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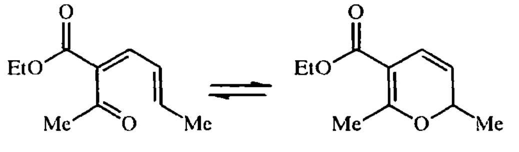
DIENONE $\rightleftharpoons$ 2H-PYRAN VALENCE ISOMERIZATION. (REVIEW)

Zh. A. Krasnaya

The researches of the author and her colleagues on the synthesis of α,α-dicarbonyl-containing dienes with various structures and study of their valence isomerization to 2H-pyrans ^1H by an ^{13}C NMR, UV, and IR spectroscopy and flash photolysis are reviewed.

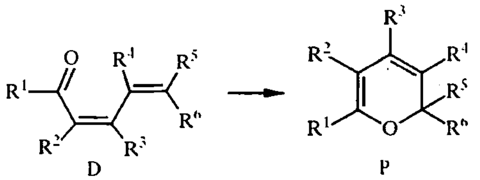
Isomerization taking place solely through the redistribution of the electrons of bonds without any migration of atoms or groups has been called valence isomerization. Although this term is imprecise and in some papers the described effect has been called "electrocyclic cyclization," "valence tautomerism," etc., we use the term "valence isomerization" as the most widely established description.

In the majority of published papers the conclusion that valence isomerization exists has been based mainly on indirect data, since it has only been possible to observe one valence isomer directly [1-8]. Examples where an equilibrium between two valence isomers was detected are given in the reviews [1, 2] and in [9-15]. Before the publication of our first paper in 1970 [16], in which the valence isomerization of 3-ethoxycarbonylhepta-3,5-dien-2-one (*E*)-(Ia) to the corresponding substituted 2H-pyran IIa was discovered, only one example (*cis*-β-ionone) in which an equilibrium between the two valence isomers had been described in the literature [17].



(*E*)-Ia IIa

Subsequently we undertook a direct systematic investigation of the dienone $\rightleftharpoons$ 2H-pyran valence isomerization for the case of various α,α-dicarbonyl-substituted dienes and functionally substituted 2H-pyrans, which were previously unknown.



D P

The results of these investigations are summarized in the present review.

We studied the effect of substituents and solvents on the position of equilibrium and determined the thermodynamic and activation parameters of the process. We also determined the effect of the solvents on the activation parameters.

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It seemed of particular interest to investigate valence isomerization in the series of δ-aminocarbonyl diene compounds. We assumed that the δ-aminodienones and 2-amino-2H-pyrans must differ significantly in the position of the absorption band in the electronic spectra, since the amino group in 2H-pyrans is withdrawn from the chain of conjugation. As a result it could be expected that the compounds would be the simplest photochromes.

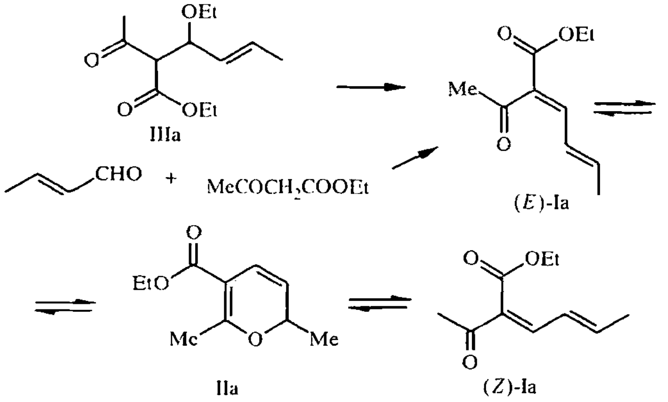
We synthesized for the first time δ-dimethylaminocarbonyl compounds containing a substituent (F, Cl, Br, CN, Me, Ph, OEt, NMe_2, *i*-Pr) at the γ-position, and we studied the δ-aminodienone ⇄ 2-amino-2-pyran valence isomerization that we detected in these compounds. δ-Heteroaryl-α,α-dicarbonyl-containing dienes have also been synthesized in recent years, and their valence isomerization has been studied.

The D ⇄ P equilibrium was studied by ^1H and ^{13}C NMR, UV, and IR spectroscopy and also by flash photolysis. Here great attention was paid to the possibilities and limits for each of the spectral methods to determine the structure of the valence isomers and the equilibrium between them.

Since the valence isomerization of dienones depends to a significant degree on their stereochemical structure, a reliable method based on the NMR spectra analysis was developed for the determination of the trisubstituted α,β-double bond configuration in the dienones [18, 19].

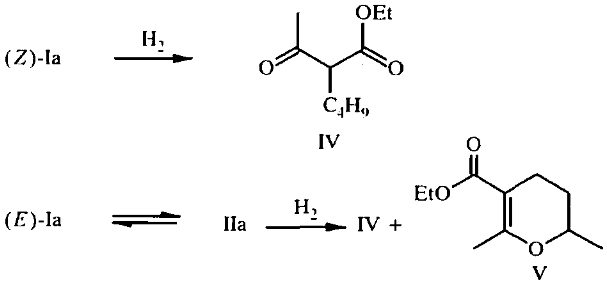
VALENCE ISOMERIZATION OF 3-ETHOXYCARBONYLHEPTA-3,5-DIEN-2-ONE (Ia)

The diene keto ester Ia and the pyran IIa in equilibrium with it were obtained by the elimination of the alcohol from the ethoxybutenyl-substituted β-ketoester IIIa and also by the Knoevenagel reaction between crotonaldehyde and acetoacetic ester [16]:



The ketoester Ia synthesized by both methods was a 3:2 mixture (GLC) of the (*E*)- and (*Z*)- isomers with respect to the α,β-double bond, which could be separated by fractional distillation. The isolated isomers had the same elemental composition and identical UV spectra, which only differed in the values of the extinction coefficient. However, study of the PMR spectra showed that one isomer was an individual (it was assigned the (*Z*)-configuration) while the second was a 1:1 mixture of the 2H-pyran IIa and the keto ester (*E*)-Ia (with the *trans*- configuration of the MeCO and Hβ), which gave one peak on the GL chromatogram. For final evidence for the presence of the 2H-pyran the keto ester (*Z*)-Ia and the mixture (*E*)-Ia ⇄ IIa were hydrogenated. As a result only the butylacetoacetic ester IV was obtained from (*Z*)-Ia, while a mixture of the ester IV and the dihydropyran V was obtained from (*E*)-Ia ⇄ IIa.

