SOME OBSERVATIONS ON THE REACTIVITY OF β-AMINOENONES TOWARDS PHENACYLAMINE HYDROCHLORIDE

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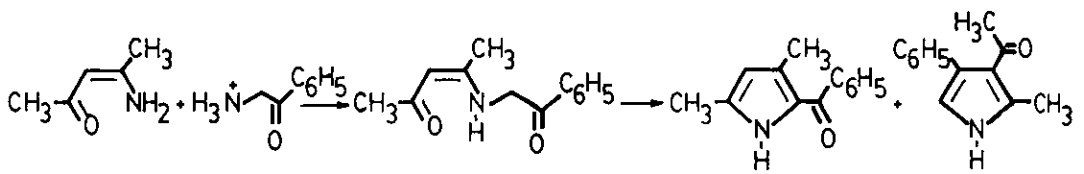
Abstract- β-Aminoenones react with phenacylamine hydrochloride to give mixture of 2- and 3-acylpyrroles. The reaction is a two steps process: formation of an isolable β-phenacylaminoenone intermediate, and cyclization of this to the final 2- and/or 3-acylpyrroles, depending on the substituents on the starting compounds.

The chemistry of pyrroles has received much attention and their synthesis has been widely studied.[1] In this sense, the starting materials more frequently used are 1,3-diketones and amino derivatives.[2] As an example, Dolphin[3] and Paine[4,5] have recently published and improved modification of the earlier Kleinspehn's method[6] using a preformed aminomalonate in the synthesis of pyrrolecarboxylates.
The transformation of 1,3-diketones into pyrroles occurs "via" an isolable β-aminoenone,[4-7] leading to a mixture of pyrrolic products, depending on the ratio of the isomeric intermediates formed in the first step.
With the object to circumvent this problem, and as a part of our continous interest in the chemistry of β-aminoenones,[8-12] we decided to examine the reactivity of these substrates towards α-aminoketone hydrochlorides, taking into account the following facts: i) β-aminoenones are regiospecifically available from isoxazoles or 1,3-diketones; ii) the primary substrates allow the regioselective preparation of N-substituted derivatives by interchange of the amino substituent.[13]



Ia II IIIa IVa Va

Scheme I

The influence of the experimental conditions (solvent, temperature, adding bases and reaction time) on the reaction was studied on 4-aminopent-3-en-2-one (Ia) as model compound, and Scheme I and Table 1 summarize the results.

Table 1. Reaction of β-aminoenone (Ia) with phenacylamine hydrochloride (II)

Run	Solvent	Temp.(°C)	Time (h)	Products (%)			
				Ia	IIIa	IVa	Va
1	Hexane	69	20	39	61	-	-
2	Benzene	76	20	86	14	-	-
3	THF	67	20	62	38	-	-
4	Acetone	56	20	20	80	-	-
5	Acetonitrile	82	2	-	100	-	-
6	Methanol	20	2	22	46	7	24
7	Methanol	20	24	-	56	10	30
8	Methanol	65	1	-	37	18	45
9	Methanol	65	2	-	-	30	70
10	Acetic Acid	117	1	-	-	40	60
11	n-Hexanol	157	0.5	-	-	36	64
12	Mesitylene	164	3	-	-	37	63
13	DMF	153	3	-	-	18	82
14	Et_3N	89	10	77	-	-	23
15	EtOH/EtONa[a]	78	2	70	-	-	30
16	EtOH/EtONa[b]	78	2	70	-	-	30

a) Ratio EtONa/II : 1/1. b) Ratio EtONa/II : 2/1.

It is interesting to note that at moderate temperature and in aprotic solvents, the reaction is easily controlled, leading to the intermediate (IIIa) (runs 1-5), while in protic solvents (runs 6-11) and/or higher temperatures (runs 10-13), the β-aminoenone is partially transformed into a mixture of acylpyrroles; the attempts to liberate the aminoketone from its hydrochloride using triethylamine as solvent or sodium ethoxide as base failed because the autocondensation of the phenacylamine.

