Benzoxazol-2(3*H*)-one and 1,3,4-Oxadiazol-2(3*H*)-one Derivatives from Substituted Enaminones and Ketoenamines (1)

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Enaminones and ketoenamines bearing a hydrazine type substituent undergo side chain thermal cyclization, the former into benzoxazol-2(3*H*)-one derivatives and the latter into 1,3,4-oxadiazol-2(3*H*)-one derivatives. Factors affecting such reactions are discussed.

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Introduction.

The reactivity of diimides of type X-N=N-CO-Y (X = CO_2Et, Y = OEt; X = CO-Ar, Y = Ar; X = Y = Ar; X = CO_2Et, Y = Ar) with enamines from cyclohexanones has been previously reported. 1,3,4-Oxadiazine derivatives, not always isomerizable into the corresponding enaminic adducts, were the products of these reactions (2-4), except in the case of diethoxycarbonyldiimide (DCD) (**3a**) which furnished trisubstituted enamines exclusively (5). With other electron rich olefins, such as vinyl ethers (6) or ketene acetals (7), such a diimide is reported to give 1,3,4-oxadiazine derivatives, although of rather low stability.

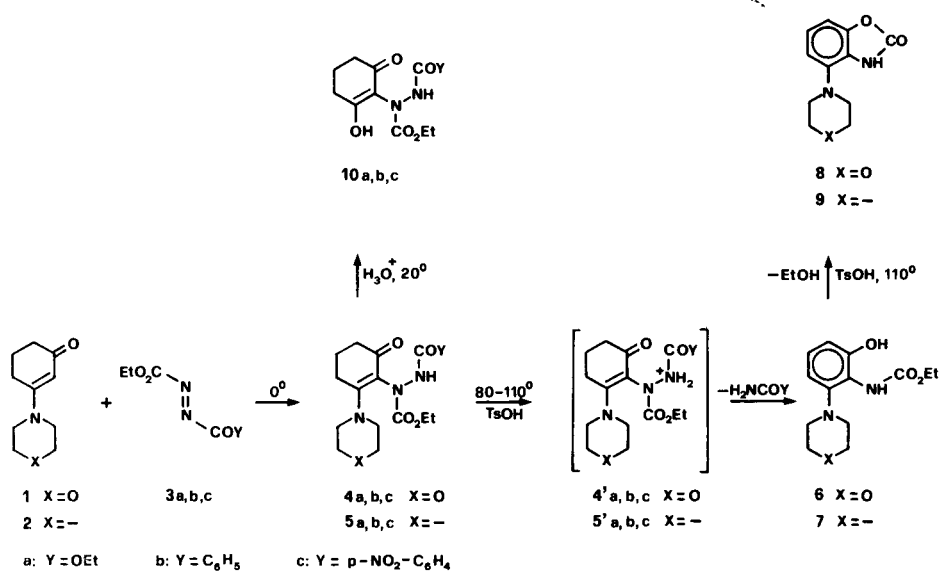
The reactions of aryl aroyl diimides with enaminones **1** and **2** and ketoenamines **11** and **12** have also been studied. They are the subject of a very recent paper (8) that will appear shortly. These substrates had been taken into consideration in order to investigate the effects of a C=O group, fully- and cross-conjugated with the N-C=C system, respectively, on their reactivity. The ketoenamines **11** and **12** reacted easily with such diimides, whilst the enaminones **1** and **2** proved to be unreactive. Such a result was rather unexpected and was explained in terms of steric hindrance of the aryl group bonded to the electrophilic nitrogen atom. In fact the same enaminones react quantitatively with DCD (9). These observations prompted us to investigate the behaviour of the same substrates **1, 2, 11,** and **12** towards aroyl ethoxycarbonyl diimides **3b,c** *i.e.* diimides less sterically hindered with respect to aryl aroyl diimides and presenting a partial structural analogy with DCD. Furthermore the reactivity of DCD (**3a**) with **11** and **12** was also investigated.

