Pergamon

*Tetrahedron* Vol. 50, No. 32, pp. 9831-9836, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $7.00+0.00

0040-4020(94)00567-2

# The Reaction of the Dianion of β-Enaminoketones with Electrophiles. Part 6#. Synthesis of γ'- and ε-Nitro-β-enaminoketones.

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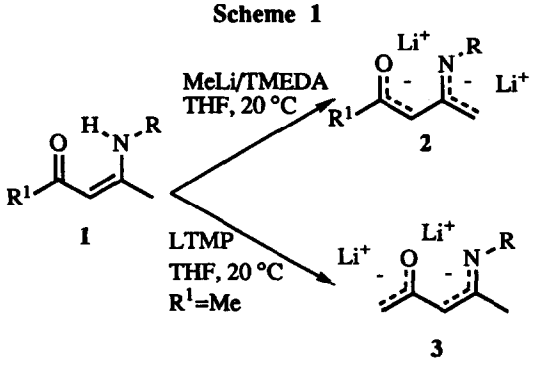
***Abstract:*** α'- And γ-dianions of acyclic β-(monoalkylamino)-α,β-unsaturated ketones can attack the double bond of nitroalkenes affording γ'- and ε-nitro-β-enaminoketones in good to high yields. In contrast to the corresponding 1,3-dicarbonyl dianions, cyclic products from intramolecular Henry reactions are never observed. Quenching the reaction with sulphuric acid ε-nitro-β-enaminoketones are converted in low yields into dihydropyrroles.

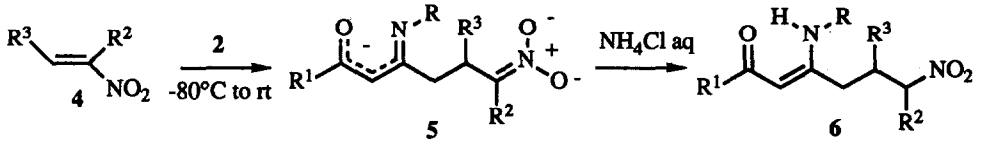
Dianions of acylic β-(monoalkylamino)-α,β-unsaturated ketones have been revealed the cornerstone of the regiocontrolled attack at the α'- and γ-positions of unsymmetrical 1,3-dicarbonyls[1]. Appropriate generation tecniques allow the almost exclusive formation of the α' or the γ dianion (scheme 1), which reacts with a large variety of electrophiles such as alkyl halides[1], oxiranes[2], nitriles[3], esters[4], aldehydes and ketones[5], leading to both straight chain and heterocyclic products.

**Scheme 1**




These results prompted us to investigate the reaction with nitroalkenes. The introduction of a nitro group in the alkyl side chain would increase the synthetic utility of these reactions, since it may be transformed in a legion of diverse functionality such as carbonyl derivatives, oximes, amines, nitrile oxides or carboxylic acids[6].

**Table 1.** Reaction of Enaminone Dianions **2** with Nitroolefins **4** at -80 °C followed by quenching with Ammonium Chloride at Room Temperature.




| Dianion | R | $R^1$ | Nitroene | $R^2$ | $R^3$ | Product | Yield (%) |
|---|---|---|---|---|---|---|---|
| **2a** | i-Pr | Ph | **4a** | H | Ph | **6aa** | 83 |
| **2a** | i-Pr | Ph | **4b** | Me | *p*-$MeOC_6H_4$ | **6ab** | 73[a] |
| **2a** | i-Pr | Ph | **4c** | Me | $PhCH_2CH_2$ | **6ac** | 67 |
| **2a** | i-Pr | Ph | **4d** | Me | Et | **6ad** | 64 |
| **2b** | Ph | Me | **4a** | H | Ph | **6ba** | 53[b] |
| **2d** | Me | Ph | **4a** | H | Ph | **6da** | 65 |
| **2e** | Me | Me | **4a** | H | Ph | **6ea** | 59 |

[a] Recovered as a mixture of diastereoisomers in about 1:1 ratio

[b] Recovered together with a 23% of the isomer **10ba**

***Synthesis of ε-Nitro-β-enaminoketones.***

γ-Dianions were prepared from β-(monoalkylamino)-α,β-unsaturated ketones and 2.5 eq of methyllithium together with 2.5 eq of *N,N,N',N'*-tetramethylethylendiamine (TMEDA). The strong complexing agent of the lithium cation was necessary to ensure that the kinetically favoured α'-dianion could isomerize to the more stable γ-isomer[1]. The reaction with nitroalkenes at -80 °C gave the expected title derivatives in good to high yields (table 1).

