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NEW SYNTHETIC METHODS FOR α,β-UNSATURATED KETONES, ALDEHYDES, ESTERS AND LACTONES BY THE PALLADIUM-CATALYZED REACTIONS OF SILYL ENOL ETHERS, KETENE SILYL ACETALS, AND ENOL ACETATES WITH ALLYL CARBONATES

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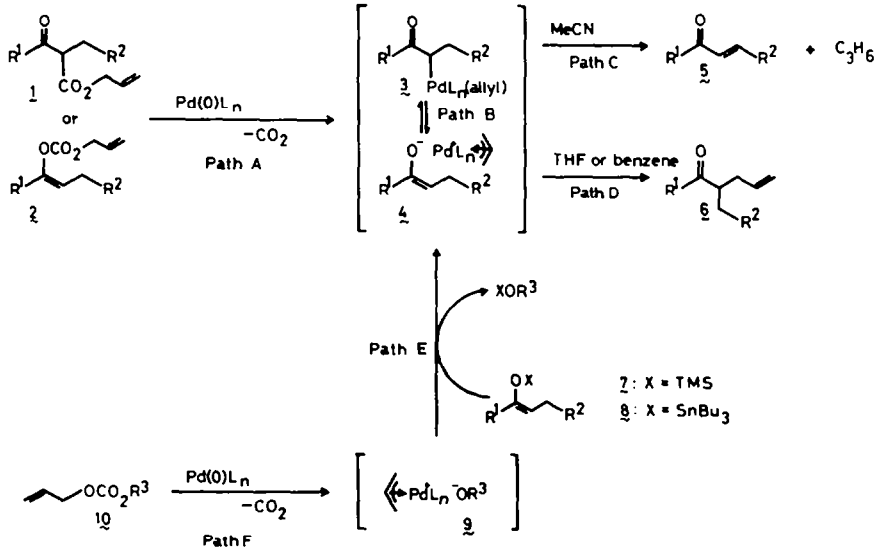
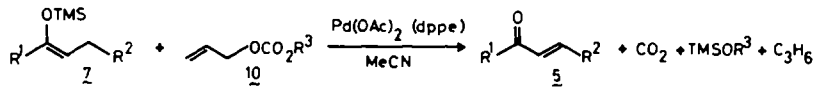
Abstract—Silyl enol ethers and ketene silyl acetals derived from ketones, aldehydes, esters and lactones are converted into α,β-unsaturated ketones, aldehydes, esters and lactones by treatment with allyl carbonates in high yields using the palladium–bis(diphenylphosphino)ethane (dppe) complex as catalyst. Phosphine-free palladium catalyst instead of the palladium–phosphine complex gives a higher selectivity for the preparation of cyclopentenone, cyclooctenone, dienones, α,β-unsaturated esters and lactones. As a solvent, the use of nitriles such as acetonitrile is essential. In other solvents, allylation takes place. Enol acetates derived from ketones are converted into α,β-unsaturated ketones by reaction with allyl carbonate in acetonitrile using the palladium complex and tributyltin methoxide as bimetallic catalysts.

INTRODUCTION

Conversion of saturated ketones, aldehydes and esters to the corresponding α,β-unsaturated compounds is one of the important synthetic methods. There are several established methods which can be carried out by the introduction of hetero-atoms such as halogens,[1] sulfur[2] and selenium,[3] followed by their elimination with β-hydrogen. But these methods still need further elaboration. During our continuing studies on the palladium-catalyzed reactions of various allylic compounds, we found the decarboxylation–allylation (path D in Scheme 1) and decarboxylation–dehydrogenation reactions (path C) of allyl β-keto carboxylates **1**.[4] As related reactions, we found the decarboxylation–allylation and decarboxylation–dehydrogenation of allyl alkenyl carbonates **2**.[5] A remarkable solvent effect was found in these reactions. The decarboxylation–dehydrogenation proceeds smoothly, using acetonitrile as the solvent, to give α,β-unsaturated ketones or aldehydes in high yields. In other solvents such as THF or benzene, the decarboxylation–allylation takes place to afford α-allyl ketones or aldehydes. It should be emphasized that in these dehydrogenation reactions, the allyl group is a hydrogen acceptor, which is converted to propene as shown by path C in Scheme 1. Thus, they offer completely new preparative methods for α,β-unsaturated ketones and aldehydes, and are useful for organic synthesis.



