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Condensation of 2-Acylcyclohexane-1,3-diones with Aromatic Aldehydes

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Abstract—Condensation of 2-propanoyl-, 2-butanoyl-, and 2-pentanoylcyclohexane-1,3-diones with aromatic aldehydes in the presence of secondary amines (diethylamine, pyrrolidine, morpholine, piperidine, and hexamethyleneimine) leads to the formation of the corresponding 2-[1-(dialkylamino)-2-alkyl-3-aryl-2-propylidene]cyclohexane-1,3-diones and derivatives of 4*H*-chromen-4,5(6*H*)-dione. A primary screening of some of the resulting enamino derivatives for fungicidal activity has been performed.

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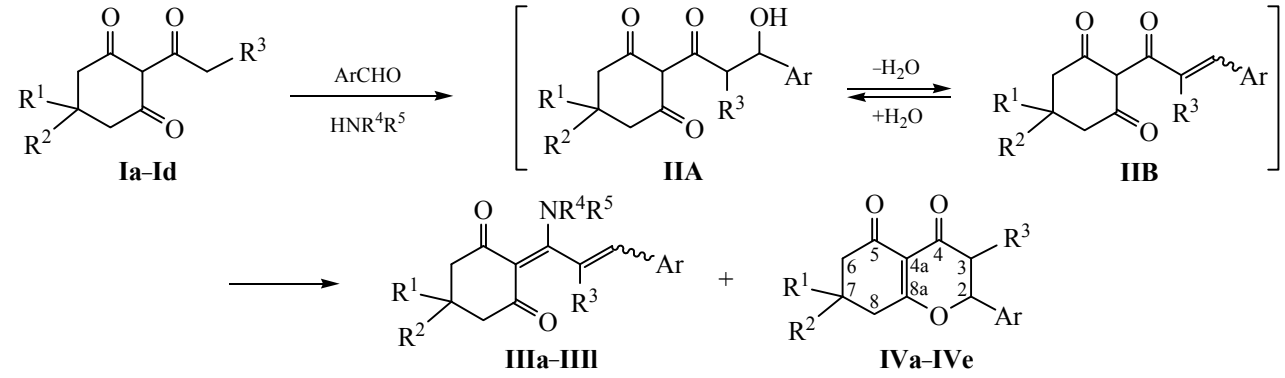
2-Acylcyclohexane-1,3-diones (cyclic β-triketones) (**I**) are interesting both as conventional synthons widely used in organic synthesis [1] and also natural substances and their analogs with diverse biological activity [2]. Compounds of this class were intensively developed in connection with the expansion of application of a number of environmentally friendly herbicide preparations on their basis [3]. Many natural compounds related to the alicyclic β-triketones contain in the acyl side chain an arylpropenoyl fragment. They are formed by condensation of 2-acetylcycloalkane-1,3-diones (**I**, R^3 = H) with aromatic aldehydes [2]. In order to search for new compounds with pesticidal activity it seems promising to investigate condensation of aromatic aldehydes with the triketones of β-cyclohexane series (**Ia–Id**), containing an acyl side chain longer than acetyl.

From the published data [1,2,4–9 the formation is expectable in this reaction of 2-(2-alkyl-3-aryl-2-propenoyl)cyclohexane-1,3-diones (**IIB**). However, it appeared that the condensation of triketones **Ia–Id** with benzaldehyde, anisaldehyde, veratric aldehyde, *p*-hydroxybenzaldehyde, and piperonal under the conditions of catalysis by secondary amine bases (diethylamine, pyrrolidine, piperidine, hexamethyleneimine, morpholine) resulted in a mixture of the enaminodiketones **IIIa–IIIl** *cis*- and *trans*-isomers and derivatives of 4*H*-chromene-4,5(6*H*)-dione **IVa–IVe**. The ratio of reaction products depends on the amount of the taken secondary amine. With 0.5 equivalents of amine the yield of enamino derivatives **IIIa–IIIe** was 45–50%, of chromenediones **IVa–IVe**, 30–40%, calculated with respect to the parent triketone. With equimolar amount of secondary amine only enamines **III** formed in the reaction in almost quantitative yield. This fact suggests that chromenediones **IV** formed in the reaction enter further reaction with the amine giving enaminodiketones **III**.

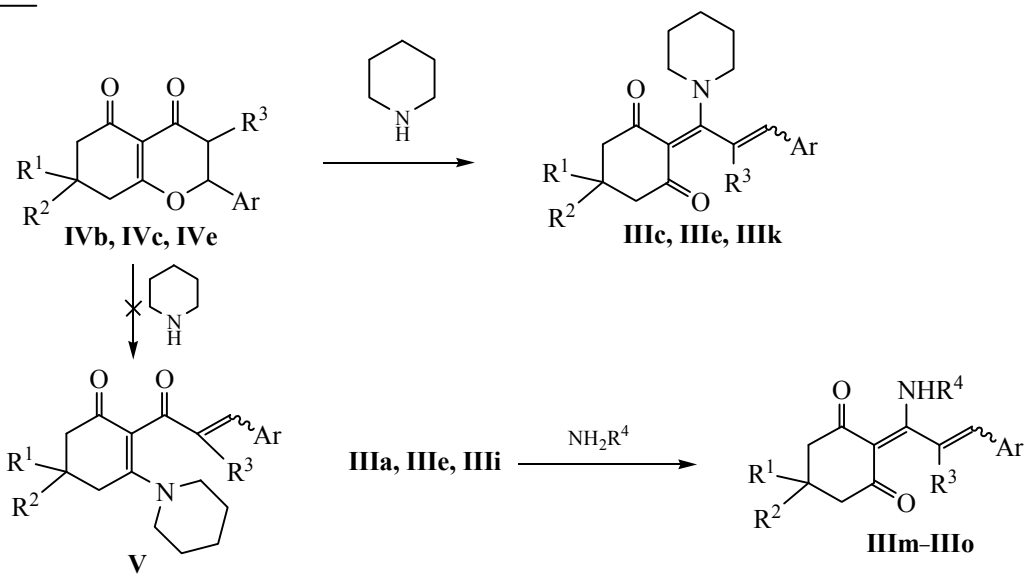
In the direct interaction of chromenediones **IVb, IVc,** and **IVe** with piperidine the corresponding piperidine enamine derivativas **IIIc, IIIe,** and **IIIk** were identified with the physicochemical and spectral properties coinciding with those of the samples obtained in the condensation reaction. This result confirms that in the course of the reaction of triketones **I** with aromatic aldehyde the enaminodiketones **III** are formed actually from the chromenediones **IV**. The formation of chromenediones **IVa–IVe** themselves can be ascribed to the intramolecular cyclization of β-triketones **IIB** or their precursors β'-hydroxytriketones **IIA**. Note that in this reaction we could not get chromenediones **IV** using other common catalysts of the aldol-crotonic condensation, including sodium hydroxide, triethylamine, trifluoroacetic acid, and hydrogen chloride.



