etherate, and 25 ml of toluene was refluxed for 2 h with a Dean–Stark trap. The reaction mass was cooled and worked up via the method described above. The yields of 2,4,6-triarylpyrylium tetrafluoroborates ranged from 31 to 50%.

The characteristics of the 2,4,6-triarylpyrylium tetrafluoroborates synthesized in the presence of an orthoester are presented in Table 1.

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ACETALS OF LACTAMS AND ACID AMIDES.

48.* REACTION OF ENAMINO DIKETONES WITH AMIDE CRYSTALS. SYNTHESIS OF DERIVATIVES OF COUMARIN AND CARBOSTYRIL

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UDC 547.421.51'262'442.3'587.51: 543.422.51

It was established that the reaction of derivatives of 2-aminomethylenecyclohexane-1,3-dione with N,N-dimethyl-diethylacetal gives dienediamines, heating of which in aqueous hydrochloric acid leads, depending on the structure, to derivatives of carbostyril and/or coumarin. This unusual reaction is based on initial attack at the α position of the enamino diketone by the ketone acetal, which exists in equilibrium with the starting amide acetal.

It has been previously established that acetals of amides and lactams are capable of undergoing condensation at the amino group of the primary enamines to give enamidines [2]. In continuing this research, in the present paper we studied the reaction of amide acetals with an enamino diketone – 2-aminomethylene-5,5-dimethylcyclohexane-1,3-dione (I), which was obtained by transamination with ammonia of 2-(N,N-dimethylaminomethylene)-5,5-dimethylcyclohexane-1,3-dione (II). The latter is readily formed in the reaction of dimedone (III) with dimethylformamide diethylacetal (IV).

The reaction of primary enamino diketone I with N,N-dimethylacetamide diethylacetal (V) proceeds extremely readily, and brief heating of the components in toluene leads to complete conversion of starting I to the reaction products; according to TLC and PMR data, two principal substances, VI and VII, the relative percentage of which is 7:3, and a small amount of a third compound (VIII) are formed in this case. Compound VIII was isolated owing to its relatively low solubility, whereas we were able to separate VI and VII by fractional crys-

*See [1] for Communication 47.

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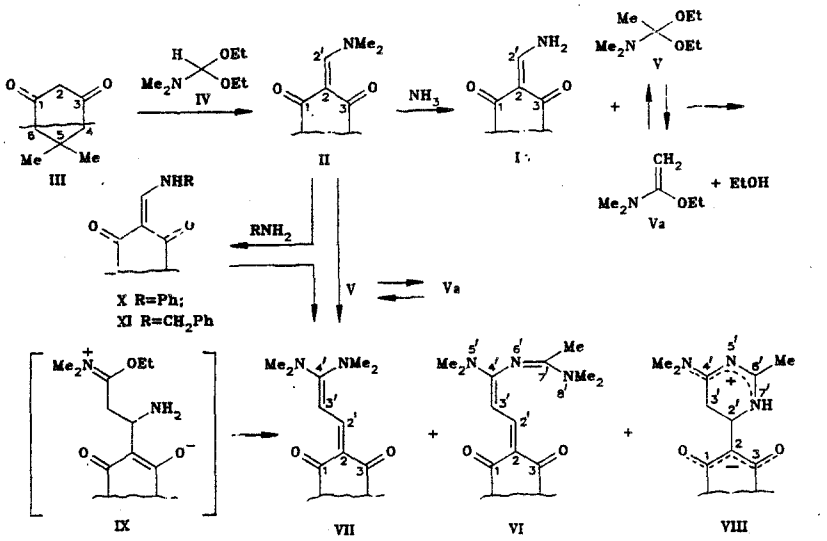
tallization from ethyl acetate. In addition to signals of the protons of C–CH_2, C–CH_3, and N–CH_3 groups, two doublets at 7.46 and 7.63 ppm (VI), as well as at 6.86 and 7.92 ppm (VII), which may be related to protons of sp^2-hybridized carbon atoms, are observed in the PMR spectra of VI and VII (see Table 1); the spin-spin coupling constants (SSCC) $^3J_{HH}$ = 14.2 (VI) and 14.7 Hz (VII) constitute evidence for a transoid orientation of these protons. An $M^{+\cdot}$ peak at 305 (33)* is observed in the mass spectrum of VI, and the principal fragmentation pathways are as follows: $[M - CH_3]^+$ 290 (7) $[M - N(CH_3)_2]^+$ 261 (13), and $[M - N(CH_3)_3{-}H{-}CH_3]^+$ 245 (15). The spectrum also contains a peak at 219 (43), which is formed by elimination of an $HN{=}C(CH_3)N(CH_3)_2$ group with migration of a hydrogen atom to this grouping. The maximally intense peak in the spectrum is located at 204 $[219 - CH_3]^+$. An $M^{+\cdot}$ peak at 264 (18) and peaks $[M - N(CH_3)_3]^+$ at 220 (33) and 219 (24) are observed in the mass spectrum of VII; the maximally intense peak is also located at 204.