As previously observed with ketones and aldehydes[5], it should be noted that bulky nitrogen substituents favoured the formation of some amounts of α' addition products, notwithstanding the negligible concentration of this dianion in the solution. However, the influence of the nitrogen substituent on product distribution was now much less important and it was observed only with the phenyl group. Therefore when a competition between the α' and γ positions is possible, a moderate size group on the nitrogen atom must be preferred.

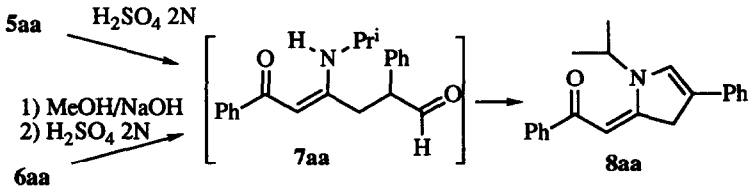
No cyclic compounds were recovered from the reaction mixture, the residue to quantitative yields being tars. It is reported that 1,3-dicarbonyl dianions[7] under similar reaction conditions gave both open chain and cyclic products. The ratio between the two isomers depends on the pH of the quenching solution. In particular basic quenching led almost exclusively to cyclic products; while after pouring the reaction mixture into 5% aqueous acetic acid straight chain products were recovered. This behaviour was explained on the basis of the quite different pKa values of the intercarbonylic and the α-nitro methylene groups. We tested unsuccessfully the reported optimum quenching conditions to obtain cyclic compounds. It is very likely that the pKa values of the α-nitro methylene and of the NH group of the enaminonic function are closer. As a consequence they are protonated at very similar pH values, so that the intramolecular Henry reaction does not occur.

When two new stereocenters were formed, generally only one diastereomer was observed, indicating that the protonation of the intermediate is also stereodirected. These findings are in agreement with those reported on

1,3-dicarbonyl dianions[7]. Since the products are oils or foams no X-ray analysis can be exploited for the determination of the structure. However, it is very likely that they have structures analogues to those proposed by Seebach[7]. Only 1-(4-methoxyphenyl)-2-nitropropene (**4b**) gave a mixture of diastereoisomers.

Treating the dianionic intermediate **5aa** and **5ac** with strong acids (e.g. $H_2SO_4$ 2 N) at 0 °C dihydropyrrole derivatives **8aa** and **8ac** were obtained in 60% and 26% yields respectively (scheme 2). These products may arise from a Nef reaction of the nitronate function followed by acid-catalyzed cyclization of the amino function on the new carbonyl. The rate of cyclisation must be very fast, because no competive hydrolysis of the enamine was observed[8].

**Scheme 2**

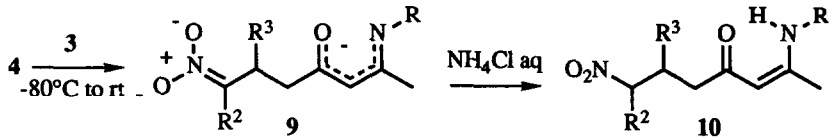



Attempts to improve the yields employing typical reactants for the Nef reaction including titanium trichloride[9] or potassium permanganate[10] were unsucessful. Moreover the cyclisation of pure **6aa** under typical Nef conditions afforded product **8aa** in comparable yields with that of the one-pot method.

***Synthesis of γ'-Nitro-β-enaminoketones.***

α'-Dianions are prepared from β-(monoalkylamino)-α,β-unsaturated ketones and 2.5 eq of a strong hindered lithium base such as lithium 2,2,6,6-tetramethylpiperidide (LTMP). To avoid a rapid intramolecular isomerisation into the more stable γ-isomer a bulky *N*-subsituent must crowd the γ position and one of the lithium ions must be strongly coordinated by both oxygen and nitrogen atoms of the enaminone moiety[1].