Results and Discussion.

a) Reactions With Enaminones 1 and 2.

Aroyl ethoxycarbonyl diimides **3b,c** reacted smoothly with the enaminones **1** and **2** always leading to the exclusive formation of the open chain adducts **4b,c** and **5b,c**, respectively, the structure of which followed from spectral data. In their ir and ^{1}H-nmr spectra the presence of NH groups was evident; furthermore the ^{1}H-nmr spectra showed no signals around δ 5. In this region the C-4a proton

SCHEME 1



resonances of 1,3,4-oxadiazine derivatives or the vinylic and C-2 proton signals of less probable trisubstituted enamine derivatives would have appeared. Such results parallel those obtained in the reactions of the same enaminones with DCD (**3a**) (9), and clearly indicate the tendency of the conjugated N-C=C-C=O system to be maintained. The adducts **4a** and **5a** undergo an aromatization reaction, on heating at 80° under acidic conditions, with formation of aromatic urethanes **6** and **7** which, in turn, can be transformed into benzoxazol-2(3*H*)-one derivatives **8** and **9** (9). Also enaminones **4b,c** and **5b,c** underwent the same transformations, but more drastic conditions were required for the reaction to occur. Under such conditions heterocyclic derivatives **8** and **9** in admixture with phenylurethanes **6** and **7** and relevant amounts of tarry products were obtained. Of importance is the separation from the crudes of amides Y-CO-NH_2 (Y = C_6H_5, *p*-NO_2-C_6H_4), since this fact indicates that the aromatization surely occurs by cleavage of the N-N bonds in the protonated species **4'a,b,c** and **5'a,b,c**, as depicted in Scheme 1. However we have not sought to establish whether the mechanism of such aromatization reactions is a concerted one or implies the intermediacy of nitrenium ions.

The formation of the benzoxazolone derivatives *via* arylurethanes from adducts **4b,c** and **5b,c** is a further proof that in the reactions with enamines the electrophilic site of the diimides **3b,c** is the nitrogen atom bearing the ethoxycarbonyl group. This conclusion was previously drawn on the basis of spectral evidence (4).

b) Reactions of Ketoenamines **11** and **12**.

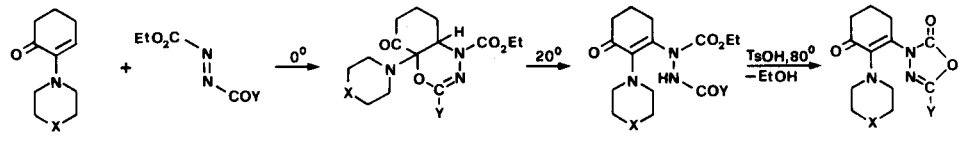
The morpholine derivative **11** reacting with **3a** gave only the ketoenaminic adduct **14a**, as shown by ir and ^{1}H-nmr spectral data. From the reaction of **11** with **3b**, besides the open chain adduct **14b**, the 1,3,4-oxadiazine derivative **13b** was formed in 20% yield. The mixture composition was determined by integration of the signal related to the C-4a proton of the oxadiazine system in the ^{1}H-nmr spectrum. Finally, when **11** reacted with **3c** only the heterocyclic derivative **13c** was obtained, as shown by spectral evidences. In fact in its ir spectrum lack of NH bands, two strong C=O absorptions at 1692 (ethoxycarbonyl C=O) and at 1725 cm^{-1} (C=O), and a weak band at 1615 cm^{-1} (C=N) were observed, while in its ^{1}H-nmr spectrum a multiplet of area 1, corresponding to the C-4a proton, was present at δ 4.85. Such 1,3,4-oxadiazine derivatives **13b,c** rearranged into the corresponding isomers **14b,c** on standing in solutions at room temperature. The rearrangements were followed monitoring the ^{1}H-nmr spectra, were the multiplets of the C-4a protons gradually disappeared, while a change in the signals of the aromatic protons, owing to the overlap with the appearing NH peaks was observed. Attempted ring openings on refluxing in various solvents (light petroleum, benzene, ethanol) led to a complete or partial heterocyclization of the side chain at C-3, as described later.

