Reaction of Dianions of Acyclic β-Enamino Ketones with Electrophiles. Part 2.† Oxiranes: Synthesis of γ'- and ε-Hydroxy-β-enamino Ketones and of α-Tetrahydrofurylidene Ketones

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β-Monoalkylamino α,β-unsaturated ketones can be regioselectively dimetallated either at the α'- or in the γ-positions. The reaction of the resulting dianions with oxiranes proceeds in good to high yields affording the corresponding hydroxyalkyl derivatives. The stereochemistry of the ring-opening reaction follows the rules of a classical S_N2 mechanism. The resulting linear products can be cyclized to furylidene ketones in high yields by treatment with hot acetic acid. Under these conditions even the product arising from reaction of trimethylsilylethylene oxide gives the ring closure instead of the elimination product.

Regiospecific alkylation of 1,3-diketones and their derivatives represents a considerable problem in organic synthesis. Several general solutions to direct the attack of carbon electrophiles at either α-, α'- or γ-positions have been proposed[1] in cyclic systems. We recently suggested[2] dianions of the β-monoalkylamino α,β-unsaturated ketones as versatile intermediates for the regioselective alkylation of the α'- and γ-positions of unsymmetrical acyclic 1,3-dicarbonylic derivatives. The regioselectivity[2] of the dimetallation can be controlled almost absolutely without resorting to classical conditions used to favour either the kinetic or the thermodynamic products. In fact, the kinetic (α'-dianion, 3) and the thermodynamic dianion (γ-dianion, 2) are preferentially formed in THF (tetrahydrofuran) at 20 °C with a slight excess of lithium tetramethylpiperidine (LiTMP, α'-conditions) or of methyllithium and N,N,N',N'-tetramethylethylenediamine (MeLi–TMEDA, γ-conditions) respectively (Scheme 1).
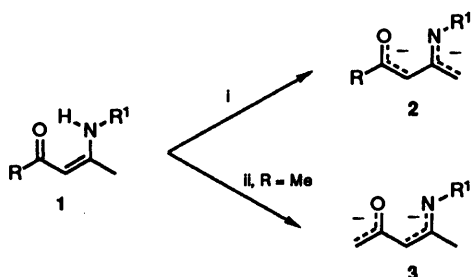
Scheme 1 *Reagents:* i, MeLi–TMEDA, 0 °C to room temp., 2 h; ii, LiTMP, 0 °C to room temp., 2 h

While under the γ-conditions, alkylation at the γ-position is observed almost exclusively, the kinetic preference for the α'-dianion is dependent on the size of the alkyl group linked to the nitrogen atom. Once formed, the α'-dianion very slowly interconverts into the more stable γ-dianion even in the presence of TMEDA, whereas, when the dianion is formed under the γ-conditions, the rate of equilibration is comparable with that of its formation, with the result that γ-dianion is exclusively formed.

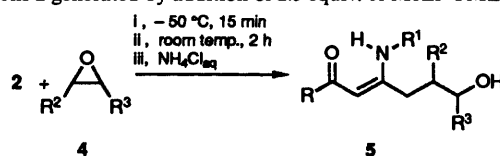The aim of giving a synthetic significance to these findings

† Part 1: ref. 2.

prompted us to test the reaction of α'- and γ-dianions with functionalised electrophiles. In this paper, we have focused our attention to the reaction with oxiranes. It is known that epoxides undergo reaction at the anion terminus of β-keto esters.[3] Subsequent cyclisation of the resulting hydroxy keto esters afford tetrahydrofurylidene acetates.[4] More recently, the conditions allowing a variety of substituents to be tolerated were found.[5] On the other hand, while enolates of simple ketones give epoxide ring cleavage products in low yields,[6] imine anions react smoothly with oxiranes to give hydroxy ketones after quenching with weak acids[7] or dihydrofurans after quenching with strong non-nucleophilic acids followed by heating.[8] Since β-monoalkylamino α,β-unsaturated ketones can resemble both imines and ketones, this system seemed to be a versatile route to the so far unknown furylidene ketones.

To test the feasibility of the reaction, the dianion 2a from 1-phenyl-3-(N-methylamino)but-2-en-1-one 1a was chosen since only the γ-position can be metallated. When oxiranes 4 are added dropwise to a cooled (−50 °C) solution of 2a followed by addition of few drops of saturated ammonium chloride, the expected ring-opening products were recovered in good to high yields (Table 1, entries 1–6).

The reaction mechanism shows the classical features of a bimolecular nucleophilic substitution. When unsymmetrical epoxides were employed to ascertain the direction of ring opening, attack at the less substituted carbon atom was always observed. In the cyclohexene oxide system, ring opening occurs with exclusive formation of the *trans*-isomer. *trans*-Methylstyrene oxide cleaves regiospecifically and stereospecifically at the α-carbon atom with formation of the corresponding R,S- and S,R-alcohol.[9] Epichlorohydrin is selectively opened without affecting the chlorine atom, according to the analogous reaction with acetoacetate anion.[10] The regiochemistry of the reaction of trimethylsilylethylene oxide resembles that of cuprates which open the three-membered ring to give β-hydroxyalkylsilanes.[11]

Once its feasibility had been established, the reaction was extended to enaminones which can give both the α'- and γ-dianions such as 4-(N-methylamino)pent-3-en-2-one 1c. As observed in reaction with alkyl halides,[2] in the presence of a powerful lithium complexing agent such as TMEDA, the more stable γ-isomer was always largely predominant and was the only recovered product, while the α'-isomer was detected in traces by HPLC–MS analysis even when the substituent on the nitrogen atom was a methyl group (Table 1, entries 8–11).
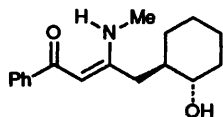
Table 1 Reaction of epoxides **4** with γ-dianions **2** generated by addition of 2.5 equiv. of MeLi–TMEDA to enaminones **1**

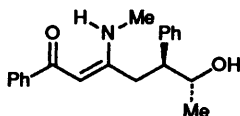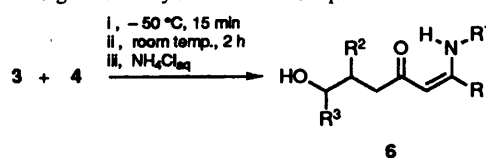|	Enaminone			Epoxide				
Entry	R^1	R		R^2	R^3	Product	α'/γ Ratio[b]	Yield (%)[a]
1	1a	Me	Ph	4a	H	H	5aa	—	92
2	1a	Me	Ph	4b	H	Et	5ab	—	98
3	1a	Me	Ph	4c	H	CH$_2$Cl	5ac	—	80
4	1a	Me	Ph	4d	–(CH$_2$)$_4$–		5ad[d]	—	98
5	1a	Me	Ph	4e[c]	Ph	Me	5ae[e]	—	87
6	1a	Me	Ph	4f	Me$_3$Si	H	5af	—	79
7	1b	Bu	Ph	4g	H	Me	5bg	—	74
8	1c	Me	Me	4a	H	H	5ca	1/13	80
9	1c	Me	Me	4b	H	Et	5cb	1/30	95
10	1c	Me	Me	4g	H	Me	5cg	1/14	84
11	1c	Me	Me	4h	H	Ph	5ch	1/50	87

[a] Calculated on the pure γ-product obtained by column chromatography. [b] α'-Product determined by HPLC/MS analysis but not isolated. [c] trans-Isomer.

