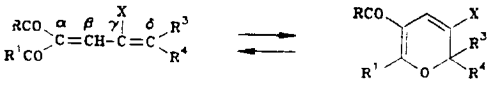
SYNTHESIS OF 2-DIMETHYLAMINO-3-SUBSTITUTED 2H-PYRANS AND STUDY OF THEIR VALENCE ISOMERIZATION TO δ-DIMETHYLAMINO DIENONES

Zh. A. Krasnaya, T. S. Stytsenko,
V. S. Bogdanov and A. S. Dvornikov

UDC 547.814'812.5'388.2'385.2:
541.141.7:543.422

It is shown that 2-dimethylamino-3-isopropyl(3-dimethylamino)-2H-pyrans are formed in the condensation of aminal acetals of α-isopropyl- or α-dimethylamino-β-dimethylaminoacroleins with β-dicarbonyl compounds. It was observed by means of ^1H and ^{13}C NMR and UV spectroscopy that they do not undergo valence isomerization to δ-dimethylamino dienones. Under the influence of pulse photoexcitation the 2H-pyrans undergo reversible cleavage of the C—O bond and isomerization to the corresponding dienones.

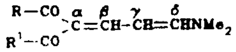
We have previously shown [1-5] that a dynamic equilibrium between open dienone form D and cyclic 2H-pyran form P is established for dienones:



D P

In view of the strong steric interaction between one of the α-substituents and the γ-proton, replacement of the latter by a CH_3 group shifted the equilibrium completely to favor 2H-pyran P [3, 4].

In unsubstituted δ-amino dienones of the type



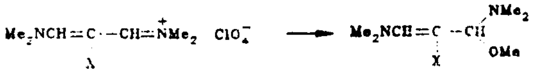
$$\underset{R^1-CO}{\overset{R-CO}{}}\!\!>\overset{\alpha}{C}{=}\overset{\beta}{C}H{-}\overset{\gamma}{C}H{=}\overset{\delta}{C}HNMe_2$$

a pyran form was not detected. However, a dynamic equilibrium between the δ-amino dienones and the corresponding 2-amino-2H-pyrans, which was studied by means of ^1H and ^{13}C NMR, UV, and IR spectroscopy and pulse photolysis, was established when Me, Ph, or Cl substituents were introduced into the γ position of these dienones (Table 1-4).

Since the amino group in the 2H-pyrans deviates from the conjugation chain, their absorption band in the electronic spectra is shifted substantially to the short-wave region as compared with the δ-amino dienones. Owing to the pronounced difference in the electronic absorption spectra of the open and cyclic forms the reversible valence isomerization δ-amino dienone ⇄ 2-amino-2H-pyran was responsible for the solvato-, thermo-, and photochromism of these compounds.

In a continuation of our study of a new class of simple photochromes, in the present research we accomplished the synthesis of δ-amino dienones that contain a bulky substituent — an iso-Pr or NMe_2 group — in the γ-position.

As the starting compounds we used the previously unknown α-isopropyl-β-dimethylamino-acrolein aminal acetal (Ia) and α-dimethylamino-β-dimethylamino-acrolein aminal acetal (Ib), which were obtained from the corresponding perchlorates by the action of MeOK in C_6H_6 as described in [11]:



$$Me_2NCH{=}\underset{X}{C}{-}CH{=}\overset{+}{N}Me_2\ ClO_4^- \longrightarrow Me_2NCH{=}\underset{X}{C}{-}CH\begin{matrix}NMe_2\\ OMe\end{matrix}$$

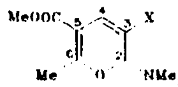
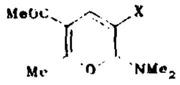
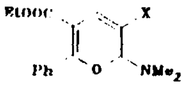
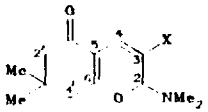
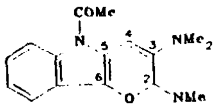
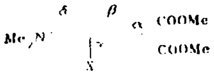
Ia,b

Ia X = i-Pr b X = NMe_2

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1325-1333, October, 1988. Original article submitted November 14, 1986; revision submitted May 14, 1988.