On the other hand, we have studied the cyclization of the isolated β-aminoenone (IIIa) at different temperatures, and the results are collected on Table 2.

The results summarized in Tables 1 and 2 show that the intermediate (IIIa) is very stable in aprotic solvents, and it is transformed into a mixture of pyrroles only after a long period of heating (runs 1, 2, Table 2) or at very high temperature (runs 3, 4). On the other hand, in protic solvents, the ratio of the isomeric acyl pyrroles IVa/Va is comparable from Ia or IIIa (compare runs 9, 11, 14, 15 and 16 from Table 1 versus runs 6-9 in Table 2); on the contrary, when DMF was used as solvent, it was necessary to add ammonium chloride to reach a similar result from IIIa than obtained from Ia (runs 4, 5 in Table 2 versus 13 in Table 1). Finally,

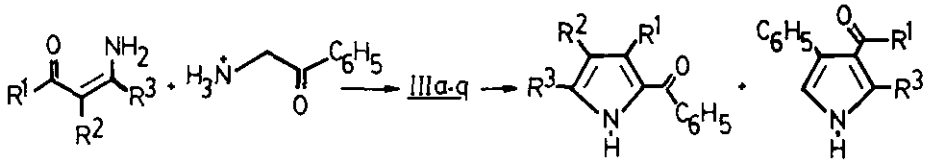
the use of a base allows to prepare regiospecifically the 3-acylpyrrole (Va) from the intermediate IIIa (runs 8 and 9 in Table 2).

Table 2. Cyclization of intermediate IIIa to acylpyrroles IVa and Va

Run	Solvent	Temp.(°C)	Time (h)	Products (%) (IVa)	(Va)
1	Hexane	69	64	33	67
2	Acetonitrile	82	50	32	68
3	Mesitylene	164	4	44	56
4	DMF	153	2	60	40
5	DMF[a]	153	2	22	78
6	Methanol	65	4	29	71
7	n-Hexanol	157	0.5	35	65
8	Et_3N	89	12	-	100
9	EtOH/EtONa	78	2	-	100
10	None	150	0.5	35	65

a) One equivalent of NH_4Cl was added.

Our interest was extended to a variety of unsymmetrically substituted β-aminoenones ($R^1 \neq R^3$) and some trisubstituted substrates ($R^2 \neq H$). The reaction was studied on two separated sets: after 1 hour at reflux of methanol (M) or ethanol (E), and until the completion of the reaction, showed by the consumption of Ia-q and IIIa-q in the mixture (tlc). Table 3 shows the obtained results.
On the substrates examined it can be observed that the rate of transamination diminishes in compounds with very high steric requeriments or two aromatic substituents (runs 24 and 25); the long period of reflux allows the hydrolysis of β-aminoenones leading to the corresponding 1,3-diketones.



Ia-q II IIIa-q IVa-q Va-q

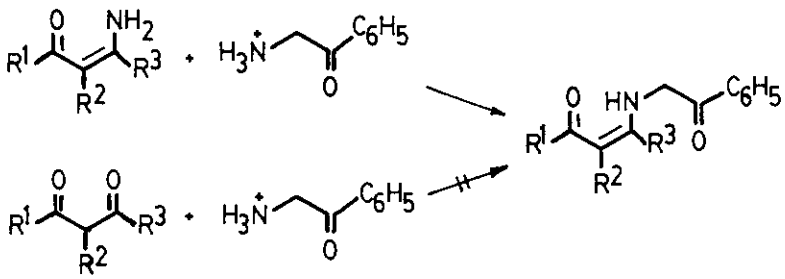
Table 3. Reactions of compouns Ia-q with phenacylamine hydrochloride II