The dihydropyran V was formed as a result of partial hydrogenation of the 2H-pyran IIa, and this agrees with the data in [20]. The fact that the valence isomers (*E*)-Ia and IIa are in equilibrium with each other followed from their PMR spectra recorded at various temperatures. If the temperature is increased, the concentration of the keto ester (*E*)-Ia increases, while the concentration of the 2H-pyran IIa decreases. On return to the original temperature the initial form of the spectrum is restored. The (*E*)- and (*Z*)- isomers of the keto ester Ia are also in equilibrium with each other, but the time for the establishment of such an equilibrium is substantially longer than for the equilibrium (*E*)-Ia $\rightleftharpoons$ IIa. In carbon tetrachloride, chloroform, and other solvents a three-component mixture (*E*)-Ia $\rightleftharpoons$ IIa $\rightleftharpoons$ (*Z*)-Ia with one and the same composition is formed from the keto ester (*Z*)-Ia and from the mixture (*E*)-Ia $\rightleftharpoons$ IIa after a month.



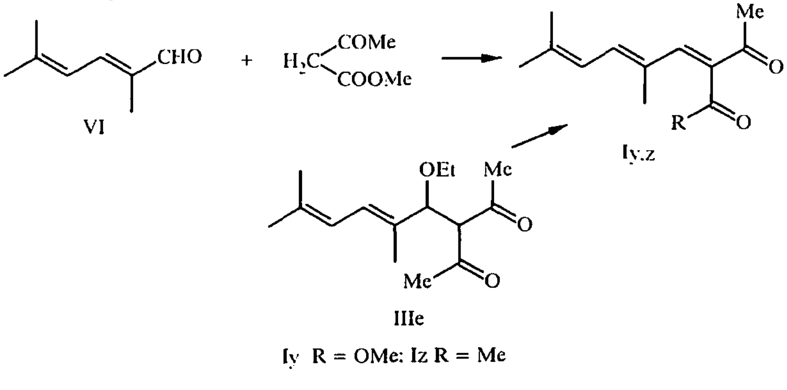
It should be noted that the synthesis of the keto ester Ia from crotonaldehyde and acetoacetic ester by the action of $TiCl_4$ in dioxane was reported in [21] but without any reference to the presence of the (*E*)- and (*Z*)-isomers and 2H-pyran.

SYNTHESIS OF α,α-DICARBONYL-SUBSTITUTED DIENES AND STUDY OF THEIR VALENCE ISOMERIZATION

In order to determine the effect of structural factors on the dienone $\rightleftharpoons$ 2H-pyran valence isomerization we synthesized a series of α,α-dicarbonyl-substituted dienes, the structure of which is shown in Table 1. Most of the compounds were obtained by the Knoevenagel reaction from α,β-unsubstituted aldehydes (with piperidine or a mixture of piperidine and glacial acetic acid as catalyst). In cases where it was not possible to obtain the α,α-dicarbonyl-substituted dienes and trienes in this way they were obtained from the β-ethoxyalkylene-substituted diketones IIId,e and keto esters IIIb,c:

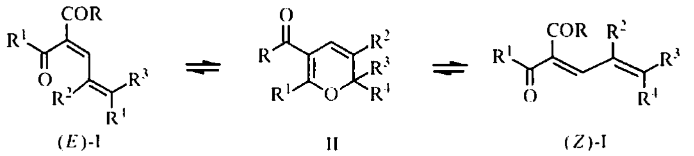
Ib, IIIb = ROEt, $R^3 = R^4 = H$; Id, IIIc R = OMe; $R^3 = R^4 = H$; Ih, IId $R = R^3 = R^4 = Me$;
Ig, IIIc $R = R^4 = Me$; $R^3 = H$ (Ih is also formed readily fromβ,β-dimethylacrolein
and acetylacetone by the Knoevenagel reaction [23])

In the Knoevenagel reaction (catalyst piperidine) the trienes Iy,z were formed with yields of not more than 15% and contain the difficultly separable initial aldehyde VI as impurity. When the procedure [21] (catalyst $TiCl_4$) was used, the triene keto ester Iy was obtained with a yield of 30%.



Iy R = OMe: Iz R = Me

TABLE 1. The Structure of α,α-Dicarbonyl-Containing Dienes and Their Equilibrium Isomeric Composition*



Compound	R	R¹	R²	R³	R⁴	Isomeric composition of reaction product in equilibrium (wt. %)			Ref.
						(*E*)-I	II	(Z)-I	
1	2	3	4	5	6	7	8	9	10
(*E*)-Ia $\rightleftarrows$ IIa $\rightleftarrows$ (*Z*)-Ia	EtO	Me	H	H	Me	30	30	40	[16]
(*E*)-Ib $\rightleftarrows$ IIb $\rightleftarrows$ (*Z*)-Ib	EtO	Me	H	H	H	45	30	25	[22]
(*E*)-Ic $\rightleftarrows$ IIc $\rightleftarrows$ (*Z*)-Ic	EtO	Me	H	Me	Me	17	68	15	[22]
(*E*)-Id $\rightleftarrows$ IId $\rightleftarrows$ (*Z*)-Id	MeO	Me	H	H	H	43	37	20	[23]
(*E*)-Ie $\rightleftarrows$ IIe $\rightleftarrows$ (*Z*)-Ie	MeO	Me	H	H	Me	40	40	20	[23]
(*E*)-If $\rightleftarrows$ IIf $\rightleftarrows$ (*Z*)-If	MeO	Me	H	Me	Me	26	62	12	[23]
Ig $\rightleftarrows$ IIg*²	Me	Me	H	H	Me	72	28	—	[23]
Ih $\rightleftarrows$ IIh*²	Me	Me	H	Me	Me	64	36	—	[23]
(*E*)-Ii $\rightleftarrows$ IIi $\rightleftarrows$ (*Z*)-Ii	*t*-BuO	Me	H	Me	Me	18	17	65	[23]