I, $R^1 = R^2 = R^3 = CH_3$ (**a**); $R^1 = R^2 = CH_3$, $R^3 = C_2H_5$ (**b**); $R^1 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3C_6H_2$, $R^3 = CH_3$ (**c**); $R^1 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3C_6H_2$, $R^3 = C_2H_5$ (**d**); **III**, $R^1 = R^2 = R^3 = CH_3$, $R^4 = R^5 = C_2H_5$, $Ar = C_6H_5$ (**a**); $R^1 = R^2 = CH_3$, $R^3 = R^4 = R^5 = C_2H_5$, $Ar = C_6H_5$ (**b**); $R^1 = R^2 = R^3 = CH_3$, $R^3 = C_3H_7$, $R^4 + R^5 = –(CH_2)_5–$, $Ar = C_6H_5$ (**c**); $R^1 = R^2 = R^3 = CH_3$, $R^4 + R^5 = –(CH_2)_6–$, $Ar = 3,4\text{-}(OCH_2O)C_6H_3$ (**d**); $R^1 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3C_6H_2$, $R^3 = CH_3$, $R^4 + R^5 = –(CH_2)_5–$, $Ar = 4\text{-}CH_3OC_6H_4$ (**e**); $R^1 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3C_6H_2$, $R^3 = C_2H_5$, $R^4 + R^5 = –(CH_2)_5–$, $Ar = 3,4\text{-}(OCH_2O)C_6H_3$ (**f**); $R^1 = R^2 = R^3 = CH_3$, $R^4 + R^5 = –(CH_2)_2O(CH_2)_2–$, $Ar = 4\text{-}CH_3OC_6H_4$ (**g**); $R^1 = R^2 = CH_3$, $R^3 = C_3H_7$, $R^4 + R^5 = –(CH_2)_2O(CH_2)_2–$, $Ar = 3,4\text{-}(CH_3O)_2C_6H_3$ (**h**); $R^1 = R^2 = R^3 = CH_3$, $R^4 + R^5 = –(CH_2)_5–$, $Ar = 4\text{-}CH_3OC_6H_4$ (**i**); $R^1 = R^2 = CH_3$, $R^3 = C_2H_5$, $R^4 + R^5 = –(CH_2)_6–$, $Ar = 3,4\text{-}(OCH_2O)C_6H_3$ (**j**); $R^1 = R^2 = CH_3$, $R^3 = C_2H_5$, $R^4 + R^5 = –(CH_2)_5–$, $Ar = C_6H_5$ (**k**); $R^1 = R^2 = R^3 = CH_3$, $R^4 + R^5 = –(CH_2)_4–$, $Ar = 4\text{-}HOC_6H_4$ (**l**); **IV**, $R^1 = R^2 = R^3 = CH_3$, $Ar = C_6H_5$ (**a**); $R^1 = R^2 = CH_3$, $R^3 = C_2H_5$, $Ar = C_6H_5$ (**b**); $R^1 = R^2 = R^3$ CH_3, $R^3 = C_3H_7$, $Ar = C_6H_5$ (**c**); $R^1 = R^2 = R^3 = CH_3$, $Ar = 3,4\text{-}(–OCH_2O–)C_6H_3$ (**d**); $R^1 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3C_6H_2$, $R^3 = CH_3$, $Ar = 4\text{-}CH_3OC_6H_4$ (**e**).

According to ^1H NMR spectra, chromenediones **IVa–IVe** are mixtures of diastereomers at the 2 and 3 positions of pyranone ring in the case of the compounds of dimedone series **IVa–IVd**, and at the 2, 3, and 7 positions in the case of compound **IVd** which has a mesityl substituent. Judging from the value of the vicinal constants of protons at C^2 and C^3 (10–11 Hz) typical of the *trans*-location of substituents, we conclude that the 2,3-*trans*-isomers prevail.

The structure of chromenedions **IVa–IVe** can be regarded as that of the intramolecular enol ether of β-



III, $R^1 = R^2 = R^3 = CH_3$, $R^4 = C_3H_7$, $Ar = 3,4\text{-}(OCH_2O)C_6H_3$ (**m**); $R^1 = R^2 = R^3 = CH_3$, $R^4 = CH_2C_6H_5$, $Ar = C_6H_5$ (**n**); $R^1 = H$, $R^2 = 2,4,6\text{-}(CH_3)_3C_6H_2$, $R^3 = CH_3$, $R^4 = 4\text{-}CH_3C_6H_4$, $Ar = 4\text{-}CH_3OC_6H_4$ (**o**).

Impact of enamines **IIIc, IIId, IIIf, IIIh,** and **IIIj** on the growth of fungi

Fungi strain	Coefficient of inhibition of fungal growth *RF*, %					
	control	**IIIc**	**IIId**	**IIIf**	**IIIh**	**IIIj**
Alternaria alternata	0	40	40	45	[a]	[a]
Aspergillus niger	0	20	20	30	20	[a]
Botridis cineria	0	40	50	45	25	[a]
Fusarium oxysporum	0	20	10	50	10	[a]
Monilia sp.	0	30	10	20	35	20
Mucor sp.	0	0	10	0	10	[a]
Penicillum lividum	0	30	20	40	20	[a]

[a] Stimulation of fungal growth.

triketone of cyclohexane series, and on this basis it is presumable that by their electronic and chemical properties these compounds should be similar to the methyl ethers of enol of 2-acylcyclohexane-1,3-dione, which react readily with amines affording enamine derivatives at the ring [10].

The analysis of IR spectra of chromenediones **IVa–IVe** shows their coincidence in the carbonyl region with the spectra of the methyl ethers of 2-acylcyclohexane-1,3-dione enol: the absorbtion of noncomjugated carbonyl group of the acyl side chain (in chromenediones it corresponds to 4-keto group) occurs at 1705–1710 cm^{-1}, the absorption of conjugated carbonyl group of the ring (5-keto group in chromenedione), at 1640–1650 cm^{-1}, and the absorption of conjugated double bonds (C^{4a}–C^{8a}), at 1610–1620 cm^{-1}.

However, we have not found such a resemblance to the enol methyl ethers in the chemical behavior of chromenediones **IVa–IVe**. As noted above, in the reaction of compounds **IVb, IVc**, and **IVe** with piperidine a mixture was isolated of (*Z*)–(*E*)-isomers of exocyclic derivatives **IIIk, IIIl** and **IIIm**, which corresponds to the nucleophilic attack of amine on the carbonyl group of the pyran ring. We did not observe formation in this reaction of regioisomeric endocyclic enaminodiketones **V** expected in the reaction of amine with chromenedione along the mechanism of vinyl substitution. This line of reaction is unusual also taking in mind that the formation of exocyclic enaminodiketones with tertiary amino group in the case of 2-acylcyclohexane-1,3-diones has been described only for their interaction with the pyrrolidine [11].

The ratio of *cis*- and *trans*-isomers of enamines **IIIa–IIIl** in the mixture is defined primarily by the length of the acyl side chain of the triketone. For 2-propanoyl derivatives **Ia** and **Ib** the preferred formation of (*E*)-isomers (**IIIa, IIId, IIIe, IIIi**, and **IIIl**) is typical while 2-butanoyl and 2-pentanoyl derivatives of cyclohexane-1,3-dione **Ib** and **Id** form in this reaction predominantly (*Z*)-isomers **IVb, IVc, IVf, IVh, IVj**, and **IVk**. The amine and aldehyde structure much less affects the ratio of isomeric reaction products.

Chromatographic mobility of *cis*-isomers of enamines **III** is higher compared with the *trans*-compounds, so their mixtures can be separated by chromatography. However, the minor condensation products readily isomerized in the course of separation, and we failed to obtain pure samples. Even when the main reaction product was isolated as a chromatographically pure crystalline compound, after preparation a sample for NMR studies the minor component appeared in an hour.