Just as in the case of VII (see below), the formation of these compounds evidently specifies the participation in the reaction with enamino diketone I of keteneacetal Va, which is known [3] to exist in equilibrium with amide acetal V. The high electron density in the β position of keteneacetal Va, which is due to the effect of two strong electron-donor substituents (Me_2N and OEt), ensures the facile addition of keteneacetal Va to the 2 position of enamino diketone I [3]. As a result, one observes the intermediate formation of a zwitterion (IX), which then is consumed via different pathways (via replacement of the alkoxy group by ammonia and dimethylamine residues liberated during the reaction).†



It is clear from the scheme why DMF acetal (IV), for which an equilibrium of the V ⇄ Va type is impossible, does not undergo this sort of reaction.‡

It should be noted that other enamino diketones (II, X, XI) also undergo this reaction – as a result, dienediamino diketone VII was isolated in all cases.

Judging from the ^1H and ^{13}C NMR spectral data, the structure of VIII differs substantially from the structures of VI and VII. Thus, in the PMR spectrum of this substance (see Experimental), in addition to signals of a dimedone fragment that are also present in the spectra of VI and VII (Table 1), one observes two multiplets centered at 2.83 (2H) and 5.15 ppm (1H), which might be assigned to a $-CH_2-CH-$ fragment (an ABX system), a singlet at 2.30 ppm (3H, C–CH_3), singlets at 3.18 and 3.38 ppm [3H each, N–$(CH_3)_2$], and a markedly broadened singlet at 11.40 ppm (a labile proton). In the ^{13}C NMR spectrum the positions and multiplicities of the signals of the carbon atoms of the dimedone fragment are close to the analogous signals of dimedone (III) (see Experimental), except for the $C_{(2)}$ atom, which in VIII is a

*Here and subsequently, the m/z values (the relative intensities with respect to the maximum ion peak in percent are given in parentheses) are given for the ion peaks.
†A detailed examination of the scheme of this unusual reaction will be given in one of the subsequent publications of this series.
‡It was specially demonstrated that DMF acetal does not react with II under these and even more severe conditions.

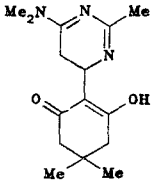
TABLE 1. PMR Spectra of the Synthesized Compounds in $CDCl_3$

Compound	Chemical shifts (δ, ppm)							$^3J_{2',3'}$ Hz
	5-$(CH_3)_2$	4,6-H_2	2'-H	3'-H	7'-CH_3	NH_2*	$N(CH_3)_2$	
I	1,07	2,35; 2,38	8,28	—	—	8,30 ($^3J_{NH,2'-H}$ = =8,85 Hz); 10,45 ($^3J_{NH,2'-H}$ = =15,75Hz)	—	—
II	1,07	2,36	8,02	—	—	—	3,40 and 3,19	—
VI	1,03	2,32	7,63	7,46	1,96	—	3,16 (6H); 3,08 (3H); 3,25 (3H)	14,2
VII	1,05	2,35	7,92	6,86	—	—	3,09 (12H)	14,7
XVII	1,93 (5-CH_2)	2,46	7,94	6,94	—	—	3,09 (12H)	14,7