0009-3122/88/2410-1095$12.50

TABLE 1. Conditions for Obtaining IIa, b—Va, b, VI, and VIIa, b and Their Characteristics

Compound		X	Reaction time, h	mp, °C	bp, °C (hPa)	n_D^{20}	Found, %				Empirical formula	Calc., %				Yield, %
							C	H	N	M		C	H	N	M	
IIa		i-Pr	2	—	62...65 (0,13)	1,5010	65,4	8,7	5,9	239	$C_{13}H_{21}NO_3$	65,2	8,8	5,8	239	72
IIb		Me₂N	24	—	78...80 (0,13)	1,5360	60,1	8,4	—	240	$C_{12}H_{20}N_2O_3$	59,9	8,3	11,6	240	76
IIIa		i-Pr	24[*1]	—	65...67 (0,33)	1,5180	69,8	9,7	—	223	$C_{13}H_{21}NO_2$	69,9	9,4	6,2	223	80
IIIb		Me₂N	48	-	82...86 (0,4)	1,5570	—	—	—	224	$C_{12}H_{20}N_2O_2$	—	—		224	90
IVa		i-Pr	48[*1]	—	120...122 (0,4)	1,5500	—	—	—	315	$C_{19}H_{25}NO_3$	72,3	7,9	4,4	315	79
IVb		Me₂N	24[*1]	69...70[*2]	—	—	68,7	7,6	9,0	316	$C_{18}H_{24}N_2O_3$	68,3	7,6	8,8	316	65
Va		i-Pr	24[*1]	88...89[*3]	—	—	73,1	9,4	5,4	263	$C_{16}H_{25}NO_2$	72,9	9,5	5,3	263	46
Vb		Me₂N	24[*1]	78...79[*4]	—	—	68,0	9,0	10,4	264	$C_{15}H_{24}N_2O_2$	68,1	9,1	10,6	264	70
VI			0,3	119...120[*5]	—	—	—	—	13,9	299	$C_{17}H_{21}N_3O_2$		—	11,0	299	75
VIIa		i-Pr	24[*1]	—	150...155 (0,13)	1,5610	—	—	—	255	$C_{13}H_{21}NO_4$	—	—	—	255	80
VIIb		Me₂N	24	72...73[*2]	—	—	56,3	7,8	10,9	256	$C_{12}H_{20}N_2O_4$	56,2	7,8	10,9	256	56

[*1] In absolute ether.

[*2] From ether.

[*3] Purified by sublimation: heating at 120°C and 13 hPa.

[*4] Eluted with ether—acetone (2:1).

[*5] From ethanol.

TABLE 2. ^{13}C NMR Spectra of 2-Dimethylamino-2H-pyrans in $CDCl_3$ (δ Relative to TMS ± 0.03 ppm; $J_{^{13}C,H}$ ± 1 Hz)

