUSED CYCLOHEXENONES[1]

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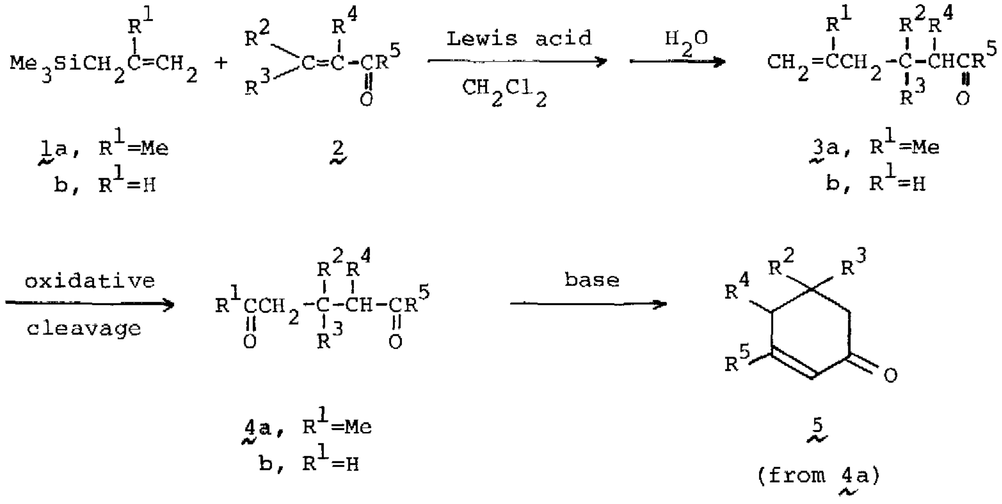
Summary: Acetonylation of α,β-enones can be achieved by reactions either with (2-methyl-2-propenyl)trimethylsilane or with allyltrimethylsilane followed by oxidative cleavage of the double bond or by the Wacker reaction, respectively. Annelation of the 1,5-diketones is also described briefly.

Acetonylation is one of the important operations in organic synthesis and a number of publications on this subject have been presented.[2] Recently we have demonstrated that allylsilanes are useful synthetic reagents with highly nucleophilic double bonds[3] and that, with α,β-enones, conjugate allylation takes place to afford δ,ε-enones generally in high yield.[4] During the course of studies on the further application of allylsilanes to organic synthesis, we have found that 2-methyl-2-propenyltrimethylsilane (**1a**) can also enter 1,4-reductive allylation and that the resultant δ,ε-enones (**3a**) are readily converted to 1,5-diketones (**4a**) by the oxidation of the olefinic part.[5] A similar process starting from allyltrimethylsilane (**1b**) resulted in the formation of **3b**[4], oxidation of which gave the corresponding δ-ketoaldehydes (**4b**) as shown in the following scheme.



1a, R^1=Me
b, R^1=H

2

3a, R^1=Me
b, R^1=H

4a, R^1=Me
b, R^1=H

5
(from **4a**)

Methyl ketones (**4a**) can also be obtained by the Wacker-type oxidation of the double bond of **3b** (<u>vide</u> <u>infra</u>).

A β-methallyl group, as well as an allyl group, can be introduced regioselectively into the β-carbon of α,β-enones by the conjugate addition of **1** in the presence of a Lewis acid such as titanium tetrachloride and boron trifluoride etherate. Since an olefinic double bond can readily be converted to a carbonyl group by the oxidative cleavage ($>C=CH_2 \xrightarrow{[O]} >C=O$), δ,ε-enones (**3**) obtained by the present reaction, can be a precursor to 1,5-dicarbonyl compounds (**4**), useful precursors to 2-cyclohexenones[6] and other compounds.

Oxidation of the δ,ε-enone (**3**) to **4**, which led to methyl ketones or aldehydes, was indeed achieved simply by the ozonation followed by reductive decomposition of the resulting ozonide with zinc-acetic acid, sodium iodide, or trimethylphosphite. Oxidation with potassium permanganate-potassium periodate is also effective. Yields of the products depend both on the structure of the starting **3** and on the oxidation method. The results are summarized in Table 1 with brief description of the reaction conditions.

Alternatively, the Wacker-type oxidation of **3b** catalyzed by palladium chloride-cuprous chloride in dimethylformamide[6a] also affords methyl ketones (**4a**). Table 1 contains the results of the type of oxidation. (runs 8 and 10).

$$\underset{\textbf{3b}}{CH_2=CHCH_2\text{-}CR^2R^3CHR^4COR^5} \xrightarrow[PdCl_2\text{-}CuCl]{O_2} \underset{\textbf{4a}}{CH_3COCH_2CR^2R^3CHR^4COR^5}$$

Therefore, the present work demonstrates that allylsilanes **1a** and **1b** can be viewed as synthetic equivalents of the acetonyl anion and/or the acetaldehyde enolate. We have previously demonstrated that **1b** can be a formyl anion equivalent in a certain case through isomerization of the double bond of the allylated product (**3b**) followed by oxidative cleavage, as shown in the next scheme.

