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A New Protocol for the Synthesis of α',β'-Unsaturated 1,3-Diketones

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Abstract: Dianions of α'-(trimethylsilyl)enaminones can be used as Peterson reagents in the reaction with aldehydes and ketones, to obtain α',β'-unsaturated enaminones or 1,3-diketones with regio and stereocontrol of the new double bond.

Recently we reported[1] the synthesis of α'- and γ-(trimethylsilyl)enaminones [*N*-(monoalkylamino) α,β-unsaturated ketones]. While the latter compounds easily hydrolyse losing the silyl group, α'-isomers are more stable and can be very important intermediates in organic synthesis.

In previous work,[2] the reaction of *N*,α'-dianions of enaminones with carbonyl derivatives was described, which exclusively affords the addition products without dehydration even in strong acidic quenching solutions.

In this paper we report the results of the addition of α'-(trimethylsilyl)enaminones *N*,α'-dianions to aldehydes and ketones, a new application of the classical Peterson reaction.[3]

Hydrolysis of the obtained α'β'-unsaturated enaminones to the corresponding diketones allows the preparation of 2,3-dihydropyranones by acidic cyclization[4] or of β'-branched 1,3-diketones by addition of Grignard reagents.[5]

Results and Discussion

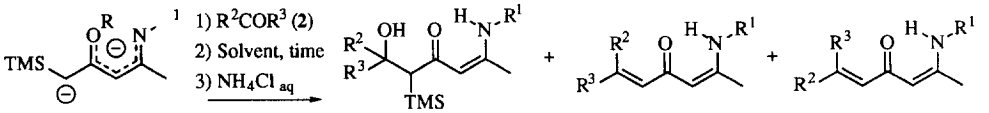
N,α'-Dianions **1** are generated by reaction of α'-(trimethylsilyl)enaminones with 2.5 equivalents of LTMP in THF at 0 °C for 2 h. Then the carbonyl compound is added at -78 °C, the reaction temperature allowed to rise to room temperature and the mixture magnetically stirred for two hours to ensure in most cases the disappearance of the starting materials.

At variance with α'-unsubstituted enaminones[2], a transmetalation reaction occurs with enolizable carbonyl compounds, so that either longer reaction times and excess of LTMP do not affect the amount of recovered starting materials.

Product distribution depends on the reaction conditions. The presence of a lithium complexing agent such as TMEDA favours the complete elimination[3] (table 1, entries 4-13), while the use of THF alone could

result either in a mixture of β'-hydroxysilylenaminones **3** and alkenes **4** (table 1, entry 1) or in the exclusive formation of product **3** (table 1, entry 2).

Table 1 Reaction of *N*,α'-Dianions of α'-(Trimethylsilyl)enaminones with Aldehydes and Ketones, followed by Quenching with Saturated Ammonium Chloride.



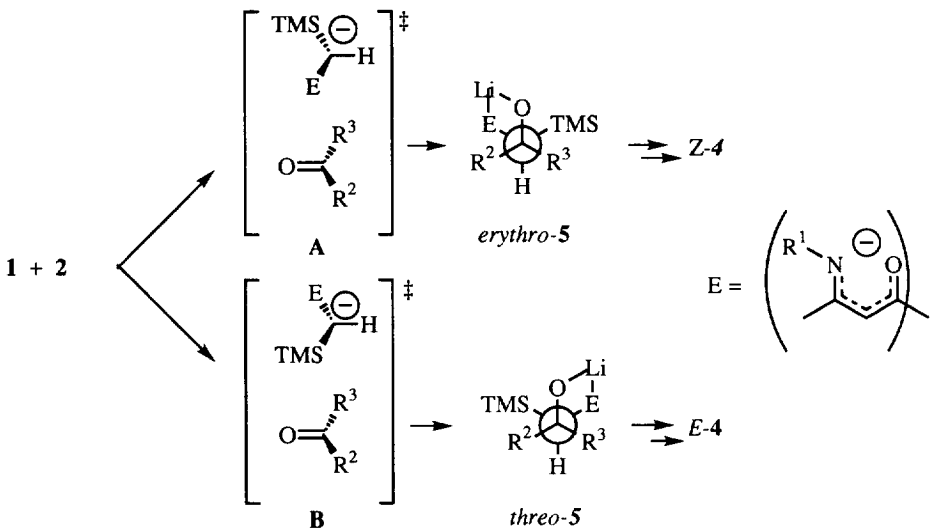
	1			3			Z-4	E-4	
Entry	Dianion	R^1	Carbonyl Compound	R^2	R^3	Method[a]	Product Yield (%) 3	Z-4	E-4
1	**1a**	*i*-Pr	**2a**	Ph	H	A	**aa** (23)	**aa** (37)	-
2	**1a**	*i*-Pr	**2b**	PhCH=CH	H	A	**ab** (51)	-	-
3	**1a**	*i*-Pr	**2c**	Et	H	A[b]	-	**ac** (35)	-
4	**1a**	*i*-Pr	**2a**	Ph	H	B	-	**aa** (53)	-
5	**1b**	Ph	**2a**	Ph	H	B	-	**ba** (82)	-
6	**1a**	*i*-Pr	**2b**	PhCH=CH	H	B	-	**ab** (65)	-
7	**1a**	*i*-Pr	**2c**	Et	H	B[c]	-	**ac** (26)	**ac** (12)
8	**1a**	*i*-Pr	**2d**	Ph	Me	B[b]	-	**ad** (45)	-
9	**1b**	Ph	**2e**	Et	Me	B[d]	-	**be** (53)	**be** (20)
10	**1a**	*i*-Pr	**2a**	Ph	H	C	-	**aa** (16)	**aa** (44)
11	**1b**	Ph	**2a**	Ph	H	C	-	-	**ba** (89)
12	**1a**	*i*-Pr	**2b**	PhCH=CH	H	C	-	-	**ab** (54)
13	**1a**	*i*-Pr	**2c**	Et	H	C[e]	-	**ac** (7)	**ac** (24)