*Due to intramolecular hydrogen bonding (IMHB) the CH_2 and NH_2 protons are unequivalent.

quaternary sp^2-hybridized atom (108.8 ppm, $CDCl_3$), whereas in dimedone it is a =C–H atom (102.6 ppm, enol form, d_6-DMSO). The remaining signals in the spectrum of VIII are five singlets at strong field and two singlets at weak field (see Experimental). Recording the ^{13}C NMR spectrum with incomplete decoupling of the protons made it possible to establish that the signal at 26.6 ppm corresponds to the carbon atom of a CH_2 group, while the signal at 42.3 ppm corresponds to the carbon atom of a methylidyne group. The remaining strong-field signals are related to the carbon atoms of the C- and N-methyl groups, while the weak-field signals (166.1 and 168.5 ppm) are related to sp^2-hybridized carbon atoms bonded directly to heteroatoms and not bonded to hydrogen atoms.

Molecular-ion peak $M^{+\cdot}$ at 277 (93) is observed in the mass spectrum of this compound, and the maximally intense peak belongs to the $[M - H]^+$ ion at 276. Elimination occurs during electron impact with the formation of ions $[M - CH_3]^+$ at 262 (20), $[M - OH]^+$ at 260 (23), $[M - CH_3N]^+$ at 248 (16), $[M - H–CHOH]^+$ at 246 (23), and $[M - OH–(CH_3)_2CCH_2]^+$ at 204 (16). Cleavage of the bond between the rings (see structure VIII) gives an ion at 138 (73) in the mass spectrum. The data obtained might have corresponded to dihydropyrimidine structure VIIIa (see [4] for information regarding the synthesis and properties of 4,5-dihydropyrimidines).

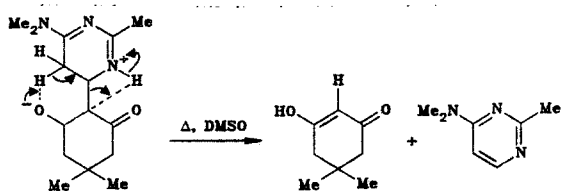


VIIIa

However, the presence in the structure of this compound of an acidic OH group (the pK_a of dimedone is 5.15) and a strongly basic imino amidine fragment made it possible to propose zwitterionic structure VIII for this compound. The latter is confirmed by the results of measurements of the ionization constants. By titration of the substance with an acid we obtained a pK_a value of 4.09 (water, 25°C), which increases on passing to 80% alcohol to pK_a 4.89. Since an increase in the percentage of alcohol leads to a decrease in both the strength of acids and the strength of bases [5], the increase in the pK_a value (the decrease in acidity) indicates that this constant pertains to the acidic group. In an attempt to determine the constant of the basic group we found that in the case of titration with an alkali (based on the fact that VIII is a zwitterion) in water or even in 96% alkali ($c = 1 \cdot 10^{-2}$ M) the substance undergoes complete dissociation; this was expressed in the coincidence of the titration curves of the substance and the solvent. Consequently, the conjugate acid is very weak, and the base corresponding to it has $pK_a > 12$. It is known that DMSO can be used for the titration of weak acids. In fact, in the case of titration in this solvent we obtained a curve with an appreciable inflection, and the determination of the pK_a value as the pH at the half-neutralization point gave a value of 15.1 ± 0.1. The use of the pK_a (DMSO)–pK_a

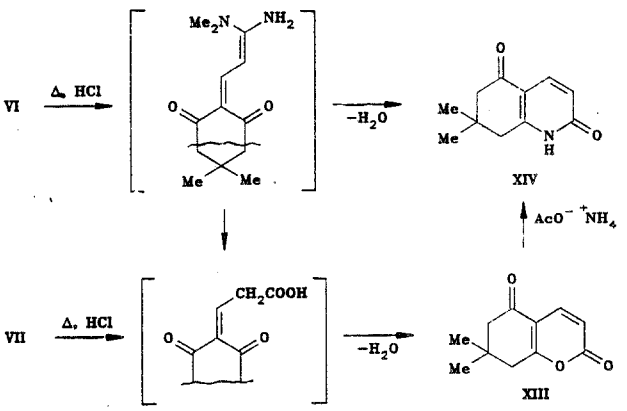
(water) correlation dependence for ammonium acids [6] gives a pK_a value (water) of ≈14.5 for VIII; this unambiguously indicates the zwitterionic structure of this substance with pK_a 4.09 (splitting out of a proton) and pK_a ≈ 14.5 (addition of a proton). The PMR spectral data also constitute evidence in favor of this structure: a certain strong-field shift of the signals of the protons of the CH_2 groups of the dimedone fragment (negatively charged in VIII) from 2.32-2.38 ppm in the case of I, II, VI, and VII to 2.10 ppm in the case of VIII.