Scheme 1.



Scheme 2.

These reactions can be explained by the formation of (π-allyl)palladium enolate complex **4** or C-bonded complex **3**, which is converted into either α-allyl ketones **6** or α,β-unsaturated ketones **5** (Scheme 1). We found that these two competitive reactions, namely, allylation (path D) and dehydrogenation (path C), are well controlled by the effects of ligands and solvents. The allylation proceeds in common solvents such as benzene or THF. On the other hand, the dehydrogenation becomes the main path when nitriles are used as the solvent, and acetonitrile is the most suitable solvent. Furthermore, the molar ratio of palladium and phosphine ligand is crucial. When the ratio is larger than two, the allylation takes place even in acetonitrile. The dehydrogenation proceeds efficiently when the ratio is less than two, or even in the absence of phosphine ligand.[6]

Mechanistic consideration for the formation of (π-allyl(palladium enolate complexes **3** and **4** as common intermediates by the intramolecular reactions of **1** or **2** leads us to find new methods of forming similar (π-allyl)palladium enolate intermediates **3** and **4** from various enol forms of carbonyl compounds by intermolecular transmetallation reactions (path E). Once the (π-allyl)palladium enolate complexes **3** or **4** are formed, we expected then either allylation or dehydrogenation to be possible. As one component of the transmetallation, we selected (π-allyl)palladium alkoxide complexes **9** which can be generated *in situ* by the reaction of allyl carbonate **10** with Pd(0) complex (path F).[7,8] Then we found that smooth transmetallation of **9** takes place with either silyl enolates **7**[9] or tin enolates **8**[10] to afford the desired (π-allyl)-palladium enolate complexes **3** and **4**. Silyl enolates can be prepared easily by well-established methods.[11] Also tin enolates can be prepared *in situ* most conveniently by the reaction of enol acetates with tin methoxide.[12] These enolates are used for the dehydrogenation. By this way, we discovered new synthetic methods for α,β-unsaturated carbonyl compounds via their silyl and tin enolates. Preliminary reports have been given[6,9b,c,10b] and the details of these reactions are presented in this paper.

RESULTS AND DISCUSSION

Preparation of α,β-unsaturated ketones, aldehydes and esters from silyl enolates

Silyl enol ethers and ketene silyl acetals, prepared from ketones, aldehydes and esters, are known to be very useful intermediates for organic synthesis.[13] Usually, they are brought into reactions by using weak Lewis acids or fluoride anion. We found that silyl enol ethers and ketene silyl acetals **7** can be converted in one step in good yields to α,β-unsaturated carbonyl compounds **5** by the reaction of allylic carbonates using the palladium–phosphine catalyst or phosphine-free palladium catalyst.[6,9c] These reactions can be explained by Scheme 2.

The results are shown in Table 1. Similar to the

Table 1. Preparation of α,β-unsaturated ketones, aldehydes, esters, and lactones from silyl enolates