a Method A: Solvent THF, reaction time 2 h. Method B: Solvent THF/TMEDA, reaction time 2 h. Method C: Solvent THF/TMEDA, reaction time 20 h.
b 54% starting material recovered.
c 44% starting material recovered.
d 15% starting material recovered.
e 25% starting material recovered.

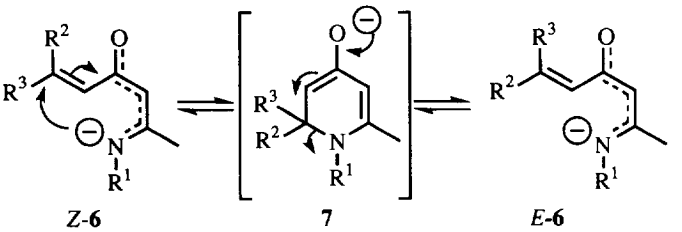
It should be noted that TMEDA cannot be added before dianion formation, since it promotes the α'-γ dianion equilibration.[6] However, once formed, the α' dianion turns very slowly into the γ-isomer, since it cannot reach a suitable conformation for the 1,5-hydrogen shift necessary for the reaction.[6] Hence the carbonyl compounds **2 a-e** dissolved in TMEDA were always added to the preformed dianion.

The most relevant feature of the reaction is the prevalent formation of the cis isomer (table 1, entries 4-9). The assignment of the double bond configuration was performed by comparing the coupling constants between the two hydrogen atoms of the double bond with the aldehyde adducts **4aa-ac,ba**, by NOE experiments with acetophenone adduct **4ad** and by evaluation of the steric compression on ^{13}C chemical shifts with 2-butanone adduct **4be**. Since the orientation of the attack of silyl carbanions to carbonyl compounds is well-established[7] the most likely reaction pattern is depicted in scheme 1.

The trimethylsilyl group is larger than the planar enaminone framework so that the carbonyl compound should face the dianion with the larger alkyl group near the smaller enaminone moiety . As a consequence the transition state **A** is favoured over the transition state **B**, the greater the difference between R^2 and R^3 is (*e.g.* with aldehydes where R^2 is an alkyl group and R^3 an hydrogen atom). Under our basic reaction conditions the *syn* elimination[3] from *erythro*-**5** is disfavoured by the mutual eclipsed conformation of the larger substituent of the carbonyl moiety and the enaminone framework. Moreover, the free rotation around the α'-β' single bond can be prevented by the lithium atom, which can chelate the two oxygen atoms giving a rigid pseudo-chair structure. TMEDA breaks this bridged structure allowing the system to reach the suitable eclipsed conformation.



