case of the sulfoxide complex it differs from the equilibrium composition.

### LITERATURE CITED

- 1. Ya. G. Mukhtarov, Dissertation, Moscow (1976).
- 2. N. Ya. Trink, Dissertation, Moscow (1977).
- 3. L. Kh. Freidlin, N. M. Nazarova, E. F. Litvin, and M. A. Annamuradov, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1978</u>, 2465.
- 4. B. Chiswell and L. M. Venanzi, J. Chem. Soc. A, 1966, 1246.
- 5. R. V. Mixer and R. F. Heck, J. Am. Chem. Soc., <u>75</u>, 4094 (1953).
- 6. Yu. A. Kopyttsev, L. Kh. Freidlin, N. M. Nazarova, and I. P. Yakovlev, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1975</u>, 997.

SYNTHESIS OF DIENIC  $\delta$ -DIMETHYLAMINO- $\gamma$ -METHYL(PHENYL)CARBONYL COMPOUNDS AND A STUDY OF THEIR VALENCE ISOMERISM EMPLOYING ULTRAVIOLET AND INFRARED SPECTROSCOPY

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The equilibrium valence isomerization of cis-dienes (I)D to 2H-pyrans (I)P was studied by us previously [1, 2].





It was shown that a  $CH_3$  group in the  $\gamma$  position of dienone (I)D, due to strong steric interaction with the substituent at  $C^{\alpha}$ , destabilizes the dienone and the equilibrium is shifted completely toward the 2H-pyran (I)P.

The pyran form was not detected in the previously studied [3, 4]  $\delta$ -aminocarbonyl compounds of the following type:

 $\begin{array}{c} R^{2}CO \\ C = CH - CH = CR^{1} - NMe_{2}(II) \\ R^{3} \end{array}$ 

R<sup>1</sup>=H, Me, Ph; R<sup>2</sup>=Me, MeO, EtO; R<sup>3</sup>=H, MeCO, MeOCO, CN, NO<sub>2</sub>

We were able to observe both valence forms for the first time in this series on the example of ketoester (III), which contains a Me group in the  $\gamma$  position [5]:



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2325-2335, October, 1980. Original article submitted October 23, 1979.

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			0.00	-	hourse					
Com- pound	Formula	Reaction tempera- ture. <sup>a</sup> °C	Yield, %	mp,°C	bp, °C ( <b>р,</b> mm Hg)	$D_D^{20}$	Empiri- cal for-	Ű	Found	% .
L]		(time)					mula	G	н	N
(à)	PhCO Me O G=CH-d=CHNMes BtOC Me Ph O NMes	20 (1 day)	20		143 - 145 (0,3)	1,6550	$G_{17}H_{21}O_3$	71,38 71,05	7,26	4,73 4,87
(IVI)	MeCO Ph G=CH-C=CHNMe <sub>2</sub> MeOC Ph MeOCO MeOCO Me	20 (1 day)	60	54-55	200 b (0,3)	1,5890	C <sub>16</sub> H <sub>19</sub> O <sub>3</sub>	69,98 70,31	6,97 7,01	5,00
(IIA)	PhGO Ph G=CH-C=CHNMe <sub>5</sub> EtOC Ph EtOCO Ph O NMe <sub>2</sub>	20 (1 day)	70	8889			$C_{22}H_{23}O_{3}$	75,60 <b>75,62</b>	6,63	4,06
(VIII) c	MeCO Me O C=CH-C=GHNMe <sub>3</sub> Me Me Me	20 (2 days)	88		59-60 (0,3)	1,5310				
p (XI)	Me Me Me Me Me Me Me	20 (2 days)	73	82-83		÷ .	C14H21O2	71,31 71,45	8,98 9,00	5,96 5,95
(X) c	Me NMe2	110 (2 h)	55		150-160 b (0,4)	1,5160				
(IX)	Me Me	100 (2 h <b>)</b>	60		180 <sup>b</sup> (0,7)	1,6200				
(XIV)e	MecoodH=CH-C=CHNMez MecoodH=CH-C=CHNMez	55 (2,5h)	24			1,6200				

TABLE 1. Dienic &-Dimethylamino-Y-methyl(phenyl)carbonyl Compounds

<sup>a</sup>Bath temperature. <sup>b</sup>The reaction product was isolated by vacuum distillation.