The exocyclic position of enamine fragment and the assignment of configuration to isomers was made on the basis of two-dimensional ^{13}C–^{15}N HMBC spectroscopy. In the NOESY experiments with compounds **IIIc** and **IIId** no interaction was observed between the protons of enamine fragment and methylene protons of cyclohexanedione, indicating that they are considerably distant from each other. In the NOESY spectrum of the cis-isomer of piperidine enaminodiketone **IIIc**, whose chromatographic mobility is higher, the interaction was observed of two of the four piperidine methylene protons (CH_2NCH_2) at 3.37 and

3.57 ppm with the *ortho*-protons of the phenyl group. These protons are likely to be located on one side of the plane of the piperidine ring. Analogous interaction was not observed in the NOESY spectra of *trans*-isomers of compounds **IIIc** and **IIId** showing lower chromatographic mobility. In the ^{13}C NMR spectrum of an isomer of enaminodiketone **IIId** with lower chromatographic mobility coupling of the carbon in the methyl group of side chains with olefinic protons is registered, with the constant equal to 8.4 Hz, which, according to [12], corresponds to the *trans*-isomer. Analysis of ^{1}H NMR spectra shows that for the *cis*-isomers of enaminodiketones **IIIa–IIIl** is characteristic an upfield shift of all signals of proton-containing groups compared with the *trans*-isomer, except for the olefinic proton. In the ^{13}C NMR spectra of the compounds of dimedone series we observed coincidence of respective chemical shifts of carbon atoms of methylene and carbonyl groups of the ring, and in the ^{1}H NMR spectra the methylene protons of cyclohexane-1,3-dione fragment appear as a broad four-proton singlet. In the IR spectra of the *trans*-isomers of enaminodiketones **IIIa–IIIl** a very strong broad absorption band is observed of the conjugated exocyclic keto group at 1550–1570 cm^{-1} and a strong absorption band of conjugated double bond at 1505–1520 cm^{-1}. In the spectra of *cis*-isomers the absorption at 1505–1520 cm^{-1} is much less intense or non-observable, and there is a very intense broad absorption band at 1580–1590 cm^{-1} belonging, apparently, both to the conjugated carbonyl groups and to the conjugated double bond.

The enaminodiketones **III** proved to be very stable chemically. Refluxing of compounds **IIIc, IIIe** and **IIIk** in a mixture of acetic and hydrochloric acid for 16 h resulted in the formation of the respective chromenediones **IVb, IVc,** and **IVe** in the yield of 40–50%. At the action of propylamine, benzylamine, or *p*-toluidine on enaminodiketones **IIIa, IIIe,** or **IIIi** in toluene at 110°C over 6–8 h respective enaminodiketones **IIIm–IIIo** formed, the products of transamination, in the yield of 50–60%.

We tested some of the synthesized compounds for the fungicidal activity in accordance with the procedure in [13, 14]. The test objects were strains of alternariosis (*Alternaria alternate*), aspergillosis (*Aspergillus niger*), gray mold of vegetable crops (*Botrytis cinerea*), root rot (fusariosis) (*Fusarium oxysporum*), as well as fungi *Mucor sp., Monilia sp.*, and *Penicillum lividum*.

It turned out that studied compounds **IIIc, IIId, IIIf, IIIh,** and **IIIj** in a concentration of 100 □g ml^{-1} showed an activity against these strains of phytopathogenic fungi, mainly by inhibiting their growth. The mycelial growth inhibition rate varies in the range of 10–50%. The maximum effect (50%) showed compound **IIId** against *Botridis cineria* and **IIIf** against *Fusarium oxysporum*.

The azepanyl derivative **IIIj** showed within 48–72 h stimulating rather than inhibiting activity toward all tested strains except for *Monilia sp*. The morpholine enamine **IIIk** stimulated the growth of *Alternaria alternata*. Most resistant to the action of the studied compounds were fungi *Mucor sp.* (the lack of effect, a slight inhibition by the compounds **IIIh** and **IIIi**, and stimulation at the action of **IIIj**) and *Monilia sp*., the degree of its suppression usually does not exceed 40%.

Inhibition of growth of colonies was calculated according to Abbott:

$$RF = \frac{D_{\text{control}} - D_{\text{exp}}}{D_{\text{control}}} \times 100,$$

where RF is growth inhibition compared with control, %; D_{control} is the diameter of growing mycelium in control test; D_{exp} is the diameter of growing mycelium in an experiment.

The results of the primary screening of the fungicidal activity of the cyclic β-triketone derivatives indicate the prospects of finding substances with fungicidal activity in this series of compounds.

EXPERIMENTAL

IR spectra of solids were recorded on a Bomem Michelson FT IR 100 instrument from the tablets with KBr, of oily substances, from the films. The NMR spectra were recorded on a Bruker Avance 500 spectrometer (operating frequency 500 MHz for ^{1}H and 125 MHz for ^{13}C) from solutions in deuteron-chloroform (TMS reference). The mass spectra were obtained on an HPLS-MS/MS system comprising an ACCELA chromatograph with a LCQ Fleet mass detector, in the APCI ionization mode with detection of positive ions. Melting points were determined on a Boetius block. The reaction course was monitored and the purity of all compounds obtained was checked by TLC on the Alufolien Kieselgel F 254 plates (Merck). The plates were developed in UV light and then sprayed with a solution of ferric chloride. For

chromatography were used Kieselgel 60 HF 254 TLC-standard (Merck) and Kieselgel 60 (Fluka).

Condensation of 2-acylcyclohexane-1,3-diones with aromatic aldehydes. *a*.To a solution of 0.05 mol of triketones **I** in 50 ml of toluene was added 0.055 mol of an aromatic aldehyde (benzaldehyde, anisaldehyde, veratric aldehyde, *p*-hydroxybenzaldehyde, or piperonal) and 0.025 mol of a secondary amine (diethylamine, pyrrolidine, morpholine, piperidine, or hexamethyleneimine). The reaction mixture was refluxed for 12–24 h with a water separator, then after cooling it was diluted with 50 ml of toluene, extracted with 2×50 ml of 20% hydrochloric acid and 50 ml of water. The toluene solution was dried over anhydrous magnesium sulfate, passed through a thin layer of silica gel, and evaporated on a rotary evaporator. The residue was crystallized from ethyl acetate–petroleum ether. Oily products were isolated by column chromatography on silica gel (eluent ethyl acetate–petroleum ether). The chromenediones **IVa–IVe** were obtained in 30–40% yield.

The combined aqueous layers were extracted with 2×25 ml of chloroform. The combined organic layers were washed with 50 ml of water, dried with anhydrous magnesium sulfate, and evaporated on a rotary evaporator. The residue was crystallized from ethyl acetate–petroleum ether to afford enaminodiketones **IIIa–IIIe, IIIl** in 45–50% yield.