Scheme 1



Scheme 2

Prolonged reaction times do not allow the Michael attack of the nitrogen anion to the α',β'-double bond, but surprisingly, we recover a mixture of isomers in which the *E*-isomer is the prevalent one (table 1, entries 10-13). Since the π-electron system of the charged enamino function is fully delocalized,[6] it is very unlikely that the α',β'-double bond will delocalize its π-electrons onto the oxygen atom. Therefore, the most probable

isomerisation is reached *via* the cyclic pyrimidone anion **7** (Scheme 2), whose stationary concentration is too low to be detected.

It is known[4,8] that α',β'-unsaturated 1,3-diketones cyclize in acidic media to 4-pyranones and that this reaction is reversible in basic media.[8] However, the reaction quenching with sulphuric acid did not afford the cyclic pyrimidone derivative but the only recovered product was the 1,3-diketone arising from hydrolysis of the enamino function, with isomerisation to the most stable *trans* isomer. Very likely the equilibrium of protonation invoked in the diketone cyclisation in the present reaction is strongly shifted toward the nitrogen atom, whose lone pair becomes no longer available.

In conclusion the reaction of α'-(trimethylsilyl)enaminones results in a stereoselective synthesis of α',β'-unsaturated enaminones or 1,3-diketones. The stereochemistry of the new double bond depends on the reaction times. Reaction yields are comparable or better than those obtained by the classical Claisen condensation reactions,[5] or by the cleavage of pyranones,[5] or finally by the Wittig reaction.[8] Finally, when a substituent is present in the γ position of the enaminone rather than a methyl group, our strategy allows a regiodirected formation of the double bond.

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Experimental

THF was purified and starting materials prepared as previously described.[1] All products were fully characterised by NMR and IR spectroscopy, mass spectrometry and elemental analysis.

Method A. Dianions **1** were prepared by adding a twofold excess of LTMP to a THF solution (1 M) of the corresponding enaminone at 0 °C for 2 h. Then, an equimolecular amount of carbonyl compound **2** dissolved in THF was added dropwise at -78 °C. After 2 h, the reaction was quenched with an ammonium chloride saturated aqueous solution, extracted with Et_2O, dried over sodium sulphate, evaporated under reduced pressure and submitted to a chromatographic separation on silica gel (hexane : ethyl acetate 8/2 as eluant). Product distribution is reported in table 1.

Method B. Dianions **1** were prepared as in method A. Then, an equimolecular amount of carbonyl compound **2** dissolved in TMEDA was added dropwise at -78 °C. After 2 h, the reaction was worked up as above described. Product distribution is reported in table 1.

Method C. As method B, but the reaction was allowed to stir for 20 h before quenching. Product distribution is reported in table 1. Physical data of all the isolated products follow.

1-Hydroxy-5-(*N*-isopropylamino)-1-phenyl-2-(trimethylsilyl)hex-4-en-3-one (**3aa**): oil, ^{1}H-NMR (200 MHz) 0.05 (s, 9H, Me_3Si); 1.17 (d, 6H, $\underline{Me_2}CH$, J = 6 Hz); 1.96 (s, 3H, 6-Me); 3.10 (d, 1H, CHSi, J = 16 Hz); 3.4-3.6 (m, 1H, $Me_2\underline{CH}$); 3.71 (d, 1H, CHOH); 4.88 (brs, 1H, OH); 5.18 (s, 1H, CH=); 7.3-7.5 (m, 5H, ArH); 11.3 (brd 1H, NH, J = 9 Hz). IR (film) ν_{max} 3300 (OH); 1591 (CO en) cm^{-1}. EI-MS (abundance) 319 (M^+, 20), 228 (77), 212 (58), 186 (223), 172 (16), 152 (52), 145 (68), 131 (68), 110 (47), 103 (48), 91 (22), 77 (52), 42 (100). Found C, 67.75; H, 9.15; N, 4.35. $C_{18}H_{29}NO_2Si$ requires C, 67.66; H, 9.15; N, 4.38 %.

