Pergamon

Tetrahedron, Vol. 52, No. 20, pp. 6983-6996, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00303-1

The Palladium-Catalysed Vinylic Substitution of Vinyl Triflates with β-Substituted-α,β-unsaturated Carbonyl Compounds. An Application to the Synthesis of Cardenolides.

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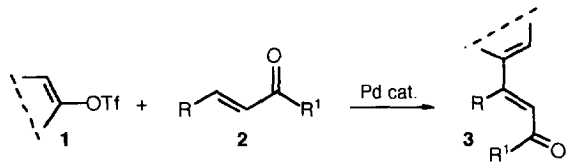
Abstract: Vinyl triflates react with β-substituted-α,β-unsaturated aldehydes, ketones, and esters in the presence of catalytic amounts of $Pd(OAc)_2$ and an excess of KOAc, omitting phosphine ligands, to give vinylic substitution products in good to high yield with high regioselectivity. The added vinyl unit is preferentially linked to the β-carbon atom. As to the stereochemistry, vinylic substitution products contain the carbonyl group on the same side of the preexisting β-substituent. The use of KOAc has been proved to be superior both to tertiary amines and to carbonate or bicarbonate bases with or without the addition of salts such as LiCl and *n*-Bu_4NCl. The application of the reaction to the synthesis of a cardenolide derivative is reported. Depending on the nature of β-substituted-α,β-unsaturated carbonyl compounds, the reaction can produce hydrovinylation (formal conjugated addition) products. Copyright © 1996 Elsevier Science Ltd

Introduction

The vinylic substitution reaction (the Heck reaction) is undoubtedly one of the most important applications of palladium chemistry. An impressive number of papers concerning synthetic applications, studies of factors affecting regio- and stereoselectivity, and improvements of traditional Heck conditions appeared in the past decades[1] and the scope of the reaction has grown continuously.

Our discovery that vinyl triflates can behave as vinyl donors in palladium-catalysed vinylic substitution reactions[2] has marked a further, significant step forward in widening the scope and the utility of the methodology. Since then, a variety of olefinic systems have been reacted with vinyl and aryl triflates in the presence of palladium catalysts.[3] Much attention has been dedicated to alkenes containing carbon-carbon double bonds conjugated to electron-withdrawing substituents. In the great majority of these studies, however, the substitution pattern of α,β-unsaturated carbonyl compounds has been quite simple. Very little has been done with β-substituted-α,β-unsaturated carbonyl compounds. Only recently intramolecular vinylic substitutions with β-substituted-α,β-unsaturated esters have been reported[4] and, as far as intermolecular reactions with β-substituted-α,β-unsaturated carbonyl compounds are concerned, only (*E*)-3-(methoxycarbonyl)-2-propenyl tetrahydropyranyl ether has been subjected to vinylic substitution conditions with steroidal vinyl triflates.[5]

Therefore, as part of an on-going program on Heck reactions involving vinyl triflates, it seemed to us of interest to explore their possible utilisation in a general synthesis of vinylic substitution derivatives **3** from β-substituted-α,β-unsaturated carbonyl compounds **2** (Scheme 1). On the other hand, β-substituted-α,β-unsaturated carbonyl compounds are widely diffused among naturally occurring and unnatural substrates and the extension of the reaction to include them appears to be especially important. Furthermore, in the presence of β-substituents, the regio- and stereochemistry of the possible elimination/readdition/elimination of HPd species from addition σ-alkylpalladium intermediates takes on significance.



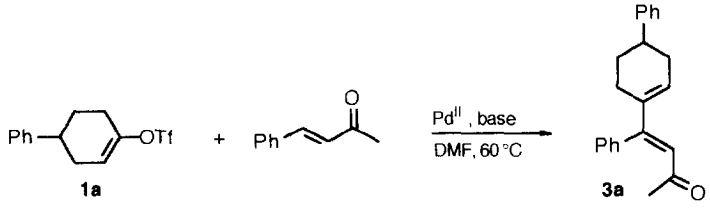
R = alkyl, aryl; R^1 = H, alkyl, OMe

Scheme 1

The results of this study are reported hereafter.

Results and Discussion

On the basis of our prior experience with the palladium-catalysed reaction of vinyl triflates with β-unsubstituted-α,β-enones and -enals in the presence of both tertiary amines and K_2CO_3/*n*-BuN_4Cl, we initially tested these conditions when the study of the reaction of 4-phenylcyclohex-1-enyl triflate with benzalacetone as the model system became.



Scheme 2

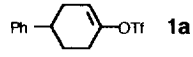
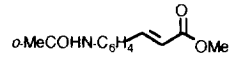
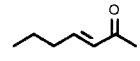
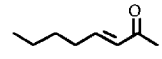
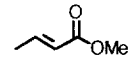
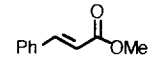
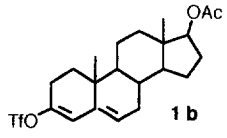
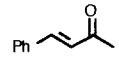
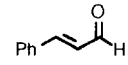
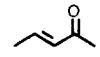
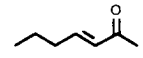
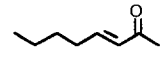
Table 1. Base, Salt, and Catalyst in the Reaction of 4-Phenyl-cyclohex-1-enyl Triflate **1a** with Benzalacetone.[a]

entry	base	salt	catalyst	vinylic substitution product **3a** yield %[b,c]
1	Et_3N[d]	–	$Pd(OAc)_2$	47 (40)
2	"	–	$Pd(OAc)_2(PPh_3)_2$	32 (68)
3	"	LiCl[e]	$Pd(OAc)_2$	4 (73)
4	"	"	$Pd(OAc)_2(PPh_3)_2$	4 (68)
5	K_2CO_3	–	$Pd(OAc)_2$	11 (55)
6	"	*n*-Bu4NCl[f]	"	45 (25)
7	$NaHCO_3$	–	"	26 (68)
8	"	*n*-Bu4NCl[f]	"	54 (40)
9	NaOAc	–	"	56 (8)
10	KOAc	–	"	82 (11)
11	*n*-Bu4NOAc[g]	–	"	64 (11)
12	KOAc	*n*-Bu4NCl[f]	"	80

[a] Unless otherwise stated, all the reactions were carried out on a 0.66 mmol scale in DMF at 60 °C (8 h) under an argon atmosphere by using the following molar ratios: **1a**: benzalacetone: base: salt (when used): Pd^{II} = 1: 1: 2.5: 1: 0.05. [b] Yields refer to single runs and are for pure, isolated products. [c] Figures in parentheses refer to the recovered benzalacetone. [d] **1a**: Et_3N: = 1: 2. [e] **1a**: LiCl = 1: 3. [f] **1a**: *n*-Bu_4NCl = 1: 1. [g] **1a**: *n*-Bu_4NOAc = 1: 2.5 .