Compound	$C_{(5)}$	$C_{(4)}$*1	$C_{(3)}$	$C_{(2)}$*1	Me	$C_{(6)}$	MeOCO		NMe_2		Ph	EtOCO			i-C_3H_7		C=O
							MeO	C=O	at $C_{(2)}$	at $C_{(3)}$		CH_3	CH_2	CO	CH	CH_3	
IIa	102,33	117,44 (161,8)	129,73	94,65 (162,8)	18,94 (129,5)	167,22	50,89 (146,1)	165,66	38,38 (134,1) (4,6)	—	—	—	—	—	30,68 (128,5)	21,81 (125,8)	—
IIb	103,72	94,79 (162)	134,22	90,99 (161)	18,17 (129)	158,46	50,88 (146)	167,54	38,25 (134)	40,19 (134)	—	—	—	—	—	—	—
IVa	104,15	118,55 (162,89)	130,99	95,31 (162,8)		162,81	—	—	38,67 (134,1)	—	136,08; 129,23; 128,8; 127,57	13,79 (126,7) (2,8)	59,79 (147,0) (4,6)	167,08 (3,7)	30,88 (127,6)	21,94 (126,6)	—
IVb	106,12	95,27 (163,5)	134,98	91,69 (162)		155,25	—	—	38,49 (134)	40,04 (134)	136,15; 128,87; 128,01; 127,47	13,77 (127,5)	59,75 (147) (4,0)	167,61			—
Va*2	109,34	113,6 (161,8)	131,66	96,29 (163,7)	28,5 (124,8)	169,79	—	—	38,32 (134,1)	-	—	—	—	—	30,74	21,8 (125,8)	194,44
Vb*2	110,8	90,2 (159)	135,3	92,2 (159)	28,5	163,4	—	—	38,2	40,1	—	—	—	—		—	194,9
VI	*3	90,81 (164)	133,92	90,74 (164)	26,93 (127,5)	138,03	-	—	38,44 (133)	40,22 (133)	115,6; 123,34; 121,22; 134,16; 122,26; 122,87	-	—				169,0

---

*1The assignment of the signals to the $C_{(2)}$ or $C_{(4)}$ atoms in IIb, IVb, and Vb was made on the basis that, without suppression of the protons, the broader signals belong to $C_{(2)}$ due to coupling with the NMe_2 group.

*2Lines of the carbon atoms in the 2', 3', and 4' positions for Va: 50.56 (127.6), 31.91 and 41.43 ppm (124); lines for Vb: 50.6, 32.1 and 40.9 ppm.

*3No signal accumulated.

TABLE 3. ^{13}C NMR Spectra of VIIa, b, VIII, and IX in $CDCl_3$ (δ Relative to TMS ± 0.03 ppm; $J_{^{13}C,\,H}$ ± 1 Hz)

Compound	$C_{(\alpha)}$	$C_{(\beta)}$	$C_{(\gamma)}$	$C_{(\delta)}$	MeCO		MeOCO		Me_2N	i-C_3H_7	
					Me	CO	MeO	CO		CH	CH_3
VIIa	112,75	144,49	106,67	147,44	—	—	52,3	166,84	44,51	28,7	23,7
VIIb	112,49	144,17*, br s	121,02	146,16 (158)	—	—	51,65 51,61 51,45 (147)	166,57 168,92 166,44	44,66 (134,5) 43,27 (139)	—	—
VIII	74,93	175,91 br s	92,39 (d 154,4)	158,45 (d 167,4)	—	—	49,98 (q 145,2)	167,89 (q 3,7)	41,57 (q 138,7) (q 3,7)	—	—
IX	89,9	177,22 br s	91,54 (d 151,1)	159,88 (d 168,3)	28,3 (q 126,7)	188,83 (q 5,5)	49,56 (q 144,2)	167,81 (q 4,6)	45,89; 41,3; 37,82	—	—

---

*The assignment of the signals to the $C_{(\beta)}$ or $C_{(\delta)}$ atoms was made on the basis of data from selective heteronuclear resonace.

TABLE 4. ^{1}H NMR Spectra of the Synthesized Compounds in Various Solvents at 25°C (δ, ppm, TMS)