6-Hydoxy-2-(*N*-isopropylamino)-8-phenyl-5-(trimethylsilyl)octa-2,7-dien-4-one (**3ab**) mp 117-118 °C. ^{1}H-NMR (200 MHz) 0.10 (s, 9H, Me_3Si); 1.06 (d, 3H, $\underline{Me_2}CH$, J = 6.3 Hz); 1.08 (d, 3H, $\underline{Me_2}CH$, J = 6.4 Hz); 1.74 (s, 3H, 1-Me); 2.30 (d, 1H, CHSi, J = 6 Hz); 3.6-3.7 (m, 1H, $Me_2\underline{CH}$); 4.49 (dd, 1H, CHOH); 4.73 (s, 1H, CH=); 5.21 (brs, 1H, OH); 6.24 (dd, 1H, =$\underline{CH}$CHOH, J = 15.1, 6.1); 6.38 (d, 1H, PhCH=); 7.3-7.5 (m, 5H, ArH), 10.4 (brd 1H, NH, J = 12 Hz). IR (film) ν_{max} 3463 (OH); 1603 (CO en) cm^{-1}. EI-MS (abundance)

345 (M^+, 10), 225 (24), 126 (100), 99 (10), 73 (27), 42 (11). Found C, 69.50; H, 9.05; N, 4.05. $C_{20}H_{31}NO_2Si$ requires C, 69.52; H, 9.04; N, 4.05 %.

(*1Z,4Z*)-5-(*N*-isopropylamino)-1-phenylhexa-1,4-dien-3-one (*Z*-**4aa**) oil; ^{1}H-NMR (200 MHz) 1.14 (d, 6H, $\underline{Me_2}CH$, J = 8 Hz); 1.80 (s, 3H, 6-Me); 3.6-3.7 (m, 1H, $Me_2\underline{CH}$); 4.96 (s, 1H, 4-CH=); 5.97 (d, 1H, 2-CH=, J = 13 Hz); 6.45 (d, 1H, 1-CH=); 7.1-7.5 (m, 5H, ArH), 10.9 (brd 1H, NH, J = 9 Hz). IR (film) ν_{max} 1592 (CO en), 697 (cis) cm^{-1}. EI-MS (abundance) 229 (M^+, 42), 214 (15), 212 (35), 152 (25) 131 (57), 115 (21), 110 (44), 103 (36), 84 (48), 77 (42), 42 (100). Found C, 78.50; H, 8.40; N, 6.10. $C_{15}H_{19}NO$ requires C, 78.56; H, 8.35; N, 6.11 %.

(*1E,4Z*)-5-(*N*-isopropylamino)-1-phenylhexa-1,4-dien-3-one (*E*-**4aa**) mp 101-102 °C; ^{1}H-NMR (200 MHz) 1.28 (d, 6H, $\underline{Me_2}CH$, J = 6.4 Hz); 2.05 (s, 3H, 6-Me); 3.7-3.8 (m, 1H, $Me_2\underline{CH}$); 5.10 (s, 1H, 4-CH=); 6.64 (d, 1H, 2-CH=, J = 17 Hz); 7.1-7.5 (m, 6H, ArH+1-CH=); 11.5 (brd 1H, NH, J = 8 Hz). IR (film) ν_{max} 1591 (CO en), 971 (trans) cm^{-1}. EI-MS (abundance) 229 (M^+, 100), 214 (19), 212 (19), 152 (43) 131 (71), 115 (24), 110 (59), 103 (46), 84 (46), 77 (47), 42 (81). Found C, 78.60; H, 8.35; N, 6.10. $C_{15}H_{19}NO$ requires C, 78.56; H, 8.35; N, 6.11 %.

(*1Z,4Z*)-5-(*N*-phenylamino)-1-phenylhexa-1,4-dien-3-one (*Z*-**4ba**) oil; ^{1}H-NMR (200 MHz) 1.96 (s, 3H, 6-Me); 5.24 (s, 1H, 4-CH=); 6.14 (d, 1H, 2-CH=, J = 12.7 Hz); 6.70 (d, 1H, 1-CH=); 7.1-7.7 (m, 10H, ArH), 12.9 (brs 1H, NH). IR (film) ν_{max} 1587 (CO en), 695 (cis) cm^{-1}. EI-MS (abundance) 263 (M^+, 11), 246 (11), 186 (100), 160 (10), 118 (12), 103 (12), 77 (30). Found C, 82.00; H, 6.50; N, 5.35. $C_{18}H_{17}NO$ requires C, 82.10; H, 6.51; N, 5.32 %.

(*1E,4Z*)-5-(*N*-phenylamino)-1-phenylhexa-1,4-dien-3-one (*E*-**4ba**) mp 98-99 °C; ^{1}H-NMR (200 MHz) 2.06 (s, 3H, 6-Me); 5.37 (s, 1H, 4-CH=); 6.69 (d, 1H, 2-CH=, J = 16 Hz); 7.2-7.7 (m, 11H, ArH+1-CH=); 13.1 (brs 1H, NH). IR (film) ν_{max} 1572 (CO en), 937 (trans) cm^{-1}. EI-MS (abundance) 263 (M^+, 13), 186 (100), 77 (18). Found C, 82.10; H, 6.50; N, 5.30. $C_{18}H_{17}NO$ requires C, 82.10; H, 6.51; N, 5.32 %.