Run	Comp.	R^1	R^2	R^3	T(h)/Sol.[a]	Products (%)			
						I	III	IV	V
1	Ia	Me	H	Me	1/M	-[b]	37	18	45
2	Ia				2/M	-[c]	-	23	64
3	Ib	Et	H	Me	1/M	13[b]	38	11	38
4	Ib				3/M	-[c]	-	15	69
5	Ic	i-Pr	H	Me	1/M	18[b]	44	2	36
6	Ic				7/M	-[c]	-	5	79
7	Id	$Ph(CH_2)_2$	H	Me	1/M	42[b]	32	4	21
8	Id				3/M	-[c]	-	13	71
9	Ie	Me	H	Et	1/M	15[b]	15	17	43
10	Ie				7/M	-[c]	-	16	64
11	If	Me	H	$Ph(CH_2)_2$	4/M	37[b,d]	-	11	33
12	If				7/M	-[c,e]	-	14	42
13	Ig	Me	Me	Me	1/M	-[c]	-	79	-
14	Ih	Me	$PhCH_2$	Me	1/M	29[b]	-	71	-
15	Ih				3/M	-[c]	-	81	-
16	Ii	Ph	H	Me	1/E	32[b]	35	4	29
17	Ii				4/E	-[c]	-	8	78
18	Ij	$4\text{-}MeOC_6H_4$	H	Me	1/E	12[b]	34	-	53
19	Ij				5/E	-[c]	-	-	73
20	Ik	$4\text{-}NO_2C_6H_4$	H	Me	4/E	60[b]	-	16	24
21	Ik				10/E	-[c]	-	30	45
22	Il	Me	H	Ph	8/E	62[b,f]	-	-	13
23					21/E	-[c,g]	-	-	34
24	Im	Ph	H	Ph	58/E	-[c,h]	-	-	30
25	In	t-Bu	H	t-Bu	42/E	20[c,i]	-	-	-
26	Io	Me	CH_2CO_2Et	Me	3/M	-[c]	-	54	-
27	Ip	Me	CO_2Et	Me	27/M	-[c,j]	-	-	-
28	Iq	Me	CH_2CN	Me	5/M	-[c]	-	10	-

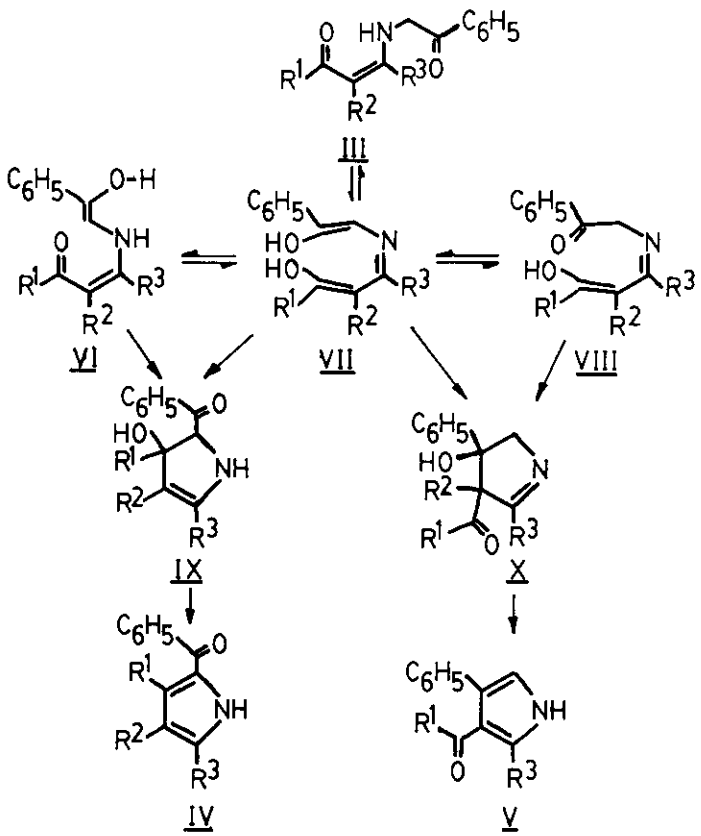
[a] The reactions were carried out at reflux of the given solvent(M: methanol, E: ethanol). [b] Yields are determined by nmr on the mixture. [c] Given yields refer to pure and isolated products. [d] In the mixture IVd (5%) and Vd (14%) were detected. [e] IVd (3%) and Vd (10%) were isolated. [f] IVi (10%) and Vi (15%) were detected on the mixture. [g] IVi (15%) and Vi (26%) were also isolated. [h] Dibenzoylmethane (70%) was isolated. [i] Dipivaloylmethane (80%) was isolated. [j] 3-Ethoxycarbonyl-2-methyl-4-phenylpyrrol (42%) was obtained.