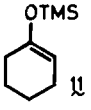
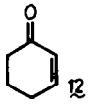
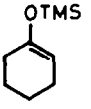
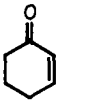
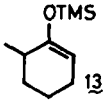
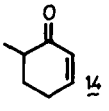
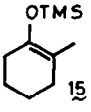
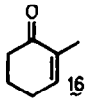
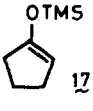
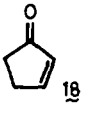
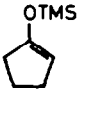
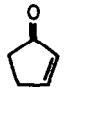
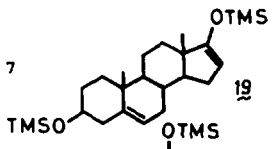
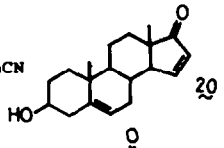
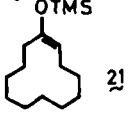
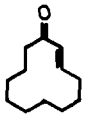
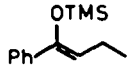
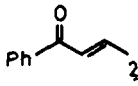
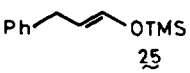
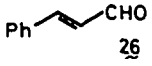
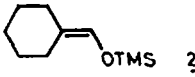
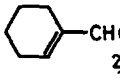
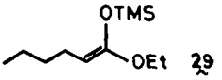
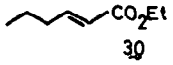
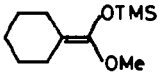
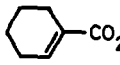
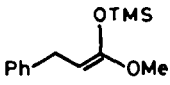
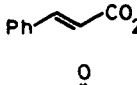
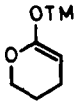
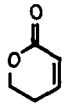
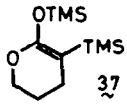
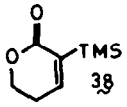
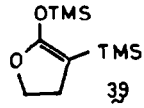
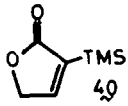
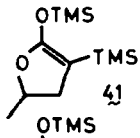
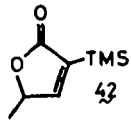
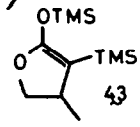
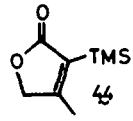
RUN	SILYL ENOLATES	METHOD[a]	SOLVENT	PRODUCT	YIELD (%)[b]
1	 11	A	MeCN	 12	(87)
2		B	MeCN		(95)
3	 13	A	MeCN	 14	(87)
4	 15	A	MeCN	 16	(81)
5	 17	A	PhCN	 18	(69)
6		C	MeCN		(81)

Table 1—*continued*

RUN	SILYL ENOLATES	METHOD[a]	SOLVENT	PRODUCT	YIELD (%)[b]
7	 19	A	PhCN	 20	52
8	 21	A	MeCN	 22	78
9	 23	A	MeCN	 24	66
10	 25	A	MeCN	 26	80
11	 27	A	MeCN	 28	(74)
12	 29	C	MeCN	 30	79
13	 31	C	PhCN	 32	75
14	 33	C	PhCN	 34	69
15	 35	C	MeCN	 36	70
16	 37	C	MeCN	 38	72
17	 39	C	MeCN	 40	90
18	 41	C	MeCN	 42	90
19	 43	C	MeCN	 44	85

a) Method A -- Silyl enolate (1 mmol), diallyl carbonate (2 mmol), $Pd(OAc)_2$ (0.05 mmol), and dppe (0.05 mmol) for 1-3 h.
Method B -- Silyl enolate (5 mmol), diallyl carbonate (7 mmol), $Pd(OAc)_2$ (0.05 mmol), dppe (0.05 mmol) for 30 h.
Method C -- Silyl enolate (1 mmol), allyl methyl carbonate (2 mmol), $Pd(OAc)_2$ (0.1 mmol) for 2-6 h.
For detail, see experimental section.

b) GLC yields in parentheses.

intramolecular reactions of allyl β-keto carboxylates **1**[4] and alkenyl allyl carbonates **2**,[5] the dehydrogenation is competitive with the allylation, and the selectivity of the reactions can be controlled by the selection of solvents and phosphine ligands. For selective dehydrogenation, nitriles, such as acetonitrile and benzonitrile, are effective solvents. As for the ligand, bis(diphenylphosphino)ethane (dppe), triphenylphosphine, is effective. The reaction proceeds at the refluxing temperature of acetonitrile. No reaction takes place at room temperature. As for the palladium catalyst, $Pd(OAc)_2$ was used most conveniently, which is reduced *in situ* to Pd(0) to form the Pd–dppe complex as an active catalyst. The relative amount of Pd catalyst for the substrate depends on the scale of the reaction. In the present studies, the reaction proceeded rapidly with 5 mol% of the palladium catalyst. For example, reaction of **11** (1 mmol) and diallyl carbonate (2 mmol) with $Pd(OAc)_2$ (0.05 mmol)–dppe (0.05 mmol) for 1 h gave 2-cyclohexenone (**12**) in 87% yield (run 1). It took 30 h to produce **12** in 95% yield with 1 mol% of $Pd(OAc)_2$ (run 2).