**Table 2.** Reaction of Enaminone Dianions **3** with Nitroolefins **4** at -80 °C followed by quenching with Ammonium Chloride at Room Temperature




| Dianion | R | $R^1$ | Nitroene | $R^2$ | $R^3$ | Product | Yield (%) |
|---|---|---|---|---|---|---|---|
| **3b** | Ph | Me | **4a** | H | Ph | **10ba** | 75 |
| **3b** | Ph | Me | **4b** | Me | *p*-$MeOC_6H_4$ | **10bb** | 64[a] |
| **3b** | Ph | Me | **4c** | Me | $PhCH_2CH_2$ | **10bc** | 77 |
| **3b** | Ph | Me | **4d** | Me | Et | **10bd** | 60 |
| **3c** | i-Pr | Me | **4a** | H | Ph | **10ca** | 68 |

[a] Recovered as a mixture of diastereoisomers in about 3:2 ratio

Under these conditions nitroalkenes exclusively undergo the attack from the α'-dianion. After the usual workup the corresponding γ-nitro-β-enaminoketones were recovered in good to high yields.

The reaction showed the same feature as the corresponding γ-alkylation: *i.e.* only one diastereomer was observed when two new stereocenters are generated except with nitroalkene **4a** and intramolecular nitroaldol reactions were never observed.

In conclusion the reaction of dianions of acylic β-(monoalkylamino)-α,β-unsaturated ketones with nitroalkenes afforded the expected conjugate addition products in good to high yields. Studies are in progress on enaminones with asymmetric nitrogen substituents in order to test the amount of asymmetric induction on the two new stereocenters formed. In a previous paper we reported the preparation of almost enantiomerically pure 1,3-diketones by the γ-alkylation of chiral enaminones.[8]

## EXPERIMENTAL

$^1$H-NMR spectra were recorded with a Bruker AW80 instrument. Chemical shifts are given in p.p.m. from $Me_4Si$ in $CDCl_3$ solutions and coupling constants are given in Hertz. IR spectra were recorded with a Perkin-Elmer FTIR spectrometer. Mass spectra were recorded with a workstation formed by an HP-5890 gaschromatograph equipped with a methyl silicone capillary column and by a HP-5970 mass detector. Melting points are uncorrected and were determined with a Kofler hot desktop. THF was dried by refluxing over sodium wires until the blue colour of benzophenone ketyl persisted and then distilling into a dry receiver under nitrogen atmosphere.

Enaminones **1a-c** were prepared according to Singh and Tandom's procedure[11]. β-Nitrostyrene is a commercial product and was used without any purification, 1-(4-methoxyphenyl)-2-nitropropene[12], 2-nitro-5-phenyl-2-pentene[13] and 2-nitro-2-pentene[13] were prepared according to the reported procedures. LTMP was prepared from equimolecular amounts of butyllithium and 2,2,6,6-tetramethylpiperidine in THF at 0 °C. Dianions **2** and **3** were prepared as previuosly described[1].

***Reaction of dianions 2 and 3 with nitroalkenes 4.***

Nitroalkenes **4** (7 mmol) were dissolved in 10 mL of THF, the solution charged in a dropping funnel and then dropped into a THF solution of the appropriate dianions **2** or **3** (5 mmol) cooling the reaction flask at -80 °C. A solid appeared and then the temperature was allowed to rise to room temperature. When the solid was dissolved the reaction mixture was quenched with saturated ammonium chloride (the mixture arising from **2a** and **4a** and that arising from **3b** and **4a** were also quenched with 5% aqueous acetic acid or with saturated aqueous sodium carbonate followed by neutralisation with 5% aqueous acetic acid), extracted with ether, washed with water, dried with anhydrous sodium sulphate and evaporated under reduced pressure. The residue was submitted to a flash-chromatographic separation on a short silica gel column (light petroleum: diethyl ether 1:1 as eluant). The following products were obtained:

1,5-diphenyl-3-(*N*-isopropylamino)-6-nitrohex-2-en-1-one **6aa**: 83%. mp 110-112 °C (diethyl ether). $\delta_H$ 1.12 (d, 3H, *J* 8); 1.22 (d, 3H, *J* 7); 2.69 (d, 2H, *J* 9, NC<u>$CH_2$</u>CH); 3.40-3.90 (m, 2H, $Me_2$CHN and $CH_2$<u>CH</u>(Ph)$CH_2$); 4.69 (d, 2H, *J* 7, $CH_2NO_2$); 5.47 (s, 1H, CH=); 6.90-7.40 (m, 8H, ArH); 7.50-7.80 (m, 2H, ArH); 11.35 (brd, 1H, *J* 10, NH). IR (KBr) $\nu_{max}$ 1598 (C=O); 1553 and 1330 ($NO_2$). m/z (%) 352 ($M^+$, 11), 306 (80), 202 (46), 146 (17), 105 (100), 77 (46). Anal calcd for $C_{21}H_{24}N_2O_3$ C, 71.57; H, 6.86; N, 7.95. Found C, 71.50; H, 6.90; N, 8.00%.