Compound	Solvent	NMe$_2$	2(δ)	4(β)	CHMe$_2$[*1]	Remaining protons
IIa	CDCl$_3$	2,28 (6H)	5,42 (1H)	6,38 (1H)	1,06 (6H, d)	2,23 (3H, MeC$_{(6)}$); 3,66 (3H, OMe)
	CD$_3$OD	2,27 (6H)	5,43 (1H)	6,35 (1H)	1,02 (6H, d)	2,27 (3H, MeC$_{(6)}$); 3,62 (3H, OMe)
	CD$_3$CN	2,25 (6H)	5,41 (1H)	6,31 (1H)	1,0 (6H, d)	2,21 (3H, MeC$_{(6)}$); 3,60 (3H, OMe)
IIb	CDCl$_3$	2.35 (6H) and 2,68 (6H)	5,41 (1H)	5,41 (1H)	—	2,3 (3H, MeC$_{(6)}$); 3,7 (3H, OMe)
	CD$_3$OD	2,31 (6H) and 2,68 (6H)	5.4 (1H)	5,45 (1H)		2,26 (3H, MeC$_{(6)}$); 3,7 (3H, OMe)
	CD$_3$CN	2,34 (6H) and 2,68 (6H)	5,35 (1H)	5,46 (1H)		2,26 (3H, MeC$_{(6)}$); 3,67 (3H, OMe)
IIIa	CDCl$_3$	2,23 (6H)	5,36 (1H)	6,26 (1H)	1,01 (6H, d)	2,16 (3H); 2,26 (3H, MeC$_{(6)}$ and MeCO)
	CD$_3$OD	2,26 (6H)	5,46 (1H)	6,36 (1H)	1,05 (6H, d)	2,18 (3H); 2,26 (3H, MeC$_{(6)}$ and MeCO)
IIIb	CDCl$_3$	2,35 (6H) and 2,72 (6H)	5,32 (1H)	5,40 (1H)	—	2,26 (6H, MeC$_{(6)}$ and MeCO)
	CD$_3$OD	2,35 (6H) and 2,70 (6H)	5,33 (1H)	5,46 (1H)		2,25 (6H, MeC$_{(6)}$ and MeCO)
IVa	CDCl$_3$	2,42 (6H)	5,53 (1H)	6,54 (1H)	1,06 (6H, d)	0,88 (3H, t, CH$_3$); 3,9 (2H, q, OCH$_2$); 7,3 (5H, m Ph)
	CD$_3$OD	2,49 (6H)	5,68 (1H)	6,55 (1H)	1,12 (6H, d)	0,92 (3H, t, CH$_3$); 3,9 (2H, q, OCH$_2$); 7.37 (5H, m, Ph)
IVb	CDCl$_3$	2,56 (6H) ; 2,76 (6H)	5,6 (1H)	5,6 (1H)	—	1,0 (3H, t, CH$_3$); 4,0 (2H, q, OCH$_2$); 7,2 ... 7,51 (5H, m, Ph); 0,95 (3H, t, CH$_3$); 3,95 (2H, q, OCH$_2$); 7,16 ... 7,43 (5H, m, Ph)
	CD$_3$OD	2,53 (6H) ; 2,70 (6H)	5,53 (1H)	5,61 (1H)		
Va	CDCl$_3$	2,25 (6H)	5,54 (1H)	6,48 (1H)	1,01 (6H, d)	1,0 (6H, Me); 2,16 (4H, CH$_2$)
Vb	CDCl$_3$	2,35 (6H) and 2,7 (6H)	5,51 (1H)	5,54 (1H)	—	1,03 (6H, Me); 2.23 (4H, CH$_2$)
	CD$_3$OD	2,35 (6H) and 2,7 (6H)	5.38 (1H)	5,63 (1H)		1,05 (6H, Me); 2.28 (4H, CH$_2$)
VI	CDCl$_3$	2,41 (6H) and 2,83 (6H)	5.53 (1H)	5,98 (1H)	—	7,01 ... 7,46 and 7,86 ... 8,06 (4H, m, Ph); 2,65 (3H, MeCO)
	CD$_3$OD	2,46 (6H) and 2,87 (6H)	5,64 (1H)	6,0 (1H)		7,08 ... 7,24 and 7,36 ... 8,07 (4H, m, Ph); 2,68 (3H, MeCO)
VIIa	CDCl$_3$	3,0 (6H)	6,37 (1H)	7,72 (1H)	1,0 (6H, d)	3,69 (6H, OMe)
	CD$_3$OD	2,83 (6H)	6,53 (1H)	7,68 (1H)	0,96 (6H, d)	3,61 (6H, OMe)
VIIb	CDCl$_3$	2,42 (6H) and 3,05 (6H)	6,26 (1H)	7,36 (1H)	—	3,7 (3H, OMe) and 3,75 (3H, OMe)
	CD$_3$OD	2,42 (6H) and 3,06 (6H)	6,56 (1H)	7,36 (1H)		3,7 (6H, OMe)
VIII[*2]	CDCl$_3$	3,02 (6H) and 3.17 (6H)	7.53 (1H, d)		—	5,0 (1H, d, γ-H); 3,62 (3H, s, OMe)
	CD$_3$OD	3,03 (3H) [*3] and 3.18 (9H)	7,53 (1H, d)		—	5,2 (1H, d, γ-H); 3,53 (3H, s OMe)
IX[*2]	CDCl$_3$	3.24 (6H) [*3] and 2,97 (3H); 3,15 · (3H)	7,52 (1H, d)		—	5,1 (1H, d., γ-H); 3,58 (3H, s, OMe); 2,45 (3H, s COMe)
	CD$_3$OD	3,13 (3H) and 3,17 (3H); 2,98 (3H) and 3,08 (3H)	7,38 (1H, d)		—	5,17 (1H, d, γ-H); 3,48 (3H, s, OMe); 2,28 (3H, s, COMe)