5,5-Dimethyl-2-[(*E,Z*)-1-(diethylamino)-2-methyl-3-phenyl-2-propylidene]cyclohexane-1,3-dione (IIIa). Yield 45%. Oily substance. IR spectrum, cm^{-1}: 1630 m, 1575 v.s, 1510 s. ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 1:1; (*Z*)-isomer, 0.78 s (6H, CH_3CCH_3), 1.06 t and 1.27 t (6H, $C\underline{H}_3CH_2)_2N$, *J* 7.2 Hz), 2.18 d (3H, $C\underline{H}_3C$=CH, *J* 1.2 Hz), 2.35 s (4H, 4-CH_2, 6-CH_2), 3.47-3.75 m [4H, $(CH_3C\underline{H}_2)_2N$], 6.84 br.s (1H, CH_3C=C$\underline{H}$), 7.10—.35 m (5H, C_6H_5); (*E*)-isomer, 1.08 s (6H, CH_3CCH_3), 1.31 t and 1.33 t (6H, $C\underline{H}_3CH_2)_2N$, *J* 7.2 Hz), 2.29 d (3H, $C\underline{H}_3C$=CH, *J* 1.0 Hz), 2.31 s (4H, 4-CH_2, 6-CH_2), 3.63 m [4H, $(CH_3C\underline{H}_2)_2N$], 6.56 d (1H, CH_3C=C$\underline{H}$), 7.10–7.35 m (5H, C_6H_5). Found, %: C 77.91, H 8.85; N 4.21. $[M + 1]^+$ 340. $C_{22}H_{29}NO_2$. Calculated, %: C 77.84, H 8.61; N 4.13. *M* 339.48.

5,5-Dimethyl-2-[(*Z*)-1-(diethylamino)-3-phenyl-2-ethyl-2-propylidene]cyclohexane-1,3-dione (IIIb). Yield 42%, mp 149–150°C. IR spectrum, cm^{-1}: 1660 v.s, 1615 s, 1585 v.s, 1555 m. ^1H NMR spectrum, δ, ppm: 1.13 s (6H, CH_3CCH_3), 1.16 t (3H, $C\underline{H}_3CH_2$, *J* 7.5), 1.45 t and 1.51 t [6H, $(C\underline{H}_3CH_2)_2N$, *J* 7.0], 2.57 q (2H, $CH_3C\underline{H}_2$, *J* 7.5), 2.68 br.s (4H, 4-CH_2, 6-CH_2), 3.89 q and 4.17 q [4H, $(CH_3C\underline{H}_2)_2N$, *J* 7.0], 6.83 s (1H, C=CH), 7.35–7.43 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 187.88 s, 187.88 s, 185.48 s, 136.91 s, 136.42 d, 133.85 s, 129.40 d, 129.40 d, 129.33 d, 128.83 d, 128.83 d, 108.96 s, 50.63 t, 50.30 t, 46.98 t, 46.98 t, 32.25 s, 28.47 q, 28.24 q, 23.76 t, 13.89 q, 13.41 q, 13.21 q. Found, %: C 78.11, H 8.95; N 4.09. $[M + 1]^+$ 354. $C_{23}H_{31}NO_2$. Calculated, %: C 78.15, H 8.84; N 3.96. *M* 353.51.

5,5-Dimethyl-2-[(*Z*)-1-(piperidyl)-2-propyl-3-phenyl-2-propenilydene]-1,3-cyclohexane-1,3-dione (IIIc). Yield 46%, mp 172–173°C. IR spectrum, cm^{-1}: 1630 w, 1570 v.s, 1510 m, 1510 m, 1400. ^1H NMR spectrum, δ, ppm: 0.93 br.s (7H, CH_3CCH_3, $NCH_2C\underline{H}_AH_B$), 0.95 t (3H, $C\underline{H}_3CH_2$, *J* 7.2), 1.40–1.60 m (6H, $CH_3C\underline{H}_2$, $NCH_2C\underline{H}_AH_BC\underline{H}_2C\underline{H}_AH_B$), 1.73 m (1H, $NCH_2CH_2CH_2CH_A\underline{H}_B$), 2.24 br.s (4H, 4-$CH_2$, 6-$CH_2$), 2.27 m and 2.46 m (2H, $CH_3CH_2C\underline{H}_A\underline{H}_B$), 3.37 m and 3.47 m (2H, $CH_2NC\ \underline{H}_A\underline{H}_B$), 3.57 (2H, $CH_AH_BNC\underline{H}_2$), 6.71 (1H, C=CH), 7.20–7.30 m (5H, C_6H_5). ^{13}C NMR spectrum, δ, ppm: 193.28 s, 193.28 s, 176.35 s, 137.93 s, 136.39 s, 132.80 d, 129.04 d, 129.04 d, 128.42 d, 128.42 d, 127.73 s, 109.86 s, 56.57 t, 52.57 t, 52.57 t, 52.02 t, 40.71 t, 30.77 c, 28.61 q, 28.61 q, 25.27 t, 25.04 t, 23.60 t, 21.22 t, 14.30 q. Found, %: C 79.48, H 8.89; N 3.72. $[M + 1]^+$ 380. $C_{25}H_{33}NO_2$. Calculated, %: C 79.11, H 8.76; N 3.69. *M* 379.54.

2-[(*E*)-1-(1-Azepanyl)-3-(1,3-benzodioxol-5-yl)-2-methyl-2-propylidene]-5,5-dimethylcyclohexane-1,3-dione (IIId). Yield 50%, mp 182–183°C. IR spectrum, cm^{-1}: 1620 m, 1600 w, 1570 v.s, 1500 v.s. ^1H NMR spectrum, δ, ppm: (*E*-isomer) 1.08 s (6H, CH_3CCH_3), 1.79 m and 1.88 m [8H, $NCH_2(C\underline{H}_2)_4CH_2$], 2.26 d (3H, CH_3C = CH, *J* 1.1 Hz), 2.30 br.s (4H, 4-CH_2, 6-CH_2), 3.76 m and 3.82 m (4H, $CH_2NC\underline{H}_2$), 5.98 s (2H, OCH_2O), 6.48 br.s (1H, CH_3C=CH), 6.80 d [1H, (5'-H)-C_6H_3, *J* 8.1 Hz], 6.84 d.d [1H, (6'-H)-C_6H_3 , J_1 1.8 Hz, J_2 1.4 Hz], 6.90 d [1H, (2'-H)-C_6 H_3, *J* 1.4 Hz]. ^{13}C NMR spectrum, δ, ppm: 193.32 s, 193.32 s, 181.48 s, 147.73 s, 147.43 s, 134.38 s, 134.19 d, 130.19 s, 124.36 d, 112.57 s, 109.31 d, 108.39 d, 101.31 t , 57.11 t, 54.19 t, 52.01 t, 52.01 t, 31.20 s, 29.63 t, 29.02 t, 28.69 q, 28.69 q, 26.92 t, 26.59 t, 19.45 q. Found, %: C 73.47, H 7.75; N 3.35. $[M + 1]^+$ 410. $C_{25}H_{31}NO_4$. Calculated, %: C 73.32, H 7.63; N 3.42. *M* 409.52.