<sup>c</sup>Compounds (VIII) and (X) are slightly contaminated (PMR spectrum) with  $Me_2NCH=C(Me)CH0$ . <sup>d</sup>Compound (IX) was isolated by cooling the evaporated reaction mass, dissolved in acetone. <sup>e</sup>Compound (XIV) was isolated by preparative chromatography-on  $Al_2O_3$  using a 2:3 acetone-hexane mixture for elution. In the present paper we established the equilibrium between the  $\delta$ -aminodienones and the isomeric 2-amino-2H-pyrans, and also studied its dependence on the solvent, temperature, and structural factors. By condensing the acetalaminals of  $\alpha$ -methyl- $\beta$ -dimethylaminoacrolein (IVa) and  $\alpha$ -phenyl- $\beta$ -dimethylaminoacrolein (IVb) with  $\beta$ -dicarbonyl compounds and with ketones we synthesized a number of previously unknown dienic  $\delta$ -dimethylaminocarbonyl compounds (V)-(XI) and (XIV), which contain either an Me or a Ph group in the  $\gamma$  position (Table 1). Compounds (V)-(XI) are depicted in Table 1 in both the dienone and 2H-pyran forms.\*

In Table 2 are given the UV and IR spectra of the obtained compounds, and for comparison also the spectra of  $\delta$ -aminodienones (XII), (XIII), and (XV), unsubstituted in the  $\gamma$  position, which exist only in the dienone form [3, 4]. The PMR spectra of (III) and (V)-(XI), and the <sup>13</sup>C NMR spectra of (III), (VI), and (VIII), are given in [6].

The  $\delta$ -aminodienones and their valence isomers, the 2-amino-2H-pyrans, are quite different in their UV spectra, since the amino group in the 2H-pyran is not included in the conjugation chain. Thus, in [5] it was mentioned that a clearly expressed solvatochromism, caused by valence isomerization, is characteristic for (III). In water, (III) exists as the  $\delta$ -aminodienone (III)D, while in hexane it exists as the 2H-pyran (III)P. A bathochromic shift of the long-wave band by 106 nm is observed when going from hexane to water.

The presence in the UV spectrum of bands in the 380-460 nm region, corresponding to the  $\delta$ -aminodienone form [3, 4], together with absorption at 235-260 and 290-350 nm, which is characteristic for substituted 2H-pyrans (I), testifies to the presence of both isomeric forms. Their amount was estimated by the values of the extinction coefficients of the long-wave absorption maximum ( $\epsilon_{d.m.}$ ). Here were taken into account the  $\epsilon_{d.m}$  values of  $\delta$ -aminocarbonyl compounds of the (II) type, which exist only in the dienone form, which values are equal to (5-6)·10<sup>4</sup> in water and in organic solvents [3, 4].

The solvent effect on the ratio of the valence isomers was studied in greatest detail on the example of (III) (Table 3). In abs. ether, as in hexane, (III) is found only as the 2H-pyran (III)P. In CHCl<sub>3</sub>,  $CH_2Cl_2$ ,  $CH_3COCH_3$ , and abs. EtOH the amount of the dienone form (III)D is 3-4%, while in abs. MeOH, MeNO<sub>2</sub>, MeCN, or 96% EtOH the amount of (III)D increases to 8-14%. The addition of water to organic solvents leads to a substantial increase in the amount of the dienone form (III)D: for example, 78% in 50% MeOH, and 52% in 50% CH<sub>3</sub>COCH<sub>3</sub>.

The data in Table 3 shows that in nearly all cases the amount of the dienone form increases with increase in the dielectric constant of the solvent ( $\epsilon$ ) and its capacity for specific solvation, which is characterized by the parameter Et. A dynamic equilibrium is established between the dienone and 2H-pyran forms (III)D and (III)P in solution, which is shifted toward (III)D when the temperature is raised. From the UV spectral data it follows that the value K = C(III)P/C(III)D is 11.5 in EtOH at 20°C, and 7.3 at 70°; it is 8.1 in MeCN at 20°, and 6.4 at 65°. The initial ratio is restored on returning to 20°.

The isomeric composition in various solvents and the temperature dependence of the equilibrium constants, obtained from the UV spectra, are confirmed by the IR spectral data.