[*1] The signal of the CH group is overlapped by the signal of the NMe$_2$ group.

[*2] $J_{\gamma\delta}$ = 12.0 Hz.

[*3] The split signal is related to the protons of the NMe$_2$ group attached to the C(δ) atom [12].

TABLE 5. UV Spectra of the Synthesized Compounds in Various Solvents

Compound	Hexane		$CHCl_3$		Abs. MeOH		EtOH		H_2O	
	λ_{max}, nm	ε	λ_{max}, nm	ε	λ_{max}, nm	ε	λ_{max}, nm	ε	λ_{max}, nm	ε
IIa	210, 232, 283	9098, 9715, 6600	235, 290	9294, 6970	203, 232, 290	13 278, 8498, 6639	—	—	203, 232, 294, 390	10 622, 6373, 5842, 1062
IIb	230, 260 sh., 326	16 086, 7783, 6227	258 sh., 330	8561, 5708	233, 260 sh., 326	16 086, 9340, 6227	235, 260 sh., 326	12 200, 9240, 6285	235, 260 sh., 326	12 330, 9138, 6115
IIIa	208, 245, 290	8358, 6766, 7960	245, 305	7885, 10 138	212, 245, 308	8773, 7275, 10 592	—	—	220, 245, 310	7272, 5563, 11 555
IIIb	241, 275, 345	13 070, 10 800, 3470	245, 287, 350	11 200, 9740, 2100	246, 282, 355 sh	10,750, 10 750, 2200	—	—	243, 285, 355sh.,	8959, 8959, 2986
IVa	230, 318	10 216, 7237	230, 320	9933, 6535	230, 318	11 454, 7289	232, 317	10 463, 6904	232, 317, 423	10 788, 5710, 6257
IVb	245, 366	16 804, 8020	250, 372	15 800, 7524	248, 370	16 552, 8025	—	—	247, 380	14 804, 8025
Va	210, 245, 293	9282, 9591, 5569	245, 302	11 820, 7092	208, 245, 304	12 190, 11 643, 7122	208, 247, 305	11 245, 11 245, 6530	208, 245, 318	9433, 10 158, 10 158
Vb	235, 270, 333	14 320, 12 690, 4320	240, 278, 350	12 690, 11 250, 4100	243, 278, 355	13, 916, 13 916, 4200	—	—	242, 273, 325, 350 sh.	10 300, 9367, 3746, 3050
VI	241, 370	23 420, 18 900	247, 377	20 590, 16 925	222, 243, 370	20 700, 25 670, 21 678	—	—	—*	—
VIIa	—	—	—	—	—	—	292, 395	3950, 17 800		
VIIb	360	25 230	370	23 003	208, 370	11 130, 29 681	212, 375	9459, 27 350	218, 390	8535, 23 890
VIII	—	—	255, 325	11 900, 28 600	—	—	256, 322	16 400, 34 900	—	—
IX	—	—	272, 325	17 400, 32 400	—	—	270, 324	20 600, 35 000	—	—

---

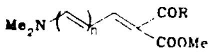
*Decomposes rapidly in H_2O.