[d] trans-Isomer:

[e] (S,R; R,S) isomer:

Table 2 Reaction of epoxides **4** with α'-dianions **3** generated by addition of 2.5 equiv. of LiTMP to enaminones **1**

	Enaminone			Epoxide				
Entry	R^1	R		R^2	R^3	Product	α'/γ Ratio[a]	Yield (%)[b]
1	1d	Pr^i	Me	4g	H	Me	6dg	3.2/1	61
2	1e	PhCHMe	Me	4a	H	H	6ea	7/1	56
3	1f	Bu^t	Me	4a	H	H	6fa	c	71
4	1f	Bu^t	Me	4g	H	Me	6fg	c	79
5	1g	Ph	Me	4b	H	Et	6gb	c	79
6	1g	Ph	Me	4d	–(CH$_2$)$_4$–		6gd[d]	c	68
7	1g	Ph	Me	4g	H	Me	6gg	c	82
8	1g	Ph	Me	4h	H	Ph	6gh	c	77
9	1g	Ph	Me	4i	H	Bu	6gi	c	83

[a] γ-Product determined by HPLC/MS analysis but not isolated. [b] Calculated on the pure α'-product obtained by column chromatography. [c] γ-Product undetectable.

[d] trans-Isomer:
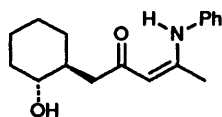
On the other hand, to obtain an almost exclusive regio-selectivity of alkylation on the α'-position, metallation should be accomplished in the absence of complexing agents and at the same time a very bulky substituent should be linked to the nitrogen atom. Under these conditions the isomerisation of the kinetically favoured α'-dianion into the more stable γ-isomer is very slow and the product arising from attack at the α'-position can be almost exclusively recovered.[2] Data reported in
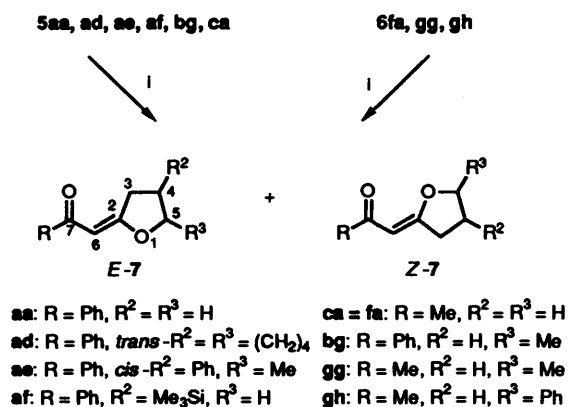
5aa, ad, ae, af, bg, ca   **6fa, gg, gh**

E-7   Z-7

aa: R = Ph, R² = R³ = H   **ca = fa**: R = Me, R² = R³ = H
ad: R = Ph, trans-R² = R³ = (CH₂)₄   **bg**: R = Ph, R² = H, R³ = Me
ae: R = Ph, cis-R² = Ph, R³ = Me   **gg**: R = Me, R² = H, R³ = Me
af: R = Ph, R² = Me₃Si, R³ = H   **gh**: R = Me, R² = H, R³ = Ph

Scheme 2 Reagents: i, CH₃CO₂H, 70 °C, 1 h

Table 3 Cyclisation of α'- and γ-products 5 and 6 carried out in acetic acid at 70 °C

Starting material	Final product	δ(3-H)[e]		(E):(Z) Ratio	Yield (%)
		(E)	(Z)		
5aa	7aa[a]	3.23	—	—	68
5ad	7ad[b]	2.62	2.56	1/8.6	66[d]
5ae	7ae[a,c]	3.68	—	—	85
5af	7af[a]	3.20	—	—	83
5bg	7bg[a]	3.25	—	—	69
5ca	7ca	3.05	2.70	2.6/1	73[d]
6fa	7ca[a]	3.05	—	—	68
6gg	7gg[a]	3.10	—	—	81
6gh	7gh[a]	3.31	—	—	66

[a] Only the main product (E)-7 had been isolated and characterized.

[b] trans Referred to the R² and R³ relationship:

[c] cis Referred to the R² and R³ relationship:

[d] Global yield. [e] For numbering see Scheme 2. Average value for the two diastereotopic protons.

Table 2 (entries 1–4) confirm this trend in the present reaction: i.e. the exclusive formation of the α'-dianion is obtained only when R¹ = Buᵗ.

However the reaction has a little synthetic applicability, since enaminone 1f is prepared in fair yields by the use of a Lewis acid and a strong dehydrating agent such as TiCl₄.[12] Since N-phenylenaminones can be obtained by simple mixing of aniline and β-diketones,[11] the degree of regioselectivity in the reaction of 4-(N-anilino)pent-3-en-2-one 1g was tested. Entries 5–9 of Table 2 show that the products from attack at the α'-position are obtained in high yields, while the γ-isomer was never detected even by HPLC–MS analysis.

The correct assignment of the products 5 and 6 as the γ- and α'-substitution products respectively was essentially made on spectroscopic evidence. For cases where assignment might be ambiguous, as in the case of enaminones 1c–g in particular, ¹³C NMR spectroscopy proved to be a very useful technique. In fact, the γ-substitution products 5 showed characteristic signals at about δ 28 for the α'-CH₃. Moreover, these compounds showed a difference between the carbonyl carbon and the carbon bound to the nitrogen of about 26 ppm. On the other hand, in the α'-products 6, the γ-CH₃ carbons resonate at about δ 19 and the difference between the carbonyl carbon and the carbon bound to the nitrogen is over 30 ppm. It should be noted that products 5aa–af, bg, ch do not exhibit a molecular ion peak in the mass spectrum, since cyclisation to the furylidene derivative occurs at the ionisation chamber temperature. Conversely, the molecular ion was detected in more volatile compounds such as 5ca, cb, cg.