It should be noted that when VIII is maintained in solution in d_6-DMSO for 2-3 h at 33 °C, it undergoes conversion to dimedone III and pyrimidine XII; this was established by means of ^{13}C and ^1H NMR spectroscopy. As this process continues, in the ^{13}C NMR spectrum one observes the appearance of additional signals, the most characteristic of which at 155.8 and 101.0 ppm are converted to doublets under conditions of recording with partial suppression of the protons. This makes it possible to assign the indicated signals to the carbon atoms of =C–H groups. In the PMR spectrum of the same solution of VIII (d_6-DMSO, 33°C) one also observes new signals, viz., doublets at 6.46 and 8.03 ppm with $^3J_{HH}$ = 6.2 Hz, which can be ascribed to the ortho protons of a heteroaromatic pyrimidine ring (the more weak-field doublet corresponds to the proton attached to the carbon atom adjacent to the heteroatom).* The probable scheme of the transformation of dihydropyrimidine VIII is presented below.



VIII III XII

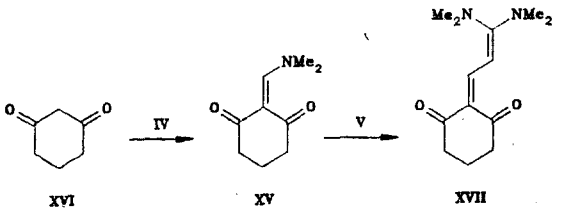
To obtain further evidence for the structures of dienes VI and VII and to study the possibility of the synthesis of heterocyclic compounds from them, a mixture of VI and VII and each of them were refluxed separately with 10% HCl solution; from the mixture of VI and VII and from individual amidine VI we obtained XIII and XIV, whereas from individual dienediamine VII we obtained only bicyclic system XIII. Data from the PMR and mass spectra, as well as a comparison of the physical constants and the spectra of the substances obtained (see Experimental) with the data in [7, 8], made it possible to unambiguously assign the 5-oxo-7,7-dimethyl-5,6,7,8-tetrahydrocoumarin structure to XIII and the 5-oxo-7,7-dimethyl-5,6,7,8-tetrahydrocarbostyril structure to XIV. Coumarin XIII was converted to carbostyril XIV by the method in [7]:



It should be pointed out that enamino diketone XV, which was obtained from dihydroresorcinol XVI, reacts with amide acetal V in the same way as enamino diketone II. The product is dienediamine XVII, the structure of which was confirmed by spectral data (see Experimental).

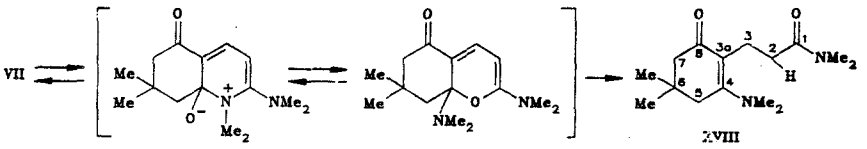
In conclusion, let us note yet another reaction that was observed during a study of the properties of dienediamine VII. During the study it was established that it is thermally

*A decrease in the $^3J_{HH}$ spin-spin coupling constant (SSCC) from 9-10 Hz (for benzene derivatives) to 6-7 Hz is characteristic for six-membered azaheterocycles.