5-Mesityl-2-[(*E,Z*)-2-methyl-3-(4-methoxyphenyl)-1-(1-piperidyl)-2-propylidene]cyclohexane-1,3-

dione (IIIe). Yield 50 %, mp 177–180°C. IR spectrum, cm^{-1}: 1640 m, 1590 v.s, 1520 m, 1250 v.s. ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 3:2; *Z*-isomer, 1.59–1.89 m [6H, $NCH_2(C\underline{H}_2)_3$], 2.16 br.s [6H, 2',6'-$(C\underline{H}_3)_2$-$C_6H_2$], 2.20 s (3H, 4'-$C\underline{H}_3C_6H_2$), 2.25 br.s (3H, $C\underline{H}_3C$=CH), 2.32 m (2H, 4-CH_A, 6-CH_B), 2.74 m (2H, 4-CH_B, 6-CH_B), 3.51–3.70 m (4H, CH_2NCH_2), 3.77 s (3H, OCH_3), 3.91 m (1H, 5-CH), 6.63 s (1H, C=CH), 6.76 s (2H, C_6H_2), 6.80 d [2H, (3',5'-$\underline{H}_2$)-C_6H_4, *J* 8.7 Hz], 7.01 d [2H (2',6'-$\underline{H}_2$)-C_6H_4, *J* 8.7 Hz]; *E*-isomer, 1.74–1.89 m [6H, $NCH_2(CH_2)_3$], 2.24 (3H, 4'-$CH_3C_6H_2$), 2.32 br.s (3H, $C\underline{H}_3C$=CH), 2.38 br.s [6H, 2',6'-$(CH_3)_2$-C_6H_2], 2.46 d.d (2H, 4-CH_A, 6-CH_A, J_1 16.8 Hz, J_2 3.7 Hz), 3.08 m (2H, 4-CH_B, 6-CH_B), 3.58–3.72 m (4H, CH_2NCH_2), 3.77 m (1H, 5-CH), 3.82 s (3H, OCH_3), 6.61 br.s (1H , C=CH), 6.83 s (2H, C_6H_2), 6.90 d (2H, (3',5'-H_2)-C_6H_4, *J* 8.7 Hz), 7.35 d [2H, (2',6'-H_2)-C_6H_4, *J* 8.7 Hz]. Found, %: C 78.86, H 8.05; N 3.13. $[M + 1]^+$ 472. $C_{31}H_{37}NO_3$. Calculated, %: C 78.95, H 7.91; N 2.97. *M* 471.64.

3,7,7-Trimethyl-2-phenyl-7,8-dihydro-2*H*-chromen-4, 5(3*H*,6*H*)dione (IVa). Yield 39%, mp 124–125°C. IR spectrum, cm^{-1}: 1700 v.s, 1640 m, 1570 v.s ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 1:4; *Z*-isomer, 1.13 d (3H, CH_3, *J* 6.6 Hz), 1.11 s (6H, CH_3CCH_3), 2.37 s (2H, 6-CH_2), 2.63 s (2H, 8-CH_2), 2.70 m (1H, 3-CH), 5.64 d (1H, 2-CH, *J* 3.1 Hz), 7.33–7.46 m (5H, C_6H_5); *E*-isomer, 0.94 d (3H, CH_3, *J* 6.8 Hz), 1.10 s (6H, CH_3CCH_3), 2.34 s (2H, 6-CH_2), 2.52 s (2H, 8-CH_2), 2.86 m (1H, 3-CH), 07.05 d (1H, 2-CH, *J* 12.7 Hz), 7.33–7.46 m (5H, C_6H_5). Found, %: C 76.18, H 7.15. $[M + 1]^+$ 285. $C_{18}H_{20}O_3$. Calculated, %: C 76.03, H 7.09. *M* 284.35.

7,7-Dimethyl-2-phenyl-3-ethyl-7,8-dihydro-2*H*-chromen-4,5(3*H*,6*H*)dione (IVb). Yield 35%, mp 113–115°C. IR spectrum, cm^{-1}: 1710 v.s, 1645 m, 1570 v.s. ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 2:1; *Z*-isomer, 0.85 t (3H, $C\underline{H}_3CH_2$, *J* 7.5 Hz), 1.13 s and 1.14 s (6H, CH_3CCH_3), 1.52–1.65 m (2H, $CH_3C\underline{H}_2$), 2.37 s (2H, 6-CH_2), 2.52 m (1H, 3-CH), 2.61 s (2H, 8-CH_2), 5.67 d (1H, 2-CH, *J* 3.1 Hz), 7.34–7.44 m (5H, C_6H_5); *E*-isomer, 0.88 t (3H, CH_3 CH_2, *J* 7.5 Hz), 1.09 s and 1.10 s (6H, CH_3CCH_3), 1.40 m (2H, $CH_3C\underline{H}_2$), 2.32 s (2H, 6-CH_2), 2.50 s (2H, 8-CH_2) , 2.78 m (1H, 3-CH), 5.33 d (1H, 2-CH, *J* 10.2 Hz), 7.33–7.44 m (5H, C_6H_5). Found, %: C 76.18, H 7.15. $[M + 1]^+$ 299. $C_{19}H_{22}O_3$. Calculated, %: C 76.48, H 7.43. *M* 298.38.

7.7-Dimethyl-3-propyl-2-phenyl-7,8-dihydro-2*H*-chromen-4,5(3*H*,6*H*)-dione (IVc). Yield 35%. Oily substance. IR spectrum, cm^{-1}: 1710 v.s, 1640 m, 1570 v.s. ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 2:1; *Z*-isomer, 0.74 t (3H, $C\underline{H}_3CH_2$, *J* 7.1 Hz), 1.11 s and 1.13 s (6H, CH_3CCH_3), 1.21–1.62 m (4H, $CH_3C\underline{H}_2C\underline{H}_2$), 2.36 s (2H, 6-$CH_2$), 2.60 m (1H, 3-CH), 2.61 s (2H, 8-CH_2), 5.66 d (1H, 2-CH, *J* 3.0 Hz), 7.33–7.43 m (5H, C_6H_5); *E*-isomer, 0.79 t (3H, CH_3 CH_2 , *J* 7.2 Hz), 1.07 s and 1.09 s (6H, CH_3CCH_3), 1.21–1.62 m (4H, $CH_3C\underline{H}_2C\underline{H}_2$), 2.31 s (2H, 6-$CH_2$), 2.50 s (2H, 8-$CH_2$), 2.82 m (1H, 3-CH), 5.31 d (1H, 2-CH, *J* 9.7 Hz), 7.33–7.43 m (5H, C_6H_5). Found, %: C 76.99, H 7.90. $[M + 1]^+$ 313. $C_{20}H_{24}O_3$. Calculated, %: C 76.89, H 7.74. *M* 312.40.

2-(1,3-Benzodioxo-5-yl)-3,7,7-trimethyl-7,8-dihydro-2*H*-chromen-4,5-(3*H*,6*H*)dione (IVd). Yield 36%. Oily substance. IR spectrum, cm^{-1}: 1710 v.s, 1660 m, 1570 v.s, 1510 s, 1500 s. ^1H NMR spectrum, δ, ppm: *E*-isomer, 0.93 t (3H, CH_3, *J* 6.74 Hz), 1.10 s (6H, CH_3CCH_3), 2.33 s (2H, 6-CH_2), 2.50 s (2H, 8-CH_2), 2.81 m (1H, 3-CH), 4.96 d (H, 2-CH, *J* 12.82 Hz), 6.02 s (2H, OCH_2O), 6.84 s and 6.88 s (3H, C_6H_3). Found, %: C 69.38, H 6.25. $[M + 1]^+$ 329. $C_{19}H_{20}O_5$. Calculated, %: C 69.50, H 6.14. *M* 328.36.