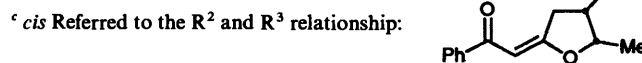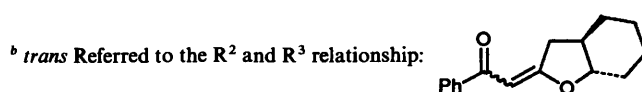*Cyclisation Reactions.*—Both compounds 5 and 6 undergo cyclisation to tetrahydrofurylidene ketones when treated with acetic acid and heated. While the latter compounds travel a classical pathway,[4] the former compounds give a formal displacement of amine (Scheme 2). The furylidene ketones were obtained in satisfactory yields (Table 3). It should be noted that, conversely from simple β-hydroxysilanes which undergo elimination to alkenes in acidic media,[11] hydroxysilane 5af cyclises to 7af under our conditions.

The (E)-isomer is the prevalent or the exclusive isomer isolated, apart from the adduct with cyclohexene epoxide, according to the literature findings on the corresponding acetates.[4] The assignment of the stereochemistry around the double bond was based on ¹H NMR evidence compared with literature data,[13] which reported that the allylic protons of the tetrahydrofuran ring resonate at lower field in the (E)- than in the (Z)-isomer (Table 3). The assignment was confirmed by measurement of the nuclear Overhauser enhancement (NOE) between the vinyl proton and the allylic protons of the tetrahydrofuran ring, when only one isomer was isolated. The

observed stereochemical trend cannot be rationalised on simple steric grounds.

In conclusion these findings demonstrate that the experimental conditions for a selective formation of α'- and γ-dianions of β-monoalkylamino α,β-unsaturated ketones are general and suitable also for functionalised electrophiles. Moreover α'-dianion can be obtained free from the γ-isomer by employing easily available anilino derivatives. Finally, an efficient access to the so far unknown furylidene ketones is reported. A very large spectrum of compounds can be prepared, because both α'- and γ-nucleophilic ring-opening products can be cyclised. Moreover, since both ring-opening and cyclisation occur with fixed stereochemistry and owing to the conformational arrangement of the enaminone, the use of a chiral alkyl group linked to the nitrogen atom appears a valuable modification to the preparation of chiral products in good optical yields, as in the preparation of ketones from metallated imines.[14]

Experimental

atmosphere and were titrated before use. All the epoxides used are commercial products or were prepared by reaction of *m*-chloroperbenzoic acid (MCPBA) and olefins.[9]

The enamino ketones **1a**–**e** were synthesized by condensation of 1,3-diketones with the corresponding alkylamine.[15] 4-(*N*-*tert*-butylamino)pent-3-en-2-one **1f** was prepared according to Weingarten's procedure.[12] 4-(*N*-phenylamino)pent-3-en-2-one **1g** was synthesized according to Boatman and Hauser's procedure.[11]

Metallation of Enaminones **1a**–**g**.[2]—γ-*Conditions*. A solution of methyllithium (12.5 mmol) was dropped into a stirred THF solution of the appropriate enaminone **1** (5 mmol) and TMEDA (12.5 mmol) at 0 °C under nitrogen. The temperature was allowed to rise to 20 °C and the mixture was stood with magnetic stirring at this temperature for 2 h.

α'-*Conditions*. A solution of LiTMP (12.5 mmol) was dropped into a stirred THF solution of the appropriate enaminone **1** (5 mmol) at 0 °C under nitrogen. The temperature was allowed to rise to 20 °C and the mixture was stood with magnetic stirring at this temperature for 2 h.

Reaction of the Dianions with Epoxides.—A THF solution of the appropriate oxirane **4** (8 mmol) was added to a cooled (−50 °C) solution of the dianion (5 mmol) and the mixture was stirred under a nitrogen atmosphere allowing the temperature to rise to room temperature. After about 30 min a gel appeared. Then, after a time varying from 1–3 h, some drops of saturated ammonium chloride solution were added to the mixture to dissolve the gel, the solution was extracted with hexane, dried (Na_2SO_4), evaporated under reduced pressure and separated on a silica gel column (hexane–ethyl acetate, 1:19 as eluent). Alchohols **5** and **6** were recovered from γ-**2** and α'-**3** dianions respectively. Yields and isomer ratios are reported in Tables 1 and 2. Physical data are reported below.

6-*Hydroxy*-3-(N-*methylamino*)-1-*phenylhex*-2-*en*-1-*one*   **5aa**. Oil (Found: C, 71.3; H, 7.8; N, 6.3. $C_{13}H_{17}NO_2$ requires C, 71.2; H, 7.8; N, 6.4%); δ_H 1.71–1.81 (m, 2 H); 2.33–2.38 (m, 2 H), 2.94 (d, *J* 5.26, 3 H), 3.33 (br s, 1 H), 3.62 (t, *J* 6.10, 2 H), 5.70 (s, 1 H), 7.30–7.40 (m, 3 H), 7.70–7.85 (m, 2 H) and 11.30 (br q, 1 H); δ_C 28.52 (t), 29.40 (t), 30.47 (q), 61.40 (t), 91.15 (d), 126.81 (d), 128.19 (d), 130.46 (d), 140.53 (s), 169.85 (s) and 187.83 (s); ν_{max}(film)/cm^{-1} 3370br, 1600, 1540, 1460 and 1330; *m/z* (%) 188 (M$^+$ − MeNH$_2$, 88), 187 (100), 111 (56), 77 (52) and 69 (87).

6-*Hydroxy*-3-(N-*methylamino*)-1-*phenyloct*-2-*en*-1-*one*   **5ab**. Oil (Found: C, 72.6; H, 8.7; N, 5.7. $C_{15}H_{21}NO_2$ requires C, 72.8; H, 8.6; N, 5.7%); δ_H 0.83 (t, *J* 7, 3 H), 1.37 (q, *J* 7, 2 H), 1.45–1.65 (m, 2 H), 2.13–2.24 (m, 1 H), 2.35–2.45 (m, 1 H), 2.81 (d, *J* 5, 3 H), 3.82 (br s, 1 H), 3.35–3.50 (m, 1 H), 5.60 (s, 1 H), 7.20–7.30 (m, 3 H), 7.65–7.80 (m, 2 H) and 11.28 (q, *J* 5, 1 H); δ_C 10.08 (q), 28.39 (t), 29.26 (t), 30.22 (t), 34.64 (q), 71.89 (t), 91.02 (d), 126.78 (d), 128.11 (d), 130.38 (d), 140.49 (s), 170.98 (s) and 187.51 (s); ν_{max}(film)/cm^{-1} 3400br, 1600, 1540, 1330, 740 and 690; *m/z* (%) 216 (M$^+$ − MeNH$_2$, 100), 215 (57), 147 (45), 105 (76), 77 (75) and 69 (62).