(*2Z,5Z,7E*)-2-(*N*-isopropylamino)-8-phenylocta-2,5,7-trien-4-one (*Z*-**4ab**) oil, ^{1}H-NMR (200 MHz) 1.23 (d, 6H, $\underline{Me_2}CH$, J = 6.4 Hz); 1.99 (s, 3H, 1-Me); 3.6-3.8 (m, 1H, $Me_2\underline{CH}$); 4.91 (s, 1H, 3-CH=); 5.85 (d, 1H, 5-CH=, J = 11 Hz); 6.43 (t, 1H, 6-CH=, J = 11 Hz); 6.67 (d, 1H, 7-CH=, J = 16 Hz); 7.2-7.6 (m, 5H, ArH); 8.43 (dd, 1H, 8-CH=, J = 11, 16 Hz); 10.8 (brd 1H, NH, J = 8 Hz). IR (film) ν_{max} 1589 (CO en), 998 (trans), 699 (cis) cm^{-1}. EI-MS (abundance) 255 (M^+, 48), 240 (34), 164 (20), 152 (21), 128 (43), 115 (30) 110 (33), 42 (100). Found C, 80.00; H, 8.30; N, 5.45. $C_{15}H_{19}NO$ requires C, 79.96; H, 8.29; N, 5.49 %.

(*2Z,5E,7E*)-2-(*N*-isopropylamino)-8-phenylocta-2,5,7-trien-4-one (*E*-**4ab**) oil, ^{1}H-NMR (200 MHz) 1.24 (d, 6H, $\underline{Me_2}CH$, J = 6 Hz); 2.01 (s, 3H, 1-Me); 3.4-3.5 (m, 1H, $Me_2\underline{CH}$); 5.04 (s, 1H, 3-CH=); 6.19 (d, 1H, 5-CH=, J = 15 Hz); 6.8-7.0 (m, 2H, 6- and 7-CH=); 7.2-7.6 (m, 6H, ArH+8-CH=); 11.5 (brd 1H, NH, J = 7 Hz). IR (film) ν_{max} 1588 (CO en), 998 (trans) cm^{-1}. EI-MS (abundance) 255 (M^+, 42), 212 (41), 178 (37), 42 (100). Found C, 80.00; H, 8.25; N, 5.50. $C_{15}H_{19}NO$ requires C, 79.96; H, 8.29; N, 5.49 %.

(*2Z,5Z*)-2-(*N*-isopropylamino)octa-2,5-dien-4-one (*Z*-**4ac**) oil, ^{1}H-NMR (200 MHz) 0.97 (t, 3H, 8-Me, J =7.4); 1.20 (d, 6H, $\underline{Me_2}CH$, J = 6.4 Hz); 1.92 (s, 3H, 1-Me); 2.67 (apparent quintet, 2H, 7-CH_2); 3.6-3.7 (m, 1H, $Me_2\underline{CH}$); 4.88 (s, 1H, 3-CH=); 5.71 (dt, 1H, 6-CH=, J = 12, 7 Hz); 5.77 (dt, 1H, 6-CH=, J = 12, 1 Hz); 11.1 (brd 1H, NH, J = 8 Hz). IR (film) ν_{max} 1596 (CO en), 796 (cis) cm^{-1}. EI-MS (abundance) 181 (M^+, 37), 138 (27), 110 (20) 99 (37), 84 (100), 71 (25), 57 (23), 55 (26), 42 (89). Found C, 72.90; H, 10.60; N, 7.75. $C_{15}H_{19}NO$ requires C, 72.88; H, 10.56; N, 7.73 %.