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10
(*E*)-Ij $\rightleftarrows$ IIj $\rightleftarrows$ (*Z*)-Ij	EtO	*p*-$O_2NC_6H_4$	H	Me	Me	84	9	7	[23]
(*E*)-Ik $\rightleftarrows$ (*Z*)-Ik	EtO	Ph	H	H	Me	67	—	33	[22]
(*E*)-Il $\rightleftarrows$ (*Z*)-Il	EtO	Ph	H	Me	Me	86	—	14	[23]
(*E*)-Im $\rightleftarrows$ (*Z*)-Im	EtO	Me	H	H	Ph	60	—	40	[22]
In*²	Me	Me	H	H	Ph	100	—	—	[23]
IIo $\rightleftarrows$ (*Z*)-Io	MeO	Me	Me	Me	Me	0	83	17	[23]
IIp	MeO	Me	Me	H	Ph	0	100	0	[25]
IIq	Me	Me	Me	Me	Me	0	100	0	[23]
IIr	Me	Me	Me	H	Ph	0	100	0	[25]
IIs	EtO	Ph	Me	Me	Me	0	100	0	[23]
(*E*)-It $\rightleftarrows$ IIt $\rightleftarrows$ (*Z*)-It	MeO	Me	H	H	*cyclo*-C_6H_{11}	30	23	47	[24]
IIu	MeO	Me	Me	H	*cyclo*-C_6H_{11}	0	100	0	[24]
(*E*)-Iv $\rightleftarrows$ IIv $\rightleftarrows$ (*Z*)-Iv	MeO	Me	H	$(CH_2)_5$		16	67	17	[24]
IIw	MeO	Me	Me	$(CH_2)_5$		0	100	0	[24]
(*E*)-Ix $\rightleftarrows$ IIx $\rightleftarrows$ (*Z*)-Ix	MeO	Me	H	$(CH_2)_4$		47	31	22	[24]
(*E*)-Iy $\rightleftarrows$ (*Z*)-Iy	MeO	Me	Me	H	$CH{=}CMe_2$	75	0	25	[25]
Iz*²	Me	Me	Me	H	$CH{=}CMe_2$	100	0	0	[25]

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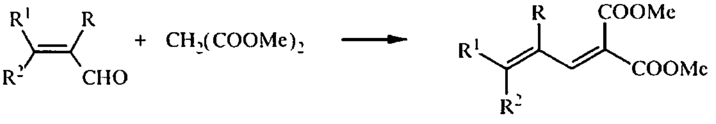
* The composition was determined by PMR in deuterochloroform at 30°C.

*² The (*E*)- and (*Z*)-isomers do not differ (topomers).

However, it was also not possible to obtain the diketone Iz by this method; it was produced with a small yield during the elimination of ethanol from the ethoxydiketone IIIf with Al_2O_3

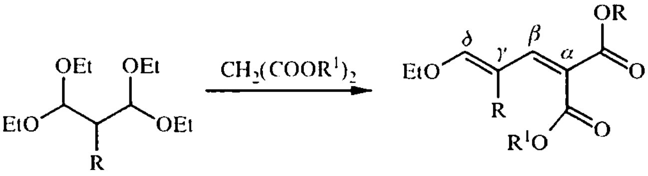
On the GL chromatogram all the synthesized diene and triene keto esters give two peaks, which were assigned by analogy with the keto ester Ia to the (*E*)- and (*Z*)-isomers; in a number of cases it was possible to separate them by fractional distillation under vacuum, fractional crystallization, or preparative chromatography.

The diene diesters VIIa-k were obtained by the condensation of conjugated aldehydes with dimethyl malonate:


VIIa-k

VIIa R = R^2 = Me; VIIb R = H, R^1 = R^2 = Me; VIIc R = R^2 = Me; VIId R = R^1 = H, R^2 = Ph;
VIIe R = Me, R^1 = H, R^2 = Ph; VIIj R= Me, R^2 = CH=CMe_2 ; VIIj R = R^1 = H, R^2 = *cyclo*-C_6H_{11};
VIIh R = Me, R^1 = H, R^2 = CH=CMe_2; VIIi R = H, R^1+R^2 = $(CH_2)_5$; VIIj R = Me, R^1+R^2 = $(CH_2)_5$;
VIIk R = H, R^1+R^2 = $(CH_2)_4$

The diene δ-ethoxydiesters VIIIa-c were obtained during the condensation of tetraethoxypropanes IXa,b with dialkyl malonates [23, 26]:


IXa,b VIIIa-c

IXa, VIIIa R = H, R^1 = Et; IXa, VIIIb R = H, R^1 = Me;
IXb, VIIIc R = R^1 = Me

It was not possible to obtain the diene δ-ethoxyketoesters and diketones from IXa,b and acetoacetic ester and acetylacetone.

The synthesized α,α-dicarbonyl-substituted dienes and trienes were studied by means of ^1H and ^{13}C NMR, UV, and IR spectroscopy. The ^1H and ^{13}C NMR spectra proved extremely informative during determination of the structure and configuration of the valence isomers.

In the ^1H NMR spectra the signals of the protons at $C_{(4)}$, $C_{(3)}$ and $C_{(2)}$ and the Me groups at $C_{(2)}$ in the 2H-pyrans were shifted upfield compared with the corresponding protons in the dienones. We determined the chemical shifts and ^{13}C, ^1H spin–spin coupling constants for α,α-dicarbonyl-substituted dienes and the corresponding 2H-pyrans for the first time [28].

The chemical shifts of $C_{(6)}$ in the 2H-pyrans amount to 160-165 ppm, while those of the corresponding C=O carbon in the MeCO (PhCO) amount to 199-203 ppm. Compared with the corresponding carbon atoms of the dienones the $C_{(2)}$,$C_{(4)}$ and $C_{(5)}$ atoms of the 2H-pyrans have significantly smaller chemical shifts. The largest difference is observed for Cδ and $C_{(2)}$, which differ from each other by hybridization.