The solvent effect on the amount of isomers in the equilibrium mixture, observed for the example of (III), is retained from the  $\delta$ -amino- $\gamma$ -methyl(phenyl)dienones (V)-(IX), obtained from the  $\beta$ -dicarbonyl compounds. In hexane they are found exclusively in the form of the 2H-pyrans (V)P-(IX)P, whereas in abs. MeOH and CHCl<sub>3</sub> they exist in both forms,<sup>†</sup> with a predominance of the 2H-pyran form (especially in CHCl<sub>3</sub>). It should be mentioned that, in contrast to (III), a greater amount of the dienone is observed in both MeOH and CHCl<sub>3</sub> for ketoesters (V) and (VII) with an  $\alpha$ -benzoyl group. Previously it was shown [2] that in the case of ketoesters (I), which have a proton in the  $\gamma$  position, replacing the acetyl group by benzoyl leads to the exclusive existence of the dienone form (I)D, R<sup>1</sup> = EtO, R<sup>2</sup> = Ph, R<sup>3</sup> = H, R<sup>4</sup> = R = Me.

A comparison of the UV spectra of ketoesters (VI) and (III), and also (VII) and (V), shows that replacing the Me group in the  $\gamma$  position by Ph leads to some decrease in the amount of the dienone form in CHCl<sub>3</sub>. Replacing the carbomethoxy group by acetyl in the  $\alpha$  position does not lead to a noticeable change in the ratio of the isomers, as can be seen from the UV spectral data for ketoester (III) and diketone (VIII) in CHCl<sub>3</sub>, MeOH, EtOH, etc.

<sup>\*</sup>When discussing the compounds, they are named as the dienone form.

<sup>&</sup>lt;sup>†</sup>With the exception of (IX), for which the dienone form was not detected in CHCl $_3$ .

				Ultraviolet spectrum, $\lambda_{max}$ , nm						
Com- pound	hex	ane		CHCl <sub>3</sub>	abs. N	1eOH	67% M	еOH	50% M	leOH
	λ <sub>max</sub>	3	λ <sub>max</sub>	8	λ <sub>max</sub>	ε	λ <sub>max</sub>	8	λ <sub>max</sub>	ε
(V)	212 232 sh 315	22 500 13 900 8200	355 400	8630 8050	250 355 410	10 820 13 200 17 900	255 355 420	10 000 11 580 25 000	255 355 sh 420	8800 8410 26 000
(VI) <sup>a</sup>	205 235 260 sh 325	$\begin{array}{c} 35\ 000\\ 23\ 500\\ 15\ 300\\ 14\ 200 \end{array}$	330 400	8740 770	205 235 262 sh 333 385	$\begin{array}{c} 25\ 200\\ 15\ 600\\ 12\ 000\\ 9640\\ 10\ 000 \end{array}$	392	35 200	392	43 800
(VII)	234 260 350	19 600 13 300 13 700	356 410 sh	14 800 3400	250 sh 360 400	10 600 17 750 14 200	250 368 405	$\begin{array}{c} 9000 \\ 15\ 600 \\ 16\ 400 \end{array}$	290 368 405	8200 11 500 23 000
(VIII) <sup>a</sup>	213 238 285	$\begin{array}{r} 15\ 000\\ 10\ 700\\ 5830 \end{array}$	250 300 390	$\begin{array}{c} 6800 \\ 5410 \\ 1400 \end{array}$	240 308 400	6750 7200 6000	212 sh 240_sh 308 410	$7020 \\ 5460 \\ 12 \ 100 \\ 13 \ 250$	208 sh 240 sh 308 410	$\begin{array}{r} 6860 \\ 5400 \\ 13700 \\ 22400 \end{array}$
(IX) <sup>a</sup>	245 254sh 263sh 300	$7060 \\ 6350 \\ 4360 \\ 4120$	250 305	9660 6750	250 300 408	14 000 6700 1340	210 245 293 408	$9000 \\ 8500 \\ 10\ 500 \\ 14\ 500$		
<b>(X</b> )	225	3780	290	4680	293	6580				
	283	6680	400	2000						
(XI)	230 245 253 345	7740 6230 5740 12 300	350 440	9690 4200	235 242 250 330 460	$\begin{array}{r} 10\ 700\\9560\\7540\\14\ 000\\870\end{array}$				
(XII)þ	255 410	9200 43 400	278 420	$3250 \\ 49 400$						
(XIII) <sup>c</sup>	250 370	4460 45 600	282 395	2560 62 500						
(XIV)			375	27 000						
(XV) d	360	39 300	395	47 100						