The reaction is regiospecific. From 2-methylcyclohexanone, the kinetically generated enolate **13** and thermodynamically stable enolate **15** were prepared and they were converted into 6-methyl-2-cyclohexenone (**14**) and 2-methyl-2-cyclohexenone (**16**), respectively (runs 3 and 4). This means that no isomerization of intermediate palladium enolates takes place.

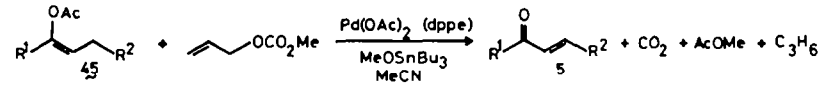
By using $Pd(OAc)_2$ and dppe in the molar ratio of 1:1, α,β-unsaturated ketones and aldehydes are obtained smoothly in most cases. However, the allylation and protonation reactions are observed in a considerable extent even when $Pd(OAc)_2$ and dppe are used in a ratio of 1:1 in acetonitrile in cases of the preparation of cyclopentenones, α,β-unsaturated esters and lactones.[6,9c] Because of these side reactions, the yields of α,β-unsaturated compounds are low with these compounds. In these cases, we found that phosphine-free Pd catalyst in nitriles is effective (see runs 6, 12–15).[6] In other solvents such as THF or benzene, Pd black is deposited immediately and almost no reaction is observed. As for the phosphine-free catalyst, $Pd(OAc)_2$ and $Pd_2(dba)_3 \cdot CHCl_3$ are effective and the $Pd(OAc)_2$–MeCN system is most convenient. In reactions catalyzed by the phosphine-free Pd, allyl carbonates of saturated primary alcohols such as allyl methyl carbonate should be used for clean transmetallation (path E). As we have reported previously, allyl carbonates of secondary alcohols and allylic alcohols are converted into the corresponding ketones or aldehydes with phosphine-free Pd catalyst.[14] Thus diallyl carbonate cannot be used. It should be pointed out that, although the phosphine-free Pd catalyst is effective for the dehydrogenation, the turnover of the catalyst is usually inferior to that of the Pd–phosphine catalyst. These results can be explained by the stabilizing effect of Pd(0) species by the phosphine ligand. Thus, preparation of cyclopentenones, cyclooctenones, dienones and α,β-unsaturated esters should be performed by using 10 mol% of the phosphine-free Pd catalyst. Other α,β-unsaturated carbonyl compounds listed in Tables 1 and 2 can be prepared with 1–5 mol% of $Pd(OAc)_2$–dppe catalyst.

The unique Pd-catalyzed dehydrogenation reaction can be applied satisfactorily to various types of ketones, aldehydes, esters and lactones as shown in Table 1. Particularly, the preparation of α,β-unsaturated esters and lactones has a high synthetic value. The conversion of ketones to α,β-unsaturated ketones via their silyl enol ethers using Pd(II) salts has been reported,[15] but the reaction requires the use of Cu(II) salt as a cocatalyst to reoxidize the Pd(0) to make the reaction catalytic. Thus the truly catalytic reaction without a reoxidant reported here offers the more convenient and useful method.