The fact that the signals belong to the (*E*)- or (*Z*)-isomer was judged from the values of the $^3J_{CO,H\beta}$ constants and the ^{13}C chemical shifts of the CO group. As a result of study of the ^{13}C NMR spectra of the wide range of (*Z*)- and (*E*)-isomers of conjugated ω-amino-, alkoxy-, alkyl-, dialkyl-, and phenyl-substituted β-dicarbonyl compounds that we synthesized it was established that the spin–pin coupling constants $^3J_{CO,H\beta}$ and the chemical shifts for ^{13}C the atoms of the CO group are stereospecific $^3J_{CO,H\beta(cis)} < {}^3J_{CO,H\beta(trans)}$ [18], δCO(*cis*) < δCO (*trans*) [19].

The UV spectra of the dienones and 2H-pyrans have a long-wave absorption maximum in practically the same region but differ substantially in intensity. In the 2H-pyrans the extinction coefficient (ε) is 3380-4660, whereas in the dienones it is significantly higher (17000-24000). In addition, in the 2H-pyrans in contrast to the dienones the most shortwave maximum (205-217 nm) is the strongest (ε = 11000-17000). This makes it possible from the UV spectra to make a qualitative judgement about the presence of valence isomeric forms in the investigated series of functionally substituted dienes.

It is significantly more difficult to establish the presence of valence isomers from the IR spectra, since the absorption bands due to the stretching vibrations of the carbonyl and the conjugated double bonds often overlap. Nevertheless, the IR spectra make it possible to gage the significance of differences in the content of the valence isomers in the pure form and in solution.

All the synthesized liquid α,α-dicarbonyl-containing dienes have practically identical IR spectra in the film (the pure substance) and in carbon tetrachloride solution [23]. This indicates insignificant change in the composition for the equilibrium mixture of valence isomers in the pure liquid substance and in the solvent. For the case of the keto ester If this was also confirmed by the PMR spectra [23].

A different picture was observed in the case of the diketone Ih. When the equilibrium mixture of Ih $\rightleftarrows$ IIh was cooled, the crystalline diketone Ih was isolated. On dissolution in organic solvents (carbon tetrachloride, ethanol) the Ih underwent valence isomerization to the 2H-pyran IIh, as a result of which the Ih $\rightleftarrows$ IIh equilibrium mixture was formed. This transformation is easily traced by means of the IR and UV spectra [23].

The content of the valence isomers in the (*E*)-dienone I $\rightleftarrows$ 2H-pyran II equilibrium mixture at 30°C in deuterochloroform, observed in the PMR spectra, is shown in Table 1. These data make it possible to examine the effect of structural factors on the D $\rightleftarrows$ P equilibrium.

Successive substitution of the hydrogen atoms at Cδ by the Me or pentamethylene group (compounds Ia-h,s) leads to an increase in the content of the 2H-pyrans. The destabilization of the dienones probably results from the increase in the steric strain between the substituents. The introduction of substituents having a stronger electron-withdrawing effect at the α-position (cf. the diketones Ig,h and the keto esters Ie,f) leads to additional stabilization of the dienones and to an increase in their content. The dienones become thermodynamically more favorable with elongation of the conjugated system by the introduction of a phenyl group (compounds Im,n) or double bond (compounds Iy,z) at the β-position.

A particularly strong shift of equilibrium, as a result of which it is possible to observe only the 2H-pyran, occurs during substitution of a hydrogen atom at Cγ by a Me group. The keto ester Il and the diketone In exist only in the dienone form, while their homologs with the Me group at the γ-position Is and Ir are fully transformed into the 2H-pyrans IIs and IIr.

The strong destabilizing effect of the bulky substituent at Cγ on the dienone is explained by the fact that in the s-*trans* conformer with respect to the β,γ-bond there is significant steric interaction between the substituent at Cα, situated in the *trans* position to Hβ, and the hydrogen or substituent at Cγ.

The spin–spin coupling constant $J_{\beta,\gamma}$ of 12-12.5 Hz for the series of α,α-dicarbonyl substituent dienes gives reason to suppose that the dienones exist predominantly in the form of s-*trans* conformers with respect to the Cβ–Cγ bond. (The s-*cis* conformation is probably realized in the transition state of valence isomerization.)

The fact that the γ-methyl-substituted trienones Iy,z only exist in the open form cannot be explained unambiguously. Since the keto ester Iy is a mixture of the (*E*)- and (*Z*)-isomers while the trienone Iz is a diketone, they do not contain stereochemical hindrances for cyclization due to isomerism with respect to the α,β-bond. It is also impossible to rule out the possibility that the trienones Iy,z may exist in the s-*cis* conformation with respect to the Cβ,γ-bond, and the Me group at Cγ will not then lead to destabilization of the open form on account of steric hindrances.

The pyran form was not detected in any of the diene diesters VIIa-k. In [26] we reported that according to the ^{1}H NMR spectra the diene δ-ethoxy diesters VIIIa,b contain 20% of the 2H-pyran. However, the assignment of the resonance signals to the 2H-pyrans proved erroneous, since they belong not to the 2H-pyrans but to the geometric isomers of the diene δ-ethoxy diesters with the (*Z*)- configuration of the protons at the γ,δ-double bond ($^3J_{\gamma,\delta}$ = 6 Hz [24].

It should be mentioned that in 1997 the reaction of certain conjugated aldehydes with substituted alkyl-3-oxobutyrates under the conditions of phase-transfer catalysis, leading to three-component mixtures of the (*E*)- and (*Z*)- isomers of the dienones and 2H-pyrans, was investigated [15]. Among the latter there are equilibrium mixtures (*E*)- Ie,f $\rightleftarrows$ IIe,f $\rightleftarrows$ (*Z*)-Ie,f, which we obtained earlier, and our data were confirmed in [15].