XVI XV XVII

unstable and undergoes a change when it is heated. Refluxing a solution of diene VII in xylene for 1.5 h leads to XVIII with the same molecular mass but a different mass spectrum: $M^{+\cdot}$ 264 (4), $[M - CH_3]^+$ 249 (0.5), 220 (10), 204 (3), and 168 (12); the maximally intense $[M - CON(CH_3)_2]^+$ peak is found at 192. In the PMR spectrum of this compound (see Experimental) the signals of the cyclic methylene groups of the dimedone fragment have different chemical shifts (2.23 and 2.43 ppm; 2H each); this constitutes evidence for their nonequivalence (in contrast to the remaining compounds investigated in this research, for which these groups are spectrally equivalent because of the symmetry of the dimedone fragment; see Table 1). Thus the spectral data indicate disruption of the symmetry of the dimedone skeleton in XVIII. Other characteristic signals of the PMR spectrum of this substance are the signals of two protons (7.30 and 7.40 ppm, $^3J_{HH}$ = 15.0 Hz), which correspond to the CH=CH grouping with a trans orientation of the protons, and signals corresponding to two dimethylamino groups. Nonequivalence of the methylene carbon atoms of the dimedone residue (43.4 and 49.9 ppm) is also observed in the ^{13}C NMR spectrum (see Experimental) of the analyzed compound. In the weak-field region there are signals of the carbon atom of a carbonyl group (194.4 ppm), of two carbon atoms of a CH=CH grouping (112.5 and 137.0 ppm), and of two sp^2-hybridized carbon atoms that are not bonded to hydrogen atoms (168.5 and 169.5 ppm), which can be ascribed to the carbon atom of a carbonyl group bonded to a heteroatom and to a carbon atom located in the α position of an enamino ketone fragment. On the basis of the data set forth above it may be concluded that the investigated compound has the XVIII structure. A possible pathway for its formation is presented in the scheme



VII XVIII

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded with Varian XL-100 and Varian XL-200 spectrometers with tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained with a Varian MAT-112 spectrometer (Phinnigan) with direct introduction of the samples into the ion source; the temperature of the ionization chamber was 180°C, and the ionizing-electron energy was 70 eV. The melting points were determined with a heating stage of the Boetius type.

The physical constants, analytical characteristics, and yields of the synthesized compounds are presented in Table 2.

5,5-Dimethylcyclohexane-1,3-dione (III). ^{13}C NMR spectrum (d_6-DMSO): 28.2 (CH_3); 46.3 ($C_{(4)}$, $C_{(6)}$]; 32.3 ($C_{(5)}$); 186.8 ($C_{(1)}$, $C_{(3)}$); 102.6 ppm ($C_{(2)}$).

2-(N,N-Dimethylaminomethylene)-5,5-dimethylcyclohexane-1,3-dione (II). A mixture of 56 g (0.4 mole) of diketone III and 112 ml (0.8 mole) of acetal IV in 60 ml of absolute benzene was refluxed for 20 min, after which it was evaporated, and the residue was triturated in petroleum ether to give 70 g (90%) of a product with mp 96°C (from ethyl acetate) (mp 93°C [9]).

2-Aminomethylene-5,5-dimethylcyclohexane-1,3-dione (I). A mixture of 70.26 g (0.36 mole) of II with 0.5 liter of ammonium hydroxide was stirred for 1 h, after which the resulting precipitate was removed by filtration and dried to give 43.76 g (70%) of a product with mp 132-133.5°C (mp 133-134°C [10]).

2-Anilinomethylene-5,5-dimethylcyclohexane-1,3-dione (X). A 2.34-g (12 mmole) sample of II was dissolved by heating in 10 ml of absolute ethanol, 1.115 g (12 mmole) of aniline was added, and the mixture was cooled. Filtration gave 2.33 g of X.