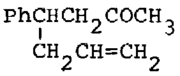
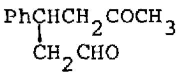
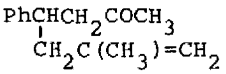
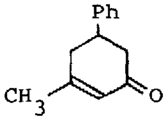
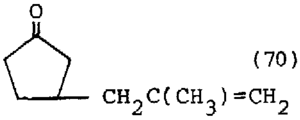
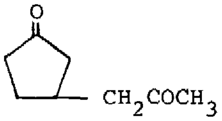
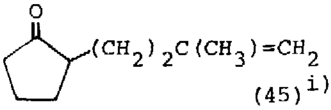
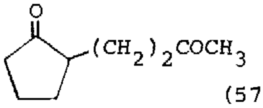
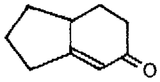
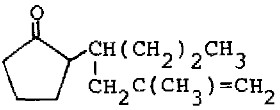
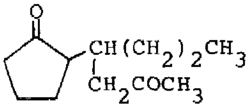
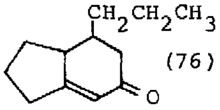
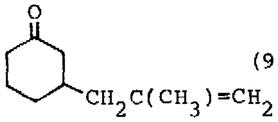
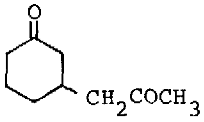
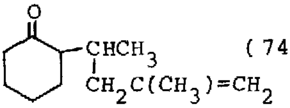
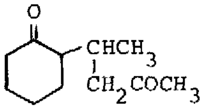
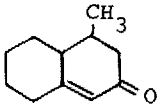
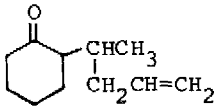
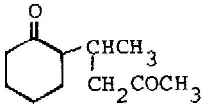
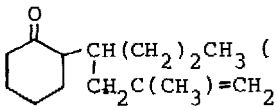
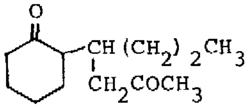
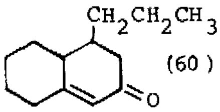
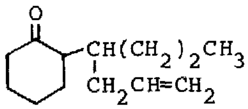
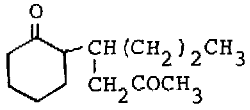
$$CH_2=CHCH_2\text{-}CR^2R^3CHR^4COR^5 \longrightarrow CH_3CH=CH\text{-}CR^2R^3CHR^4COR^5 \longrightarrow OCH\text{-}CR^2R^3CHR^4COR^5$$

Further useful application of the conjugate allylation may be displayed by cyclization, especially by the Robinson-type annelation of the oxidation products **4a** to cyclic α,β-enones. Thus, 1,5-diketones (**4a**, $R^4,R^5=-(CH_2)_n-$; n=3,4) obtained by the oxidation of the corresponding **3a** can be converted to fused cyclic α,β-enones (**5**) under a basic condition, representative examples being listed in Table 1.

The characteristic feature of the present annelation reaction stems in that the method consists of [3C + 3C] reactions; namely a three-carbon unit is introduced to an α-alkylidenecycloalkanone which may be obtained selectively from a cycloalkanone. The method can avoid the use of rather unstable methyl vinyl ketone or its equivalent in the [4C + 2C] reaction of the enolate[8] or enamine[9] of cyclohexanone.

Acknowledgment: We thank to Toshiba Silicone Co., Ltd., and the Mitsubishi Foundation for gifts of chlorosilanes and a partial support to the work. Our thanks are also due to Prof. A. Yoshikoshi, Tohoku University, for communicating to us his results prior to publication.[10]

Table 1. Synthesis of δ,ε-enones (**3**) followed by oxidation to 1,5-dicarbonyl compounds (**4**) and cyclization to cyclohexenones (**5**)

Entry	δ,ε-Enone (%yield)[a]	1,5-Dicarbonyl Compound (%yield)[a]	Cyclohexenone (%yield)[a]
1	 $\underset{CH_2CH=CH_2}{PhCHCH_2COCH_3}$ (95)[b]	 $\underset{CH_2CHO}{PhCHCH_2COCH_3}$ (72)[c] (63)[d]	
2	 $\underset{CH_2C(CH_3)=CH_2}{PhCHCH_2COCH_3}$ (69)[e]	$PhCH(CH_2COCH_3)_2$ (33)[c] (69)[f]	 (69)[j]
3	 (70)[g]	 (67)[h]	
4	 (45)[i]	 (57)[h]	 (76)[j]
5	 (82)[k]	 (72)[h]	 (76)[j]
6	 (99)[l]	 (61)[h]	
7	 (74)[m]	 (85)[h]	 (82)[j]
8	 (45)[n]	 (72)[o]	
9	 (67)[p]	 (65)[h]	 (60)[j]
10	 (52)[q]	 (64)[o]	

Caption to the Table.