TABLE 6. Rate Constants and Activation Parameters of the Valence Isomerization D → P

Compound	In n-heptane			In iso-PrOH				
	λ_{max}*, nm	k (20°C), sec^{-1}	$\Delta G^{\neq}$ (20°C),** kJ/mole	λ_{max}*, nm	k (20°C), sec^{-1}	ΔH,* kJ/mole	$\Delta S^{\neq}$, eu	$\Delta G^{\neq}$ (20°C),** kJ/mole
IIa	<330	0,15	74,3	<330	6	51,6	−16	71,0
IIIa	<340	0,1	76,4	<340	6	—	—	71,0
IVa	380	0,1	76,4	420	0,06	—	—	79,4
IIb	360	0,027	79,2	350	0,7	41,9	−25	72,1
IVb	—	—	—	<420	—	—	—	—
Va	—	—	—	440	2000	58,5	—	53,5

*The dienone form.

**The error in the determination of $G^{\neq}$ is 10%.

TABLE 7. UV Spectra of  [12]

Compound	*n*	R	λ_{max}, nm (ε), in EtOH
XII	0	OMe	244 (5760), 288 (19 600)
X	1	OMe	235 (7000), 374 (54 400)
XIII	0	Me	251 (9100), 312 (15 616)
XI	1	Me	241 (6400), 266 (6900), 400 (57 000)

Acetals Ia, b have high reactivities: in the absence of a catalyst at room temperature they undergo condensation at the active methylene group with various β-dicarbonyl compounds. The resulting IIa-VIIa, VI, and IIb-VIIb are presented in Table 1; their structures were established on the basis of the ^{13}C and ^1H NMR spectra (Table 2 and 4) and UV spectra (Table 5). It follows unambiguously from these data that all of the compounds, except for diesters VIIa and VIIb, exist only in the cyclic 2H-pyran form.

Thus in the ^{13}C NMR spectra of IIa, b, IVa, b, Va, b, and VI in $CDCl_3$ one observes one set of resonance signals, which was assigned to the 2H-pyran form on the basis of a comparison of the chemical shifts (CS) with the CS of the previously studied 2-amino-2H-pyrans and δ-amino dienones [5, 10].

One set of resonance signals is also observed in the ^1H NMR spectra (Table 4) of IIa-Va, IIb-Vb, and VI in $CDCl_3$ and CD_3OD. The CS for solutions in $CDCl_3$ and CD_3OD differ very slightly, and their comparison with the CS of the previously studied valence isomers shows that the synthesized compounds exist only in the 2H-pyran form in both solvents.

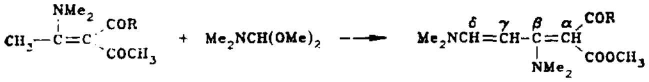
The UV spectral data (Table 5) also provide evidence for the absence of an effect of the solvent on opening of the 2H-pyran ring. The absorption bands and extinction coefficients of the synthesized compounds in hexane, $CHCl_3$, absolute MeOH, EtOH, and H_2O are close, and their values also confirm that these compounds, regardless of the solvent, exist only in the 2H-pyran form, in contrast to the previously studied 2-dimethylamino-2H-pyrans with Me, Ph, or Cl substituents in the 3 position, for which the equilibrium was shifted substantially to favor the δ-amino dienones with an increase in the capacity of the solvent for specific solvation [6, 7, 10]. It follows from the data in Table 5 that only 2H-pyrans IIa and IVa undergo slight isomerization to δ-dimethylamino dienones in water, as evidenced by the appearance in the UV spectra of a long-wave absorption band with λ_{max} 390 and 423 nm for IIa and IVa, respectively, with small extinction coefficients.