7-*Chloro*-6-*hydroxy*-3-(N-*methylamino*)-1-*phenylhept*-2-*en*-1-*one* **5ac**. Oil (Found: C, 62.9; H, 6.7; N, 5.2. $C_{14}H_{18}ClNO_2$ requires C, 62.8; H, 6.8; N, 5.2%); δ_H 1.64–1.85 (m, 2 H), 2.25–2.54 (m, 2 H), 2.93 (d, *J* 5, 3 H), 3.47 (dq, J_{AB} 5.4, *J* 11, 2 H), 3.75–3.82 (m, 1 H), 3.98 (br s, 1 H), 5.65 (s, 1 H), 7.30–7.40 (m, 3 H), 7.75–7.85 (m, 2 H) and 11.30 (br q, 1 H); δ_C 27.97 (t), 29.42 (q), 31.94 (t), 49.73 (t), 70.29 (d), 91.01 (d), 126.77 (d), 128.12 (d), 130.43 (d), 140.34 (s), 168.92 (s) and 187.87 (s); ν_{max}(film)/cm^{-1} 3320br, 1600, 1540, 1320, 1065, 740 and 695; *m/z* (%) 238 (32), 236 (M$^+$ − MeNH$_2$, 90), 235 (100), 159 (55), 105 (56) and 77 (91).

2-[2-(N-*Methylamino*)-4-*oxo*-4-*phenylbut*-2-*enyl*]*cyclohex-anol* **5ad**. Oil (Found: C, 74.9; H, 8.6; N, 5.2. $C_{17}H_{23}NO_2$ requires C, 74.7; H, 8.5; N, 5.1%); δ_H 0.80–1.25 (m, 2 H), 1.50–1.80 (m, 4 H), 1.90–2.10 (m, 6 H), 3.05 (d, *J* 5, 3 H), 3.25 (br s, 1 H), 5.65 (s, 1 H), 7.30–7.45 (m, 3 H), 7.80–7.85 (m, 2 H) and 11.30 (br q, 1 H); δ_C 24.84 (t), 25.36 (t), 29.76 (t), 30.62 (d), 35.60 (t), 36.04 (t), 44.47 (q), 74.68 (d), 92.72 (d), 126.86 (d), 128.13 (d), 130.31 (d), 140.69 (s), 159.15 (s) and 187.22 (s); ν_{max}(film)/cm^{-1} 3390br, 1730, 1600, 1530, 1320, 745 and 700; *m/z* (%) 242 (M$^+$ − MeNH$_2$, 58), 147 (100), 105 (61), 77 (54) and 69 (35).

6-*Hydroxy*-3-(N-*methylamino*)-1,5-*diphenylhept*-2-*en*-1-*one* **5ae**. Oil (Found: C, 77.8; H, 7.6; N, 4.4. $C_{20}H_{23}NO_2$ requires C, 77.6; H, 7.5; N, 4.5%); δ_H 1.08 (d, *J* 6.3, 3 H), 2.50–2.65 (m, 2 H); 2.70 (br s, 1 H), 2.81–2.87 (m, 1 H), 2.86 (d, *J* 5.4, 3 H), 4.00–4.15 (m, 1 H); 5.57 (s, 1 H), 7.20–7.40 (m, 8 H), 7.70–7.75 (m, 2 H) and 11.35 (br q, 1 H); δ_C 21.55 (q), 29.64 (q), 34.44 (t), 51.51 (d), 69.16 (d), 92.63 (d), 126.86 (d), 127.30 (d), 128.11 (d), 128.58 (d), 128.99 (d), 130.36 (d), 139.51 (s), 140.58 (s), 167.94 (s) and 187.54 (s); ν_{max}(film)/cm^{-1} 3460br, 1610, 1550, 1330 and 700; *m/z* (%) 278 (M$^+$ − MeNH$_2$, 25), 147 (89), 105 (55), 77 (100) and 69 (45).

6-*Hydroxy*-3-(N-*methylamino*)-1-*phenyl*-5-(*trimethylsilyl*)-*hex*-2-*en*-1-*one* **5af**. M.p. 118–119 °C (hexane) (Found: C, 65.8; H, 8.6; N, 4.7. $C_{16}H_{25}NO_2Si$ requires C, 65.9; H, 8.6; N, 4.8%); δ_H 0.09 (s, 9 H), 1.17 (tdd, *J* 7.8, 3.7, 5.8, 1 H), 2.25 (br s, 1 H), 2.42 (d, *J* 7.8, 2 H), 3.00 (d, *J* 5.3, 3 H), 3.72 (dd, *J* 5.8, 10.7, 1 H), 3.82 (dd, *J* 3.7, 10.7, 1 H), 5.70 (s, 1 H), 7.30–7.40 (m, 3 H), 7.80–7.90 (m, 2 H) and 11.45 (br s, 1 H); δ_C −2.37 (q), 29.06 (d), 29.47 (q), 29.94 (t), 62.51 (t), 91.86 (d), 126.75 (d), 128.04 (d), 130.28 (d), 140.39 (s), 170.30 (s) and 187.19 (s); ν_{max}(Nujol)/cm^{-1} 3400br, 1590, 1540, 1130, 1065, 830, 750 and 700; *m/z* (%) 260 (M$^+$ − MeNH$_2$, 5), 170 (33), 105 (100) and 73 (84).

3-(N-*Butylamino*)-6-*hydroxy*-1-*phenylhept*-2-*en*-1-*one*   **5bg**. Oil (Found: C, 74.0; H, 9.0; N, 5.2. $C_{17}H_{25}NO_2$ requires C, 74.1; H, 9.1; N, 5.1%); δ_H 0.90 (t, *J* 7.2, 3 H), 1.18 (d, *J* 6.1, 3 H), 1.34–1.46 (m, 2 H), 1.52–1.70 (m, 2 H), 2.21–2.51 (m, 2 H), 2.20–2.55 (m, 2 H), 3.00 (br s, 1 H), 3.26 (q, *J* 6.5, 2 H), 3.79 (sext, *J* 6.1, 1 H), 5.62 (s, 1 H), 7.35–7.40 (m, 3 H), 7.75–7.85 (m, 2 H) and 11.45 (br s, 1 H); δ_C 13.75 (q), 20.04 (q), 23.64 (t), 28.71 (t), 32.14 (t), 37.22 (t), 42.61 (t), 66.86 (d), 90.85 (d), 126.81 (d), 128.11 (d), 130.32 (d), 140.57 (s), 169.21 (s) and 187.59 (s); ν_{max}(film)/cm^{-1} 3390br, 1600 and 1580; *m/z* (%) 202 (M$^+$ − BuNH$_2$, 72), 201 (73), 125 (42), 105 (54), 77 (92) and 69 (100).