TABLE 2	2.	Ultraviolet	and	Infrared	Spectra	of	Compounds	(V) - (XV)

<sup>a</sup>Ultraviolet spectrum in H<sub>2</sub>O: (VI) 400 nm ( $\varepsilon$  53,400), (VIII) 305 nm ( $\varepsilon$  6300), 410 nm ( $\varepsilon$  22,700), (IX) 240 nm ( $\varepsilon$ 8200), 295 ( $\varepsilon$ 15,500), 400 ( $\varepsilon$  21,400).

NMe<sub>2</sub>.

 $^{C}$  (MeCO)<sub>2</sub> C=CH-CH=CHNMe<sub>2</sub>.

d o

Ъ

NMe<sub>2</sub>.

	Ultravi	iolet spe	ectrum,	λ <sub>max</sub> ,	Infrared spectrum, $v$ , cm <sup>-1</sup> (neat)			
10% M	еOH	abs. M	eCN	Eto	ЭH			
λ <sub>max</sub>	8		8	λ <sub>max</sub>	8	C=0	C=C-C=C-N	
255 355 slт 420	8040 8200 27 300			248 350 410	9000 11 700 14 200	1690	1615, 1540, ~1380, 1230	1665sh , 1600sh , 1290, 1100, 1065
396 290	46 000 2100					1705		1630, 1565, 1300, 1090, 1075
250         7540           290         8530           405         29 000				240 360 410	12 200 20 400 12 900	1710		1630, 1565, 1300, 1095, 1070
		$242 \\ 295 \\ 385$	$5100 \\ 10\ 600 \\ 6480$	245 300 395	8400 9060 3140	1680		1650, 1560, 1290, 1070
		247 305	11 700 6600	240 295 400	5700 11 100 12 000	1665 sh		1645, 1600, 1 <b>295,</b> 1065
235 sh 293 418	3070 6260 1540	294 395	4040 1540	225 sh 286 410	4170 5220 1570			1600, 1290, 1060
235 242 250 330	5440 5150 4720 9740	250 344 438	7040 10 350 4840	240 sh 335 455	5600 10 000 4760			1665, 1600, 1 <b>275,</b> 1090, 1060
400	4000			280 415	9200 36 000	1650	1635 sh 1585, 1530,	
				240 289 400	3660 6850 60 000	1635sh	1610, 1535, 1480	
				385	28 700			
			-:	393	<b>3</b> 3 600	1640	1615, 1535, 1380	

From the UV spectra of (VIII) in MeCN and in EtOH, taken at 20 and 65°, it follows that, as for (III), the equilibrium is shifted toward the dienone form (VIII)D when the temperature is raised.

In contrast to (VIII), in cyclic ketone(IX) the dienone form (IX)D was not detected at all in CHCl<sub>9</sub>, while in MeOH its amount is exceedingly small. In all cases the addition of water to a methanol solution of compounds (V)-(IX) leads to a substantial shift of the equilibrium toward the dienone form. In water both ketoester (VI) and ketone (VIII), the same as (III), are found only as the  $\delta$ -aminodienones (VI)D and (VIII)D.\* The dienic  $\delta$ -amino- $\gamma$ -methyl ketones (X), (XI), and (XIV) differ substantially from the above discussed  $\delta$ -amino- $\gamma$ -methyldicarbonyl compounds (III), (V), (VIII), and (IX). Based on the UV and PMR spectral data, the acyclic dienic  $\delta$ -amino ketone (XIV) is found only in the dienone form, with a trans configuration of the  $\alpha,\beta$ -double bond (J = 15 Hz).

\*Estimating the amount of isomers in water for the other compounds is made difficult due to the poor solubility of (V) and (VII) or the rapid hydrolysis of (IX).