TABLE 2. Characteristics of the Synthesized Compounds

Compound	T_{mp}*, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
VI	182—183	66,7	9,2	13,8	$C_{17}H_{27}N_3O_2$	66,9	8,9	13,8	7
VII	162—163	68,0	8,8	11,0	$C_{15}H_{24}N_2O_2$	68,2	9,1	10,6	13 (from I), 70 (from II), 70 (from X) 43 (from XI)
VIII	162—163	65,0	8,6	15,2	$C_{15}H_{23}N_3O_2$	65,0	8,3	15,2	13
X	138—140 (137 [11])	73,8	7,2	5,6	$C_{15}H_{17}NO_2$	74,1	7,0	5,8	80
XI	188—189 (176—178 [12])	75,0	7,5	5,4	$C_{16}H_{19}NO_2$	74,7	7,4	5,4	94
XVII	139—140	66,3	8,6	11,9	$C_{13}H_{20}N_2O_2$	66,1	8,5	11,9	50
XVIII	153—155	68,1	9,2	10,4	$C_{15}H_{24}N_2O_2$	68,2	9,1	10,6	65

*The compounds were crystallized: VI, VII, X, and XVIII from ethyl acetate, VIII from acetonitrile, XI from methanol, and XVII from toluene.

2-(N-Benzylaminomethylene)-5,5-dimethylcyclohexane-1,3-dione (XI). This compound was similarly obtained. The yield was 2.9 g.

2-(γ-N,N-Dimethylamino-γ-N',N'-dimethylacetamidino-propylidene)-5,5-dimethylcyclohexane-1,3-dione (VI), 2-(γ,γ-Bis-N,N-dimethylaminopropylidene)-5,5-dimethylcyclohexane-1,3-dione (VII), and 2-Methyl-4-(5,5-dimethyl-1,3-dioxocyclohexyl)-6-N,N-dimethyl-amino-4,5-dihydropyrimidine Betaine (VIII). A) A mixture of 3.34 g (0.02 mole) of I and 9 g (0.056 mole) of V in 16 ml of absolute toluene was refluxed for 30 min, after which it was evaporated to give 5.5 g of a mixture of VI-VIII with mp 145-155°C. The mixture was refluxed in 40 ml of ethyl acetate, cooled rapidly to 25°C, and filtered to give 0.7 g of VIII. The precipitate that formed from the mother liquor during standing was removed by filtration, refluxed in 30 ml of ethyl acetate, cooled, and filtered rapidly to give 0.7 g of VII. A 3-g sample of a mixture of VI-VIII was isolated from the mother liquor. The mother liquors were evaporated, and the precipitate was crystallized from ethyl acetate to give 0.45 g of VI.

B) For VII. A mixture of 0.01 mole of II (or X or XI) and 6.56 g (0.04 mole) of V in 8 ml of absolute toluene was refluxed for 1 h, after which it was evaporated, and the residue was triturated in toluene to give VII.

^{13}C NMR spectrum ($CDCl_3$) of betaine VIII: 2.27 (6'-CH_3); 26.6 ($C_{(3')}$); 28.6 [5-$(CH_3)_2$]; 31.1 ($C_{(5)}$), 38.4 and 38.0 [$N(CH_3)_2$]; 42.3 ($C_{(2')}$); 50.0 ($C_{(4)}$, $C_{(6)}$); 108.8 ($C_{(2)}$); 166.09 and 168.55 ($C_{(4')}$, $C_{(6')}$); 190.7 ppm ($C_{(1)}$, $C_{(3)}$).

PMR spectrum ($CDCl_3$) of betaine VIII: 0.98 [6H, 5-$(CH_3)_2$]; 2.10 (4H, 4,6-CH_2); 2.30 (3H, 6'-CH_3); 3.18 and 3.38 [6H, $N(CH_3)_2$]; 5.15 (1H, 2'-H); 2.83 (2H, 3'-CH_2); 11.40 ppm (1H, 7'-NH).

5-Oxo-7,7-dimethyl-5,6,7,8-tetrahydrocoumarin (XIII). A solution of 0.45 g (1.7 mmole) of diene VII in 5 ml of 10% aqueous HCl was refluxed for 30 min, after which it was cooled and filtered to give 0.21 g (96%) of coumarin XIII with mp 88-91°C (from heptane (mp 89-92 °C [8])). PMR spectrum ($CDCl_3$: 1.16 [s, 6H, 7-$C(CH_3)_2$]; 2.43 (s, 2H, 8-H_2); 2.74 (s, 2H, 6-H_2); 6.25 (d, 1H, 3-H); 7.84 ppm (d, 1H, 4-H), $^3J_{34}$ = 9.5 Hz. Mass spectrum: M^+· 192 (60), $[M - CH_3]^+$ 177 (10), $[M - CO]^+$ 164 (26), $[M - CH_2C(CH_3)_2]^+$ 136 (100), $[M - CH_2C(CH_3)_2 - CO]^+$ 108 (92).