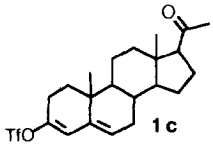
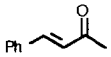
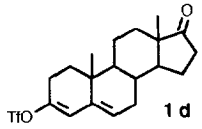
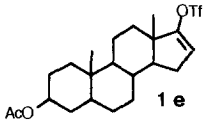
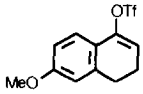
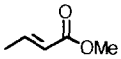
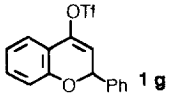
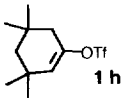
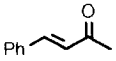
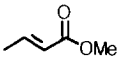
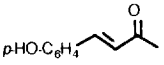
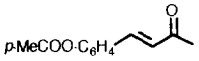
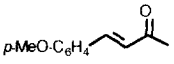
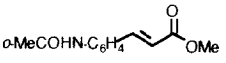
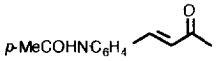
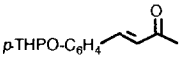
However, with Et_3N as the base **3a** was isolated in only moderate yield (Table 1, entries 1 and 2) and the addition of LiCl, reported to act as a ligand exchanger in the initially formed vinyl palladium triflate and often to produce better yields,[6] resulted in a complete failure (Table 1, entries 3 and 4). A slight increase of the yield, still unsatisfactory from a synthetic point of view, was observed in the presence of $NaHCO_3$ or K_2CO_3 and *n*-Bu_4NCl[7] (Table 1, entries 6 and 8). Switching to NaOAc or *n*-Bu_4NOAc led to a further increase of the yield (Table 1, entries 9 and 11), but the best conditions with regard to both the yield and simplicity of the procedure appeared to be those using KOAc and $Pd(OAc)_2$ without ammonium salt and triphenylphosphine Under these conditions compound **3a** was isolated in 82% yield (Table 1, entry 10). The addition of *n*-Bu_4NCl to KOAc did not produce any substantial change (Table 1, entry 12). Then, a variety of vinyl triflates and β-substituted-α,β-unsaturated carbonyl compounds have been reacted in the presence of $Pd(OAc)_2$ and KOAc (Table 2).

Table 2. Palladium-Catalysed Reaction of Vinyl Triflates with β-Substituted-α,β-unsaturated Carbonyl Compounds in the Presence of $Pd(OAc)_2$ and KOAc.[a]

entry	vinyl triflate **1**	β-substituted-α,β-unsaturated carbonyl compound **2**	reaction time (h)	vinylic substitution product **3**	yield %[b]
1	 **1a**		1	**3b**	47
2	"		24	**3c**	48[c]
3	"		24	**3d**	49 (5)[d]
4	"		"	"	30 (4)[d,e]
5	"		24	**3e**	56 (6)[f]
6	"		8	**3f**	70
7	"		24	**3g**	61
8	 **1b**		24	**3h**	88
9	"		29	**3i**	67
10	"		6	**3j**	81[g]
11	"		7	**3k**	75[h]
12	"		24(8)[h]	**3l**	53(76)[h]

(continued)

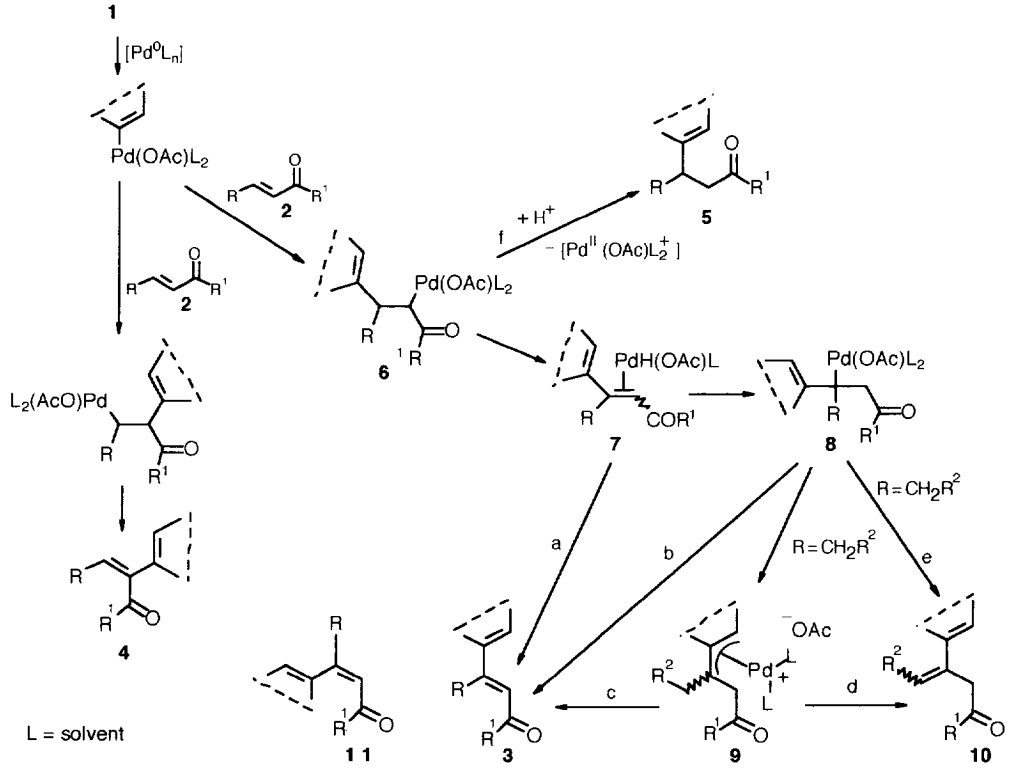
Table 2. (continued)

entry	vinyl triflate **1**	β-substituted-α,β-unsaturated carbonyl compound **2**	reaction time (h)	vinylic substitution product **3**	yield %[b]
13	 **1c**		24	**3m**	77
14	 **1d**	"	24	**3n**	79
15	 **1e**	"	24(24)[c]	**3o**	71(42)[c,l]
16	 **1f**		24	**3p**	49
17	 **1g**	"	"	**3q**	34
18	 **1h**		9	**3r**	84
19	"		8	**3s**	80
20	"		6	**3t/11t**	64[m]
21	"		7	**3u**	77
22	"		7	**3v**	78
23	"		8	**3w**	56[n,c]
24	"		6	**3x**	57
25	"		6	**3y**	76

[a] Unless otherwise stated, reactions were carried out in DMF at 60 °C under an argon atmosphere, by using the following molar ratios: **1**: **2**: KOAc: $Pd(OAc)_2$ = 1: 1: 2.5: 0.05. [b] Yields refer to single runs and are for pure, isolated products. [c] At 80 °C. [d] Yield of **10d** (Scheme 3). [e] In the presence of $NaHCO_3$ and n-Bu_4NCl. [f] Yield of **10e** (Scheme 3). [g] **1**: **2**: KOAc: $Pd(OAc)_2$ = 1: 3: 2.5: 0.05. [h] **1**: **2**: KOAc: $Pd(OAc)_2$ = 1: 2: 2.5: 0.05. [i] **1e** and benzalacetone were recovered in 66 and 95% yield, respectively. [l] **1e** and benzalacetone were recovered in 9 and 48% yield, respectively. [m] As an about 55/45 stereoisomeric mixture. [n] The regioisomeric vinylic substitution product **4w** (Scheme 3) was isolated in 9% yield.

A possible explanation for the effect of acetate anions is that they can stabilise palladium(0) through the formation of acetate anion-associated anionic palladium(0) species in a manner similar to that suggested by Amatore and Jutand in the presence of phosphine ligands[8] and provide a more efficient route for the generation of vinylic substitution products that most probably involves the intermediacy of σ-vinylpalladium acetates. Acetate anions might also participate in the elimination step, favouring the displacement of palladium from addition σ-alkylpalladium intermediates through basic intramolecular attack of the acetate moiety ligated to palladium on the β-hydrogen.[9] Whatever the real effect of acetate anions may be, it remains that they play a pivotal role in determining the success of the reaction and that they are more efficient than chloride anions.

The reaction is highly regioselective and preferential β-attack of vinyl units (as determined by NOE and NOESY experiments)[10] is invariably observed. This result supports further the notion that electronic effects, favouring the formation of σ-alkylpalladium intermediates **6** (Scheme 3), play a dominant role in controlling the direction of the carbopalladation step in the vinylic substitution of olefinic systems bearing electron-withdrawing substituents. Regioisomeric vinylic substitution products **4**, derived from the reverse addition of σ-vinylpalladium complexes to the carbon-carbon double bond, have been isolated in only a few cases and in low yield (see, for example, Table 2, entry 23).