3-(*N*-isopropylamino)-5-(4-methoxyphenyl)-6-nitro-1-phenylhept-2-en-1-one **6ab**: overall yield 73%. First isomer: 44%. oil. $\delta_H$ 1.04 (d, 3H, *J* 6.3, i-Pr); 1.20 (d, 3H, *J* 6.5, i-Pr); 1.33 (d, 3H, *J* 6.2, Me); 2.50-2.80 (ABX, 2H, NC<u>$CH_2$</u>CH); 3.20-3.70 (m, 2H, $Me_2$CHN and $CH_2$<u>CH</u>(Ar)$CH_2$); 3.70 (s, 3H, OMe); 4.64-5.06 (m, 1H, $CHNO_2$); 5.25 (s, 1H, CH=); 6.73-7.16 ($A_2B_2$, 4H, ArH); 7.21-7.44 and 7.54-7.76 (m, 5H, ArH); 11.33 (brd, 1H, *J* 9.2, NH). IR (film) $\nu_{max}$ 1598 (C=O); 1549 and 1334 ($NO_2$). m/z (%) 396 ($M^+$, 11), 350 (48), 263 (23), 216 (27), 202 (30), 148 (24), 146 (27), 105 (100), 77 (40). Anal calcd for $C_{23}H_{28}N_2O_4$ C, 69.68; H, 7.12; N, 7.07. Found C, 69.60; H, 7.15; N, 7.00%. Second isomer: 56%. oil. $\delta_H$ 1.07 (d, 3H, *J* 6.0, i-Pr); 1.20 (d, 3H, *J* 6.5, i-Pr); 1.50 (d, 3H, *J* 6.7, Me); 2.38-3.00 (ABX, 2H, NC<u>$CH_2$</u>CH); 3.20-3.70 (m, 2H, $Me_2$CHN and $CH_2$<u>CH</u>(Ar)$CH_2$); 3.70 (s, 3H, OMe); 4.67-5.06 (m, 1H, $CHNO_2$); 5.46 (s, 1H, CH=); 6.70-7.20 ($A_2B_2$, 4H, ArH); 7.21-7.50 and 7.54-8.00 (m, 5H, ArH); 11.42 (brd, 1H, *J* 8.4, NH). IR (film) $\nu_{max}$ 1598 (C=O); 1549 and 1332 ($NO_2$). m/z (%) 396 ($M^+$, 8), 350 (40), 263 (19), 216 (23), 202 (24),

148 (23), 146 (27), 105 (100), 77 (36). Anal calcd for $C_{23}H_{28}N_2O_4$ C, 69.68; H, 7.12; N, 7.07. Found C, 69.70; H, 7.10; N, 7.00%.

1,7-diphenyl-3-(*N*-isopropylamino)-5-(1-nitroethyl)hept-2-en-1-one **6ac**: 67%. oil. $\delta_H$ 1.20 (d, 6H, *J* 6.3); 1.24 (d, 3H, *J* 6); 1.40-1.80 (m, 2H); 2.10-2.80 (m, 5H); 3.30-3.75 (m, 1H, CHN); 4.50-4.90 (m, 1H, $CHNO_2$); 5.54 (s, 1H, CH=); 6.80-7.40 (m, 8H, ArH); 7.70-8.00 (m, 2H, ArH); 11.50 (brd, 1H, *J* 9.3, NH). IR (film) $\nu_{max}$ 1598 (C=O); 1545 and 1329 ($NO_2$). m/z (%) 394 ($M^+$, 2), 364 (14), 320 (13), 105 (100), 98 (23), 96 (11), 91 (23), 77 (26). Anal calcd for $C_{24}H_{30}N_2O_3$ C, 73.07; H, 7.66; N, 7.10. Found C, 73.10; H, 7.65; N, 7.10%.