	Ultraviolet s	spectrum	Dienone	E <sub>t</sub> ,†		
Solvent	λ <sub>max</sub> , nm	8	(III)D, %*	kcal/ mole	at 25°	
C <sub>6</sub> H <sub>14</sub>	210 235 294	9500 9600 4800	0	30,9	1,89	
Et <sub>2</sub> O	208 233 294	16 400 8790 6850	0	34,6	4,34	
CHCl <sub>3</sub>	294 294 385	6420 1540	3	39,1	4,7	
Me <sub>2</sub> CO	380	1360	3	42,2	20,7	
CH <sub>2</sub> Cl <sub>2</sub>	292 382	6200 2090	4	41,1	8,9	
abs. EtOH	235 300 400	9200 6990 2110	4	51,9	24,3	
95 % E <b>t</b> OH	205 236 296 405	$\begin{array}{r} 14770\\ 10250\\ 7080\\ 4020\end{array}$	. 8	:		
MeCN	205 235 293 385	13 700 7740 7050 5460	11	46	36,2	
abs. MeOH	203 235 292 400	$ \begin{array}{r} 10\ 400 \\ 6340 \\ 6600 \\ 6010 \end{array} $	12	55,5	32,6	
MeNO <sub>2</sub>	385	6800	14	46,3	38,6	
80% Et OH	300 405	6800 10 800	22	53,7		
5 <b>0%</b> Me <sub>2</sub> CO	400	25 400	52			
66% MeOH	203 235 292 400	10 700 7160 7850 31 500	64			
5 <b>0%</b> MeOH	290 400	4600 38 000	78			
H <sub>2</sub> O	290 400	33C0 49 000	100	63,1	78,5	

TABLE 3. Solvent Effect on Amount of Valence Isomers (III)D and (III)P at  $\sim 25^{\circ}$ 

\*The amount of (III)D was estimated on the basis of the  $\epsilon_{d.m}$  at 380-405 nm, taking into account the fact that the  $\epsilon$  of the 100% dienone form (III)D is 49,000 (in H<sub>2</sub>O).

<sup>T</sup>The  $\varepsilon$  and E<sub>t</sub> values were taken from [7].

Both isomers were detected in the cyclic dienic  $\delta$ -amino ketones (X) and (XI) in CHCl<sub>3</sub>, MeCN, or EtOH, with a substantial predominance of the 2H-pyran (X)P and (XI)P. It should be mentioned that, in contrast to (III) and (V)-(IX), in ketones (X) and (XI) in MeOH the dienone form is practically absent, and its amount hardly increases when water is added. The obtained data show that when the 2H-pyran lacks a substituent containing the carbonyl group, in solvents that are capable of specific solvation, the concentration of the dienone form increases slightly. In MeCN, which has a high electron-donor capacity [8], the amount of the dienone form (X)D and (XI)D is somewhat higher than in MeOH. Additional data on the structure and isomerization of dienic  $\delta$ -aminocarbonyl compounds were obtained from the IR spectra (see Table 2). Ketoester (III) was studied in greatest detail, which, depending on the aggregate state, is found in either the 2H-pyran or the dienone form. Compound (III), isolated as an oil by distillation, is, based on the PMR spectrum [5], 2H-pyran (III)P, which, either on long standing or when cooled, changes to the crystalline dienone form (III)D with mp 70-72°. On melting, (III)D is again converted to (III)P. The interconversions of (III)D and (III)P could be observed via the IR spectra of both the solid and liquid phases, which are quite different. The spectral traits of (III)D and (III)P were used to identify the valence isomers in a number of dienic  $\delta$ -aminocarbonyl compounds.

When compared with (III)P, in (III)D the  $\pi$ -electron density is delocalized over the entire conjugation chain. Due to this, in the IR spectrum of the crystalline (III)D the absorption bands of the C=O group, and also those caused by involvement in the vibrations of the other multiple bonds (1690, 1610, 1500 cm<sup>-1</sup>), are shifted toward the low-frequency region when compared with the analogous vibrations in (III)P (1710, 1670, 1600 cm<sup>-1</sup>). A broad intense band at 1360 cm<sup>-1</sup> and a narrower band at 1250 cm<sup>-1</sup> are also observed in the spectrum of (III)D, whereas in the spectrum of (III)P the 1250 cm<sup>-1</sup> band is absent, while a number of narrow, substantially weaker bands are present in the 1360 cm<sup>-1</sup> region. Bands at 1290 and 1080 cm<sup>-1</sup> are characteristic for (III)P, which are apparently caused by the vibrations of the ether linkages of the pyran ring. Additional data, which confirm the validity of the indicated assignment, were obtained from the IR spectra of authentic dienones (XII), (XIII), (XV) (see Table 2), and substituted 2H-pyrans (I)P [1].