TABLE 2. The Thermodynamic and Activation Parameters of Valence Isomerization in Deuterochloroform

Compound	$\Delta H^0 = H^0_P - H^0_D$, kcal/mole	$\Delta S^0 = S^0_P - H^0_D$, kcal/mole
(*E*)-Id $\rightleftharpoons$ IId $\rightleftharpoons$ (*Z*)-Id	-2.07	-5.6
(*E*)-If $\rightleftharpoons$ IIf $\rightleftharpoons$ (*Z*)-If	-3.73	-10.2
Ih $\rightleftharpoons$ IIh	-2.22	-8.7
Ih $\rightleftharpoons$ IIh*	—	—
Ih $\rightleftharpoons$ IIh*2	—	—

Compound	Dienone → pyran			Pyran → dienone		
	$\Delta H^{\#}$, cal/mole	$\Delta S^{\#}$, cal/mole·deg	$\Delta G^{\#}$, cal/mole	$\Delta H^{\#}$, cal/mole	$\Delta S^{\#}$, cal/mole·deg	$\Delta G^{\#}$, cal/mole
(*E*)-Id $\rightleftharpoons$ IId $\rightleftharpoons$ (Z)-Id	18.09	-14.4	22.45	19.03	-10.9	22.33
(*E*)-If $\rightleftharpoons$ IIf $\rightleftharpoons$ (*Z*)-If	16.21	-18.3	21.75	16.38	-19.5	22.29
Ih $\rightleftharpoons$ IIh	14.93	-24.6	22.38	15.01	-23.2	22.04
Ih $\rightleftharpoons$ IIh*	13.21	-30.3	22.39	13.37	-29.0	22.16
Ih $\rightleftharpoons$ IIh*2	17.68	-17.1	22.86	17.97	-12.91	21.88

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* In CD_3OD.

*2 In CD_3CN.

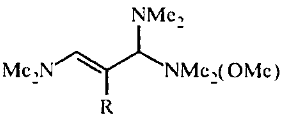
Study of the effect of solvents [$CDCl_3$, CD_3OD, CD_3NO_2, CD_3CN, $(CD_3)_2SO$] on the position of equilibrium for the valence isomers showed that the equilibrium is shifted appreciably toward the formation of the dienones in aprotic dipolar solvents [27]. The thermodynamic parameters of the valence isomers and the activation parameters of valence isomerization were determined for the case of compounds Id,f,h, in which both valence isomers are observed (Table 2) [27]. The kinetic measurements were carried out by the equilibration method.

To determine the effect of the solvent on the activation parameters of the diketone Ih the measurements were made in $CDCl_3$, CD_3OD and CD_3CN.

In all cases the enthalpies of the dienones (H_D^0) were appreciably higher than the enthalpies of the 2H-pyrans, and this agrees with the observed increase in the content of the dienones with increase of temperature. As expected, for the more ordered cyclic form the entropy of the pyrans is lower than the entropy of the dienones. In all the investigated cases the obtained $\Delta G^{\#}$ values (21.88-22.86) differ slightly.

SYNTHESIS OF DIENE AND TRIENE ω-DIMETHYLAMINO-γ-SUBSTITUTED α-CARBONYL COMPOUNDS AND STUDY OF THEIR VALENCE ISOMERIZATION TO 2-DIMETHYLAMINO-3-SUBSTITUTED 2H-PYRANS

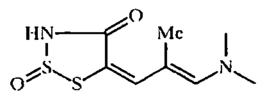
The 2H-pyran form was not detected in diene δ-dimethylamino diketones and keto esters $RCO-C(COR^1)=CH-CH=CHNMe_2$ [29]. In view of the fact that the introduction of the Me group at the γ-position of the dienones Ip-s led to a complete shift of the equilibrium toward the 2H-pyrans we synthesized the previously unknown δ-aminocarbonyl compounds containing a substituent at the γ-position. As starting compounds for the synthesis of such compounds we used the aminals (or aminal-acetals) of α-substituted β-dimethylaminoacroleins Xa-i [30, 31].



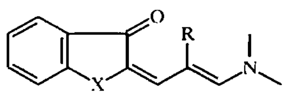
Xa-i

a R = Me, b Ph, c Cl, d Br, e OEt, f CN, g F, h *i*-Pr, i NMe_2

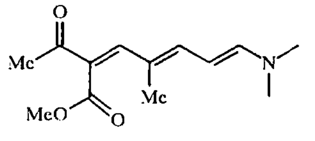
It was found that the aminals Xa-i had high reactivity. Their condensation with compounds containing an active methylene group does not require a catalyst and is hardly accompanied at all by the formation of side products. The substances XI-XIV obtained here are shown in Table 3, and the formulas of the compounds XV-XXIII synthesized similarly are given below.



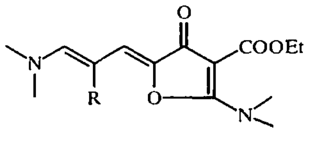
XV [37]



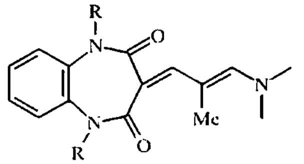
XVIa-d [38]



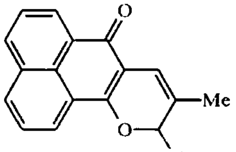
XVII [25]



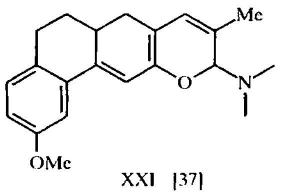
XVIIIa,b [37]



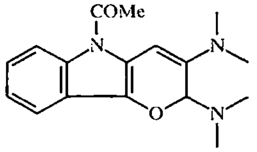
XIXa,b [39]



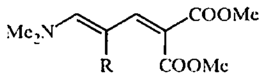
XX [39]



XXI [37]



XXII [37]



XXIIIa-i [30, 32-36]

XVIa X = NH; XVIb,c,d X = CO; XVIa,b,, XVIII, XIXb, XXIIIa R = Me; XVIc, XVIIIb, XXIIIb R = Cl;
XVId, XXIIIc R = CN; XIXa R = H; XXIIId R = Ph: XXIIIe R = Br; XXIIIf R = OEt; XXIIIg R = F;
XXIIIh R = *i*-Pr; XXIIIi R = NMe_2

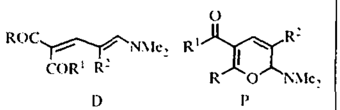
The triene keto ester XVII was obtained by the reaction of the keto ester XIa with the Iotsich reagent [25].