As for the pyrrolidine derivative **12**, the reactions with **3a,b,c** always furnished adducts of ketoenaminic type, *i.e.* **15a,b** and **17c**, respectively. The latter had as a substituent at C-3 an 1,3,4-oxadiazolone ring deriving from cyclization of the side chain.

Factors affecting the formation and the stability of the 1,3,4-oxadiazine *versus* enamine derivatives have already been discussed (4,8).

As for the structure of **17c**, its ^{1}H-nmr spectrum showed no ester ethyl resonances and in its ir spectrum the absorption characteristic of a γ-lactone C=O group was present at 1770 cm^{-1}. The analogous compounds **16b,c** and **17b** were obtained from adducts **14b,c** and **15b**, respectively, on refluxing in benzene by acidic catalysis (Scheme 2). These results were rather unexpected, since the corresponding *N*-aroyl-*N'*-ethoxycarbonylhydrazines were recovered unchanged when heated under the same conditions, and to obtain the 5-phenyl-1,3,4-oxadiazol-2(3*H*)-one from the corresponding hydrazine more drastic conditions were required (10). The ease of cyclization of the side chains of these adducts must be correlated with the electronwithdrawing effect of the C=C-C=O system that should increase the acidity of the NH protons. A further important factor should be the basic strength of the amine moiety, the nitrogen of which could be involved in the detachment of the NH proton, through a six membered ring transition state. The presence of an electronwithdrawing group in the aromatic ring can aid the proton abstraction process. In this way the direct formation of **17c** is explained.

SCHEME 2



11 X=O
12 X=–

3a,b,c

13b,c X=O

14a,b,c X=O
15a,b X=–

16b,c X=O
17b,c X=–

a: Y=OEt b: Y=C_6H_5 c: Y=p-NO_2-C_6H_4

As far as derivatives **14a** and **15a** are concerned, they did not give an analogous cyclization in their side chains, but it is also worth noting that they resisted any aromatization and were recovered unchanged from their reaction solutions, when treated under the same conditions as those determining the transformations of **4a** and **5a** into **6** and **7** or **8** and **9**, respectively. Attempts of heterocyclization or aromatization by employing higher boiling solvents such as toluene or xylene were unsuccessful and resulted in extensive formation of tarry products.

c) Hydrolysis Reactions.

The hydrolyses of adducts **4a,b,c** and **5a,b,c** were very slow; in fact only after 30 days the corresponding 2-substituted 1,3-cyclohexanediones **10a,b,c** were obtained, albeit in poor yields. As for the ketoenaminic adducts **14a,b,c, 15a,b, 16b,c**, and **17b,c** they proved very resistant to hydrolysis. Even over a very long time (30 days), they were partly recovered unchanged and partly gave a mixture of unidentified products (tlc) from which no type of ketone could be isolated, after column or plate chromatography.

On the other hand, these results are not surprising considering the data reported in literature on the hydrolysis of enaminones (11) and unsubstituted ketoenamines (12).

EXPERIMENTAL

Melting points are uncorrected and were determined on a Büchi apparatus. Unless otherwise stated, ir spectra were measured for Nujol mulls with a Perkin-Elmer 297 spectrophotometer with polystyrene calibration. ^{1}H-nmr spectra were recorded at 60 MHz for deuteriochloroform solutions, unless otherwise noted, at 20° with a JEOL JNM spectrometer; a number of spectra were obtained on a Bruker WP Pulsed Fourier Transform spectrometer operating at 80 MHz; chemical shifts are reported in ppm downfield from tetramethylsilane; exchangeable protons were detected by deuterium oxide-d_2 addition. Microanalyses were carried out on a Hewlett-Packard 185 instrument. Analytical tlc and column chromatography were performed on silica gel G (Merck) and silica gel 60 (Merck, 70-230 mesh ASTM), respectively.