The transformation of β-aminoenones into acylpyrroles by reaction with phenacylamine hydrochloride can be depicted as a two-steps process, being the former a

fast regioselective interchange of the amino moiety leading to the intermediate III. The rate of this step is depending on the bulk of the substituents, decreasing with the steric requeriments or their aromatic character. On the other hand, 1,3-diketones, resulting from the hydrolysis of I, can not be an intermediate because they were recovered unchanged after heating with II in identical conditions.



The second step, that is the rate determining, is the cyclization of the intermediate III or its enolic forms VI, VII, or VIII.[14] It is unclear how the steric and conformational factors influence on the distribution of the enols, but the electronic efects play an important role on the ratio of VI, VII and VIII in the



equilibrium. Thus, enols VII and VIII would be more stable than VI because its extended conjugation, and any additional conjugation will contribute to increase their concentration in the mixture.[15-17]

On the other hand, the electron withdrawing or donating ability of the group R^1 must be translated to the nucleophilic attack on the corresponding carbonyl group; thus compound Ij (R^1 = 4-$MeOC_6H_4$) leads "via" VIIj or VIIIj to Vj as a single product, while compound Ik (R^1= 4-$NO_2C_6H_4$) gives a mixture of IVk and Vk as a consequence of a competing attack on the more electrodefficient carbonyl in VIk or VIIIk.

As expected, the cyclization of 2-substituted β-aminoenones Ig, Ih, Io and Ip ($R^2 \neq H$) leads to the 2-acylpyrrole IV as a single product because the unability of their intermediates X to be transformed into the aromatic system.

Finally, the formation, in low yields of IVd and Vd from If, and IVi and Vi from Il is a well documented process[18] and could be due to an initial competing 1,2-addition process or, more probable to the isomerization of the starting aminoenone.

EXPERIMENTAL

Mp's were measured on a Büchi apparatus, in an open capillary tube and are uncorrected. Nmr were recorded on either a Varian T 60A or Bruker AC80 spectrometers and chemical shifts are given downfield from TMS as internal standard. Mass spectra were measured on a Hewlett-Packard 5988A mass spectrometer. Elemental analysis were determined on a Perkin-Elmer 240B analyzer. Starting β-aminoenones were prepared as previously described.[8,10]

Synthesis of 4-phenacylamino-3-penten-2-one (IIIa). A mixture of 990 mg (10 mmol) of 4-amino-3-penten-2-one and 1.89 g (11 mmol) of phenacylamine hydrochloride in 25 ml of acetonitrile was refluxed for 2 h. The solvent was eliminated (rotavapor) and the residue was stirred in anhydrous THF. The inorganic precipitate was filtered off and the THF solution was concentrated to dryness. The residue was recristallized from carbon tetrachloride, giving 2.06 g. (95%) of IIIa. White solid, mp 110-111°C (from CCl_4). Nmr ($CDCl_3$): 1.92 (s, 3H); 2.00 (s,3H); 4.75 (d, 2H, J= 6 Hz); 5.10 (s, 1H); 7.30-8.10 (m, 5H); 11.10 (broad s, 1H). $C_{13}H_{15}NO_2$ requires: C, 71.87; H, 6.96; N, 6.44. Found: C, 71.78; H, 6.72; N, 6.56.