An increase in the temperature also did not lead to isomerization of the 2-amino-2H-pyrans to δ-amino dienones. This was shown by ^1H NMR spectroscopy in the case of IIa and IIb in $CDCl_3$ and CD_3CN at 100°C and by UV spectroscopy in the case of 2H-pyran IIIa in CH_3CN and EtOH at 75°C.

Pulse irradiation of 2H-pyrans IIa-IVa and IIb-Vb in a polar solvent (iso-PrOH), which stabilizes the open dienone form, leads to photocleavage of the C—O bond of the pyran ring with the formation of the corresponding dienones as in the case of previously investigated 2H-pyrans [9, 10]. Photochemical opening of the pyran ring in Va could not be detected in iso-PrOH or in heptane. In nonpolar media (n-heptane) photoisomerization to the dienone form could be observed for 2H-pyrans IIa-IVa and IIb. After the action of UV light is discontinued, the dienone form is converted to the starting 2H-pyran.

The kinetic and activation parameters of the cyclization of the dienones to 2H-pyrans obtained as in [9], as well as the spectral characteristics of the dienone forms, are presented in Table 6. The free energies of activation ($\Delta G^{\neq}$) are close to those obtained previously for 2-dimethylamino-3-methyl-2H-pyrans [9] and substantially lower (by ~20 kJ/mole) than those found for 2H-pyrans that do not contain an NMe_2 group [3].

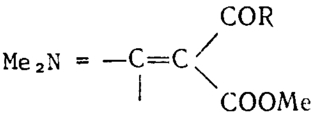
Since a strong effect of the γ-substituent on the position of the δ-amino dienone $\rightleftarrows$ 2-amino-2H-pyran equilibrium was observed in a number of examples, it seemed of interest to compare the effect of the same substituent as a function of its position in the polymethine chain. With this end in mind we synthesized diester VIII and keto ester IX, which have an NMe_2 group in the β position:



VIII, IX

VIII R=OMe; IX R=Me

It follows from the ^{13}C and ^1H NMR and UV spectral data (Tables 3-5) that keto ester IX, like diester VIII, has an acyclic structure and does not contain the 2H-pyran form. Keto ester IX was isolated in the form of two crystalline modifications with mp 128-130°C and 165-167°C; crystallization ensues (at ~150°C) after the low-melting form melts, after which the substance melts again. Both forms crystallize with 1 mole of H_2O and have identical ^1H NMR, UV, and mass spectra.

It should be noted that a comparison of the UV spectra of esters VIII and IX (Table 5) and the analogous unsubstituted X and XI (Table 7) shows that the Me_2N =  $-\overset{|}{C}=C\begin{smallmatrix}\diagup COR\\ \diagdown COOMe\end{smallmatrix}$ chromophore makes the chief contribution to the absorption in the case of the first pair of examined compounds, which have electronic spectra that are similar to the spectra of enamino carbonyl compounds XII and XIII; this leads to a significant hypsochromic shift of the long-wave band as compared with esters X and XI.

EXPERIMENTAL

The UV spectra were measured with a Specord UV-vis spectrophotometer. The ^1H NMR spectra were obtained with Bruker WM-250 and Tesla BS-467 spectrometers with ^1H nuclei operating frequencies of 250 and 60 MHz, respectively. The high-resolution ^{13}C NMR spectra and $^{13}C\{H\}$ spectra were recorded with a Bruker WM-250 spectrometer with a ^{13}C nuclei operating frequency of 62.89 MHz. Pulse photoexcitation was accomplished with a pulse-photolysis apparatus [13].