Enaminones **1** (13), **2** (12) and ketoenamines **11** (14) and **12** (15) were prepared by azeotropic removal of water (16) from the appropriate ketones and 1.5 excess amines in refluxing benzene, in the dark. Diethoxycarbonyldiimide (**3a**) was purchased from Aldrich Chemicals Co. and distilled prior to use. Diimides **3b** (17) and **3c** (4) were prepared by oxidation of the corresponding *N,N'*-disubstituted hydrazines with *N*-bromosuccinimide.

a) Reactions of Enaminones **1, 2** and Ketoenamines **11, 12** With Diimides **3a,b,c**.

General Procedure.

A solution of diimide (10 mmoles) in 10 ml of anhydrous benzene was added dropwise and under nitrogen to a stirred solution of an equimolar amount of enaminic reagent in 20 ml of the same solvent cooled in an ice-bath. The mixture was set aside at 0° for 48-72 hours, until the red colour of the diimide was discharged. Removal of the solvent under reduced pressure and at room temperature left a semisolid residue which crystallized by addition of anhydrous ether and after short standing at 0°.

The reactions of **1** and **2** with **3a** have been already reported (9). From **1** and **2**, by reaction with **3b,c** the corresponding adducts **4b,c** and **5b,c** were obtained.

The reactions of **11** and **12** with diimide **3a** furnished **14a** and **15a**, respectively, in quantitative yields.

2-(Morpholin-4-yl)-3-(*N,N'*-diethoxycarbonyl)hydrazinocyclohex-2-en-1-one (**14a**).

This compound was obtained as off white crystals, mp 116-119° (triturated with anhydrous ether); ir: 3295 (NH), 1765, 1700 (ethoxycarbonyl C=O), 1660 (C=O), 1625 cm^{-1} (N-C=C); ^{1}H-nmr: δ 7.98 (broad s, NH, 1H).

Anal. Calcd. for $C_{16}H_{25}N_3O_6$: C, 54.07; H, 7.09; N, 11.82. Found: C, 54.17; H, 7.17; N, 11.9.

2-(Pyrrolidin-1-yl)-3-(*N,N'*-diethoxycarbonyl)hydrazinocyclohex-2-en-1-one (**15a**).

This compound was obtained as pale yellow crystals, mp 103-105°

Table

Compound	Formula	Analysis Calcd./Found C	H	N	Mp (°C)	Yield (%)	IR (cm^{-1}) (a) NH	CO_2Et	COY	C=N	^{1}H-nmr (δ) (a) H-4a	NH
4b	$C_{20}H_{25}N_3O_5$	62.0 (62.3)	6.50 (6.55)	10.85 (10.75)	126-127 (b)	67	3180	1740	1670			8.9 (br s, 1)
4c	$C_{20}H_{24}N_4O_7$	55.55 (55.7)	5.59 (5.62)	12.96 (12.89)	166-167 (c)	65	3160	1730	1675			9.5 (br s, 1)
5b	$C_{20}H_{25}N_3O_4$	64.67 (64.6)	6.78 (6.75)	11.31 (11.25)	144-146 (b)	59	3180	1735	1670			8.9 (br s, 1)
5c	$C_{20}H_{24}N_4O_6$	57.69 (57.80)	5.81 (5.83)	13.45 (13.32)	174-175 (c)	50	3240	1705	1680			9.1 (br s, 1)
13b + 14b	$C_{20}H_{25}N_3O_5$	62.0 (62.3)	6.50 (6.55)	10.85 (10.81)	50-75 (d)	80	3300 (e)	1700 br	1680	1620 br	4.85 (m,0.2)	(f)
14b		(61.8)	(6.53)	(11.0)	60-82 (d,g)	100	3300 (e)	1720	1680			(f)
13c	$C_{20}H_{24}N_4O_7$	55.55 (55.75)	5.59 (5.42)	12.96 (13.0)	130-132 (h)	60		1692		1615	4.85 (m,1)	
14c		(55.3)	(5.57)	(13.1)	94-95 (h)	100	3280	1725	1680			(f)
15b	$C_{20}H_{25}N_3O_4$	64.67 (64.7)	6.78 (6.75)	11.31 (11.29)	104-105 (i)	58	3360	1735	1680			8.65 (br s, 1)