7-Mesityl-3-methyl-2-(4-methoxyphenyl)-7,8-dihydro-2*H*-chromen-4,5-(3*H*,6*H*)-dione (IVe). Yield 37%. mp 182–185°C. IR spectrum, cm^{-1}: 1705 v.s, 1640 m, 1620 m, 1570 s, 1520 m, ^1H NMR spectrum, δ, ppm: (four diastereomers) 0.94 d, 0.96 d, 1.00 d and 1.01 d (3H, CH_3, *J* 7.0 Hz), 2.25 s (3H, 4'-$C\underline{H}_3C_6H_2$), 2.37 br.s [6H, 2',6'-$(C\underline{H}_3)_2C_6H_2$], 2.51–2.65 m (2H, 6-$CH_A$, 8-$CH_A$), 2.86–2.97 m (1H, 3-CH), 3.03–3.11 m (1H, 6-CH_B), 3.21–3.37 m (1H, 8-CH_B), 3.78–3.87 m (1H, 7-CH), 3.84 s (3H, OCH_3), 5.03 d (0.56H, *J* 13.3 Hz), 5.9 d (0.29H, *J* 12.6 Hz), 5.63 d (0.1H, *J* 3.1 Hz) and 5.66 d (0.05H, *J* 3.7 Hz) (1H, 2-CH); 6.85 s (2H, C_6H_2), 6.94–7.01 m [2H, 3",5"-($\underline{H}_2$)-C_6H_4], 7.52–7.36 m [2H, 2",6"-($\underline{H}_2$)-C_6H_4]. Found, %: C 77.16, H 7.11. $[M + 1]^+$ 405. $C_{26}H_{28}O_4$. Calculated, %: C 77.20, H 6.98. *M* 404.51.

b. To a solution of 0.05 mol of triketone **I** in 50 ml of toluene was added 0.055 mol of aromatic aldehyde and 0.05 mole of a secondary amine. The reaction mixture was refluxed for 8–10 h with a water separator. After cooling, the reaction mixture was placed in a freezer, the precipitated crystals were filtered off, washed with 20 ml of cold toluene, recrystallized from ethyl acetate–petroleum ether, and then dried in a vacuum. Yield of the enaminodiketones **III** 85–95%. Enaminodiketone **IIId** described above was obtained by method *b* in 90% yield.

2-[(*Z*)-3-(1,3-Benzodioxol-5-yl)-1-(1-piperidyl)-2-ethyl-2-propylidene]-5-mesitylcyclohexane-1,3-dione (IIIf). Yield 95%, mp 236–238°C (ether). IR spectrum, cm^{-1}: 1660 m, 1590 v.s, 1500 s. ^1H NMR spectrum, δ, ppm: 1.15 t (3H, $C\underline{H}_3CH_2$, *J* 7.4 Hz), 1.54–1.84 m [6H, $NCH_2(C\underline{H}_2)_3$], 2.23 s (3H, 4'-$C\underline{H}_3C_6H_2$), 2.31 br.s [6H, 2',6'-$(C\underline{H}_3)_2C_6H_2$], 2.35 d.d (1H, 4-$CH_A$, J_1 12.6 Hz, J_2 4.5 Hz), 2.48 br.s (1H, 6-CH_A), 2.56 m (2H, $CH_3C\underline{H}_2$), 2.96 m (1H, 4 CH_B, 6-CH_B), 3.51–3.72 m (5H, 5-CH, CH_2NCH_2), 5.95 s (2H, OCH_2O), 6.64 s (1H, C=CH), 6.77 s [2H, (5',6'-H_2)C_6H_3], 6.80 s (2H, C_6H_2), 6.83 s [1H, (2'-H)C_6H_3]. Found, %: C 76.74, H 7.68; N 2.91. $[M + 1]^+$ 500. $C_{32}H_{37}NO_4$. Calculated, %: C 76.92, H 7.46; N 2.80. *M* 499.64.

5,5-Dimethyl-2-[(*E*,*Z*)-2-methyl-3-(4-methoxyphenyl)-1-(4-morpholinyl)-2-propylidene]cyclohexane-1,3-dione (IIIg). Yield 87%, mp 158–159°C. IR spectrum, cm^{-1}: 1605 m, 1580 v.s, 1510 s, 1400, 1240 s. ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 4:1; *Z*-isomer, 0.85 br.s (6H, CH_3CCH_3), 2.13 d (3H, $C\underline{H}_3C$=CH, *J* 1.3 Hz), 2.19 br.s (4H, 4-CH_2, 6-CH_2), 3.37–3.58 m (4H, CH_2NCH_2), 3.70–4.00 m (4H, CH_2OCH_2), 3.78 s (3H, OCH_3), 6.64 br.s (1H, CH_3C=C$\underline{H}$), 6.80 d [2H, 3',5'-$(H_2)C_6H_4$, *J* 8.8 Hz]; 7.7 d [2H, 2',6'-$(H_2)C_6H_4$, *J* 8.8 Hz]; *E*-isomer, 1.08 s (6H, CH_3CCH_3), 2.28 d (3H, $C\underline{H}_3C$=CH, *J* 1.0 Hz), 2.32 br.s (4H, 4-CH_2, 6-CH_2), 3.46 t (4H, CH_2NCH_2, *J* 5.0 Hz), 3.83 t (4H, CH_2OCH_2, *J* 5.0 Hz), 3.82 s (3H, OCH_3), 6.55 br.s (1H, CH_3C=C$\underline{H}$), 6.88 d [2H, 3',5'-$(H_2)C_6H_4$ *J* 8.8 Hz], 7.31 d [2H, 2',6'-(H_2)-C_6H_4, *J* 8.8 Hz]. ^{13}C NMR spectrum, δ, ppm: *Z*-isomer, 193.56 br, 176.07, 159.62, 134.35, 130.44, 130.02, 130.02, 128.65, 114.06, 114.06, 109.79, 66.28, 66.10, 55.80, 55.45, 52.55 , 52.55, 51.05, 30.68, 28.41 br, 24.14; *E*-isomer, 193.82 br, 180.73, 159.62, 134.56, 132.60, 130.02, 130.02, 128.54, 114.06, 114.06, 112.55, 66.99, 66.65, 55.66, 52.55, 52.55, 52.25, 51.77, 31.05, 28.73, 28.73, 19.79. Found, %: C 72.11, H 7.85; N 3.77. $[M + 1]^+$ 384. $C_{23}H_{29}NO_4$. Calculated, %: C 72.04, H 7.62; N 3.65. *M* 383.49.

5,5-Dimethyl-2-[(*Z*)-3-[3,4-dimethoxyphenyl]-1-(morpholinyl)-2-propyl-2-propenilydene]-1,3-cyclohexane-1,3-dione (IIIh). Yield 95%, mp 147–151°C. IR spectrum, cm^{-1}: 1640, 1590 v.s, 1520 v.s, 1250 v.s. ^1H NMR spectrum, δ, ppm: 0.91 t (3H, $C\underline{H}_3CH_2$, *J* 7.3), 1.02 s (6H, CH_3CCH_3), 1.39 m (2H, $CH_3C\underline{H}_2$), 2.24 m (1H, $CH_3CH_2C\underline{H}_A$), 2.32 s (4H, 4-CH_2, 6-CH_2), 2.36 m (1H, $CH_3CH_2C\underline{H}_B$), 2.97 m, 3.14 m, 3.38 m, and 3.95 m (4H, CH_2NCH_2), 3.51 m and 3.64 m (4H, CH_2 CH_2), 3.80 s and 3.88 s (6H, $(OCH_3)_2$), 6.75 s (1H, C=CH), 6.81 d [1H, (3')-H-C_6H_3, *J* 8.3], 6.86 d [1H, (2')-H-C_6 H_3, *J* 8.3], 7.01 s [1H, (6')-H-C_6H_3]. Found, %: C 70.64, H 8.05; N 3.09. $[M + 1]^+$ 442. $C_{26}H_{35}NO_5$. Calculated, %: C 70.72, H 7.99; N 3.17. *M* 441.56.