(*2Z,5E*)-2-(*N*-isopropylamino)octa-2,5-dien-4-one (*E*-**4ac**) oil, ^{1}H-NMR (200 MHz) 0.98 (t, 3H, 8-Me, J =6.4); 1.20 (d, 6H, $\underline{Me_2}CH$, J = 6 Hz); 1.97 (s, 3H, 1-Me); 2.11 (apparent quintet, 2H, 7-CH_2); 3.6-3.7 (m, 1H, $Me_2\underline{CH}$); 4.94 (s, 1H, 3-CH=); 5.99 (dt, 1H, 5-CH=, J = 15, 1 Hz); 6.72 (dt, 1H, 6-CH=, J = 15, 6 Hz); 11.4 (brd 1H, NH, J = 9 Hz). IR (film) ν_{max} 1596 (CO en), 974 (trans) cm^{-1}. EI-MS (abundance) 181 (M^+,

40), 152 (36), 124 (35), 110 (54) 99 (26), 84 (73), 83 (38), 58 (23), 55 (47), 42 (100). Found C, 72.85; H, 10.60; N, 7.70. $C_{15}H_{19}NO$ requires C, 72.88; H, 10.56; N, 7.73 %.

(*2Z,5Z*)-2-(*N*-isopropylamino)-6-phenylhepta-2,5-dien-4-one (*Z*-**4ad**) oil, ^{1}H-NMR (200 MHz) 1.18 (d, 6H, $\underline{Me_2}CH$, J = 6.3 Hz); 1.78 (s, 3H, 1-Me); 2.11 (d, 3H, 7-Me, J = 1.4 Hz); 3.6-3.8 (m, 1H, $Me_2\underline{CH}$); 4.62 (s, 1H, 3-CH=); 6.00 (q, 1H, CH=, Enhanced on irradiation of 7-Me in a difference NOE experiment); 7.2-7.4 (m, 5H, ArH); 10.8 (brd 1H, NH, J = 8 Hz). Relevant ^{13}C-NMR (200 MHz) 18.7 (q), 26.9 (q), 97.1 (2d). IR (film) ν_{max} 1591 (CO en) cm^{-1}. EI-MS (abundance) 243 (M^+, 25), 226 (36), 200 (50) 159 (19), 145 (25), 115 (46), 91 (25), 84 (46), 42 (100). Found C, 78.95; H, 8.70; N, 5.75. $C_{15}H_{19}NO$ requires C, 78.97; H, 8.70; N, 5.76 %.

(*2Z,5Z*)-2-(*N*-phenylamino)-6-methylocta-2,5-dien-4-one (*Z*-**4be**) oil, ^{1}H-NMR (200 MHz) 1.11 (t, 3H, $\underline{Me}CH_2$, J = 7.6 Hz); 1.86 (d, 3H, 6-Me, J= 1.5 Hz); 2.02 (s, 3H, 1-Me); 2.72 (q, 2H, $MeCH_2$); 5.16 (s, 1H, 3-CH=); 5.84 (q, 1H, CH=); 7.2-7.4 (m, 5H, ArH); 12.8 (brs 1H, NH). Relevant ^{13}C-NMR (200 MHz) 13.0 (q), 20.2 (q), 24.9 (t), 26.5 (q), 100.2 (2d). IR (film) ν_{max} 1592 (CO en) cm^{-1}. EI-MS (abundance) 229 (M^+, 64), 200 (67) 160 (75), 132 (100), 120 (56), 118 (39), 93 (40), 77 (61). Found C, 78.50; H, 8.35; N, 6.15. $C_{15}H_{19}NO$ requires C, 78.56; H, 8.35; N, 6.11 %.

(*2Z,5E*)-2-(*N*-phenylamino)-6-methylocta-2,5-dien-4-one (*E*-**4be**) oil, ^{1}H-NMR (200 MHz) 1.00 (t, 3H, $\underline{Me}CH_2$, J = 7.4 Hz); 1.96 (s, 3H, 1-Me); 2.07 (q, 2H, $MeCH_2$); 2.14 (d, 3H, 6-Me, J= 1.3 Hz); 5.11 (s, 1H, 3-CH=); 5.80 (q, 1H, CH=); 7.0-7.3 (m, 5H, ArH); 12.8 (brs 1H, NH). Relevant ^{13}C-NMR (200 MHz) 12.5 (q), 18.8 (q), 20.3 (q), 34.2 (t), 100.4 (2d). IR (film) ν_{max} 1578 (CO en) cm^{-1}. EI-MS (abundance) 229 (M^+, 40), 200 (100) 160 (39), 132 (51), 120 (50), 118 (26), 93 (27), 77 (38). Found C, 78.60; H, 8.35; N, 6.10. $C_{15}H_{19}NO$ requires C, 78.56; H, 8.35; N, 6.11 %.

(*1Z,4E*)-5-hydroxy-1-phenylhexa-1,4-dien-3-one (*E*-**8**) recognized by comparison with literature data.[8]

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