7-*Hydroxy*-4-(N-*methylamino*)*hept*-3-*en*-2-*one*   **5ca**. Oil (Found: C, 61.0; H, 9.5; N, 8.8. $C_8H_{15}NO_2$ requires C, 61.1; H, 9.6; N, 8.9%); δ_H 1.55–1.70 (m, 2 H), 1.85 (s, 3 H), 2.15–2.24 (m, 2 H), 2.82 (d, *J* 5.4, 3 H), 3.52 (t, *J* 6.1, 2 H), 4.30 (br s, 1 H), 4.87 (s, 1 H) and 10.63 (br q, 1 H); δ_C 28.04 (q), 30.39 (q), 30.71 (t), 32.69 (t), 61.12 (t), 94.86 (d), 168.04 (s) and 196.84 (s); ν_{max}(film)/cm^{-1} 3325br, 1610, 1565, 1315 and 1050; *m/z* (%) 157 (M$^+$, 21), 142 (16), 126 (43), 113 (100), 98 (47) and 71 (74).

7-*Hydroxy*-4-(N-*methylamino*)*non*-3-*en*-2-*one*   **5cb**. Oil (Found: C, 64.9; H, 10.3; N, 7.5. $C_{10}H_{19}NO_2$ requires C, 64.8; H, 10.3; N, 7.6%); δ_H 0.96 (t, *J* 7.5, 3 H), 1.50 (m, *J* 7.5, 2 H), 1.50–1.77 (m, 2 H), 2.01 (s, 3 H), 2.14 (br s, 1 H), 2.19–2.29 (m, 1 H), 2.38–2.49 (m, 1 H), 2.96 (d, *J* 6.0, 3 H), 3.54–3.62 (m, 1 H), 5.00 (s, 1 H) and 11.80 (br q, 1 H); δ_C 9.93 (q), 27.91 (t), 30.29 (q), 32.57 (t), 24.57 (t), 38.17 (q), 72.12 (d), 93.98 (d), 168.39 (s) and 194.68 (s); ν_{max}(film)/cm^{-1} 3360br, 1610, 1560, 1355 and 1315; *m/z* (%) 185 (M$^+$, 16), 156 (41), 126 (27), 113 (70), 98 (100), 71 (66) and 56 (46).

7-*Hydroxy*-4-(N-*methylamino*)*oct*-3-*en*-2-*one*   **5cg**. Oil (Found: C, 63.0; H, 10.1; N, 8.2. $C_9H_{17}NO_2$ requires C, 63.1; H, 10.0; H, 8.2%); δ_H 1.20 (d, *J* 6.2, 3 H), 1.58–1.66 (m, 2 H), 1.96 (s, 3 H), 2.15–2.42 (m, 2 H), 2.60 (br s, 1 H), 2.92 (d, *J* 5.3, 3 H), 3.75–3.85 (m, 1 H), 4.95 (s, 1 H) and 10.75 (br s, 1 H); δ_C 23.67

(q), 27.93 (t), 28.75 (q), 29.18 (q), 36.75 (t), 66.97 (d), 94.03 (d), 168.08 (s) and 194.82 (s); v_{max}(film)/cm^{-1} 3350br, 1600, 1300, 1070 and 740; m/z (%) 171 (M$^+$, 5), 126 (43), 113 (100), 98 (41) and 71 (84).

7-Hydroxy-4-(N-methylamino)-7-phenylhept-3-en-2-one **5ch**. Oil (Found: C, 72.0; H, 8.1; N, 6.0. C$_{14}$H$_{19}$NO$_2$ requires C, 72.1; H, 8.2; N, 6.0%); δ_H 1.82 (s, 3 H), 1.70–1.90 (m, 2 H), 2.10–2.30 (m, 2 H), 2.72 (d, *J* 5.3, 3 H), 4.50 (br s, 1 H), 4.62 (dd, *J* 7.5, 5.3, 1 H), 4.85 (s, 1 H), 7.15–7.30 (m, 5 H) and 10.55 (br q, 1 H); δ_C 27.73 (t), 28.46 (q), 29.00 (q), 36.84 (t), 72.69 (d), 93.98 (d), 125.75 (d), 127.28 (d), 128.27 (d), 144.65 (s), 168.47 (s) and 194.45 (s); v_{max}(film)/cm^{-1} 3320br, 1605, 1560, 1310 and 700; m/z (%) 202 (M$^+$ − MeNH$_2$, 88), 187 (15), 159 (36), 117 (70), 91 (42) and 85 (100).

7-Hydroxy-2-(N-isopropylamino)oct-2-en-4-one **6dg**. Oil (Found: C, 66.2; H, 10.5; N, 7.0. C$_{11}$H$_{21}$NO$_2$ requires C, 66.3; H, 10.6; N, 7.0%); δ_H 0.75 (d, *J* 6.2, 3 H), 0.80 (d, *J* 6.4, 6 H), 1.20–1.32 (m, 2 H), 1.55 (s, 3 H), 1.93 (t, *J* 4.6, 2 H), 3.25–3.46 (m, 1 H), 3.34 (m, 1 H), 4.45 (br s, 1 H), 4.50 (s, 1 H) and 10.40 (br d, 1 H); δ_C 18.25 (q), 23.19 (q), 23.38 (q), 34.89 (t), 37.85 (t), 44.30 (t), 66.74 (d), 94.16 (d), 162.26 (s) and 196.79 (s); v_{max}(film)/cm^{-1} 3380br, 1605, 1560 and 1440; m/z (%) 199 (M$^+$, 7), 184 (7), 156 (21), 141 (30), 126 (97), 99 (65) and 84 (100).