Reaction of β-aminoenones with phenacylamine hydrochloride. General procedure. A mixture of β-aminoenone Ia-q (10 mmol) and phenacylamine hydrochloride (11 mmol) in 25 ml of the appropiate solvent was refluxed until total disappearance of I and III (tlc). The solvent was evaporated to dryness and the residue redissolved in anhydrous THF. The insoluble precipitate was filtered off, the solvent eliminated and the residue recrystallized or chromatographed on silica gel using ethylacetate/toluene (1/5) as eluent.

The physical and spectroscopic properties of the acylpyrroles obtained are given in the following paragraphs.

2-Benzoyl-3,5-dimethylpyrrole (IVa). White solid, mp 118-119°C (from MeOH),(lit.[19] mp 119°C). Nmr($CDCl_3$): 1.87 (s, 3H); 2.23 (s, 3H); 5.83 (d, 1H, J=3 Hz); 7.20-7.80 (m, 5H); 10.20 (broad s, 1H). Ms: m/z (%): 199(M^+); (61); 77 (100).

3-Acetyl-2-methyl-4-phenylpyrrole (Va). White solid, mp 150-151°C (from MeOH)(lit.[20] mp 150-151°C) Nmr($CDCl_3$): 2.06 (s, 3H); 2.50 (s, 3H); 6.50 (d, 1H, J=2 Hz); 7.33 (s,

5H); 9.60 (broad s, 1H). Ms: m/z (%): 199 (M^+, 50); 184 (100).

2-Benzoyl-3-ethyl-5-methylpyrrole (IVb). White solid, mp 77-78°C (from hexane-benzene). Nmr ($CDCl_3$): 1.00 (t, 3H, J=8 Hz); 2.26 (s, 3H); 2.30 (q, 2H, J=8 Hz); 5.93 (d, 1H, J= 2 Hz); 7.20-7.80 (m, 5H); 10.20 (broad s, 1H). Ms: m/z (%): 213 (M^+,43); 77 (100). $C_{14}H_{15}NO$ requires: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.70; H, 7.22; N, 6.74.

2-Methyl-4-phenyl-3-propionylpyrrole (Vb). White solid, mp 118-119°C (from MeOH). Nmr ($CDCl_3$): 0.96 (t, 3H, J= 7 Hz); 2.40 (q, 2H, J= 7 Hz); 2.46 (s, 3H); 6.45 (d, 1H, J= 2 Hz); 7.26 (s, 5H); 9.90 (broad s, 1H). Ms: m/z (%): 213 (M^+, 27); 184 (100). $C_{14}H_{15}NO$ requires: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.67; H, 7.26; N, 6.75.

2-Benzoyl-5-methyl-3-isopropylpyrrole (IVc). White solid, mp 122-123°C (from hexane-benzene). Nmr ($CDCl_3$): 1.06 (d, 6H, J= 7 Hz); 2.26 (s, 3H); 2.85 (m, 1H, J= 7 Hz); 5.95 (d, 1H, J= 2 Hz); 7.10-7.80 (m, 5H); 9.60 (broad s, 1H). Ms: m/z (%): 227 (M^+, 39); 77 (100). $C_{15}H_{17}NO$ requires: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.35; H, 7.36; N, 6.34.

3-isoButyryl-2-methyl-4-phenylpyrrole (Vc). White solid, mp 123-124°C (from MeOH). Nmr ($CDCl_3$): 0.96 (d, 6H, J= 7 Hz); 2.40 (s, 3H); 2.80 (m, 1H, J= 7 Hz); 6.50 (d, 1H, J=2 Hz), 7.25 (s, 5H); 9.60 (broad s, 1H). Ms: m/z (%): 227 (M^+,15); 184 (100). $C_{15}H_{17}NO$ requires: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.43; H, 7.71; N, 6.34.

2-Benzoyl-5-methyl-3-phenethylpyrrole (IVd). White solid, mp 96-97°C (from hexane-benzene). Nmr ($CDCl_3$): 2.26 (s, 3H); 2.65 (s, 4H); 5.92 (d, 1H, J= 2 Hz); 6.70-7.70 (m, 10H); 9.40 (broad s, 1H). Ms: m/z (%): 289 (M^+, 30); 198 (100). $C_{20}H_{19}NO$ requires: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.90; H, 6.55; N, 4.96.