Scheme 3

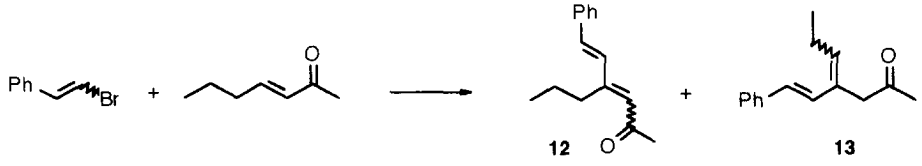
As far as the stereochemistry is concerned, tested vinyl triflates and β-substituted-α,β-unsaturated carbonyl compounds produced vinylic substitution products containing the added vinylic unit *trans* to the carbonyl group. Usually there is no evidence of any stereoisomer. The lone exception to this observation was the reaction of 3,3,5,5-tetramethylcyclohex-1-enyl triflate with 4-(*p*-hydroxyphenyl)butenone (Table 2, entry 20) that afforded the vinylic substitution product as an *E*/*Z* mixture. Most probably, the stereoisomeric mixture is

generated through the base-catalysed isomerization, favoured by the free phenolic group, of the initially stereodefined vinylic substitution product. The preparation of the stereoisomer **3t** from **3y** and its treatment under usual reaction conditions to verify its possible conversion into a stereoisomeric mixture could prove this hypothesis. Unfortunately, the hydrolysis of **3y** under mild conditions (TsOH 10 mol%, MeOH, room temperature, 0.5 h) generated a mixture of **3t** and **11t** (80% yield) only leaving room for the supposition that the great ease with which the isomerization takes place under acidic conditions might reflect the tendency of **3t** to isomerise even under basic conditions.

The configuration of compounds **3** was determined by NOE and NOESY experiments.[10]

The stereochemical outcome of the reaction could be accounted for by assuming that the formation of **3** may result from a marked tendency of η^2-palladium complexes **7** to undergo an irreversible elimination of HPd species (Scheme 3, a). This tendency could be dependent on the substitution pattern of the olefinic moiety, controlling the electron density transferred from olefinic π-electrons to palladium or/and on the presence of acetate anions.[9] However, the parallel or alternative formation of **3** through the elimination of HPd from readdition σ-allylpalladium complexes **8** (Scheme 3, b) or, more likely, π-allylpalladium complexes **9**,[11] derived from σ-to-π isomerization (Scheme 3, c), cannot be excluded. On the contrary, the formation of the regioisomeric olefinic derivatives **10d** and **10e** on reacting **1a** with 3-hepten-2-one and 3-octen-2-one (Table 2, entries 3-5) provides evidence that, at least in some cases, the elimination/readdition/elimination sequence may be operating and that, presumably, π-allylpalladium intermediates may be present in the reaction medium.

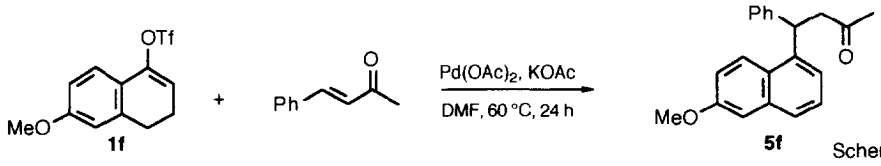
Interestingly, **3d** and **3e**, the main products of the reaction of **1a** with 3-hepten-2-one and 3-octen-2-one, were isolated as the only stereoisomers. This result allows us to make the following considerations. If compounds **3d** and **3e** do not arise from their corresponding π-allylpalladium complexes, the latter have to lie on a different reaction pathway. Alternatively, if **3d** and **3e** are generated from their corresponding π-allylpalladium complexes (whether this represents the only reaction pathway or a reaction pathway parallel to that leading from **6** to **3**), it must be assumed that the elimination of HPd from π-allylpalladium complexes favours the formation of the same vinylic substitution derivatives generated through the elimination of HPd from σ-alkylpalladium intermediates **6**. This tendency could reflect, at least in part, the steric effects related to the substitution pattern of the vinyl unit transferred to the β-carbon atom. Substituents on the vinyl group could in fact influence the relative stability of the π-conformers possibly involved in the elimination of HPd. If this hypothesis is correct, the addition of a less steric demanding vinyl unit (in these two reactions, as in all of the reactions reported in Table 2, a disubstituted vinyl unit has been added to the β-carbon) could alter the relative stability of π-conformers and lead to the formation of both stereoisomers. In the effect, treatment of 3-hepten-2-one with 2-phenyleth-1-enyl bromide, precursor of a monosubstituted vinyl unit, afforded an about 55/45 mixture of stereoisomeric vinylic substitution products **12** (25% yield) along with 27% of the regioisomeric olefinic derivatives **13** (Scheme 4).



Scheme 4

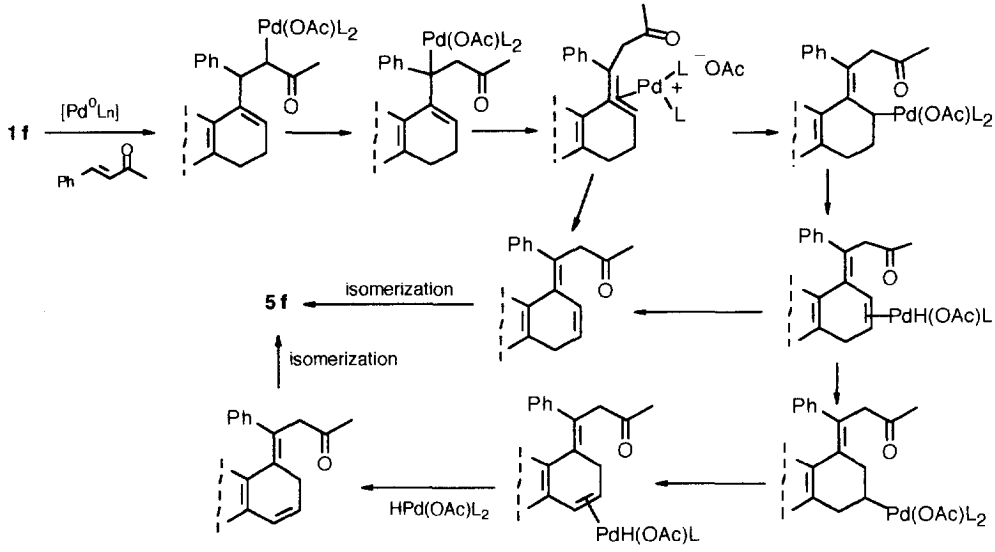
The utilization of 2-phenyleth-1-enyl triflate instead of the corresponding bromide would have been more consistent, but its preparation by using standard methods[12] met with failure. At any rate, it can be reasonably presumed that the nature of the anion coming from the vinyl donor does not affect the stereochemical course of the reaction to a large extent.

The possible presence of π-allylpalladium complexes in the reaction mixture, at least in some cases, appears to be further supported by the isolation of **5f** (22% yield) in the reaction of **1f** with benzalacetone (Scheme 5).



Scheme 5

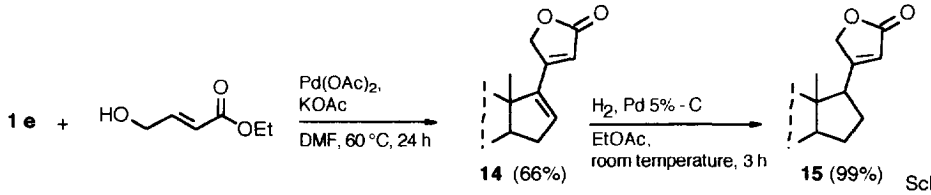
A π-allylpalladium complex might be involved in this reaction which most probably proceeds through to the migration of palladium along the carbon chain according to the sequence outlined in Scheme 6. The migration of palladium along carbon chains is a well-known process that Larock has thoroughly investigated.[13] In the present reaction, aromatisation is the likely driving force of the final, isomerization steps.