[a] Yields after isolation by TLC. [b] $Me_3SiCH_2CH=CH_2$ (1b), $PhCH=CHCOCH_3$, $TiCl_4$, CH_2Cl_2, -30°, 5 min. [c] 1) O_3, CH_2Cl_2 or MeOH, -78°; 2) NaI, AcOH, MeOH, 0°, 1h. [d] 1) O_3, CH_2Cl_2, -78°; 2) $P(OMe)_3$, rt, 20 min. [e] $Me_3SiCH_2C(CH_3)=CH_2$ (1a), $PhCH=CHCOCH_3$, $TiCl_4$, CH_2Cl_2, -78°, 30 sec. [f] KIO_4, $KMnO_4$, K_2CO_3, H_2O, rt, 19h. [g] 1a, 2-Cyclopentenone, $TiCl_4$, CH_2Cl_2, -78°, 10 min. [h] 1) O_3, CH_2Cl_2, -78°; 2) Zn, AcOH, H_2O, rt, 1h. [i] 1a, 2-Methylenecyclopentanone, $BF_3 \cdot OEt_2$, CH_2Cl_2, -78°, 1h. [j] 2% KOH-H_2O, MeOH, reflux, 3h. [k] 1a, 2-Butylidenecyclopentanone, $TiCl_4$, -78°, 30 min. [l] 1a, 2-Cyclohexenone, $TiCl_4$, -78°, 10 min. [m] 1a, 2-Ethylidenecyclohexanone, $TiCl_4$, CH_2Cl_2, -78°, 1h. [n] 1b, 2-Ethylidenecyclohexanone,[11] $TiCl_4$, CH_2Cl_2, -78°, 2h. [o] $PdCl_2$, CuCl, O_2, DMF, H_2O, rt, 2h. [p] 1a, 2-Butylidenecyclohexanone, $TiCl_4$, CH_2Cl_2, -78°, 30 min. [q] 1b, 2-Butylidenecyclohexanone,[11] $TiCl_4$, CH_2Cl_2, -78°, 2h.

References and Notes

1. Chemistry of Organosilicon Compounds. 135.
2. a) R. M. Jacobson, R. A. Raths, and J. H. McDonald III, J. Org. Chem., 42, 2545 (1977); b) T. Nakai, J. Syn. Org. Chem., Japan, 36, 49 (1978), and references cited therein.
3. For recent reports, see a) A. Hosomi, H. Hashimoto, and H. Sakurai, J. Org. Chem., 43, 2551 (1978); b) A. Hosomi and H. Sakurai, Tetrahedron Lett., 2589 (1978); c) A. Hosomi, M. Saito, and H. Sakurai, ibid., 429 (1979).
4. A. Hosomi and H. Sakurai, J. Am. Chem. Soc., 99, 1673 (1977).
5. Satisfactory spectral data and elemental analyses were obtained for all products.
6. For recent reports, see a) J. Tsuji, I. Shimizu, and K. Yamamoto, Tetrahedron Lett., 2975 (1975); b) K. Narasaka, K. Soai, and T. Mukaiyama, Chem. Lett., 1223 (1974).
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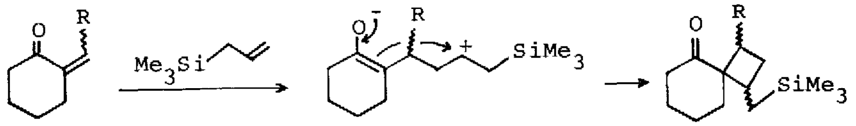
8. a) J. A. Marshall and W. I. Fanta, J. Org. Chem., 29, 2501 (1964); b) N. C. Ross and R. Levine, ibid., 29, 2341 (1964).
9. a) G. Stork, A. Brizzolara, H. H. Landesman, J. Szmuszkovicz, and R. Terrell, J. Am. Chem. Soc., 85, 216 (1963); b) W. G. Dauben, G. W. Schaffer, and N. D. Vietmeyer, J. Org. Chem., 33, 4060 (1968).
10. Professor A. Yoshikoshi and his coworkers are carrying out a work according to a similar synthetic design. See, T. Yanami, M. Miyashita, and A. Yoshikoshi, Chem. Commun., 525(1979).
11. In these cases, 6 was isolated by GLC as a by-product. Details will be reported later.



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