2-Methyl-4-phenyl-3-(β-phenyl)propionylpyrrole (Vd). White solid, mp 87-88°C (from MeOH). Nmr ($CDCl_3$): 2.40 (s, 3H); 2.73 (m, 4H); 6.43 (d, 1H, J= 2 Hz); 6.70-7.40 (m, 5H); 7.25 (s, 5H); 9.10 (broad s, 1H). Ms: m/z (%): 289 (M^+, 41); 184 (100). $C_{20}H_{19}NO$ requires: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.17; H, 6.50; N, 4.72.

2-Benzoyl-5-ethyl-3-methylpyrrole (IVe). Yellow oil. Nmr (CCl_4): 1.20 (t, 3H, J= 7 Hz); 1.83 (s, 3H); 2.65 (q, 2H, J= 7 Hz); 5.80 (d, 1H, J= 2 Hz); 7.00-7.80 (m, 5H); 11.00 (broad s, 1H). Ms: m/z (%): 213 (M^+, 64); 212 (100). $C_{14}H_{15}NO$ requires: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.95; H, 7.22; N, 6.44.

3-Acetyl-2-ethyl-4-phenylpyrrole (Ve). White solid, mp 104-105°C (from hexane-benzene). Nmr ($CDCl_3$): 1.30 (t, 3H, J= 7 Hz); 2.10 (s, 3H); 3.00 (q, 2H, J= 7 Hz); 6.60 (d, 1H, J= 2 Hz); 7.40 (s, 5H); 9.80 (broad s, 1H). Ms: m/z (%): 213 (M^+,45); 198 (100). $C_{14}H_{15}NO$ requires: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.98; H, 7.19 N, 6.68.

2-Benzoyl-5-(β-phenyl)ethyl-3-methylpyrrole (IVf). Yellow oil. Nmr ($CDCl_3$): 1.94 (s, 3H); 2.90 (s, 4H); 5.90 (d, 1H, J= 2 Hz); 7.13 (s, 5H); 7.00-7.70 (m, 5H); 9.30 (broad s, 1H). Ms: m/z (%): 289 (M^+, 9); 77 (100). $C_{20}H_{19}NO$ requires: C,83.01 H, 6.62; N, 4.84. Found: C, 82.86; H, 6.56; N, 4.96.

3-Acetyl-2-(β-phenyl)ethyl-4-phenylpyrrole (Vf). White solid, mp 157-158°C (from MeOH). Nmr ($CDCl_3$): 2.03 (s, 3H); 3.08 (m, 4H); 6.46 (d, 1H, J= 2 Hz); 7.17 (s,5H); 7.30 (s, 5H); 8.90 (broad s, 1H). Ms: m/z (%): 289 (M^+, 26); 198 (100). $C_{20}H_{19}NO$ requires: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.17; H, 6.51; N, 4.93.

2-Benzoyl-3,4,5-trimethylpyrrole (IVg). White solid, mp 134-135°C (from MeOH). (lit.[21] mp 136°C). Nmr (CCl_4): 1.72 (s, 3H); 1.86 (s, 3H); 2.23 (s, 3H); 7.20-7.80 (m, 5H); 11.20 (broad s, 1H). Ms: m/z (%): 213 (M^+, 45); 77 (100).

2-Benzoyl-4-benzyl-3,5-dimethylpyrrole (IVh). White solid, mp 112-113°C (from MeOH). Nmr (CCl_4): 1.70 (s, 3H); 2.25 (s, 3H); 3.70 (s, 2H); 7.05 (s, 5H); 7.20-7.80 (m, 5H); 11.20 (broad s, 1H). Ms: m/z (%): 289 (M^+, 82); 77 (100). $C_{20}H_{19}NO$ requires: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.18; H, 6.57; N, 4.71.