5-ethyl-3-(*N*-isopropylamino)-6-nitro-1-phenylhept-2-en-1-one **6ad**: 64%. oil. $\delta_H$ 1.00 (t, 3H, *J* 6, MeCH$_2$); 1.28 (d, 6H, *J* 6.2); 1.42-1.55 (m, 5H, MeCH+MeCH$_2$); 2.14-2.55 (m, 3H) 3.50-4.00 (m, 1H, CHN); 4.47-4.92 (m, 1H, $CHNO_2$); 5.59 (s, 1H, CH=); 7.26-7.51 and 7.70-8.00 (m, 5H, ArH); 11.53 (brd, 1H, *J* 9.3, NH). IR (film) $\nu_{max}$ 1599 (C=O); 1548 and 1329 ($NO_2$). m/z (%) 318 ($M^+$, 4), 105 (100), 98 (38), 96 (11), 77 (43). Anal calcd for $C_{18}H_{26}N_2O_3$ C, 67.90; H, 8.23; N, 8.80. Found C, 68.00; H, 8.25; N, 8.70%.

7-nitro-3-(*N*-phenylamino)-6-phenylhept-3-en-2-one **6ba**: 53% foam. $\delta_H$ 2.02 (s, 3H, Me); 2.63 (d, 2H, *J* 8, NCCH$_2$CH); 3.49 (quintet, 1H, CH$_2$CH(Ph)CH$_2$); 4.47 (d, 2H, *J* 8, $CH_2NO_2$); 5.16 (s, 1H, CH=); 6.60-7.50 (m, 10H, ArH); 12.22 (brs, 1H, NH). IR (film) $\nu_{max}$ 1597 (C=O); 1554 and 1379 ($NO_2$). m/z (%) 324 ($M^+$, 41), 281 (44), 278 (90), 253 (58), 232 (75), 160 (92), 118 (53), 77 (58), 43 (100). Anal calcd for $C_{19}H_{20}N_2O_3$ C, 70.35; H, 6.21; N, 6.99. Found C, 70.40; H, 6.25; N, 7.00%.

1,5-diphenyl-3-(*N*-methylamino)-6-nitrohex-2-en-1-one **6da**: 65%. foam. $\delta_H$ 2.64 [d,*J* 7.4, 2H, NCCH$_2$CH(Ph)]; 2.81 (d, *J* 5.4, 3H, MeN); 3.65-3.85 (m, 1H); 4.55-4.80 (ABX, 2H, $CH_2NO_2$); 5.46 (s, 1H, CH=); 7.2-7.4 and 7.6-7.7 (m, 8+2H, ArH); 11.29 (brq, 1H, NH). IR (film) $\nu_{max}$ 1605 (C=O); 1555 and 1385 ($NO_2$). m/z (%) 324 ($M^+$, 33), 288 (50), 278 (35), 259 (14), 219 (21), 191 (29), 183 (27), 105 (100), 77 (57). Anal calcd for $C_{19}H_{20}N_2O_3$ C, 70.35; H, 6.21; N, 6.99. Found C, 70.40; H, 6.20; N, 7.00%.

3-(*N*-methylamino)-7-nitro-6-phenylhept-3-en-2-one **6ea**: 59%. oil. $\delta_H$ 1.90 (s, 3H, MeCO) 2.73 (d, 2H, *J* 5.4, NCCH$_2$CH); 2.84 (d, 3H, *J* 5.3, NMe); 3.55-3.75 (m, 1H, CH$_2$CH(Ph)CH$_2$); 4.55-4.73 (ABX, 2H, $CH_2NO_2$); 4.80 (s, 1H, CH=); 7.00-7.40 (m, 5H, ArH); 10.62 (brq, 1H, NH). IR (film) $\nu_{max}$ 1605 (C=O); 1550 and 1390 ($NO_2$). m/z (%) 262 ($M^+$, 30), 247 (17), 219 (28), 216 (69), 191 (82), 91 (65), 59 (65), 43 (100). Anal calcd for $C_{14}H_{18}N_2O_3$ C, 64.11; H, 6.92; N, 10.68. Found C, 64.20; H, 6.95; N, 10.65%.