Preparation of α,β-unsaturated ketones from enol acetates

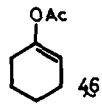
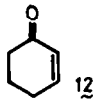
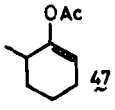
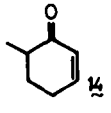
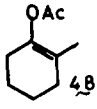
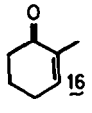
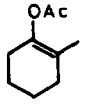
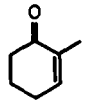
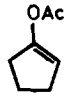
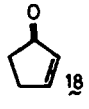
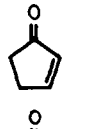
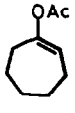
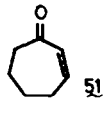
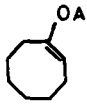
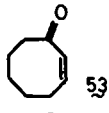
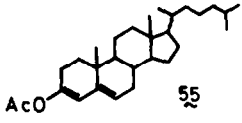
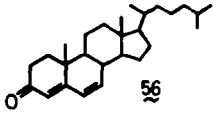
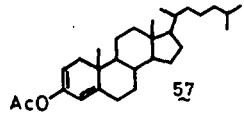
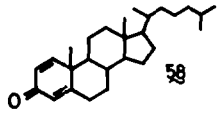
Encouraged by the successful reaction of silyl enolates, we then attempted to extend the reaction with other metal enolates, and tin enolates were selected as the next candidate. Tin enolates are reactive enolates and their allylation with allylic acetates by means of the Pd–phosphine catalyst is known.[16] But tin enolates are usually sensitive to moisture and somewhat difficult to handle. Tin enolates are prepared from enol acetates **45** and tin methoxide **59**.[12] Recently, *in situ* formation of tin enolates from enol acetates or silyl enol ethers followed by Pd-catalyzed arylation[17] and vinylation[18] has been reported. Thus we examined the reaction of allyl carbonates with tin enolates formed *in situ*. From mechanistic considerations, tin methoxide **59** would be regenerated after the transmetallation of tin enolate **8** with (π-allyl)Pd methoxide complex **60** (path B in Scheme 4). Thus we expected that the reaction should proceed with catalytic amounts of both the Pd complex and tin methoxide. We were pleased to find that reaction of 1-acetoxy-1-cyclohexene (**46**) with allyl methyl carbonate in the presence of $Pd(OAc)_2$–dppe–$MeOSnBu_3$ catalyst in boiling acetonitrile gave 2-cyclohexenone (**12**) in almost quantitative yield (run 1). Without the tin methoxide, no reaction was observed at all. Thus we discovered unique bimetallic catalysis. The reaction can be explained by Scheme 3.

The reaction can be applied most satisfactorily to the enol acetates derived from ketones. This is not a good method for the preparation of α,β-unsaturated aldehydes. As shown in Table 2, other enol acetates were also converted to the corresponding enones in good yields. Similar to the reaction of silyl enolates, phosphine-free Pd catalyst is effective for some cases. For example, cyclopentenones were obtained in high yields by the use of phosphine-free Pd catalyst.[6] For the preparation of 6-methyl-2-cyclohexenone (**14**), $Pd(OAc)_2$–dppe–$MeOSnBu_3$ is a good catalyst (run 2), but phosphine-free catalyst must be used for the preparation of 2-methyl-2-cyclohexenone (**16**) from 1-



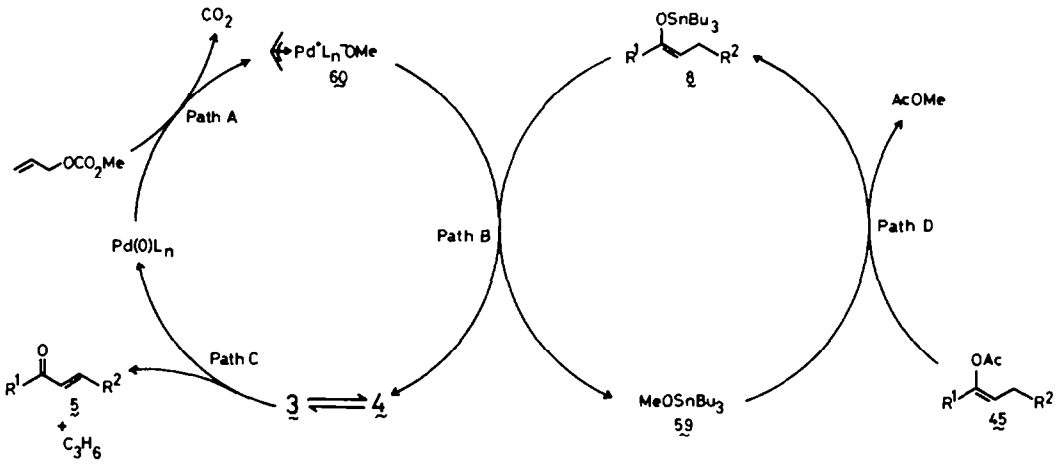
Scheme 3.