Scheme 6

Clearly, even though there is some evidence that the reaction of vinyl triflates with β-substituted-α,β-unsaturated carbonyl compounds may generate π-allylpalladium intermediates, further work is needed to establish whether π-allylpalladium intermediates are the precursors of vinylic substitution products and, in case, whether this represents their general behaviour or a behaviour depending on the nature of reagents.

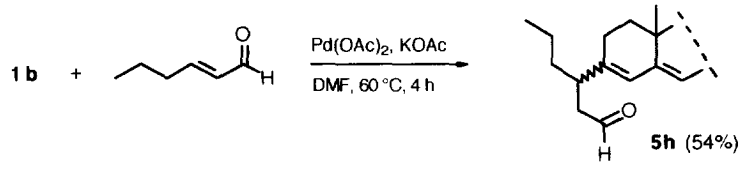
The present procedure has been successfully applied to the synthesis of the cardenolide **15**[14] starting from **1e** and ethyl 4-hydroxy-2-pentenoate (Scheme 7). The key step of the process is the regio- and stereoselective vinylic substitution reaction followed by the *in situ* cyclization to **14**. It is worth emphasising that no reaction was reported to occur when **1e** was reacted with ethyl 4-hydroxy-2-pentenoate in the presence of $Pd(OAc)_2$, PPh_3, and triethylamine.[5] Furthermore, according to the data reported in Table 1, when we carried out the reaction employing the $NaHCO_3$/*n*-Bu_4NCl or K_2CO_3/*n*-Bu_4NCl combinations, the butenolide **14** was isolated only in trace amounts.



14 (66%) **15** (99%)

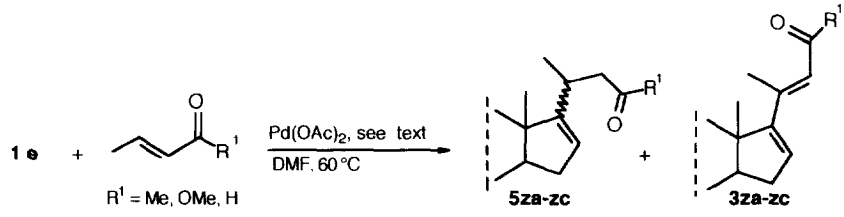
Scheme 7

Finally, we have to mention that, in agreement with our expectations, only trace amounts, if any, of hydrovinylation (formal conjugated addition)[15] products **5** (Scheme 3f) have been usually detected. Indeed, the hydrovinylation pathway is encouraged by the availability of protons promoting the substitution of the C_α-H bond for the C_α-Pd bond before σ-alkylpalladium intermediates **6** undergo the rotation/elimination sequence.[16] In addition, to maintain the catalytic cycle, the substitution of the C_α-H bond for the C_α-Pd bond has to combine with the reduction of Pd^{II} to Pd^0. The conditions employed in the present reaction do not favour the formation of hydrovinylation derivatives. Protons originate sparingly from the competing vinylic substitution and from the reduction of palladium acetate to Pd^0 by the olefin in the early stages of the reaction. Furthermore, there are no reducing agents such as HCOOH[17] or even tertiary amines.[19] In spite of these considerations, however, some β-substituted-α,β-unsaturated carbonyl compounds showed an "intrinsic" tendency to enter the hydrovinylation catalytic cycle. We did not investigate this point thoroughly. At any rate, according to our previous studies,[17] α,β-enals have been found to be more prone to give hydrovinylation derivatives than α,β-enones [compare the results obtained in the reaction of **1b** with 2-hexenal (Scheme 8) and 3-pent-2-enone (Table 2, entry 11)]. Even the nature of β-substituents may affect the vinylic substitution/hydrovinylation balance [compare the results obtained in the reaction of **1b** with 2-hexenal (Scheme 8) and with cinnamaldehyde (Table 2, entry 9)]. In cases where the formation of the hydrovinylation products appears to be favoured, the utilization of an excess of α,β-unsaturated carbonyl compounds as the reducing agents gave some interesting results. For example, exposure of **1b** to a 3 equiv excess of 2-hexenal afforded **5h** in 54% yield as an about 60/40 diastereoisomeric mixture.



Scheme 8

When we investigated the reaction of the steroidal vinyl triflate **1e** with butenal, 3-pentenone, and methyl 2-butenoate (Scheme 9) as a model for evaluating the potential of the present methodology for the construction of the C-17 side chain from androstane precursors, vinylic substitution and/or hydrovinylation products have been obtained depending on the nature of the carbonyl group and on the reaction medium. The results obtained are summarised in Table 3.



Scheme 9

As expected, the highest relative percentage of the hydrovinylation derivative **5** was obtained with butenal (Table 3, entry 1). Of particular interest is the possibility of influencing the reaction outcome by controlling the concentration of proton donors able to trap σ-alkylpalladium intermediates **6**. Lowering the amount of AcOH through the addition of $NaHCO_3$ to the usual reaction mixture caused an increase of the **3/5** ratio (Table 3, compare entry 2 with entry 4) and substituting $NaHCO_3$ for KOAc reversed the trend of the reaction; **3zb** was isolated as the major one, albeit a lower reactivity was observed (Table 3, entry 5). In the

presence of the *n*-Bu_3N/CF_3COOH combination, the highest relative percentage of **5zb** was observed (Table 3, entry 6).

Table 3. The reaction of 3β-Acetoxyandrost-16-en-17-yl Triflate **1e** with Butenal, 3-Pentenone, and Methyl 2-Butenoate.[a]

entry	reaction conditions	R^1	reaction time (h)	relative percentages[b] **5**		**3**		total yield %[c]
1	KOAc (2.5 equiv)	H	7	100	**5za**	-	**3za**	28 (11)[d]
2	"	Me	"	77	**5zb**	23	**3zb**	76
3	"	OMe	9	-	**5zc**	100	**3zc**	49
4	KOAc (2.5 equiv)/$NaHCO_3$ (1 equiv)	Me	8	53	**5zb**	47	**3zb**	72
5	$NaHCO_3$ (2.5 equiv)/ *n*-BuN_4Cl (1 equiv)	"	7	28	**5zb**	72	**3zb**	26 (45)[d]
6	*n*-Bu_3N (4.5 equiv)/ CF_3COOH (2.6 equiv)	"	24	75	**5zb**	25	**3zb**	30 (26)[d]

[a] Reactions were carried out in DMF at 60 °C, under an argon atmosphere, in the presence of $Pd(OAc)_2$ (5 mol%) and an excess of the α,β-unsaturated carbonyl compound (**1e**: α,β-unsaturated carbonyl compound = 1: 3). [b] By NMR analysis. [c] Total yields are given on pure, isolated products. [d] Recovered starting material.

What comes out from these data is that the vinylic substitution/hydrovinylation balance depends on an intriguing combination of steric, electronic, and medium effects.

In conclusion, the results reported here show that in the presence of potassium acetate the reaction of vinyl triflates with β-substituted-α,β-unsaturated carbonyl compounds is a synthetically useful reaction that affords stereodefined vinylic substitution derivatives. With α,β-unsaturated carbonyl compounds bearing nucleophilic centres on the β-substituent the reaction holds promise as a powerful tool for the development of new routes to the synthesis of hetero- and carbocycles. Finally, even though the results reported here in the hydrovinylation (formal conjugated addition) of β-substituted-α,β-unsaturated carbonyl compounds are only preliminary, they allow to foresee new applications of vinyl triflates as C_{sp^2} donors in palladium-catalysed carbon-carbon bond forming reactions.