General Method for the Synthesis of 2-Dimethylamino-3-substituted 2H-pyrans IIa-Va, IIb-Vb, and VI and Diesters VIIa, b. A mixture of equimolar amounts of the β-dicarbonyl compound and aminal acetal Ia or Ib in absolute ether or without a solvent was allowed to stand at room temperature for the length of time indicated in Table 1, after which the reaction mass was evaporated in vacuo, and the residue was either fractionated (IIa-IVa, IIb, IIIb, and VIIa) or stirred with absolute ether and cooled to −70°C (IVb, Va, b, VI, and VIIb).

Methyl α-Carbomethyoxy-β,δ-bis(dimethylamino)butadienecarboxylate (VIII). A mixture of 0.2 g (1.3 mmole) of methyl α-carbomethoxy-β-dimethylamino-β-methylacrylate and 0.26 g (2.2 mmole) of DMF acetal was heated for 20 min at 90°C, after which it was evaporated. Absolute ether was added to the residue, and 0.2 g (60%) of diester VIII was separated in the form of a yellow precipitate with mp 194-195°C (from acetone) and M 256. Found: C 56.0; H 8.0; N 11.2%. $C_{12}H_{20}N_2O_4$. Calculated: C 56.2; H 7.8; N 10.9%.

Methyl α-Acetyl-β,δ-bis(dimethylamino)butadienecarboxylate (IX). A mixture of 1 g (5.5 mole) of methyl α-acetyl-β-dimethylamino-β-methyl-acrylate and 1.3 g (11 mmole) of DMF acetal was heated for 20 min at 90°C, after which it was evaporated in vacuo. Absolute ether (5 ml) was added to the crystalline residue, and, after washing, 1.2 g (91%) of ester

IX was isolated in the form of a cream-colored precipitate with a double melting point: 128-130°C and 165-167°C, The product had molecular weight M 240. Found: C 56.0; H 8.8; N 11.1; H_2O 7.0%. $C_{12}H_{20}N_2O_3 \cdot H_2O$. Calculated: C 55.7; H 8.5; N 10.8; H_2O 6.9%.

The substance with mp 128-130°C was dissolved in $CHCl_3$, the solution was evaporated, and ether was added to the residue to give a precipitate with mp 165-167°C and M 240. Found: C 55.9; H 8.7; N 11.2; H_2O 7.1%. $C_{12}H_{20}N_2O_3 \cdot H_2O$. Calculated: C 55.7; H 8.5; N 10.8; H_2O 6.9%.

The substance with mp 165-167°C was dissolved in acetone, and the solution was cooled to give a precipitate with mp 128-130°C.

LITERATURE CITED

1. Zh. A. Krasnaya, E. P. Prokof'ev, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2318 (1970).
2. Zh. A. Krasnaya, E. P. Prokof'ev, M. Sh. Zaripova, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2356 (1973).
3. E. P. Prokof'ev, Zh. A. Krasnaya, and K. M. Litvak, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 766 (1979).
4. Zh. A. Krasnaya, E. P. Prokof'ev, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 816 (1979).
5. E. P. Prokof'ev and Zh. A. Krasnaya, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1011 (1980).
6. Zh. A. Krasnaya, E. P. Prokof'ev, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 123 (1978).
7. Zh. A. Krasnaya, E. P. Prokof'ev, I. P. Yakovlev, and E. D. Lubuzh, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2325 (1980).
8. E. P. Prokof'ev and Zh. A. Krasnaya, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2284 (1980).
9. A. S. Dvornikov, Zh. A. Krasnaya, and Ya. N. Malkin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 390 (1981).
10. Zh. A. Krasnaya, T. S. Stytsenko, V. S. Bogdanov, E. D. Daeva, and A. S. Dvornikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1075 (1985).
11. Zh. A. Krasnaya and T. S. Stytsenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 850 (1983).
12. E. P. Prokof'ev, Zh. A. Krasnaya, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2013 (1973).
13. Yu. E. Borisevich, A. S. Tatikolov, and V. A. Kuz'min, Khim. Vys. Énerg., 12, 474 (1978).