(a) br = broad. (b) Off white powder, after washing with anhydrous ether. (c) Yellow crystals, from absolute ethanol. (d) Glass-like off white product, after washing with light petroleum bp 30-50°. (e) Recorded in carbon tetrachloride solution. (f) Missing, superimposed with aromatic protons. (g) Homogeneous on tlc (eluant: benzene-acetone 9:1). (h) Yellow crystals, after washing with anhydrous ether. (i) Pale yellow crystals, after washing with anhydrous ether.

(ligroin); ir: 3280 (NH), 1745, 1700 (ethoxycarbonyl C=O), 1670 (C=O), 1595 cm^{-1} (N-C=C); ^{1}H-nmr: δ 7.5 (broad s, NH, 1H).

Anal. Calcd. for $C_{16}H_{25}N_3O_5$: C, 56.62; H, 7.42; N, 12.38. Found: C, 56.8; H, 7.36; N, 12.3.

From the reaction between **11** and **3b** a mixture of 2-phenyl-4-ethoxycarbonyl-8-oxo-1,3,4-oxadiazine (**13b**) and the isomeric 2-(morpholin-4-yl)-3-(*N*-ethoxycarbonyl-*N'*-benzoyl)hydrazinocyclohex-2-en-1-one (**14b**) in a 1:4 ratio was obtained.

From **11** and **3c** the 1,3,4-oxadiazine derivative **13c** was obtained exclusively. Both **13b,c** rearranged quantitatively into the corresponding enaminic isomers **14b,c** within 48 hours, on standing at room temperature in chloroform solution.

From ketoenamine **12** and **3b** the adduct **15b** was formed, while in the reaction with **3c** the heterocyclic derivative **17c** was obtained (see under section c). Yields, physical, analytical and the more significant spectral data for structural assignments of adducts **4b,c**, **5b,c**, **13b,c** **14b,c**, and **15b** are reported in the Table.

b) Thermolysis of Adducts **4b,c** and **5b,c**.

Toluene solutions of the title adducts and *p*-toluenesulphonic acid in a 15:1 molar ratio were refluxed under nitrogen for 4 days in the dark until tlc (eluant: benzene-acetone 4:1) indicated the disappearance of starting materials and the presence of the benzoxazol-2(3*H*)-one derivatives **8** and **9**, the amides H_2N-CO-Y (Y = C_6H_5, *p*-NO_2-C_6H_4), and the 2-hydroxy-6-aminophenylurethanes **6** and **7**, the latter ones as the minor components, together with other unidentified products. By treatment of the crudes with acetonitrile, **8** and **9** were isolated (30-35%), while on column chromatography (eluant: benzene-acetone, gradient polarity) phenylurethanes **6** and **7** (10-15%) and the amides (50-55%) were separated. Authentic samples of **6** and **7** were prepared by refluxing **4a** and **5a** in benzene for 24 hours, in the presence of *p*-toluenesulphonic acid (9). Authentic samples of **8** and **9** (9), were obtained from **6** and **7**, respectively, when heated in toluene for 24 hours, in the presence of catalytic amounts of *p*-toluenesulphonic acid.

2-Hydroxy-6-(morpholin-4-yl)phenylurethane (**6**).