Table 2. Preparation of α,β-unsaturated ketones from enol acetates

RUN	ENOL ACETATES	METHOD[a]	PRODUCT	YIELD (%)[b]
1	 46	D	 12	(97)
2	 47	D	 14	(87)
3	 48	D	 16	(9)
4		E		(90)
5	 49	D	 18	(59)
6		E		(100)
7	 50	D	 51	70
8	 52	E	 53	80
9	 54	D	 22	85
10	 55	E	 56	78
11	 57	E	 58	69

a) Method D -- Enol acetate (1 mmol), allyl methyl carbonates (2 mmol), $Pd(OAc)_2$ (0.05 mmol), dppe (0.05 mmol), and $MeOSnBu_3$ (0.2 mmol), for 5-10 h.
Method E -- Enol acetate (1 mmol), allyl methyl carbonate (2 mmol), $Pd(OAc)_2$ (0.1 mmol), $MeOSnBu_3$ (0.2 mmol), for 5-10 h.
For detail, see experimental section.

b) GLC yields in parentheses.



Scheme 4.

acetoxy-2-methylcyclohexene (**48**) (runs 3 and 4). With Pd–phosphine catalyst, 2-allyl-2-methylcyclohexanone (**61**) was obtained in 90% yield from **48**. It should be noted that from the corresponding silyl enolate **15**, enone **16** rather than α-allyl ketone **61** was obtained. Cyclooctenone was obtained in 80% yield with the phosphine-free Pd catalyst (run 8). The phosphine-free Pd catalyst is also effective for the preparation of dienones. For example, 3-acetoxy-3,5-cholestadiene (**55**) and 3-acetoxy-2,4-cholestadiene (**57**) were prepared from 4-cholesten-3-one and they were converted to 4,6-cholestadien-3-one (**56**) and 1,4-cholestadien-3-one (**58**), respectively, without forming regioisomers (runs 10 and 11). However, the turnover of the phosphine-free Pd catalyst is lower than that of the Pd–dppe catalyst.

This unique bimetallic catalysis can be explained by Scheme 4. The *in situ* formation of tin enolate **8** by the reaction of enol acetate **45** with tributyltin methoxide (**59**) is known (path D in Scheme 4).[12] The transmetallation of tin enolate **8** (path B) with (π-allyl)Pd methoxide complex **60**, formed by the oxidative addition of allyl methyl carbonate to Pd(0) complex (path A),[7,8] gives (π-allyl)Pd enolate complexes **3** and **4**. Regeneration of tributyltin methoxide (**59**) renders the reaction catalytic. Finally the β-elimination of **4** (path C) gives the enones and regenerates the Pd(0) complex.

Enol acetates are prepared easily from ketones and they are stable compounds. But owing to their stability, their use in organic synthesis is rather limited. Now we have established that α,β-unsaturated ketones can be prepared easily from enol acetates. As a related reaction, it has been reported that some enol acetates can be converted to enones by electrochemical anodic oxidation.[19]

EXPERIMENTAL

General. ^{1}H-NMR spectra were recorded on a JEOL Model FX-90Q Fourier transform spectrometer in $CDCl_3$ soln at 90 MHz or a Hitachi Model R-24A in CCl_4 soln at 60 MHz using TMS as internal standard. ^{13}C-NMR spectra were recorded on a JEOL Model FX-90Q in $CDCl_3$ soln at 22.5 MHz using TMS as internal standard. IR spectra were obtained on a JASCO Model IRA-2 spectrometer. GLC for qualitative and quantitative analyses were performed on a Shimadzu Model GC-4C(PT) gas chromatograph. The column was 3 m × 3 mm, 15% silocone DC 550 on 60/80 Uniport B. Preparative GLC was performed on a Varian Model 920 gas chromatograph. The column was 3 m × 5 mm, 15% silicon DC 550 on 60/80 Uniport B. The carrier gas was He. Acetonitrile and benzonitrile were distilled over P_2O_5 and stored under Ar. Allyl methyl carbonate and diallyl carbonate were prepared by the procedure reported previously.[20] Silyl enol ethers **11**, **13**, **15**, **17**, **19**, **21**, **23**, **25**, **27**,[11a] ketene silyl acetals **29**, **31**, **33**, **35**,[11b] **37**, **39**, **41**, **43**[11c] and enol acetates **46**, **47**, **48**, **49**, **50**, **52**, **54**, **55**, **57**[21] were prepared by known methods.