2-Benzoyl-5-methyl-3-phenylpyrrole (IVi). White solid, mp 156-157°C (from EtOH). Nmr ($CDCl_3$): 2.40 (s, 3H); 6.10 (d, 1H, J= 2 Hz); 7.00 (s, 5H); 7.00-7.60 (m, 5H); 11.20 (broad s, 1H). Ms: m/z (%): 261 (M^+, 94); 260 (100). $C_{18}H_{15}NO$ requires: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.86; H, 5.66; N, 5.24.

3-Benzoyl-2-methyl-4-phenylpyrrole (Vi). White solid, mp 230-231°C (from EtOH) (lit.[22] mp 231°C). Nmr ($CDCl_3$/DMSO-d_6): 2.26 (s, 3H); 6.75 (d, 1H, J= 2 Hz); 7.03 (s, 5H); 7.10-7.70 (m, 5H); 11.20 (broad s, 1H). Ms: m/z (%): 261 (M^+, 73); 260 (100).

3-(p-Methoxy)benzoyl-2-methyl-4-phenylpyrrole (Vj). White solid, mp 222-223°C (from EtOH). Nmr ($CDCl_3$/DMSO-d_6): 2.30 (s, 3H); 3.83 (s, 3H); 6.90 (d, 2H, J= 10 Hz); 6.93 (d, 1H, J= 2 Hz); 7.20 (s, 5H), 7.80 (d, 2H, J= 10 Hz); 11.20 (broad s, 1H). Ms: m/z (%): 291 (M^+, 79); 290 (100). $C_{19}H_{17}NO_2$ requires: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.51; H, 6.01; N, 4.68.

2-Benzoyl-5-methyl-3-(p-nitrophenyl)pyrrole (IVk). Yellow solid, mp 227-228°C (from EtOH). Nmr ($CDCl_3$/DMSO-d_6): 2.36 (s, 3H); 6.20 (d, 1H, J= 2 Hz); 7.00-7.70 (m,7H); 7.93 (d, 2H, J= 8 Hz); 11.90 (broad s, 1H). Ms: m/z (%): 306 (M^+, 100). $C_{18}H_{14}N_2O_3$ requires: C, 70.58; H, 4.61; N, 9.14. Found: C, 70.48; H, 4.72; N, 9.28.

2-Methyl-3-(p-nitrobenzoyl)-4-phenylpyrrole (Vk). Yellow solid, mp 250-251°C (from EtOH). Nmr ($CDCl_3$/DMSO-d_6): 2.38 (s, 3H); 6.80 (d, 1H, J= 2 Hz); 7.03 (s, 5H);7.70 (d, 2H, J= 8 Hz); 8.00 (d, 2H, J= 8 Hz); 11.50 (broad s, 1H). Ms: m/z (%): 306 (M^+, 100). $C_{18}H_{14}N_2O_3$ requires: C, 70.58; H, 4.61; N, 9.14. Found: C, 70.77; H, 4.72; N, 9.30.

3-Acetyl-2,4-diphenylpyrrole (Vl). White solid, mp 208-209°C (from EtOH). Nmr ($CDCl_3$): 2.00 (s, 3H); 6.76 (d, 1H, J= 2 Hz); 7.26 (s, 5H); 7.20-7.70 (m, 5H); 11.20 (broad s, 1H). Ms: m/z (%): 261 (M^+, 54); 246 (100). $C_{18}H_{15}NO$ requires: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.58; H, 5.66; N, 5.47.

3-Benzoyl-2,4-diphenylpyrrole (Vm). White solid, mp 183-184°C (from EtOH). Nmr ($CDCl_3$): 6.75 (d, 1H, J=2 Hz); 7.00-8.20 (m, 15H); 9.50 (broad s, 1H). Ms:m/z (%): 323 (M^+, 93); 246 (100). $C_{23}H_{17}NO$ requires: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.51; H, 5.24; N, 4.28.