7-Hydroxy-2-[N-(1-phenylethyl)amino]hept-2-en-4-one **6ea**. Oil (Found: C, 72.6; H, 8.5; N, 5.7. C$_{15}$H$_{21}$NO$_2$ requires C, 72.8; H, 8.6; N, 5.7%); δ_H 1.44 (d, *J* 7.5, 3 H), 1.70 (s, 3 H), 1.79 (m, *J* 7, 2 H), 2.36 (t, *J* 7, 2 H), 3.59 (t, *J* 7, 2 H), 4.25 (br s, 1 H); 4.58 (q, *J* 7.5, 1 H), 4.94 (s, 1 H), 7.10–7.30 (m, 5 H) and 11.10 (br d, 1 H); δ_C 19.22 (q), 24.64 (q), 28.65 (t), 39.02 (t), 53.11 (d), 62.51 (t), 95.37 (d), 125.47 (d), 127.23 (d), 128.84 (d), 144.00 (s), 163.42 (s) and 197.81 (s); v_{max}(film)/cm^{-1} 3340br, 1605, 1560 and 1275; m/z (%) 247 (M$^+$, 11), 203 (30), 161 (22), 105 (100) and 84 (24).

7-Hydroxy-2-(N-tert-butylamino)hept-2-en-4-one **6fa**. Oil (Found: C, 66.2; H, 10.5; N, 7.1. C$_{11}$H$_{21}$NO$_2$ requires C, 66.3; H, 10.6; N, 7.0%); δ_H 1.37 (s, 9 H) 1.53–1.70 (m, 2 H), 2.02 (s, 3 H), 2.20 (br s, 1 H), 2.38 (t, *J* 7.2, 2 H), 3.63 (t, *J* 6.2, 2 H), 4.89 (s, 1 H) and 11.30 (br s, 1 H); δ_C 20.52 (q), 30.68 (q), 35.09 (t), 39.17 (t), 52.50 (s), 61.56 (t), 95.82 (d), 164.30 (s) and 196.15 (s); v_{max}(film)/cm^{-1} 3350br, 1600, 1300, 1070 and 740; m/z (%) 199 (M$^+$, 13), 155 (27), 140 (15) and 84 (100).

7-Hydroxy-2-(N-tert-butylamino)oct-2-en-4-one **6fg**. Oil (Found: C, 67.7; H, 10.8; N, 6.7. C$_{12}$H$_{23}$NO$_2$ requires C, 67.6; H, 10.9; N, 6.6%); δ_H 1.15 (d, *J* 6.0, 3 H), 1.36 (s, 9 H), 1.58–1.78 (m, 2 H), 1.80 (br s, 1 H), 2.04 (s, 3 H), 2.28–2.46 (m, 2 H), 3.73–3.84 (m, 1 H), 4.85 (s, 1 H) and 11.30 (br s, 1 H); δ_C 20.32 (q), 23.27 (q), 30.50 (q), 34.71 (t), 38.08 (t), 52.26 (s), 67.48 (d), 95.64 (d), 163.99 (s) and 196.37 (s); v_{max}(film)/cm^{-1} 3380br, 1605 and 1230; m/z (%) 213 (M$^+$, 3), 156 (26), 113 (26), 98 (22) and 84 (100).

7-Hydroxy-2-(N-phenylamino)non-2-en-4-one **6gb**. Oil (Found: C, 72.7; H, 8.6; N, 5.7. C$_{15}$H$_{21}$NO$_2$ requires C, 72.8; H, 8.6; N, 5.7%); δ_H 0.93 (t, *J* 7.0, 3 H), 1.40–1.88 (m, 4 H), 1.97 (s, 3 H), 2.51 (td, *J* 7.0, 1.9, 2 H), 3.48–3.65 (m, 2 H), 5.20 (s, 1 H), 7.03–7.35 (m, 5 H) and 12.40 (br s, 1 H); δ_C 9.93 (q), 19.82 (q), 30.21 (t), 32.19 (t), 38.44 (t), 72.85 (d), 97.03 (d), 124.57 (d), 125.59 (d), 128.94 (d), 138.38 (s), 160.99 (s) and 198.99 (s); v_{max}(film)/cm^{-1} 3400br, 1600, 1320, 1270, 750 and 700; m/z (%) 247 (M$^+$, 7), 175 (31), 160 (100), 133 (35) and 77 (32).

2-[2-Oxo-4-(N-phenylamino)pent-3-enyl]cyclohexanol **6gd**. Oil (Found: C, 74.7; H, 8.4; N, 5.0. C$_{17}$H$_{23}$NO$_2$ requires C, 74.7; H, 8.5; N, 5.1%); δ_H 1.00–1.25 (m, 4 H), 1.55–1.75 (m, 4 H), 1.92–2.02 (m, 1 H), 1.98 (s, 3 H), 2.27 (dd, *J* 4.7, 14.8, 1 H), 2.60 (dd, *J* 6.6, 14.8, 1 H), 3.15–3.25 (m, 1 H), 4.20 (br s, 1 H), 5.19 (s, 1 H), 7.02–7.35 (m, 5 H) and 12.50 (br s, 1 H); δ_C 19.83 (q), 24.72 (t), 25.63 (t), 32.45 (t), 35.43 (t), 42.67 (d), 47.28 (t), 75.33 (d), 97.62 (d), 124.57 (d), 125.68 (d), 128.94 (d), 138.23 (s), 161.35 (s) and 198.79 (s); v_{max}(film)/cm^{-1} 3400br, 1600, 1280,

1065, 750 and 700; m/z (%) 273 (M$^+$, 8); 175 (66), 160 (100) and 133 (42).

7-Hydroxy-2-(N-phenylamino)oct-2-en-4-one **6gg**. Oil (Found: C, 72.0; H, 8.2; N, 6.1. C$_{14}$H$_{19}$NO$_2$ requires C, 72.1; H, 8.2; N, 6.0%); δ_H 1.18 (d, *J* 6.2, 3 H), 1.64–1.82 (m, 2 H), 1.97 (s, 3 H), 2.44–2.52 (m, 2 H), 3.65 (br s, 1 H), 3.78–3.86 (m, 1 H), 5.20 (s, 1 H), 7.03–7.35 (m, 5 H) and 12.40 (br s, 1 H); δ_C 19.65 (q), 23.19 (q), 34.49 (t), 38.29 (t), 67.25 (d), 96.88 (d), 124.36 (d), 125.43 (d), 128.84 (d), 138.20 (s), 160.86 (s) and 198.72 (s); v_{max}(film)/cm^{-1} 3400br, 1605, 1275, 1070, 750 and 700; m/z (%) 233 (M$^+$, 9), 175 (34), 160 (100), 133 (31) and 118 (34).