This compound was obtained as white crystals, mp 108-109° (absolute ethanol); ir: 3280 (OH), 3140 (NH), 1685 cm^{-1} (ethoxycarbonyl C=O); ^{1}H-nmr: δ 1.43 (t, CH_3, 3H), 4.24 (q, CH_2, 2H), 6.75 (m, aromatic, 3H), 7.73 (broad s, NH, 1H), 9.2 (broad s, OH, 1H).

Anal. Calcd. for $C_{13}H_{16}N_2O_4$: C, 58.64; H, 6.81; N, 10.52. Found: C, 58.50; H, 6.89; N, 10.58.

2-Hydroxy-6-(pyrrolidin-1-yl)phenylurethane (**7**).

This compound was obtained as white crystals, mp 72-74° (benzene-light petroleum); ir: 3270-3250 (OH + NH), 1695, 1675 cm^{-1} (ethoxycarbonyl C=O); ^{1}H-nmr: δ 1.33 (t, CH_3, 3H), 4.27 (q, CH_2, 2H), 6.9 (m, aromatic, 3H), 7.3 (broad s, NH, 1H), 8.95 (broad s, OH, 1H).

Anal. Calcd. for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.48; H, 7.22; N, 11.13.

4-(Morpholin-4-yl)benzoxazol-2(3*H*)-one (**8**).

This compound was obtained as white crystals, mp 232-234° (acetonitrile); ir: 3180 (NH), 1760 cm^{-1} (C=O); ^{1}H-nmr (acetone-d_6): δ 7.0 (m, aromatic, 3H), 10.45 (broad s, NH, 1H).

Anal. Calcd. for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 60.11; H, 5.51; N, 12.80.

4-(Pyrrolidin-1-yl)benzoxazol-2(3*H*)-one (**9**).

This compound was obtained as off white crystals, mp 205-206° (acetonitrile); ir: 3280 (NH), 1755 cm^{-1} (C=O); ^{1}H-nmr (acetone-d_6): δ 6.65 (m, aromatic, 3H), 10.83 (broad s, NH, 1H).

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.80; H, 5.96; N, 13.78.

c) Side Chain Heterocyclization Reactions.

Ketoenaminic adduct **14b** was refluxed in anhydrous benzene for 6 hours, in the presence of catalytic amounts of *p*-toluenesulphonic acid, leading quantitatively to **16b**. The analogous compounds **16c** and **17b** were obtained, also in quantitative yields, on heating the adducts **14c** and **15b**, respectively, under the same conditions but only for 10 minutes.

2-(Morpholin-4-yl)-3-(5-phenyl-1,3,4-oxadiazol-2(3*H*)-on-3-yl)cyclohex-2-en-1-one (**16b**).

This compound was obtained as white crystals, mp 162-164° (absolute ethanol); ir: 1770 (heterocyclic C=O), 1680 (carbocyclic C=O), 1620, 1600, 1570 cm^{-1} (N-C=C, monosubstituted benzene, C=N).

Anal. Calcd. for $C_{18}H_{19}N_3O_4$: C, 63.33; H, 5.61; N, 12.31. Found: C, 63.38; H, 5.60; N, 12.30.

2-(Morpholin-4-yl)-3-(5-*p*-nitrophenyl-1,3,4-oxadiazol-2(3*H*)-on-3-yl)cyclohex-2-en-1-one (**16c**).

This compound was obtained as pale orange crystals, mp 196-198° (absolute ethanol); ir: 1775 (heterocyclic C=O), 1680 (carbocyclic C=O), 1620, 1600, 1580 cm^{-1} (N-C=C, disubstituted benzene, C=N).

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 55.96; H, 4.70; N, 14.5. Found: C, 55.7; H, 4.67; N, 14.45.

2-(Pyrrolidin-1-yl)-3-(5-phenyl-1,3,4-oxadiazol-2(3*H*)-on-3-yl)cyclohex-2-en-1-one (**17b**).