Ethyl (2-benzoyl-3,5-dimethyl)-4-pyrrolylacetate(IVo). White solid, mp 111-112°C (from MeOH). Nmr ($CDCl_3$): 1.20 (t, 3H, J= 7 Hz); 1.85 (s, 3H); 2.25 (s, 3H); 3.35 (s, 2H); 4.10 (q, 2H, J= 7 Hz); 7.20-7.80 (m, 5H); 10.30 (broad s, 1H). Ms: m/z (%): 285 (M^+, 31); 77 (100). $C_{17}H_{19}NO_3$ requires: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.68; H, 6.61; N, 4.73.

2-Benzoyl-4-cyanomethylene-3,5-dimethylpyrrole(IVq). White solid, mp 148-149°C (from MeOH). Nmr ($CDCl_3$/DMSO-d_6): 1.87 (s, 3H); 2.22 (s, 3H); 3.38 (s, 2H); 7.10-7.90 (m, 5H); 10.70 (broad s, 1H). Ms: m/z (%): 238 (M^+, 99); 210 (100). $C_{15}H_{14}N_2O$ requires: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.46; H, 5.80; N, 11.89.

Reaction of β-aminoenones Ia-q with phenacylamine hydrochloride in alcohols at reflux for 1 h. A mixture of 1 mmol of β-aminoenone Ia-q and 1.1 mmol of phenacylamine hydrochloride was refluxed in 2.5 ml of anhydrous methanol or ethanol for 1 h. The solvent was eliminated to dryness and the product was taken in 5 ml of anhydrous THF. The residue of ammonium chloride was filtered off and the solvent of the filtrate was eliminated. The residue was disolved in $CDCl_3$ and the nmr was registered. The ratio of products on the mixture was determined by integration of the proton at the conjugated system on III versus the protons at C-4 (in pyrroles IV) and C-5 (in pyrroles V).

The nmr data for intermediates IIIb-j are as follows:

5-Phenacylaminehex-4-en-3-one (IIIb). Nmr ($CDCl_3$): 1.07(t, 3H, J= 7 Hz); 1.93(s, 3H); 2.25(q, 2H, J= 7 Hz); 4.71(d, 2H, J= 6 Hz); 5.08(s, 1H); 7.30-8.00(m, 5H); 11.16(t, 1H, J= 6 Hz).

6-Phenacylamine-2-methylhept-5-en-4-one (IIIc). Nmr ($CDCl_3$): 1.08(d, 6H, J= 7 Hz); 1.92(s, 3H); 2.45(m, 1H, J= 7 Hz); 4.72(d, 2H, J= 6 Hz); 5.10(s, 1H); 7.30-8.00(m, 5H); 11.23(broad, 1H).

5-Phenacylamine-1-phenylhex-4-en-3-one (IIId). Nmr ($CDCl_3$): 1.88(s, 3H); 2.74(m, 4H); 4.65(d, 2H, J= 6 Hz); 5.10(s, 1H); 7.25(s, 5H); 7.30-8.00(m, 5H); 11.30(t, 1H, J= 6 Hz).

4-Phenacylaminehex-3-en-2-one (IIIe). Nmr ($CDCl_3$): 1.13(t, 3H, J= 7 Hz); 2.02(s, 3H); 2.18(q, 2H, J= 7 Hz); 4.70(d, 2H, J= 6 Hz); 5.07(s, 1H); 7.30-8.00(m, 5H); 11.20(broad, 1H).

1-Benzoyl-2-phenacylaminepropene (IIIi). Nmr ($CDCl_3$): 2.03(s, 3H); 4.95(d, 2H, J= 6 Hz); 5.85(s, 1H); 7.30-8.20(m, 10H); 11.70(t, 1H, J= 6 Hz).

1-(p-Methoxyphenyl)-2-phenacylaminepropane (IIIj). Nmr ($CDCl_3$): 2.10(s, 3H); 3.77 (s, 3H); 5.03(d, 2H, J= 6 Hz); 5.90(s, 1H); 7.06(d, 2H, J= 9 Hz); 7.10-7.90(m, 5H); 8.02(d, 2H, J= 9 Hz); 11.70(m, 1H).

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