7-Hydroxy-7-phenyl-2-(N-phenylamino)hept-2-en-4-one **6gh**. Oil (Found: C, 77.4; H, 7.2; N, 4.6. C$_{19}$H$_{21}$NO$_2$ requires C, 77.3; H, 7.2; N, 4.7%); δ_H 1.96 (s, 3 H), 2.00–2.15 (m, 2 H), 2.42–2.53 (m, 2 H), 4.70–4.83 (m, 2 H), 5.17 (s, 1 H), 7.03–7.40 (m, 10 H) and 12.45 (br s, 1 H); δ_C 19.84 (q), 34.78 (t), 38.21 (t), 73.55 (d), 97.12 (d), 124.53 (d), 125.64 (d), 125.78 (d), 126.90 (d), 128.11 (d), 129.05 (d), 138.35 (s), 145.03 (s), 161.08 (s) and 198.57 (s); v_{max}(film)/cm^{-1} 3400br, 1600, 1270, 750 and 700; m/z (%) 295 (M$^+$, 5); 277 (73), 220 (22), 160 (100), 118 (42) and 77 (68).

7-Hydroxy-2-(N-phenylamino)undec-2-en-4-one **6gi**. Oil (Found: C, 74.3; H, 9.2; N, 5.0. C$_{17}$H$_{25}$NO$_2$ requires C, 74.1; H, 9.2; N, 5.1%); δ_H 0.83 (t, *J* 7.1, 3 H), 1.20–1.90 (m, 8 H), 1.88 (s, 3 H), 2.38–2.57 (m, 2 H), 3.50–3.65 (m, 2 H), 5.19 (s, 1 H), 7.00–7.35 (m, 5 H) and 12.40 (br s, 1 H); δ_C 13.95 (q), 19.78 (q), 22.65 (t), 27.80 (t), 32.68 (t), 37.20 (t), 38.42 (t), 71.43 (d), 97.02 (d), 124.52 (d), 125.54 (d), 128.96 (d), 138.38 (s), 160.87 (s) and 198.96 (s); v_{max}(film)/cm^{-1} 3400br, 1600, 1270, 750 and 700; m/z (%) 275 (M$^+$, 8), 175 (43), 160 (100), 133 (50) and 118 (36).

Cyclisation of the ε-Hydroxy- 5 or the γ'-Hydroxy-enamino Ketones 6 to Furylidene Ketones.—The appropriate compound **5** or **6** (1 mmol) was dissolved in acetic acid (2 cm^3) and water (0.5 cm^3), then heated at 70 °C for 1 h. The mixture was then neutralised with saturated aqueous NaHCO$_3$, extracted with dichloromethane, dried (Na$_2$SO$_4$), evaporated under reduced pressure and submitted to a chromatographic separation on a silica gel column (hexane–ethyl acetate, 95:5 as eluent). Yields and isomer ratios are reported in Table 3. Physical data are reported below.

(E)-α-*(Tetrahydro-2-furylidene)acetophenone* (E)-**7aa**. Oil (Found: C, 76.5; H, 6.3. C$_{12}$H$_{12}$O$_2$ requires C, 76.6; H, 6.4%); δ_H 2.07 (m, *J* 7.5, 2 H, 4-H), 3.23 (dt, *J* 1.6, 7.5, 2 H, 3-H), 4.21 (t, *J* 7.5, 2 H, 5-H), 6.51 (t, *J* 1.6, 1 H, 6-H), 7.35–7.45 (m, 3 H, ArH) and 7.85–7.90 (m, 2 H, ArH); δ_C 23.72 (t), 31.44 (t), 71.87 (t), 95.03 (d), 127.54 (d), 128.29 (d), 131.67 (d), 139.81 (s), 179.22 (s) and 190.13 (s); v_{max}(film)/cm^{-1} 3430br, 1650, 1585 and 700; m/z (%) 188 (M$^+$, 88), 187 (100), 11 (56), 77 (52), 69 (88) and 51 (28).

(E)-α-(trans-*Octahydro-2-benzo[b]furylidene)acetophenone* (E)-**7ad**. M.p. 78–80 °C (Found: C, 79.4; H, 7.5. C$_{16}$H$_{18}$O$_2$ requires C, 79.3; H, 7.5%); δ_H 1.20–1.37 (m, 4 H), 1.57–1.87 (m, 4 H), 1.95–2.09 (m, 1 H), 2.38 (dd, *J* 16.5, 6.1, 1 H, 3a-H), 2.87 (dd, *J* 16.5, 6.0, 1 H, 3b-H), 3.17–3.25 (m, 1 H, 5-H), 6.20 (s, 1 H, 6-H), 7.35–7.55 (m, 3 H) and 7.80–7.90 (m, 2 H); δ_C 24.95 (t), 25.49 (t), 31.70 (t), 35.81 (t), 47.94 (d), 54.10 (t), 74.85 (d), 97.18 (d), 126.99 (d), 128.72 (d), 132.69 (d), 134.67 (s), 182.32 (s) and 198.08 (s); v_{max}(Nujol)/cm^{-1} 1585, 1550, 1430, 1265, 750 and 680; m/z (%) 242 (M$^+$, 15), 163 (49), 162 (26), 161 (37), 147 (63), 105 (100), 77 (72) and 69 (73).

(Z)-α-(trans-*Octahydro-2-benzo[b]furylidene)acetophenone* (Z)-**7ad**. Oil (Found: C, 79.2; H, 7.5); δ_H 1.00–1.40 (m, 4 H), 1.50–1.80 (m, 4 H), 1.90–2.05 (m, 1 H), 2.21 (dd, *J* 14.3, 8.9, 1 H, 3a-H), 2.91 (dd, *J* 14.3, 4.5, 1 H, 3b-H), 3.17–3.26 (m, 1 H, 5-H), 6.20 (s, 1 H, 6-H), 7.35–7.50 (m, 3 H) and 7.90–7.80 (m, 2 H); δ_C 24.95 (t), 25.49 (t), 31.27 (t), 35.81 (t), 43.29 (t), 43.45 (d), 74.39 (d), 97.18 (d), 126.99 (d), 128.59 (d), 132.29 (d), 134.67 (d), 182.32 (s) and 198.08 (s); v_{max}(film)/cm^{-1} 3390br, 1605, 1570,

1160, 765 and 695; m/z (%) 242 (M^+, 48), 163 (31), 161 (18), 147 (100), 105 (86) and 77 (53)

(E)-α-(cis-*Tetrahydro-5-methyl-4-phenyl-2-furylidene)aceto-phenone* (E)-7ae. Oil (Found: C, 79.9; H, 6.4. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%); δ_H 1.02 (d, J 6.5, 3 H, Me), 3.57–3.67 (m, 2 H, 3a-H, 4-H), 3.73–3.83 (m, 1 H, 3b-H), 4.84 (q, J 6.5, 1 H, 5-H), 6.65 (t, J 1.6, 6-H), 7.10–7.15 (m, 2 H), 7.20–7.30 (m, 3 H), 7.45–7.55 (m, 3 H) and 7.95–8.00 (m, 2 H); δ_C 16.38 (q), 38.38 (t), 46.17 (t), 82.94 (d), 95.34 (d), 127.19 (d), 127.68 (d), 128.04 (d), 128.42 (d), 128.60 (d), 131.82 (d), 138.68 (s), 139.80 (s), 178.25 (s) and 190.32 (s); v_{max}(film)/cm^{-1} 3370br, 1635, 1560, 1450, 1370, 1160 and 705; m/z (%) 278 (M^+, 46), 160 (44), 147 (100), 105 (74), 77 (98), 69 (56) and 51 (43).