General procedure for the preparation of α,β-unsaturated carbonyl compounds from silyl enolates (*Table* 1)

Method A. A soln of $Pd(OAc)_2$ (11 mg, 0.05 mmol) and dppe (20 mg, 0.05 mmol) in acetonitrile (1 ml) was heated under Ar. As soon as the soln began to reflux, a mixture of silyl enolate (1 mmol) and diallyl carbonate (280 mg, 2 mmol) in acetonitrile (4 ml) was added in one portion. The mixture was refluxed for 1–3 h. After the reaction was complete (TLC and/or GLC analysis), the resultant soln was filtered through florisil. Then pure α,β-unsaturated product was isolated by column chromatography on silica gel or by preparative GLC. In runs 5 and 7, benzonitrile (0.5 ml + 0.5 ml) was used instead of acetonitrile.

Method B. The reaction was carried out using silyl enolate (5 mmol), diallyl carbonate (1 g, 7 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol) and dppe (20 mg, 0.05 mmol) in acetonitrile (5 ml + 25 ml) for 30 h by the same procedure as method A.

Method C. A soln of $Pd(OAc)_2$ (22 mg, 0.1 mmol), silyl enolate (1 mmol) and allyl methyl carbonate (230 mg, 2 mmol) in acetonitrile (5 ml) was refluxed for 2–6 h under Ar. After the reaction was complete (TLC and/or GLC analysis), α,β-unsaturated compound was isolated by the same work-up as described above. In runs 14 and 15, benzonitrile (1 ml) was used instead of acetonitrile.

General procedure for the preparation of α,β-unsaturated carbonyl compounds from enol acetates (*Table* 2)

Method D. A soln of enol acetate (1 mmol), allyl methyl carbonate (230 mg, 2 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol) and dppe (20 mg, 0.05 mmol) in acetonitrile (5 ml) was stirred at room temp for 10 min. Then tributyltin methoxide (64.2 mg, 58 μl, 0.2 mmol) was added and the mixture was refluxed for 5–10 h. After the reaction was complete (TLC and/or GLC analysis), the enone was isolated by the usual work-up.

Method E. A soln of enol acetate (1 mmol), allyl methyl carbonate (230 mg, 2 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol) and tributyltin methoxide (64.2 mg, 58 μl, 0.2 mmol) in

acetonitrile (5 ml) was refluxed for 5–10 h. After the reaction was complete, the enone was isolated by the usual work-up.

Spectral data

α,β-Unsaturated carbonyl compounds **12**, **14**, **16**, **18**, **22**, **26**, **28**, **30**, **32**, **34** and **51** were identified by comparison of their spectral data with those of authentic samples.

3-*Hydroxy*-5,15-*androstadiene*-17-*one* (**20**). ^{1}H-NMR (CCl_4) δ 1.10 (s, 6H), 1.50–2.50 (m, 17H), 5.20–5.60 (m, 1H), 5.98 (dd, J = 6 and 2 Hz, 1H), 7.35 (d, J = 6 Hz, 1H). IR (KBr) 3400, 2900, 1680, 1560, 1050, 825 cm^{-1}. M.p. 200–202° (lit.[22] 202–205°).

1-*Phenyl*-2-*butene*-3-*one* (**24**) (*E*, *Z mixture*). ^{1}H-NMR ($CDCl_3$) δ 1.98 (d, J = 5.3 Hz, 3H), 6.78–7.86 (m, 5H), 7.89–7.92 (m, 2H). IR (neat) 1670, 1650, 1625, 1600, 1580, 1450, 1300, 1220, 1025, 960, 920, 830, 760, 690 cm^{-1}.

2-*Pentenolide* (**36**). ^{1}H-NMR ($CDCl_3$) δ 2.37–2.57 (m, 2H), 4.43 (t, J = 6 Hz, 2H), 6.02 (dt, J = 10 and 4 Hz, 1H), 6.96 (dt, J = 10 and 4 Hz, 1H). IR (neat) 2900, 1720, 1625, 1400 cm^{-1}.