5,5-Dimethyl-2-[(*E*,*Z*)-2-methyl-3-(4-methoxyphenyl)-1-(1-piperidyl)-2-propylidene]cyclohexane-1,3-dione (IIIi). Yield 92%, mp 125–126°C. IR spectrum, cm^{-1}: 1610 m, 1580 v.s, 1570 v.s, 1565 v.s, 1535 m, 1510 m, 1250 v.s. ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 1:1; *Z*-isomer, 0.63 br.s and 0.87 br.s (6H, CH_3CCH_3), 1.51–1.85 m [6H, $CH_2N(C\underline{H}_2)_3$], 2.10 br.s (4H, 4-$CH_2$, 6-$CH_2$), 2.20 d (3H, $C\underline{H}_3C$=CH, *J* 1.3 Hz), 3.45 m (1H, $C\underline{H}_AH_BNCH_AH_B$), 3.51–3.60 m (2H, $CH_A\underline{H}_BNCH_A\underline{H}_B$), 3.77 s (3H, OCH_3), 3.85 m (1H, $CH_AH_BNC\underline{H}_AH_B$), 6.57 br.s (1H, CH_3C=C$\underline{H}$), 6.76 d [2H, 3',5'-(H_2)-C_6H_4, *J* 8.7 Hz], 7.00 d [2H, 2',6'-(H_2)-C_6H_4, *J* 8.7 Hz]; *E*-isomer, 1.08 s (6H, CH_3CCH_3), 1.49–1.83 m [6H, $CH_2N(C\underline{H}_2)_3$], 2.29 br.s (3H, $C\underline{H}_3C$ =CH), 2.31 br.s (4H, 4-CH_2, 6-CH_2), 3.55 m and 3.65 m (4H, CH_2NCH_2), 3.81 s (3H, OCH_3), 6.54 s (1H, CH_3C=C$\underline{H}$), 6.87 d [2H, 3',5'-(H_2)-C_6H_4, *J* 8.8 Hz], 7.31 d [2H, 2',6'-(H_2)-C_6H_4, *J* 8.8 Hz]. ^{13}C NMR spectrum, δ, ppm: *Z*-isomer, 193.56, 193.56, 176.24, 159.19, 133.11, 130.82, 129.94, 129.94, 128.53, 113.67, 113.67, 109.97, 56.17, 55.32, 52.33, 52.33, 51.53, 30.49, 28.59 br, 26.05, 25.93, 24.30, 23.53. Found, %: C 75.71, H 8.09, N 3.80. $[M + 1]^+$ 382. $C_{24}H_{31}NO_3$. Calculated, %: C 75.56; H 8.19; N 3.67. *M* 381.52.

2-[(*E*,*Z*)-1-(1-Azepanyl)-3-(1,3-benzodioxol-5-yl)-2-ethyl-2-propylidene]-5,5-dimethylcyclohexane-1,3-dione (IIIj). Yield 93%. Oily substance. IR spectrum, cm^{-1}: 1570 v.s, 1500, 1490 o.s. ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 3:2; *Z*-isomer, 0.99 s (6H, CH_3CCH_3), 1.05 t (3H, $C\underline{H}_3CH_2$, *J* 7.5 Hz), 1.16–1.30 m and 1.48–1.80 m [8H, $NCH_2(C\underline{H}_2)_4CH_2$], 2.25–2.34 m (1H, $C\underline{H}_AH_BCH_3$), 2.28 s (4H, 4-CH_2, 6-CH_2), 2.40–2.48 m (1H, $CH_A\underline{H}_BCH_3$), 3.02 m (1H, $C\underline{H}_AH_BNCH_CH_D$), 3.64 d.d (1H, $CH_A\underline{H}_BNCH_CH_D$, J_1 15.2 Hz, J_2 7.9 Hz), 3.80 d.d (1H, $CH_AH_BNC\underline{H}_CH_D$, J_1 15.3 Hz, J_2 10.2 Hz), 3.94 m (1H, $CH_AH_BNCH_C\underline{H}_D$), 5.93 s and 5.94 s (2H, OCH_2O), 6.58 s (1H, C=CH), 6.74 d [1H, (5'-H)C_6H_3, *J* 7.9 Hz], 6.79 d [1H, (6'-H)C_6 H_3, *J* 7.9 Hz], 6.81 br.s [1H, (2'-H)-C_6H_3]; *E*-isomer, 1.02 s (6H, CH_3CCH_3), 1.14 t (3H, $C\underline{H}_3CH_2$, *J* 7.5 Hz), 1.70–1.90 m [8H, $NCH_2(C\underline{H}_2)_4CH_2$], 2.38 br.s (4H, 4-$CH_2$, 6-$CH_2$), 2.54 q (2H, $CH_3C\underline{H}_2$, *J* 7.5 Hz), 4.2 m (4H, CH_2NCH_2), 5.97 s (2H, OCH_2O), 6.75 s (1H, CH_3C=C$\underline{H}$), 6.80 d [1H, (5'-H)-C_6H_3, *J* 8.5 Hz], 6.93 d [1H, (6'-H)-C_6H_3, *J* 8.5 Hz], 6.95 br.s [1H, (2'-H)-C_6H_3]. Found, %: C

73.67, H 9.15; N 3.23. $[M + 1]^+$ 424. $C_{26}H_{33}NO_4$. Calculated, %: C 73.73; H 7.85; N 3.31. *M* 423.54.

5,5-Dimethyl-2-[(*Z*)-1-(piperidyl)-3-phenyl-2-ethyl-2-propenylidene]-1,3-cyclohexane-1,3-dione (IIIk). Yield 89%, mp 173–178°C. IR spectrum, cm^{-1}: 1630 w, 1580 v.s, 1540 m, 1500 w. ^1H NMR spectrum, δ, ppm: 0.88 br.s (6H, CH_3CCH_3), 1.01 m [1H, $N(CH_2CH_2)_2C\underline{H}_A$], 1.12 t (3H, $C\underline{H}_3CH_2$, *J* 7.4), 1.43–1.76 m [5H, $N(CH_2C\underline{H}_2)_2C\underline{H}_B$], 2.22 br.s (4H, 4-$CH_2$, 6-$CH_2$), 2.33 m (1H, $CH_3C\underline{H}_A$), 2.56 m (1H, $CH_3C\underline{H}_B$), 5.98 s (2H, OCH_2O), 3.37–3.65 m (4H, CH_2NCH_2), 6.69 s (1H, C=CH), 7.17–7.31 m (5H, C_6H_5). Enaminodiketone **IIIk**) was also obtained with the yield 48%, along with chromenedione **IVb** (yield 31%), by the method *a*.