The structure of the synthesized substances was established on the basis of the ^1H and ^{13}C NMR and UV spectra data from which it follows conclusively that the compounds having the F atom or CN group at the γ-position and also all the diesters XIIIa-i exist only in the open dienone form; the compounds having the *i*-Pr or NMe_2 group at the γ-position exist only in the cyclic form as 2H-pyrans. Compounds XV, XVIa-d, XVII, XVIIIa,b, XIXa,b, XX-XXII exist in the form of the single valence isomer shown above. According to X-ray crystallographic analysis and ^{13}C NMR, the triene keto ester XVII is the (*Z*)- isomer with respect to the α,β-double bond [25].

The ketones XIIId-g, which contain a five-membered ring, are the (*E*)- isomers (with the *trans* arrangement of the CO and Cγ). Unlike them, the ketones XIIIa-c, containing a six-membered ring, are mixtures of 2H-pyrans and dienones in the form of the (*E*)- isomers.

In compounds XIa-e,j,k,n,s,t, XIIIa-c, and XIVa,b, containing Cl, Br, Me, Ph, or OEt at the γ-position a dynamic D $\rightleftharpoons$ P equilibrium is established in a number of solvents.

TABLE 3. The Structure and Yields of the Functionally γ-Substituted δ-Dimethylaminodienones and 2H-Pyrans

Compound	Valence isomer *	 D P			Yield, %	Reference
		R	R^1	R^2		
XIa	D $\rightleftarrows$ P	Me	OMe	Me	90	[30.32]
XIb	D $\rightleftarrows$ P	Me	OMe	Ph	60	[32]
XIc	D $\rightleftarrows$ P	Me	OMe	Cl	88	[33]
XId	D $\rightleftarrows$ P	Me	OMe	Br	70	[34]
XIe	D $\rightleftarrows$ P	Me	OMe	OEt	45	[34]
XIf	D	Me	OMe	CN	80	[34]
XIg	D	Me	OMe	F	94	[35]
XIh	P	Me	OMe	*i*-Pr	72	[36]
XIi	P	Me	OMe	NMe$_2$	76	[36]
XIj	D $\rightleftarrows$ P	Ph	OEt	Me	60	[32]
XIk	D $\rightleftarrows$ P	Ph	OEt	Ph	70	[32]
XIl	D	Ph	OEt	Cl	53	[33]
XIm	D	Ph	OEt	Br	64	[34]
XIn	D $\rightleftarrows$ P	Ph	OEt	OEt	64	[34]
XIo	D	Ph	OEt	CN	50	[34]
XIp	D	Ph	OEt	F	78	[35]
XIq	P	Ph	OEt	*i*-Pr	79	[36]
XIr	P	Ph	OEt	NMe$_2$	65	[36]
XIs	D $\rightleftarrows$ P	Me	Me	Me	88	[32]
XIt	D $\rightleftarrows$ P	Me	Me	Br	51	[34]
XIu	D	Me	Me	CN	80	[34]
XIv	P	Me	OMe	*i*-Pr	80	[36]
XIw	P	Me	OMe	NMe$_2$	90	[36]

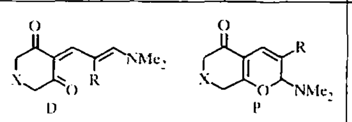
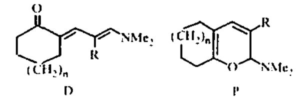
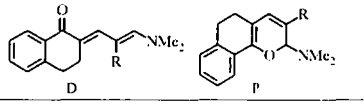
		 D P			
		X	R		
XIIa	D $\rightleftarrows$ P^{*2}	CMe$_2$	Me	73	[32]
XIIb	D $\rightleftarrows$ P^{*2}	CMe$_2$	Cl	63	[33]
XIIc	D $\rightleftarrows$ P^{*2}	CMe$_2$	OEt	40	[34]
XIId	D	CMe$_2$	CN	44	[34]
XIIe	D	CMe$_2$	F	10	[35]
XIIf	P	CMe$_2$	*i*-Pr	46	[36]
XIIg	P	CMe$_2$	NMe$_2$	70	[36]
XIIh	D $\rightleftarrows$ P^{*2}	CH$_2$	Me	60	[37]
XIIi	D $\rightleftarrows$ P^{*2}	CH$_2$CH$_2$	Me	30	[37]

TABLE 3 (continued)

Com-paund	Valence isomer			Yield, %	Reference
		n	R		
XIIIa	D ⇄ P	1	Me	55	[32]
XIIIb	D ⇄ P	1	Cl	10	[33]
XIIIc	D ⇄ P	1	OEt	44	[34]
XIIId	D	0	Me	41	[32]
XIIIe	D	0	Cl	38	[33]
XIIIf	D	0	Br	10	[34]
XIIIg	D	0	OEt	52	[34]
					
		R			
XIVa	D ⇄ P	Me		60	[32]
XIVb	D ⇄ P	Cl		65	[33]

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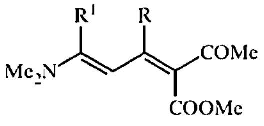
*D ⇄ P, the compound is present in the form of an equilibrium mixture of the valence isomers, the content of which depends on the solvent; D, the compound is present only in the dienone form; P, the compound is present only in the pyran form.

*[2]The D ⇄ P equilibrium is shifted largely toward the 2H-pyran.

The presence of both valence isomers is indicated by two sets of signals in the ^{13}C and ^{1}H NMR spectra and also by the data from the UV spectra, in which there are absorption bands for both valence isomers.*

Table 4 shows the contents of the keto esters XIa-i, x valence isomers, differing only in the nature of the substituent at Cγ, in the same solvents. The data in Table 4 make it possible to conclude that the content of the 2H-pyran form increases with increase in the size of the substituent at Cγ, irrespective of its electronic nature. This relationship is also observed in other γ-substituted dienones. It should be noted that the keto esters XIg,f,x, which exist only in the dienone form, represent mixtures of the (*E*)- and (*Z*)- isomers with respect to the α,β double bond, i.e., they contain the (*E*)- isomer, in which cyclization is possible.