It should be mentioned that both (III)D and (III)P when dissolved in either  $CHCl_3$  or  $CD_3CN$  give the same IR spectra, in which the bands of both valence isomers are present. A similar result is observed in the UV spectra when (III)D and (III)P are dissolved in EtOH,  $CHCl_3$ , MeOH, MeCN, etc. From this it follows that equilibrium is established in solution between (III)D and (III)P, with the same ratio independent of the starting state of (III). On the basis of measuring the integral intensities of the 1290 cm<sup>-1</sup> band in the IR spectrum of (III) in hexane, where only (III)P is present, and then in  $CHCl_3$  and  $CD_3CN$ , in which both isomers exist, we obtained the values of C(III)P and  $C_{(III)D}$  in these solvents, and in this way determined the equilibrium constant  $K = C_{(III)P}/C_{(III)D}$ . The values  $K_{CHCl_3} = 31$  and  $K_{CD_3CN} = 8$ , as well as the change in the latter in the range from 20 to 70°, are very close to those found from the UV spectra (see Table 3). The equilibrium constant is independent of the concentration, and the value of  $C_{(III)P}/C_{(III)D}$  in MeCN is practically constant in the range from  $3 \cdot 10^{-5}$  to  $3 \cdot 10^{-3}$  mole/liter (UV spectrum), and in  $CD_3CN$  in the range from  $1 \cdot 10^{-2}$  to  $4 \cdot 10^{-1}$  mole/liter (IR spectrum).

The IR spectral data for compounds (V)-(XI) neat made it possible to establish in which form of the valence isomer they exist.

On the basis of the spectral differences, observed for the 2H-pyran and dienone forms, it may be assumed that (VI)-(XI) are 2H-pyrans. It should be mentioned that the presence of quite intense bands at 1565 cm<sup>-1</sup> in the spectra of (VI)-(VIII), indicating as it were the dienone form, is explained by the effect of the phenyl substituent at C<sup>3</sup> in (VI) and (VII), and of the acetyl group at C<sup>5</sup> in (VIII), on the vibrations of the pyran ring. This follows from the fact that in the IR spectra of (VI)-(VIII) is hexane (in which only the pyran form exists) the band at 1565 cm<sup>-1</sup> remains practically the same as in the spectra neat (without a solvent). Of all of the studied compounds, only in (V) is the 2H-pyran-dienone equilibrium observed, which is evidently facilitated by the benzoyl substituent in the  $\alpha$  position. The broad intense band at 1540 cm<sup>-1</sup>, which is present in the spectrum of (V) neat and is characteristic for the dienone form, disappears completely in the IR spectrum of (V) in hexane. Above it was mentioned that in aqueous and aqueous methanol solutions of compounds (V)-(IX) the dienone-2H-pyran equilibrium is shifted toward the dienone form.

Based on the UV and PMR spectral data, the aqueous and aqueous methanol solutions remain unchanged for some time; in addition, after evaporating the water in vacuo at 20° samples remain that are identical with the original samples. However, irreversible changes take place on longer standing. Thus, for example, for (III) after 10-12 h, and for (VIII)-(IX) after one hour, a hypsochromic shift of the long-wave band by 20-48 nm is observed in the UV spectrum, while in the PMR spectrum is observed a decrease in the integral intensity of the signal of the methine protons and the appearance of two singlets downfield in the 7.34-7.64 and 8.98-9.22 ppm regions. The transformation products of (III) and (VIII) could not be isolated from the aqueous methanol solution due to their lability. However, (IX) forms a more stable product (XVIII), which was isolated in the crystalline form. The elemental analysis and mass spectrum of (XVIII) correspond to the formula  $C_{14}C_{21}NO_2 \cdot H_2O$ .

From the UV, IR, and PMR spectral data for (XVIII), which are given in the Experimental section, it follows that (XVIII) in H<sub>2</sub>O, MeOH, or MeCN represents the  $\delta$ -dimethylaminoaldehyde (XVIII)A, while neat and in CHCl<sub>3</sub> solution it represents its valence isomer, namely 2H-pyran (XVIII)P:



In a similar manner, from (III) and (VIII) are apparently formed the  $\delta$ -aminoaldehydes COR Me

Me-C = C - CH = C - CHO, where R = MeO and Me.

NMe.