7-nitro-2-(*N*-phenylamino)-6-phenylhept-2-en-4-one **10ba** 75%. oil. $\delta_H$ 1.94 (s, 3H, Me); 2.74 (d, 2H, *J* 8, NCCH$_2$CH); 4.04 (m, 1H, CH$_2$CH(Ph)CH$_2$); 4.61-4.79 (ABX, 2H, $CH_2NO_2$); 5.11 (s, 1H, CH=); 6.90-7.50 (m, 10H, ArH); 12.43 (brs, 1H, NH). IR (film) $\nu_{max}$ 1596 (C=O); 1552 and 1379 ($NO_2$). m/z (%) 324 ($M^+$, 4), 160 (100), 148 (45), 145 (20), 118 (22), 77 (26). Anal calcd for $C_{19}H_{20}N_2O_3$ C, 70.35; H, 6.21; N, 6.99. Found C, 70.40; H, 6.25; N, 7.00%.

2-(*N*-phenylamino)-6-(4-methoxyphenyl)-7-nitrooct-2-en-4-one **10bb**: 64% (recovered as a mixture of diastereomers in a 3:2 ratio by NMR and GC/MS). major isomer $\delta_H$ 1.26 (d, 3H, *J* 6.8, MeCHNO$_2$); 1.85 (s, 3H, γ-Me); 2.50-2.90 (m, 2H, NCCH$_2$CH); 3.60-3.80 (m, 1H, CH$_2$CH(Ar)CH$_2$); 3.74 (s, 3H, OMe); 4.60-4.90 (m, 1H, $CHNO_2$); 4.97 (s, 1H, CH=); 6.60-7.50 (m, 9H, ArH); 12.23 (brs, 1H, NH). IR (film) $\nu_{max}$ 1590 (C=O); 1530 and 1370 ($NO_2$). m/z (%) 368 ($M^+$, 0.4), 322 (7), 189 (7), 160 (100), 118 (10), 77 (11). minor isomer $\delta_H$ 1.46 (d, 3H, *J* 6.6, MeCHNO$_2$); 1.88 (s, 3H, γ-Me); 2.50-2.90 (m, 2H, NCCH$_2$CH); 3.60-3.80 (m, 1H, CH$_2$CH(Ar)CH$_2$); 3.69 (s, 3H, OMe); 4.60-4.90 (m, 1H, $CHNO_2$); 5.03 (s, 1H, CH=); 6.60-7.50 (m, 9H, ArH); 12.29 (brs, 1H, NH). IR (film) $\nu_{max}$ 1590 (C=O); 1530 and 1370 ($NO_2$). m/z (%) 368 ($M^+$, 0.5), 322 (7), 189 (12), 160 (100), 118 (7), 77 (10). Anal calcd for $C_{21}H_{24}N_2O_4$ C, 68.46; H, 6.57; N, 7.60. Found for the mixture C, 68.40; H, 6.55; N, 7.60%.

1,8-diphenyl-2-(*N*-phenylamino)-6-(1-nitroethyl)oct-2-en-4-one **10bc**: 77%. oil. $\delta_H$ 1.49 (d, 3H, *J* 6.5 MeCHNO$_2$); 1.50-1.80 (m, 2H); 1.97 (s, 3H, γ-Me); 2.30-2.80 (m, 5H); 4.50-4.95 (m, 1H, $CHNO_2$); 5.16 (s, 1H, CH=); 6.90-7.40 (m, 10H, ArH); 12.48 (brs, 1H, NH). IR (film) $\nu_{max}$ 1596 (C=O); 1545 and 1379 ($NO_2$). m/z (%) 366 ($M^+$, 3), 336 (11), 216 (12), 160 (100), 148 (14), 132 (13), 118 (31), 91 (24), 77 (25). Anal calcd for $C_{22}H_{26}N_2O_3$ C, 72.11; H, 7.15; N, 7.64. Found C, 72.20; H, 7.15; N, 7.60%.

6-ethyl-2-(*N*-phenylamino)-7-nitrooct-2-en-4-one **10bd**: 60%. oil. $\delta_H$ 0.93 (t, 3H, *J* 7, MeCH$_2$); 1.35 (m, 2H); 1.47 (d, 3H, *J* 7, MeCHNO$_2$); 1.99 (s, 3H, γ-Me); 2.20-2.50 (m, 3H); 4.50-4.92 (m, 1H, $CHNO_2$);

5.16 (s, 1H, CH=); 7.00-7.51 (m, 5H, ArH); 12.50 (brs, 1H, NH). IR (film) $\nu_{max}$ 1597 (C=O); 1546 and 1380 ($NO_2$). m/z (%) 290 ($M^+$, 2), 160 (100), 148 (34), 132 (13), 130 (12), 118 (24), 77 (36). Anal calcd for $C_{16}H_{22}N_2O_3$ C, 66.18; H, 7.64; N, 9.65. Found C, 66.20; H, 7.65; N, 9.60%.