This compound was obtained as yellow crystals, mp 108° (benzene-ligroin); ir: 1780 (heterocyclic C=O), 1680 (carbocyclic C=O), 1615, 1600, 1590, 1575 cm^{-1} (N-C=C, monosubstituted benzene, C=N).

Anal. Calcd. for $C_{18}H_{19}N_3O_3$: C, 66.45; H, 5.89; N, 12.91. Found: C, 66.65; H, 5.91; N, 12.82.

2-(Pyrrolidin-1-yl)-3-(5-*p*-nitrophenyl-1,3,4-oxadiazol-2(3*H*)-on-3-yl)cyclohex-2-en-1-one (**17c**).

This compound was obtained as orange crystals, mp 192° (acetone); ir: 1770 (heterocyclic C=O), 1680 (carbocyclic C=O), 1610, 1590, 1580 cm^{-1} (N-C=C, disubstituted benzene, C=N).

Anal. Calcd. for $C_{18}H_{18}N_4O_5$: C, 58.37; H, 4.90; N, 15.13. Found: C, 58.45; H, 4.94; N, 15.06.

d) Hydrolysis of Enaminic Adducts **4a,b,c** and **5a,b,c**.

To a stirred solution of the title compounds in acetone-10% hydrochloric acid was added until acidity. The solutions were kept for 30 days at room temperature in the dark. The reactions were followed on tlc (eluant: benzene-acetone 4:1). After neutralization with sodium bicarbonate, the solvent was removed under reduced pressure and at room temperature, furnishing the 2-substituted-1,3-cyclohexanedione derivatives **10a,b,c**. The exclusive enolic forms of such ketones were substantiated by their ^{1}H-nmr spectra showing singlets of area 1 around δ 11 for OH groups.

2-(*N,N'*-Diethoxycarbonyl)hydrazino-1,3-cyclohexanedione (**10a**).

This compound was obtained as white crystals, mp 80° (washed with diethyl ether), (40%); ir: 3240 broad (NH + OH), 1735, 1690 cm^{-1} (ethoxycarbonyl C=O); ^{1}H-nmr: δ 8.38 (broad s, NH, 1H), 10.62 (broad s, OH, 1H).

Anal. Calcd. for $C_{12}H_{18}N_2O_6$: C, 50.35; H, 6.34; N, 9.79. Found: C, 50.25; H, 6.33; N, 9.70.

2-(*N*-Ethoxycarbonyl-*N'*-benzoyl)hydrazino-1,3-cyclohexanedione (**10b**).

This compound was obtained as white crystals, mp 163-164° (40%) (benzene-ligroin 1:1); ir: 3220 broad (NH + OH), 1725 (ethoxycarbonyl C=O), 1650 sh, 1630 cm^{-1} (C=O); ^{1}H-nmr: δ 10.05 (broad s, OH, 1H). The NH signal is hidden by the multiplet of the aromatic protons.

Anal. Calcd. for $C_{16}H_{18}N_2O_5$: C, 60.37; H, 5.70; N, 8.80. Found: C, 60.42; H, 5.57; N, 8.88.

2-(*N*-Ethoxycarbonyl-*N'*-*p*-nitrobenzoyl)hydrazino-1,3-cyclohexanedione (**10c**).

This compound was obtained as off white crystals, mp 185-187° (45%)

(ethanol); ir: 3180 broad (NH + OH), 1725 (ethoxy-carbonyl C=O), 1655 sh, 1635 cm^{-1} (C=O); ^{1}H-nmr: δ 11.0 (broad s, NH, 1H), 11.8 (broad s, OH, 1H). The ^{1}H-nmr spectrum of 1,3-cyclohexanedione, recorded in the same solvent shows the signal of the OH proton at δ 11.65.

Anal. Calcd. for $C_{16}H_{17}N_3O_7$: C, 52.89; H, 4.72; N, 11.57. Found: C, 52.79; H, 4.67; N, 11.5.

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