### EXPERIMENTAL

The UV spectra were measured on a Specord UV-VIS instrument, and the PMR spectra were measured on a Tesla BS-497 instrument (100 MHz) with HMDS as the internal standard. The IR spectra were obtained on UR-20, Specord 75-IR, and Perkin-Elmer-577 spectrophotometers, for the solids as KBr pellets, and for the liquids as a thin layer between KBr plates. The solutions in hexane,  $CHCl_3$  or  $CD_3CN$  were studied in standard NaCl cells with a thickness of 1-0.05 mm. The concentration of the solutions was 0.4-0.01 mole/liter. To obtain the integral intensities the spectra of the solutions were recorded on the logarithmic scale on a secondary automatic recorder attached to the UR-20 instrument.

The starting acetalaminals (IVa) and (IVb) were obtained as described in [5, 9]. Compounds (V), (VIII)-(XI), and (XIV) were obtained by condensing (IVa) with benzoylacetic ester, acetylacetone, dimedon, cyclohexanone, 1-tetralone, and acetone; (VI) and (VII) were obtained by condensing (IVb) with acetoacetic and benzoylacetic esters. The reaction conditions, yields, and constants are given in Table 1. Diketone (XII) (bp 185-186°) was obtained in 85% yield from dimedon and  $\beta$ -dimethylaminoacrolein acetalaminal similar to (IX).

PMR spectrum of (XII) ( $\delta$ , ppm and CD<sub>3</sub>OD): 0.95 (6H, Me<sub>2</sub>C), 2.27 (4H, CH<sub>2</sub>), 3.08 and 3.27 (6H, Me<sub>2</sub>N), 7.22 (1H, H<sup> $\gamma$ </sup>), 7.71 (1H, H<sup> $\delta$ </sup>), 7.80 (1H, H<sup> $\beta$ </sup>), J<sub> $\beta$ ,  $\gamma$ </sub> = 14, J<sub> $\gamma$ ,  $\delta$ </sub> = 12 Hz.

<u>Hydrolysis of (IX)</u>. In the UV spectrum of a solution of 0.4 g of (IX) in 15 ml of 66% aqueous MeOH the band at 408 nm disappears in one hour and a band appears at 360 nm. After evaporation in vacuo (bath temperature below 30°) the residue was treated with hexane, and the pale yellow precipitate was separated and washed with hexane to give 0.35 g of (XVIII) with mp 78-80°. Found: C 66.00; H 9.24; N 5.40; H<sub>2</sub>O 7.1%.  $C_{14}H_{21}NO_2 \cdot H_2O$ . Calculated: C 66.37; H 9.15; N 5.53; H<sub>2</sub>O 6.63%.

Infrared spectrum (with KBr,  $\nu$ , cm<sup>-1</sup>): 1645 s, 1610 s, 1520 w, 1295 w; (in CD<sub>3</sub>CN) 1655 s, 1620 m, 1570 m, 1480-1500 s.br. The IR spectrum of the crystalline sample corresponds to the structure of (XVIII)P, while in CD<sub>3</sub>CN solution it corresponds to (XVIII)A.

Mass spectrum (m/e): 235 (M)<sup>+</sup>. Ultraviolet spectrum ( $\lambda_{max}$ , nm, in H<sub>2</sub>O): 220 ( $\varepsilon$  7660), 295 ( $\varepsilon$  14,600), 360 ( $\varepsilon$  9880); (MeOH) 218 ( $\varepsilon$  6550), 294 ( $\varepsilon$  11,800); 360 ( $\varepsilon$  9150); (MeCN) 208 ( $\varepsilon$  11,100), 245 plateau ( $\varepsilon$  6800), 290 ( $\varepsilon$  9380), 373 ( $\varepsilon$  10,100); (in CHCl<sub>3</sub>) 250 ( $\varepsilon$  9670), 290 ( $\varepsilon$  6800). The UV spectrum in H<sub>2</sub>O, MeOH, or MeCN corresponds to (XVIII)A, while in CHCl<sub>3</sub> it corresponds to (XVIII)P. After short holding in CHCl<sub>3</sub>\* ( $\sim$ 10 min), and evaporation in vacuo the residue in either MeOH or H<sub>2</sub>O gives UV spectra that correspond to (XVIII)A.