In the case of bulky substituents the destabilization of the dienone form, which leads to the equilibrium mixture D ⇄ P or to P alone, is due to steric interaction between the C=O of the acetyl group and the substituent at Cγ in the (*E*)- isomer of the keto ester, capable of cyclization.



XXIVa,b

a R = H, R^1 = Me [36], b R = Me, R^1 = H [36]

The introduction of substituents at the β- or δ- position (keto esters XXIVa,b) does not lead to the appearance of the 2H-pyran form.

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*In the ^{1}H ^{13}C and NMR spectra of the keto esters XIa,b there is only one set of signals even in solvents where according to the UV spectra both valence isomers are present in comparable amounts. Such an averaged pattern in the NMR spectra must be explained by the relatively low energy barrier of the valence isomerization [40].

TABLE 4. The Content of the 2H-Pyran in the D $\rightleftarrows$ P mixture of the keto esters XIa-i,x in various solvents

Compound	R	R_B[*2], Å	Content of 2H-pyran*, %		
			$CDCl_3$	CD_3CN	CD_3OD
XIx	H	1,2	0	0	0
XIg	F	1,35	0	0	0
XIf	CN	—	0	0	0
XIc	Cl	1,80	73	27	16
XId	Br	1,95	89	50	75[*3]
XIe	OEt	—	92	56	47
XIa	Me	2,0	97[*4]	89[*4]	88[*4]
XIb	Ph	1,7	98[*4]	70[*4]	67[*4]
XIi	NMe_2	—	100	100	100
XIh	*i*-Pr	—	100	100	100

---

* According to the PMR spectrum.

[*2] The van der Waals radius.

[*3] At -35°C.

[*4] According to the UV spectra.

It was shown by ^1H and ^{13}C NMR, UV, and IR spectroscopy that the series of γ-substituted δ-dimethylaminodienones exhibit solvato- and thermochromic characteristics. The solvents have a very strong effect on the position of the D $\rightleftarrows$ P equilibrium [40]. Thus, the keto esters XIa-e,j,k and the diketones XIs,t are present in the 2H-pyran form in hexane, $Cl_2C = CCl_2$ and carbon tetrachloride and in the δ-aminodienone form in water.

As supposed, the δ-aminodienones and their valence isomers, the 2H-pyrans, differ significantly in their UV spectra. A significant bathochromic shift ($\Delta\lambda_{max}$ 90-125 nm) is observed in the UV spectra during the transition from hexane (λ_{max} 294-300 nm, ε 4500-6500) to water (λ_{max} 390-420 nm, ε 40000-50000).

In a series of organic solvents both valence isomers are present. With increase of the solvent capacity for specific solvation, characterized by the parameter E_T the content of the dienone form is substantially increased. There is a particularly strong shift of the equilibrium with increase of the water content in the organic solvents. In the cyclic diketones XIIa-c,h,i the equilibrium in the organic solvents is shifted substantially toward the 2H-pyran form. In the cyclic ketones XIIIa-c and XIVa,b the effect of the solvent on the D $\rightleftarrows$ P equilibrium is insignificant. The obtained data show that in the absence of a substituent containing a carbonyl group in the 2H-pyran the concentration of the dienone form in solvents capable of specific solvation is hardly increased at all. The existence of the δ-amino ketones in the form of one or the other valence isomer can be affected by the aggregation state. Thus, the keto ester XIa and the ketone XIIIc are dienones in the crystalline state and 2H-pyrans in the melt. In the case of the keto esters XIa,e,n it was shown that as also in the diene ketoesters not containing the NMe_2 group the D $\rightleftarrows$ P equilibrium is shifted toward the dienone form.

THE PHOTOCHROMISM OF γ-SUBSTITUTED δ-DIMETHYLAMINODIENONES

Study of the series of synthesized γ-substituted δ-dimethylaminodienones by flash photolysis showed that many of them exhibit photochromic characteristics [33, 34, 41]. Thus, the impulsed exposure of compounds XIa,c,e,n and XIIIc in heptane to UV light at the absorption frequency of the 2H-pyrans (290 nm) leads to photochemical opening of the pyran ring with the formation of the (*Z*)-isomers of the dienones ((λ_{max} 380-400 nm), which at the end of irradiation isomerize to the (*E*)-isomers (λ_{max} 350-370 nm) followed by their cyclization to 2H-pyrans. In the ketone XIIIc the observed isomerization corresponds to the (*E*) → (*Z*) → P transition. The 2H-pyrans that are valence isomers of the corresponding diketones XIs, XIIc also undergo reversible photoisomerization to the dienone form.

Above it was shown that δ-dimethylaminodienones containing the *i*-Pr or NMe_2 group at the γ-position exist only in the 2H-pyran form, irrespective of the solvent. However, the impulsed irradiation of these 2H-pyrans in a polar solvent (isopropyl alcohol), which stabilizes the open diene form, leads to the reversible photocleavage of the C–O bond of the pyran ring with the formation of the corresponding dienone forms. For some of these compounds it was also possible to observe photoisomerization to the dienone form in nonpolar media.

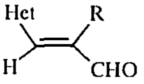
The kinetic and activation parameters of the photoisomerization D(*Z*) → D(*E*) and the cyclization D → P were given in [34].

For all the investigated compounds the free energies of activation for cyclization ($\Delta G^{\#}$) are close (17-19 kcal/mole) and substantially lower (by 3-5 kcal/mole) than $\Delta G^{\#}$ for the cyclization of the diene α,α-dicarbonyl compounds not containing the NMe_2 group examined above. The obtained $\Delta G^{\#}$ values are close to the corresponding $\Delta G^{\#}$ values for the cyclization of the merocyanine forms of spiropyrans to the spirocyclic forms with closure of the C–O bond [42].

The relatively low values of the free energy of activation for (*Z*),(*E*)- isomerization about the Cα=Cβ bond (13-14 kcal/mole) agree with the data from the ^1H and ^{13}C NMR spectra, in which the lines of the (*E*)- and (*Z*)-isomers in XIa, c, e, n at 20°C are not observed individually. This is probably due to the averaging of their chemical shifts as a result of rapid rotation about the Cα=Cβ bond, characteristic of the analogous diene δ-amino-α,α-dicarbonyl compounds not containing a substituent at Cγ [43].