(E)-α-[*Tetrahydro-4-(trimethylsilyl)-2-furylidene]acetophen-one* (E)-7af. Oil (Found: C, 69.1; H, 7.8. $C_{15}H_{20}O_2Si$ requires C, 69.2; H, 7.7%); δ_H 0.05 (s, 9H), 1.57 (tt, J 12.3, 8.4, 1 H, 4-H), 2.75 (ddd, J 2, 12.3, 18.8, 1 H, 3a-H), 3.65 (dd, J 18.8, 8.4, 1 H, 3b-H), 3.95 (dd, J 12.4, 8.7, 1 H, 5a-H), 4.45 (t, J 8.7, 1 H, 5b-H), 6.50 (d, J 2, 1 H, 6-H), 7.35–7.48 (m, 3 H) and 7.85–7.95 (m, 2 H); δ_C −3.17 (q), 25.23 (d), 34.07 (t), 74.52 (t), 94.43 (d), 127.42 (d), 128.06 (d), 131.51 (d), 139.68 (s), 179.56 (s) and 190.09 (s); v_{max}(film)/cm^{-1} 1655, 1590, 1165, 955, 835 and 700; m/z (%) 260 (M^+, 7), 245 (12), 187 (15), 170 (34), 105 (100) and 73 (87).

(E)-α-(*Tetrahydro-5-methyl-2-furylidene)acetophenone* (E)-7bg. Oil (Found: C, 77.1; H, 7.0. $C_{13}H_{13}O_2$ requires C, 77.2; H, 7.0%); δ_H 1.32 (d, J 6.3, 3 H, Me), 1.60–1.70 (m, 1 H, 4a-H), 2.15–2.27 (m, 1 H, 4b-H), 3.00–3.15 (m, 1 H, 3a-H), 3.40–3.50 (m, 1 H, 3b-H), 45.11 (m, J 8.1, 1 H, 5-H), 6.45 (s, 1 H), 7.35–7.45 (m, 3 H) and 7.85–7.90 (m, 2 H); δ_C 20.38 (q), 30.89 (t), 32.20 (t), 80.82 (d), 94.90 (d), 127.57 (d), 128.34 (d), 130.04 (d), 131.74 (s), 179.62 (s) and 190.73 (s); v_{max}(film)/cm^{-1} 3405br, 1645, 1585 and 710; m/z (%) 202 (M^+, 93), 201 (92), 147 (50), 125 (87), 105 (96) and 77 (100).

(E)-α-(*Tetrahydro-2-furylidene)acetone* (E)-7ca. Oil (Found: C, 66.6; H, 7.9. $C_7H_{10}O_2$ requires C, 66.7; H, 8.0%); δ_H 1.99 (q, J 7.4, 2 H, 4-H), 2.01 (s, 3 H, Me), 3.05 (td, J 7.9, 1.7, 2 H, 3-H), 4.12 (t, J 7.9, 2 H, 5-H) and 5.70 (t, J 1.7, 1 H, 6-H); δ_C 23.66 (t), 30.86 (q), 31.04 (t), 71.50 (t), 98.48 (d), 176.71 (s) and 197.32 (s); v_{max}(film)/cm^{-1} 3460br, 1670, 1590 and 1135; m/z (%) 126 (M^+, 29), 111 (53) and 69 (100).

(Z)-α-(*Tetrahydro-2-furylidene]acetone* (Z)-7ca. Oil (Found: C, 66.7; H, 7.9); δ_H 2.00–2.01 (m, 2 H, 4-H), 2.21 (s, 3 H, Me), 2.70 (td, J 1.1, 7.7, 2 H, 3-H), 4.40 (t, J 6.8, 2 H, 5-H) and 5.15 (t, J 1.1, 1 H, 6-H); δ_C 23.12 (q), 30.86 (t), 32.16 (t), 74.38 (t), 100.32 (d), 176.71 (2) and 197.32 (s); v_{max}(film)/cm^{-1} 3460br, 1670, 1590 and 1135; m/z (%) 126 (M^+, 60), 111 (68) and 85 (100).

(E)-α-(*Tetrahydro-5-methyl-2-furylidene)acetone* (E)-7gg. Oil (Found: C, 68.5; H, 8.5. $C_8H_{12}O_2$ requires C, 68.6; H, 8.6%); δ_H 1.34 (d, J 6.1, 3 H, 5-Me), 1.62 (dq, J 8.7, 12.5, 1 H, 4a-H); 2.09 (s, 3 H, COMe), 2.14–2.25 (m, 1 H, 4b-H), 2.87–3.00 (m, 1 H, 3a-H), 3.21–3.36 (m, 1 H, 3b-H), 4.50 (dq, J 6.1, 8.1, 1 H, 5-H) and 5.75 (s, 1 H); δ_C 20.37 (q), 30.92 (t), 31.12 (t), 31.53 (q), 80.22 (d), 98.29 (d), 176.57 (s) and 197.58 (s); v_{max}(film)/cm^{-1} 1670, 1590, 1140 and 950; m/z (%) 140 (M^+, 42), 125 (50) and 69 (100).

(E)-α-(*Tetrahydro-5-phenyl-2-furylidene)acetone* (E)-7gh. Oil (Found: C, 77.1; H, 7.0. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%); δ_H 2.19 (s, 3 H), 2.60–2.75 (m, 2 H, 4-H), 3.00–3.38 (m, 1 H, 3a-H), 3.35–3.50 (m, 1 H, 3b-H), 5.48–5.55 (m, 1 H, 5-H), 5.90 (s, 1 H, 6-H) and 7.25–7.40 (m, 5 H); δ_C 28.93 (q), 30.95 (t), 31.34 (t), 81.19 (d), 98.73 (d), 125.24 (d), 128.42 (d), 136.24 (d), 139.33 (s), 176.13 (s) and 242.65 (s); v_{max}(film)/cm^{-1} 1775, 1675, 1590, 1130, 750 and 690; m/z (%) 202 (M^+, 34), 159 (19), 117 (28), 85 (100) and 69 (54).

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