Experimental

Melting points were determined with a Büchi apparatus and are uncorrected. All the catalysts, ligands, amines, salts, and solvents are commercially available and were used without further purification. Vinyl triflates **1a**,[20] **1b**,[21] **1c-d**,[20] **1e**,[5] **1f**,[22] and **1h**[22] were prepared according to reference 12. 4-(*o*-acetamidophenyl)-, 4-(*p*-acetamidophenyl)-, 4-(*p*-methoxyphenyl)-, 4-(*p*-acetoxyphenyl)-, 4-[*p*-(2,3,5,6-tetrahydropyran-2-yloxy)-phenyl]-but-3-en-2-one and methyl 3-(*p*-acetamidophenyl)- and 3-(*o*-acetamidophenyl)-propenoate, were prepared from the corresponding aryl iodides (in turn prepared from commercially available *p*-amino-, *o*-amino- and *p*-hydroxyphenyl iodide according to standard methods) and α,β-unsaturated carbonyl compounds through palladium-catalysed vinylic substitution reactions in the presence of KOAc and K_2CO_3 according to ref. 23. The palladium-catalysed reactions of vinyl triflates with β-substituted-α,β-unsaturated carbonyl compounds were carried out on a 0.50 - 0.65 mmol scale. Reaction products were purified on axially compressed columns, packed with SiO_2 25-40 μm (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with *n*-hexane/ethyl acetate mixtures. ^1H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra ($CDCl_3$, unless otherwise stated; TMS as internal standard) were recorded with a Bruker AM 200 spectrometer. IR spectra were recorded with a Nicolet 5DX FT/IR spectrometer. MS spectra were recorded with a Hewelett Packard HP 5980A spectrometer equipped with a Data System 5934A. All the isolated new products gave satisfactory microanalyses.

General Procedure of Reaction of α,β-Unsaturated Carbonyl Compounds (2) with Vinyl Triflates (1). This is exemplified by the reaction of 4-phenyl-cyclohex-1-enyl triflate **1a** with benzalacetone. To a solution of triflate **1a** (0.200 g, 0.65 mmol) and benzalacetone (0.096 g, 0.65 mmol) in DMF (2 mL) were added KOAc (0.160 g, 1.63 mmol) and palladium diacetate (0.007 g, 0.033 mmol) under an argon atmosphere. The mixture was warmed at 60 °C and stirred for 9 h. Then EtOAc and water were added, the organic layer was separated, washed with water, dried (Na_2SO_4) and concentrated under vacuum. The residue was chromatographed on silica gel eluting with *n*-hexane/EtOAc (95/5 v/v) to afford 0.161 g (82%) of **3a**. The following compounds were prepared and isolated according to this procedure.

4-(4-Phenylcyclohex-1-enyl)-4-phenyl-3-buten-2-one (3a): mp 78-80 °C; IR (KBr) 1688, 753, 703 cm^{-1}; ^1H NMR δ 7.57–7.09 (m, 10 H), 6.27 (s, 1 H), 5.77 (m, 1 H), 3.03-2.63 (m, 1 H), 1.68 (s, 3 H); ^{13}C NMR δ 199.1, 146.4, 145.9, 139.1, 135.0, 128.5, 126.8, 126.3, 124.7, 39.6, 34.6, 29.2, 27.3, 24.7; MS *m/e* (relative intensity) 302 (M^+, 19), 273 (49), 197 (100). Anal. Calcd. for $C_{22}H_{22}O$: C, 87.38; H,.7.33. Found: C, 87.25; H, 7.25.

4-(4-Phenylcyclohex-1-enyl)-3-penten-2-one (3b): mp oil; IR (liquid film) 1688, 753, 703 cm^{-1}; ^1H NMR δ 7.63-7.20 (m, 5 H), 6.42 (m, 1 H), 6.28 (bs, 1 H), 3.00-2.60 (m, 1 H),2.30 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR δ 199.6, 152.7, 146.3, 137.7, 131.2, 128.5, 126.2, 121.1. Anal. Calcd. for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.07; H, 8.34.

Methyl 3-(4-Phenylcyclohex-1-enyl)-3-(*o*-acetamidophenyl)-2-propenoate (3c): mp 127-8 °C; IR (KBr) 1729, 1668,876, 827, 761, 703 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.67 (bs, 1 H), 7.65 (d, J = 7.9 Hz, 1H), 7.36-7.12 (m, 7 H), 6.99 (d, J = 7.5 Hz, 1 H), 6.08 (s, 1 H), 5.59 (bs, 1 H), 3.49 (s, 3 H), 2.01 (s, 3 H); ^{13}C NMR δ 167.2, 147.6, 137.6, 129.9, 128.9, 128.3, 127.7, 117.1, 56.8, 52.3; MS *m/e* (relative intensity) 375 (M^+, 2), 301 (100). Anal. Calcd. for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.73. Found: C, 76.68; H, 6.65; N, 3.51.

4-(4-Phenylcyclohex-1-enyl)-4-phenyl-3-hepten-2-one (3d): mp 56-8 °C; IR (KBr) 1671, 761, 703 cm^{-1}; ^1H NMR δ 7.27-7.15 (m, 5 H), 6.28 (m, 1 H), 6.13 (bs, 1 H), 2.17 (s, 3 H), 0.96 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 199.1, 158.4, 146.3, 136.7, 130.5, 128.5, 126.8, 126.2, 120.7; MS *m/e* (relative intensity) 268 (M^+, 38), 225 (100). Anal. Calcd. for $C_{19}H_{24}O$: C, 85.03; H, 9.01. Found: C, 85.11; H, 9.09.

4-(4-Phenylcyclohex-1-enyl)-4-phenyl-3-octen-2-one (3e): mp 42-44 °C; IR (KBr) 1671, 761, 703 cm^{-1}; ^1H NMR δ 7.63–7.12 (m, 5 H), 6.37 (m, 1 H), 6.22 (bs, 1 H), 2.21 (s, 3 H), 0.93 (t, 3H); ^{13}C NMR δ 198.9, 158.7, 146.3, 136.7, 130.4, 128.5, 126.8, 126.2, 120.5. Anal. Calcd. for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 84.97; H, 9.35.

Methyl 4-(4-Phenylcyclohex-1-enyl)-2-butenoate (3f): mp 101-2 °C; IR (KBr) 1700, 1600, 1145, 800, 733 cm^{-1}; ^1H NMR δ 7.35-7.16 (m, 5 H), 6.34 (m, 1 H), 5.86 (s, 1 H), 3.71 (s, 3 H), 2.90-2.60 (m, 1 H), 2.36 (s, 3 H); ^{13}C NMR δ 168.0, 154.8, 146.3, 137.4, 130.3, 128.5, 126.8, 126.2, 113.2, 51.0, 39.5, 34.4, 29.8, 26.4, 14.9; MS *m/e* (relative intensity) 256 (M^+, 100), 224 (27), 197 (30). Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.77; H, 7.91.

Methyl 3-(4-Phenylcyclohex-1-enyl)-3-phenyl-2-propenoate (3g): mp 120-1 °C; IR (KBr) 1725, 1600, 850, 800, 736 cm^{-1}; ^1H NMR δ 7.38-7.09 (m, 10 H), 6.00 (s, 1 H), 5.73 (bs, 1 H), 3.53 (s, 3 H), 2.87-2.71 (m, 1 H); ^{13}C NMR δ 166.9, 157.5, 146.1, 138.6, 137.6, 51.0, 39.4, 34.6, 29.7, 26.4; MS *m/e* (relative intensity) 318 (M^+, 39), 287 (10), 258 (31), 181 (68), 155 (100). Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 82.88; H, 6.88.