2-(*N*-isopropylamino)-7-nitro-6-phenylhept-3-en-4-one **10ca**: 68%. oil. $\delta_H$ 1.15 (d, 6H, *J* 6); 1.84 (s, 3H, γ-Me); 2.58 (d, 2H, *J* 9, NC<u>$CH_2$</u>CH); 3.31-4.19 (m, 2H, N<u>CH</u>$Me_2$ and $CH_2$<u>CH</u>(Ph)$CH_2$); 4.58-4.76 (ABX, 2H, $CH_2NO_2$); 4.81 (s, 1H, CH=); 6.80-7.40 (m, 5H, ArH); 12.81 (brd, 1H, *J* 8, NH). IR (film) $\nu_{max}$ 1602 (C=O); 1559 and 1379 ($NO_2$). m/z (%) 290 ($M^+$, 6), 244 (18), 145 (25), 126 (75), 114 (100), 108 (15), 84 (67), 42 (65). Anal calcd for $C_{16}H_{22}N_2O_3$ C, 66.18; H, 7.64; N, 9.65. Found C, 66.10; H, 7.60; N, 9.60%.

The reaction mixtures containing intermediates **5aa** and **5ac** were quenched with 10 mL of sulphuric acid 2 N, cooling the reaction flask with an ice bath. The mixture was then carefully neutralized with solid sodium carbonate extracted with ether, the organic layer washed with water, dried over sodium sulphate and evaporated under reduced pressure. The residue was submitted to a flash-chromatographic separation on a short silica gel column (light petroleum: diethyl ether 3:1 as eluant) leading to the following products:

(1-isopropyl-2,3-dihydro-4-phenyl-1*H*-pyrrol-2-ylidene)acetophenone **8aa**: 60%. oil. $\delta_H$ 1.41 (d, 6H, *J* 6.7); 4.20 (heptet, 1H, N<u>CH</u>$Me_2$); 4.24 (s, 2H, $CH_2$); 6.24 (s, 1H, CH=); 6.90-7.50 and 7.80-8.15 (m, 11H, ArH). IR (film) $\nu_{max}$ 1599 (C=O). m/z (%) 303 ($M^+$, 21), 198 (100), 156 (45), 128 (11), 77 (13). Anal calcd for $C_{21}H_{21}NO$ C, 83.13; H, 6.98; N, 4.62. Found C, 83.10; H, 7.00; N, 4.60%.

[1-isopropyl-2,3-dihydro-4-(2-phenylethyl)-1*H*-pyrrol-2-ylidene]acetophenone **8ac**: 26%. oil. $\delta_H$ 1.39 (d, 6H, *J* 7.1); 2.05 (s, 3H); 2.40-3.00 (m, 4H, $CH_2CH_2$); 4.23 (s, 2H, $CH_2$); 4.32 (heptet, 1H, N<u>CH</u>$Me_2$); 5.78 (s, 1H, CH=); 6.95-7.60 and 7.86-8.21 (m, 10H, ArH). IR (film) $\nu_{max}$ 1600 (C=O). m/z (%) 345 ($M^+$, 17), 254 (100), 212 (32), 197 (27), 105 (16), 91 (17), 77 (15). Anal calcd for $C_{24}H_{27}NO$ C, 83.44; H, 7.88; N, 4.05. Found C, 83.50; H, 7.90; N, 4.05%.

Pure product **6aa** (3 mmol) was dissolved in MeOH (3mL) and crushed NaOH pellets were added (4 mmol). The mixture was carefully added with sulphuric acid 2 N, cooling the reaction flask with an ice bath. The methanol was then evaporated and the crude product was worked up as above described. Product **8aa**, was recovered in 74% yield (61% calculated with respect to enaminone **1a**).

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#. Part 5, ref. 4
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(*Received in UK* 23 *May* 1994; *revised* 21 *June* 1994; *accepted* 24 *June* 1994)