2-*Trimethylsilyl*-2-*pentenolide* (**38**). ^{1}H-NMR ($CDCl_3$) δ 0.19 (s, 9H), 2.42 (dt, J = 4.3 and 6.2 Hz, 2H), 4.35 (t, J = 6.2 Hz, 2H), 7.13 (t, J = 4.3 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ −1.7, 25.3, 66.2, 135.4, 153.1, 165.5. IR (neat) 2950, 1700, 1600, 1250, 840 cm^{-1}. (Found: C, 56.99; H, 8.33. Calc for $C_8H_{14}O_2Si$: C, 56.43; H, 8.29%.)

2-*Trimethylsilyl*-2-*butenolide* (**40**). ^{1}H-NMR ($CDCl_3$) δ 0.25 (s, 9H), 4.82 (d, J = 1.54 Hz, 2H), 7.62 (t, J = 1.54 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ −2.2, 72.6, 134.9, 160.3, 176.4. IR (neat) 2940, 1740, 1590, 1250, 1155, 1050, 840 cm^{-1}. (Found: C, 53.83; H, 7.97. Calc for $C_7H_{12}O_2Si$: C, 53.81; H, 7.74%.)

4-*Methyl*-2-*trimethylsilyl*-2-*butenolide* (**42**). ^{1}H-NMR ($CDCl_3$) δ 0.25 (s, 9H), 1.41 (d, J = 6.8 Hz, 3H), 5.05 (dq, J = 1.4 and 6.8 Hz, 1H), 7.55 (d, J = 1.4 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ −2.0, 18.8, 79.8, 134.1, 165.3, 175.7. IR (neat) 2960, 1740, 1600, 1250, 1165, 845 cm^{-1}. (Found: C, 56.63; H, 8.23. Calc for $C_8H_{14}O_2Si$: C, 56.43; H, 8.29%.)

3-*Methyl*-2-*trimethylsilyl*-2-*butenolide* (**44**). ^{1}H-NMR ($CDCl_3$) δ 0.29 (s, 9H), 2.14 (d, J = 0.7 Hz, 3H), 4.61 (d, J = 0.7 Hz, 2H). ^{13}C-NMR ($CDCl_3$) δ −1.1, 14.8, 74.6, 125.9, 130.5, 172.8. IR (neat) 2900, 1720, 1610, 1250, 1130, 840 cm^{-1}. (Found: C, 57.18; H, 8.00. Calc for $C_8H_{14}O_2Si$: C, 56.43; H, 8.29%.)

2-*Cyclooctenone* (**53**). ^{1}H-NMR (CCl_4) δ 1.20–2.10 (m, 6H), 2.10–2.80 (m, 4H), 5.96 (d, J = 14.4 Hz, 1H), 6.36 (dt, J = 14.4 and 6 Hz, 1H). IR (neat) 2950, 1660, 850 cm^{-1}.

4,6-*Cholestadien*-3-*one* (**56**). ^{1}H-NMR ($CDCl_3$) δ 0.78 (s, 6H), 0.86 (d, J = 6.2 Hz, 6H), 0.92 (d, J = 4.6 Hz, 3H), 1.00–2.40 (m, 24H), 6.03 (dd, J = 9.7 and 1.9 Hz, 1H), 6.23 (dd, J = 10.1 and 1.9 Hz, 1H), 7.06 (d, J = 10.1 Hz, 1H). IR (KBr) 2950, 1660, 1610, 1585, 900, 740 cm^{-1}. M.p. 80–82°, UV λ_{max}^{EtOH} 284 nm (lit.[23] m.p. 80–81.5°, λ 284 nm).

1,4-*Cholestadien*-3-*one* (**58**). ^{1}H-NMR ($CDCl_3$) δ 0.73 (s, 6H), 0.86 (d, J = 6.2 Hz, 9H), 1.00–2.50 (m, 24H), 6.07 (br s, 1H), 6.22 (dd, J = 1.8 and 10.1 Hz, 1H), 7.05 (d, J = 10.1 Hz, 1H). IR (KBr) 2950, 1670, 1625, 1605, 915, 895, 740 cm^{-1}. M.p. 110–112°, UV λ_{max}^{EtOH} 246 nm (lit.[23] m.p. 110–112°, λ 246 nm).

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