4-(17β-Acetoxyandrosta-3,5-dien-3-yl)-4-phenyl-3-buten-2-one (3h): mp 171-4 °C; IR (KBr) 1729, 1647, 777, 703 cm^{-1}; ^1H NMR δ 7.56-7.33 (m, 3 H), 7.33-7.07 (m, 2 H), 6.30 (s, 1 H), 5.82 (bs, 1 H), 5.57-5.37 (m, 1 H), 4.80-4.51 (m, 1 H), 2.02 (s, 3 H), 1.67 (s, 3 H), 0.94 (s, 3 H), 0.82 (s, 3 H); ^{13}C NMR δ 194.3, 171.2, 162.5, 142.3, 138.4, 136.1, 134.2, 131.1, 130.2, 128.4, 128.0, 124.9. Anal. Calcd. for $C_{31}H_{38}O_3$: C, 81.18; H, 8.35. Found: C, 81.25; H, 8.41.

4-(17β-Acetoxyandrosta-3,5-dien-3-yl)-4-phenyl-3-butenal (3i): mp 193-5 °C; IR (KBr) 1729, 1655, 769, 712 cm^{-1}; ^1H NMR δ 9.29 (d, J = 8.25 Hz, 1 H), 7.42-7.36 (m, 3 H), 7.25-7.19 (m, 2 H), 6.23 (d, J = 8.25 Hz, 1 H), 5.95 (s, 1 H), 5.53 (bs, 1 H), 4.65-4.57 (m, 1 H), 2.05 (s, 3 H), 0.96 (s, 3 H), 0.82 (s, 3 H); ^{13}C NMR δ 194.1, 171.1, 162.4, 142.3, 138.3, 136.1, 134.2, 131.1, 130.1, 128.3, 127.9, 124.8, 82.6; MS *m/e* (relative intensity) 444 (M^+, 100). Anal. Calcd. for $C_{30}H_{36}O_3$: C, 81.04; H, 8.16. Found: C, 80.92; H, 8.09.

4-(17β-Acetoxyandrosta-3,5-dien-3-yl)-3-penten-2-one (3j): mp 153-6 °C; IR (KBr) 1729, 1671 cm^{-1}; ^1H NMR 6.53 (bs, 1H), 6.31 (bs, 1 H), 5.82-5.63 (m, 1 H), 4.82-4.52 (m, 1 H), 2.31 (s, 3 H), 2.22 (s, 3 H), 2.02 (s, 3 H), 0.92 (s, 3 H), 0.82 (s, 3 H); ^{13}C NMR δ 199.4, 171.2, 152.5, 142.3, 134.4, 132.6, 128.4, 121.4. Anal. Calcd. for $C_{26}H_{36}O_3$: C, 78.75; H, 9.15. Found: C, 78.86; H, 9.21.

4-(17β-Acetoxyandrosta-3,5-dien-3-yl)-3-hepten-2-one (3k): mp 133-5 °C; IR (KBr) 1737, 1680 cm^{-1}; ^1H NMR δ 6.47 (bs, 1 H), 6.24 (s, 1 H), 5.80-5.58 (m, 1 H), 4.77-4.52 (m, 1 H), 2.20 (s, 3 H), 2.02 (s, 3 H),1.00 (t, J = 6.0 Hz, 3 H), 0.91 (s, 3H), 0.82 (s, 3 H); ^{13}C NMR δ 198.7, 171.2, 158.0, 142.4, 133.5, 132.1, 128.2, 120.8. Anal. Calcd. for $C_{28}H_{40}O_3$: C, 79.20; H, 9.49. Found: C, 79.13; H, 9.44.

4-(17β-Acetoxyandrosta-3,5-dien-3-yl)-3-octen-2-one (3l): mp 98-9 °C; IR (KBr) 1729, 1680 cm^{-1}; ^1H NMR δ 6.49 (bs, 1 H), 6.24 (s, 1 H), 5.81-5.62 (m, 1 H), 4.78-4.51 (m, 1 H), 2.22 (s, 3H), 2.04 (s, 3 H), 0.93 (s, 3 H) 0.84 (s, 3 H); ^{13}C NMR δ 198.7, 171.3, 158.3, 142.4, 133.5, 132.2, 128.3, 120.6. Anal. Calcd. for $C_{29}H_{42}O_3$: C, 79.41; H, 9.65. Found: C, 79.38; H, 9.70.

4-(17β-Acetylandrosta-3,5-dien-3-yl)-4-phenyl-3-buten-2-one (3m): mp 167-9 °C; IR (KBr) 1696, 1647, 777, 712 cm^{-1}; ^1H NMR δ 7.35-7.32 (m, 3 H), 7.32-7.09 (m, 2 H), 6.29 (s, 1 H), 5.80 (bs, 1 H), 5.59-5.38 (m, 1 H), 2.10 (s, 3 H), 1.66 (s, 3 H), 0.92 (s, 3 H), 0.63 (s, 3 H); ^{13}C NMR δ 209.4, 200.6, 154.6, 142.2, 138.5, 137.1, 134.7, 129.5, 129.2, 128.2, 128.0, 125.4. Anal. Calcd. for $C_{31}H_{38}O_2$: C, 84.12; H, 8.65. Found: C, 84.21; H, 8.59.

4-(17-Oxoandrosta-3,5-dien-3-yl)-4-phenyl-3-buten-2-one (3n): mp 159-161 °C; IR (KBr) 1737, 1639, 868, 760, 704 cm^{-1}; ^1H NMR δ 7.57-7.32 (m, 3 H), 7.32-7.12 (m, 2 H), 6.31 (s, 1 H), 5.82 (bs, 1 H), 5.59-5.41 (m, 1 H), 1.69 (s, 3 H), 0.96 (s, 3 H), 0.89 (s, 3 H); ^{13}C NMR δ 220.8, 200.6, 154.4, 142.3, 138.4, 136.8, 134.9, 129.3, 128.8, 128.2, 128.0, 125.5. Anal. Calcd. for $C_{29}H_{34}O_2$: C, 84.02; H, 8.27. Found: C, 83.91; H, 8.32.

4-(3β-Acetoxyandrost-16-en-17-yl)-4-phenyl-3-buten-2-one (3o): mp 137-9 °C; IR (KBr) 1734, 1646, 721, 705 cm^{-1}; ^1H NMR δ 7.56-7.10 (m, 5 H), 6.35 (bs, 1 H), 5.65-5.50 (m, 1 H), 4.97-4;47 (m, 1 H), 2.01 (s, 3 H), 1.67 (s, 3 H), 1.01 (s, 3 H), 0.87 (s, 3 H). Anal. Calcd. for $C_{31}H_{40}O_3$: C, 80.83; H, 8.75. Found: C, 80.73; H, 8.68.

Methyl 3-(6-Methoxy-3,4-dihydronaphth-1-yl)-2-butenoate (3p): mp oil; IR (liquid film): 1721, 1040, 888, 827 cm^{-1}; ^1H NMR (Acetone-d_6) δ 6.95 (d, J = 8.2 Hz, 1 H), 6.81-6.74 (m, 2 H), 5.94 (t, J = 4.84 Hz, 1 H); 5.87 (q, J = 1.4 Hz, 1 H), 3.78 (s, 3 H), 3.68 (s, 3 H), 2.76-2.67 (m, 2 H), 2.31 (d, J = 1.4 Hz, 3 H), 2.29-2.19 (m, 2 H); ^{13}C NMR δ 167.3, 158.7, 157.7, 142.1, 138.6, 126.2, 124.1, 117.7, 113.4, 110.9, 55.2, 50.9, 28.5, 23.0, 19.3; MS *m/e* (relative intensity) 258 (M^+, 73). Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 7.31; H, 6.04.