PMR spectrum of (XVIII) ( $\delta$ , ppm, in CD<sub>3</sub>OD): 1.02 (6H, Me<sub>2</sub>C), 1.59 (3H, MeC=), 2.64 (6H, Me<sub>2</sub>N), 2.23 (4H, CH<sub>2</sub>), 7.34 (1H, CH=), 9.28 (1H, HC=O); (in CD<sub>3</sub>CN): 0.98 (6H, Me<sub>2</sub>C), 1.56 (3H, MeC=), 2.5 (6H, Me<sub>2</sub>N), 2.14 (4H, CH<sub>2</sub>), 7.24 (1H, CH=), 9.26 (1H, HC=O). The PMR spectra in CD<sub>3</sub>OD and in CD<sub>3</sub>CN confirm structure (XVIII)A. PMR spectrum of (XIV) ( $\delta$ , ppm, in CDCl<sub>3</sub>): 1.82 (Me), 2.1 (MeCO), 2.97 (Me<sub>2</sub>N) 5.65 (H<sup>\alpha</sup>), 6.18 (H<sup>\delta</sup>), 7.02 (H<sup>\beta</sup>), J<sub>\alpha,\beta</sub> = 15 Hz.

### CONCLUSIONS

1. Some previously unknown dienic  $\delta$ -dimethylaminocarbonyl compounds, containing a substituent (Me or Ph) in the  $\gamma$  position, were synthesized. The  $\delta$ -aminodienone-2-amino-2H-pyran

\*Compound (XVIII) is unstable when held for a longer time in CHCl3, and also in MeCN.

valence isomerization was discovered and studied (via the UV and IR spectra) for the first time on the example of these compounds.

2. The existence of a dynamic equilibrium between both valence isomers was established. The equilibrium is shifted toward the  $\delta$ -aminodienones with increase in the temperature, and also the dielectric constant of the solvent and its capacity for specific solvation. An especially strong change occurs when the amount of water in organic solvents is increased.

3. The dienic  $\delta$ -amino- $\gamma$ -methyl(phenyl)carbonyl compounds exhibit a clearly expressed solvatochromism, the nature of which depends on the valence isomerization.

4. The aggregate state can exert an effect on the existence of the  $\delta$ -aminodienones as either valence isomer; 6-dimethylamino-3-carbomethoxy-5-methyl-3,5-hexadien-2-one in the crystalline state represents the dienone, while in the molten state it represents the 2H-pyran.

## LITERATURE CITED

- L. Zh. A. Krasnaya, E. P. Prokof'ev, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 816.
- E. P. Prokof'ev, Zh. A. Krasnaya, and K. M. Litvak, Izv. Akad. Nauk SSSR, Ser. Khim., 1979, 766.
- 3. E. P. Prokof'ev, Zh. A. Krasnaya, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 2218; 1973, 2013.
- 4. Zh. Z. Krasnaya, T. S. Stytsenko, E. P. Prokof'ev, V. A. Petukhov, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 595.
- 5. Zh. A. Krasnaya, E. P. Prokof'ev, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 123.
- 6. E. P. Prokof'ev and Zh. A. Krasnaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 2284.
- 7. H. Reichardt, Solvents in Organic Chemistry [Russian translation], Khimiya (1973), p. 137.
- 8. T. Kagiya, Y. Sumida, and T. Jnoue, Bull. Chem. Soc. Jpn., <u>41</u>, 767 (1968).
- 9. Zh. A. Krasnaya and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 1064.

# REACTION OF PHTHALODINITRILE WITH O-PHENYLENEDIAMINE

AND 1,2,4-TRIAMINOBENZENE

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In a previous communication [1] we discussed in detail the condensation of phthalodinitrile (I) with aromatic o-cyanoamines and, in particular, with 3,3'-dicyano-4,4'-diaminodiphenylmethane, as a result of which a macroheterocyclic compound, containing condensed isoindole and quinazoline rings in its composition, is formed in high yield.

It seems very interesting to obtain macroheterocycles from (I) that also contain other condensed rings in their composition. The present paper is devoted to the synthesis of macro-heterocyclic compounds, containing condensed isoindole and benzimidazole rings, from (I) and bis(o-phenylenediamines).

The possibility of forming the following system of condensed rings was first studied on the example of the model reaction of (I) with o-phenylenediamine (III):

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2335-2339, October, 1980. Original article submitted October 31, 1979.

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