2-[(*E*)-3-(4-Hydroxyphenyl)-2-methyl-1-(pyrroli-inyl)-2-propenilydene]-5,5-dimethyl-1,3-cyclohexane-1,3-dione (IIIl). Yield 95%, mp 199–203°C. IR spectrum, cm^{-1}: 1610 m, 1570 v.s, 1540 v.s, 1510 v.s. ^1H NMR spectrum, δ, ppm: 1.10 s (6H, CH_3CCH_3), 2.05 m and 2.12 m (4H, $NCH_2C\underline{H}_2C\underline{H}_2$), 2.22 s (3H, $C\underline{H}_3C$=CH), 2.36 s (4H, 4-CH_2, 6-CH_2), 3.73 t and 3.78 t (4H, CH_2NCH_2, *J* 6.8), 6.45 s (1H, C=CH), 6.69 d and 6.95 d (4H, C_6H_4, *J* 8.6), 10.03 br.s (1H, OH).

Reaction of chromenediones IVb, IVc, and IVe with piperidine. To a solution of 2 mmol of a chromenedione in 50 ml of toluene was added 2.2 mmol of piperidine. The reaction mixture was refluxed with a water separator for 6–8 h, cooled to room temperature, passed through a thin layer of silica gel, and evaporated in a rotary evaporator. The residue was crystallized from ethyl acetate–petroleum ether. The yields of enaminodiketones: **IIIc**, 82%, **IIId**, 95% **IIIk,** 88%.

Transamination of enaminodiketones IIIa, IIIe and IIIi. To a solution of 2 mmol of a enaminodiketone **IIIa**, **IIIe**, or **IIIi** in 25 ml of toluene was added 2.4 mmol of an amine. The reaction mixture was refluxed for 6–8 h without access of air moisture, cooled to room temperature, passed through a thin layer of silica gel, and evaporated on a rotary evaporator. By column chromatography of the residue on silica gel (ethyl acetate–petroleum ether) respective enaminodiketone **IIIm–IIIo** were isolated. Yield 50–60%.

2-[(*E*)-3-(1,3-Benzodioxol-5-yl)-2-methyl-1-(*n*-propylamino)-2-propenilydene]-5,5-dimethyl-1,3-cyclohexane-1,3-dione (IIIm). Yield 52%. Oily substance. IR spectrum, cm^{-1}: 1650 s, 1550 v.s, 1500 m. ^1H NMR spectrum, δ, ppm: 0.86 t (3H, $NCH_2CH_2C\underline{H}_3$, *J* 7.4 Hz), 1.07 s (6H, CH_3CCH_3), 1.17 t (3H, $CH_2C\underline{H}_3$, *J* 7.4 Hz), 1.34–1.47 m (2H, $NCH_2C\underline{H}_2CH_3$), 2.16 m (1H, $C\underline{H}_AH_BCH_3$), 2.34 s and 2.46 s (4H, 4-CH_2, 6-CH_2), 2.43 m (1H, $CH_A\underline{H}_BCH_3$), 3.00 m (1H, $NC\underline{H}_AH_B$), 3.24 m (1H, $NCH_A\underline{H}_B$), 5.90 s (2H, OCH_2O), 6.33 br.s (1H, C=CH), 6.62–6.68 m (3H, C_6H_3), 13.17 br.s (1H, NH···O). Found, %: C 71.37, H 7.65; N 3.60. $[M + 1]^+$ 370. $C_{22}H_{27}NO_4$. Calculated, %: C 71.52, H 7.37; N 3.79. *M* 369.46.

2-[(*E*,*Z*)-1-(benzylamino)-2-methyl-3-phenyl-2-propylidene]-5,5-dimethylcyclohexane-1,3-dione (IIIn). Yield 60%. Oily substance. IR spectrum, cm^{-1}: 1650 s, 1580 v.s, 1550 v.s. ^1H NMR spectrum, δ, ppm: (*Z*):(*E*) = 2:1; *Z*-isomer, 1.06 s (6H, CH_3CCH_3), 2.12 d (3H, $C\underline{H}_3C$=CH, *J* 1.3 Hz), 2.34 s and 2.45 s (4H, 4-CH_2, 6-CH_2), 4.63 br.d (2H, $NHCH_2Ph$, J_2 6.0 Hz), 6.21 br.s (1H, CH_3C=CH), 7.00–7.38 m (10H, $C_6H_5CH_2C_6H_5$), 13.45 br.s (1H, NH); *E*-isomer, 1.04 s and 1.06 s (6H, CH_3CCH_3), 2.07 d (3H, $C\underline{H}_3C$=CH, *J* 1.3 Hz), 2.34 s and 2.44 s (4H, 4-CH_2, 6-CH_2), 4.22 d.d (1H, $NHC\underline{H}_ACH_BPh$, J_1 15.3 Hz, J_2 5.0 Hz), 4.55 d.d (1H, $NHCH_AC\underline{H}_BPh$, J_1 15.3 Hz, J_2 6.0 Hz), 6.51 br.d (1H, CH_3C=C$\underline{H}$), 7.00–7.38 m (10H, $C_6\underline{H}_5CH_2C_6\underline{H}_5$), 13.36 br.s (1H, NH). Found, %: C 80.47, H 7.15; N 3.58. $[M + 1]^+$ 374. $C_{25}H_{27}NO_2$. Calculated, %: C 80.40, H 7.29; N 3.75. *M* 373.49.

5-Mesityl-2-[(*E*,*Z*)-2-methyl-3-(4-methoxyphenyl)-1-(4-toluidine)-2-propenilydene]-1,3-cyclohexane-1,3-dione (IIIo). Yield 55%, mp 157°C. IR spectrum, cm^{-1}: 1650 s, 1600, 1540 v.s, 1510 m. ^1H NMR spectrum, δ, ppm: 2.01 d and 2.07 d [3H, 4'-($C\underline{H}_3$)-C_6H_4, *J* 1.3 Hz], 2.25 s and 2.27 s (3H, 4'-$C\underline{H}_3C_6H_2$), 2.32 s and 2.34 s (3H, $C\underline{H}_3C$=CH), 2.42 br.s [6H, 2',6'-$(C\underline{H}_3)_2C_6H_2$], 2.55–2.72 m (2H, 4-$CH_A$, 6-$CH_A$), 2.96–3.11 m (1H, 4-$CH_B$), 3.23–3.33 m (1H, 6-$CH_B$), 3.62 m and 3.86 m (1H, 5-CH), 3.82 s (3H, OCH_3), 6.18 s and 6.25 s (1H, C=CH), 6.68–7.15 m (10H, aromatic), 14.42 br (1H, NH···O). Found, %: C 80.42, H 7.05; N 2.98. $[M + 1]^+$ 494. $C_{33}H_{35}NO_3$. Calculated, %: C 80.29, H 7.15; N 2.84. *M* 493.64.

Hydrolysis of enaminodiketones (IIIc, IIIe, and IIIk). To a mixture of 10 ml of acetic acid and 2 ml of concn. hydrochloric acid was added 2 mmol of a enaminodiketone. The mixture was refluxed for 16 h, then cooled, 50 ml of water was added, and the mixture was extracted with 2×50 ml of toluene. The combined organic solution was washed with water,

washed with 25 ml of saturated sodium carbonate solution, dried over magnesium sulfate, passed through a thin layer of silica gel, and evaporated on a rotary evaporator. The residue was crystallized from ethyl acetate–petroleum ether. Yield of chromenediones: **IVb** 42%, **IVc** 40%, **IVe** 50%.

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