Methyl 3-(2-Phenyl-3-chromen-4-yl)-2-butenoate (3q): mp 75-76 °C; IR (KBr) 1729, 1639, 925, 867, 766 cm^{-1}; ^1H NMR δ 7.48-6.86 (m, 9 H), 6.00 (q, J = 1.4 Hz, 1 H), 5.84 (AA' part of an AA'BB' system, J = 3.7 Hz, 1 H), 5.77 (BB' part of an AA'BB' system, J = 3.7 Hz, 1 H), 3.74 (s, 3 H), 2.40 (d, J = 1.4 Hz, 3 H); ^{13}C NMR δ 166.8, 154.6, 153.6, 140.0, 139.0, 129.9, 128.7, 128.5, 127.1, 125.3, 122.2, 121.4, 120.9, 119.3, 116.9, 76.5, 51.2, 19.3; MS *m/e* (relative intensity) 306 (M^+, 35), 274 (100). Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.52; H, 5.84.

4-(3,3,5,5-Tetramethylcyclohex-1-enyl)-4-phenyl-3-buten-2-one (3r): mp 73-74 °C; IR (KBr) 1635, 760, 720 cm^{-1}; ^1H NMR δ 7.40–7.34 (m, 3 H), 7.15-7.10 (m, 2 H), 6.19 (s, 1 H), 5.38 (bs, 1 H),

2.00 (bs, 2 H), 1.70 (s, 3 H), 1.36 (s, 2 H), 1.00 (s, 6 H), 0.94 (s, 6 H); ^{13}C NMR δ 200.9, 155.5, 145.1, 138.8, 134.6,129.3, 128.0, 127.9, 125.3, 49.1, 39.7, 33.6, 31.0, 30.7, 30.2, 29.9; MS *m/e* (relative intensity) 282 (M^+, 25), 239 (27), 225 (100). Anal. Calcd. for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 85.15; H, 9.20.

Methyl 3-(3,3,5,5-Tetramethylcyclohex-1-enyl)-2-butenoate (3s): mp oil; IR (liquid film) 1730, 1620, 850 cm^{-1}; ^{1}H NMR δ 5.89 (t, J=1.5 Hz, 1 H), 5.82 (q, J = 1.2 Hz, 1 H), 3.70 (s, 3 H), 2.34 (d, J = 1.2 Hz, 3 H), 1.92 (d, J = 1.5 Hz, 2 H), 1.35 (s, 2 H), 2.05 (s, 6 H), 0.96 (s, 6 H); ^{13}C NMR δ 167.9, 156.4, 138.8, 134.4, 113.4, 50.9, 49.2, 39.8, 33.3, 31.4, 30.7, 29.9, 15.5; MS *m/e* (relative intensity) 236 (M^+, 14). Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found:C, 76.34; H, 10.28.

4-(3,3,5,5-Tetramethylcyclohex-1-enyl)-4-(*p*-hydroxyphenyl)-3-buten-2-one (3t/11t): mp oil; IR (liquid film) 3394, 1696, 1655, 910, 843, 736 cm^{-1}; ^{1}H NMR δ 7.50-7.57 (bs, 1 H), 7.40-6.80 (m, 4 H), 6.20 (s, 0.16 H), 6.17 (s, 0.84 H), 5.49 (bs, 1 H), 2.34 (s, 0.32 H), 1.97 (s, 1.68 H), 1.80 (s, 3 H), 1.36 (s, 0.32 H), 1.05 (s, 1.68 H), 1.00 (s, 6 H), 0.96 (s, 6 H); ^{13}C NMR δ 203.4, 157.6, 156.6, 145.7, 136.2, 49.2; MS *m/e* (relative intensity) 298 (M^+, 31), 241 (100).

4-(3,3,5,5-Tetramethylcyclohex-1-enyl)-4-(*p*-acetoxyphenyl)-3-buten-2-one (3u): mp 41-2 °C; IR (nujol) 1769, 1655, 909, 851 cm^{-1}; ^{1}H NMR δ 7.13 (s, 4 H), 6.19 (s, 1 H), 5.40 (t, J = 1.5 Hz, 1 H), 2.31 (s, 3 H) 2.00 (d, J = 1.5 Hz, 2 H), 1.75 (s, 3 H), 1.36 (s, 2 H), 1.00 (s, 6 H), 0.96 (s, 6 H); ^{13}C NMR δ 200.7, 169.0, 154.6, 150.5, 145.2, 136.1, 134.5, 130.3, 125.5, 121.2, 49.1, 39.8, 33.6, 31.0, 30.7, 30.4, 29.9, 21.2; MS *m/e* (relative intensity) 340 (M^+, 27), 283 (100). Anal. Calcd. for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29. Found: C, 77.49; H, 8.20.

4-(3,3,5,5-Tetramethylcyclohex-1-enyl)-4-(*p*-methoxyphenyl)-3-buten-2-one (3v): mp oil; IR (liquid film) 1721, 1655, 835 cm^{-1}; ^{1}H NMR δ 7.06 (AA' part of an AA'BB' system, J = 8.8 Hz, 2 H), 6.91 (BB' part of an AA'BB' system, J = 8.8 Hz, 2 H), 6.15 (s, 1 H), 5.43 (s, 1 H), 3.84 (s, 3 H), 1.98 (s, 2 H), 1.73 (s, 3 H), 1.36 (s, 2 H), 1.00 (s, 6 H), 0.96 (s, 6 H); ^{13}C NMR δ 201.3, 159.6, 155.6, 144.6, 134.8,130.7, 125.3, 113.4, 55.0, 49.1, 39.9, 33.5, 31.0, 30.7, 30.1, 29.8; MS *m/e* (relative intensity) 312 (M^+, 32), 297 (37), 269 (22), 255 (100). Anal. Calcd. for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.82; H, 9.11.

Methyl 3-(3,3,5,5-Tetramethylcyclohex-1-enyl)-3-(*o*-acetamidophenyl)-2-propenoate (3w): mp 134-6 °C; IR (KBr) 3361, 1712, 1688, 769, 753 cm^{-1}; ^{1}H NMR δ 8.05 (d, J = 6.7 Hz, 1 H), 7.36 (t, J = 5.7 Hz, 1 H), 7.16 (t, J = 5.7 Hz, 1 H),7.03 (bs, 1 H), 6.95 (d, J = 6.7 Hz, 2 H), 6.12 (s, 1H), 5.42 (s, 1H), 3.55 (s, 3 H), 1.96 (s, 2 H), 1.93 (s, 3 H), 1.36(s, 2 H), 0.95 (s, 6 H), 0.90 (s, 6 H); ^{13}C NMR δ 167.9, 166.5, 154.5, 145.5, 134.6, 132.1, 129.9, 128.7, 128.4, 124.1, 122.4, 115.8, 51.3, 48.9, 39.2, 33.5, 33.2, 31.0, 30.6, 30.1, 29.5, 24.3; MS *m/e* (relative intensity) 355 (M^+, 3), 281 (86), 266 (100). Anal. Calcd. for $C_{22}H_{29}NO_3$: C, 74.33; H, 8.22; N, 3.94. Found: C, 74.22; H, 8.14.

4-(3,3,5,5-Tetramethylcyclohex-1-enyl)-4-(*p*-acetamidophenyl)-3-buten-2-one (3x): mp 59-60 °C; IR (KBr) 3312, 1672, 1647, 843, 728 cm^{-1}; ^{1}H NMR δ 8.75 (s, 1 H), 7.56 (d, J = 8.9 Hz, 2 H), 7.05 (d, J = 8.9 Hz, 2 H), 6.20 (s, 1 H), 5.53 (s, 1 H), 2.18 (s, 3 H), 2.00 (s, 2 H), 1.83 (s, 3 H), 1.35 (s, 2 H), 1.00 (s, 6 H), 0.90 (s, 6 H); ^{13}C NMR δ 171.1, 169.0, 156.0, 145.5, 138.5, 134.5, 133.9, 129.8, 124.4, 119.1, 49.0, 39.8, 33.6, 31.0, 29.7, 24.3, 20.9; MS *m/e* (relative intensity) 339 (M^+, 30), 324 (41), 282 (100). Anal. Calcd. for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.70; H, 8.55; N, 4.02.