5-Oxo-7,7-dimethyl-5,6,7,8-tetrahydrocarbostyril (XIV). A solution of 2 g (6.6 mmole) of VI (or a mixture of VI and VII) in 20 ml of 10% aqueous HCl was refluxed for 30 min, after which it was cooled and filtered to give 0.65 g (51%) [or 0.95 g (71%)] of coumarin XIII. The mother liquor was evaporated, and the residue was washed with 5 ml of water. Filtration gave 0.56 g (45%) [or 0.21 g (28%)] of carbostyril XIV with mp 276°C (from ethyl acetate) (mp 276°C [7]). PMR spectrum ($CDCl_3$): 1.15 [s, 6H, 7-$C(CH_3)_2$]; 2.44 (s, 2H, 8-CH_2); 2.84 (s, 2H, 6-CH_2); 6.48 (d, 1H, 3-H); 8.06 ppm (d, 1H, 4-H), $^3J_{34}$ = 9.5 Hz. Mass spectrum: M^+· 191 (52), $[M - CH_3]^+$ 176 (5), $[M - CH_2C(CH_3)_2]^+$ 135 (100), $[M - CH_2C(CH_3)_2 - CO]^+$ 107 (7), $[M - CO]^+$ 163 (3).

2-N,N-Dimethylaminomethylenecyclohexane-1,3-dione (XV). This compound was obtained by a procedure similar to that used to prepare II. The yield was 3.3 g (100%), and the product had mp 115-117°C (from butyl acetate) (mp 118°C [9]).

2-(γ,γ-Bis-N,N-dimethylaminopropylidene)cyclohexane-1,3-dione (XVII). This compound was obtained by a procedure (method B) similar to that used to prepare VII. PMR spectrum ($CDCl_3$): 1.93 (q, 2H, 5-CH_2); 2.46 (t, 4H, 4,6-CH_2); 3.09 [s, 12H, 5',6'-$N(CH_3)_2$]; 6.94 (d, 1H, 3'-H); 7.94 ppm (d, 1H, 2'-H), $^3J_{2',3'}$ = 14.7 Hz. Mass spectrum: M^+· 236 (48), $[M - CH_3]^+$ 221 (3), $[M - N(CH_3)_2]^+$ 192 (100).

β-(2-N,N-Dimethylamino-4,4-dimethyl-6-oxo-1-cyclohexen-1-yl)-acrylic Acid Dimethylamide (XVIII). A suspension of 1 g (3.8 mmole) of VII in 10 ml of absolute xylene was refluxed for 1.5 h, after which it was evaporated, and the residue was triturated in 1 ml of ethyl acetate. Filtration gave amide XVIII. ^{13}C NMR spectrum ($CDCl_3$): 28.3 [6-$(CH_3)_2$]; 30.0 ($C_{(6)}$); 43.4 ($C_{(5)}$); 49.9 ($C_{(7)}$); 35.5 and 37.1 [1-$N(CH_3)_2$]; 43.7 [4-$N(CH_3)_2$]; 106.2 ($C_{(3a)}$); 112.5 ($C_{(2)}$); 137.0 ($C_{(3)}$); 168.6 ($C_{(1)}$); 169.5 ($C_{(4)}$); 194.4 ppm ($C_{(8)}$). PMR spectrum ($CDCl_3$): 1.06 [s, 6H, 6-$C(CH_3)_2$]; 2.23 (s, 2H, 5-CH_2); 2.43 (s, 2H, 7-CH_2); 3.03 and 3.16 [two s, 3H each, 1-$N(CH_3)_2$]; 3.16 [s, 6H, 4-$N(CH_3)_2$]; 7.30 (d, 1H, 2-H); 7.40 ppm (d, 1H, 3-H), $^3J_{23}$ = 15.0 Hz.

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