4-(3,3,5,5-Tetramethylcyclohex-1-enyl)-4-[*p*-(2-tetrahydropyranyloxy)phenyl]-3-buten-2-one (3y): mp oil; IR (liquid film) 1671, 761, 704 cm^{-1}; ^{1}H NMR δ 7.04 (s, 4 H), 6.13 (s, 1 H), 5.43 (m, 2 H), 3.85-4.05 (m, 1 H), 3.60-3.75 (m, 1 H), 1.71 (s, 3 H), 1.63 (s, 2 H), 1.35 (s, 2 H), 0.99 (s, 6 H), 0.95 (s, 6 H); ^{13}C NMR δ 201.67, 157.3, 155.8, 144.6, 134.7, 131.8, 130.7, 125.6, 115.9, 96.7, 62.4, 49.3; MS *m/e* (relative intensity) 382 (M^+, 1), 298 (43), 283 (35), 241 (100), 227 (15). Anal. Calcd. for $C_{25}H_{34}O_3$: C, 78.49; H, 8.96. Found:C, 78.64; H, 8.89.

4-[(*E*)-2-Phenylethenyl]-hept-3-en-2-one (12): IR (liquid film) 1672, 753 cm^{-1}; ^1H NMR δ 8.30 (d, J = 16.5 Hz, 0.5 H), 7.20-7.60 (m, 5 H), 7.00 (d, J = 16.5 Hz, 0.5 H), 6.99 (d, J = 16.1 Hz, 0.5 H), 6.70 (d, J = 16.1 Hz, 0.5 H), 6.26 (s, 0.5 H), 6.07 (s, 0.5 H), 2.56-2.58 (m, 1 H), 2.35-2.45 (m, 1 H), 2.25 (s, 3 H), 1.50-1.75 (m, 2 H), 1.80-1.10 (m, 3 H); ^{13}C NMR δ 198.4, 197.9, 154.9, 152.8,35.8, 31.9, 29.3, 22.9, 22.5, 14.2, 13.8; MS *m/e* (relative intensity) 214 (M^+, 8). Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.23; H, 8.42.

4-[(*E*)-2-Phenylethenyl]-hept-4-en-2-one (13): IR (liquid film) 1712, 753, 695 cm^{-1}; ^1H NMR δ 7.50-7.15 (m, 5 H), 7.12 (d, J = 16.4 Hz, 0.4 H), 6.80 (d, J = 16.3 Hz, 0.6 H), 6.45 (d, J = 16.4 Hz, 0.4 H), 6.35 (d, J = 16.3 Hz, 0.6 H), 5.83 (t, J = 7.3 Hz, 0.6 H), 5.55 (t, J = 7.3 Hz, 0.4 H), 3.40 (s, 1.2 H), 3.30 (s, 0.8 H), 2.50-2.10 (m, 2 H), 2.16 (s, 3 H), 1.20-1.00 (m, 3 H); ^{13}C NMR δ 207.7, 206.3, 50.2,42.5, 28.3, 27.9, 21.9, 20.9, 13.9, 13.6; MS *m/e* (relative intensity) 214 (M^+, 73). Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.27; H, 8.41.

4-Phenyl-4-(6-methoxynapht-1-yl)-butan-2-one (5f): mp oil; IR (liquid film) 1712, 851, 826, 796, 753, 704 cm^{-1}; ^1H NMR δ 8.03 (d, J = 10.2 Hz, 1 H), 7.63 (d, J = 10.2 Hz, 1 H), 7.39 (t, J = 8.0 Hz, 1 H), 7.26-7.08 (m, 8 H), 5.36 (t, J = 7.5 Hz, 1 H), 3.68 (s, 3H), 3.27 (d, J = 8.0 Hz, 2 H), 2.09 (s, 3 H); ^{13}C NMR δ 207.0, 157.2, 55.3, 50.2, 41.7, 30.6, 29.7; MS (CI) *m/e* (relative intensity) 305 (MH^+,19), 247 (100). Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 83.05; H, 6.57.

3-(3β-Acetoxyandrost-16-en-17-yl)-butanale (5za): IR (KBr) 1729, 1253, 1023 cm^{-1}; ^1H NMR δ 9.68 (s, 1 H), 5.39 (bs, 1 H), 4.77-4.61 (m, 1 H), 2.54-2.80 (m, 2 H), 2.03 (s, 3 H), 1.14 (d, J = 6.7 Hz, 2 H), 0.85 (s, 3 H), 0.81 (s, 3 H); ^{13}C NMR δ 230.0, 170.8, 158.9, 123.2, 73.7; MS *m/e* (relative intensity) 386 (M^+, 16). Anal. Calcd. for $C_{25}H_{38}O_3$: C, 77.68; H, 9.91. Found: C, 77.49; H, 9.83.

3-(3β-Acetoxyandrost-16-en-17-yl)-3-buten-2-one (5zb) and 3-(3β-Acetoxyandrost-16-en-17-yl)-butan-2-one (3zb): ^1H NMR δ 6.28 (bs, 0.25 H), 6.17 (m, 0.25 H), 5.35 (bs, 0.75 H), 4.80-4.55 (m, 1 H), 2.12 (s, 3 H), 2.03 (s, 3 H), 0.85 (s, 3 H), 0.79 (s, 3 H); ^{13}C NMR δ 208.6, 199.51, 170.8, 159.8, 156.3, 135.5, 121.9.

Methyl 3-(3β-Acetoxyandrost-16-en-17-yl)-2-butenoate (3zc): mp 123-24 °C; IR (KBr) 1737, 1614, 1245, 1146 cm^{-1}; ^1H NMR δ 6.13 (m, 1 H), 5.90 (bs, 1 H), 4.77-4.61 (m, 1 H), 3.70 (s, 3 H), 2.30 (d, 3 H, J = 1.14 Hz, 2.02 (s, 3 H), 0.95 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR δ 170.7, 167.8, 156.0, 150.9, 134.3, 114.0, 73.6; MS *m/e* (relative intensity) 414 (M^+, 60). Anal. Calcd. for $C_{26}H_{38}O_4$: C, 75.32; H, 9.24. Found: C, 75.11; H, 9.14.

3-(17β-Acetoxyandrosta-3,5-dien-3-yl)-hexanal (5h): ^1H NMR δ 9.66 (t, J = 2.4 Hz, 1 H), 5.77 (m, 1 H), 5.34 (m, 1 H), 4.61 (t, J = 7.5 Hz, 1 H), 2.04 (s, 3 H), 0.88 (s, 3 H), 0.83 (s, 3 H); ^{13}C NMR δ 202.6, 171.2, 141.4, 137.1, 125.9, 122.1, 82.7, 51.3; Anal. Calcd. for $C_{27}H_{40}O_3$: C, 78.60; H, 9.77. Found: C, 78.41; H, 9.68.

Acknowledgements. The authors are greatly indebted to Consiglio Nazionale delle Ricerche (CNR) and to Ministero dell'Università e della Ricerca Scientifica (MURST) for financial support of this research. The authors are also indebted to Dr. Luciana Turchetto of the Istituto Superiore di Sanità for obtaining the mass spectra of new products.

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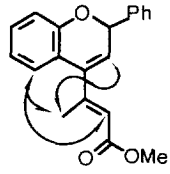
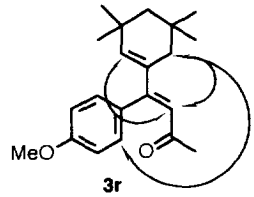


3q



3r

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(*Received in UK* 8 *February* 1996; *revised* 19 *March* 1996; *accepted* 21 *March* 1996)