THE SYNTHESIS OF δ-HETEROARYL-α,α-DICARBONYL-CONTAINING DIENES AND STUDY OF THEIR VALENCE ISOMERIZATION

In order to study the effect of heteroaryl substituents at the δ position of α,α-dicarbonyl-containing dienes on their valence isomerization the Knoevenagel reaction was realized between the α,β-unsaturated β-heteroaryl aldehydes XXVa-i and the methyl and ethyl esters of acetoacetic XXVIa, b or malonic XXVIIa, b acid [44].



XXVa-i

XXVa Het = 2-furyl, R = H; XXVb Het = 2-thienyl, R = H; XXVc Het = 2-pyridyl, R = H;
XXVd Het = 3-pyridyl, R = H; XXVe Het = 4-pyridyl, R = H; XXVf Het = 2-furyl, R = Me;
XXVg Het = 2-thienyl, R = Me; XXVh Het = 2-pyridyl, R = Me; XXVi Het = 3-pyridyl, R = Me

The initial aldehydes XXVa,b,f-h were obtained as a result of the aldol condensation of heterocyclic aldehydes with acetaldehyde and propionaldehyde [45-47]. It should be noted that the recently developed method of aldol condensation in a heterophase system [47] proved suitable for the synthesis of the α-methyl-substituted aldehydes XXVg,h and also XXVi. It was, however, unsuitable for the synthesis of β-pyridylacroleins XXVc-e.

It has been stated many times in the literature that the condensation of acetaldehyde with aldehydes of the pyridine series gives very low yields [48, 49]. The best method for the synthesis of β-pyridylacroleins XXVc-e was the Wittig reaction between the corresponding pyridinecarbaldehydes and (formylmethylene)triphenylphosphorane [50], in spite of the need to prepare the latter. We were also able to obtain β-(2-pyridyl)acrolein XXVc with a 15% yield by the fairly simple procedure proposed for the synthesis of β-(4-pyridyl)acrolein XXVe by the aldol condensation of 2-pyridinecarbaldehyde with acetaldehyde in benzene in the presence of morpholine acetate [49]. An attempt to obtain this compound by the condensation of 2-pyridinecarbaldehyde with the lithium derivative of the Schiff base $CH_3CH=N(t\text{-}Bu)$ [51] was unsuccessful.

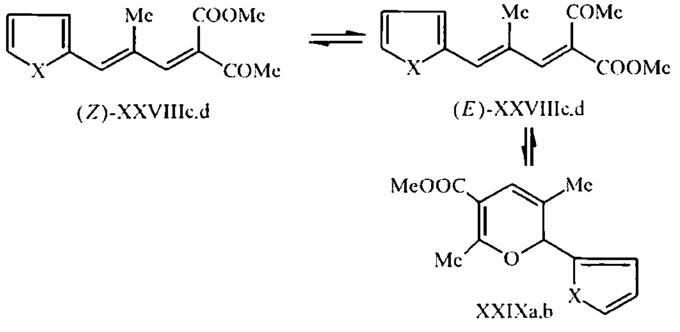
The condensation of the aldehydes XXVa-i with the esters XXVI and XXVIIa,b was carried out in the presence of a catalyst (piperidine or a mixture of piperidine and glacial acetic acid). The structure of the obtained products was established by means of the ^1H and ^{13}C NMR and UV spectra.

The diene keto esters XXVIIIa,b are formed from β-furyl- and β-thienylacroleins XXVa,b and the keto ester XXVIa as an equilibrium mixture of the (*E*)- and (*Z*)- isomers with respect to the α,β double bond (the partion of (*E*)- isomer is 54 and 60% respectively).

(*Z*)-XXVIIIa.b (*E*)-XXVIIIa.b

X = O, S

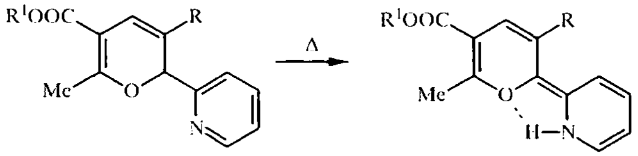
The 2H-pyrans XXIXa,b (12-13%) are formed from the α-methyl-substituted β-furyl- and β-thienylacroleins XXVf, g and the keto ester XXVIa in addition to the (*Z*) and (E) isomers of the dienes (XXVIIIc,d).



(*Z*)-XXVIIIc.d (*E*)-XXVIIIc.d

XXIXa.b

During the condensation of α-methyl-β-(2-pyridyl)acrolein XXVh with the keto esters (XXVIa,b) only the pyrans XXIXc,d are formed:

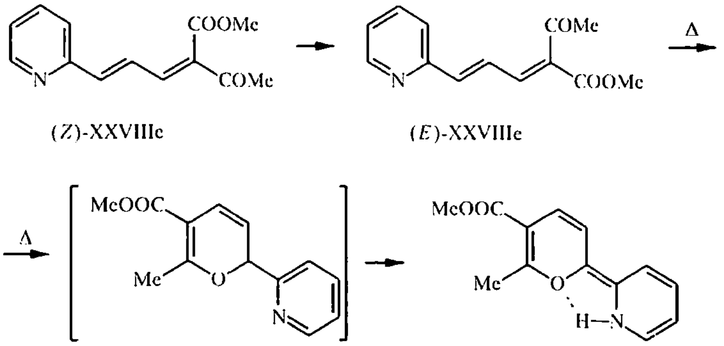


XXIXc.d XXXa.b

XXIXc. XXX R = R^1 = Me: XXIXd.XXXb R = Me, R^1 = Et

It was found that the pyrans XXIXc,d were unexpectedly converted during distillation or heating into 3,6-dimethyl-5-alkoxycarbonyl-2-(2-pyridyl)pyrans XXXa,b, which are chelates with an intramolecular hydrogen bond.

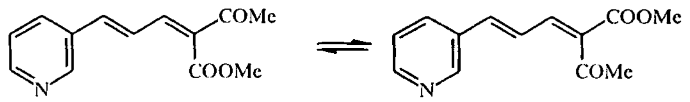
The reaction of β-(2-pyridyl)acrolein XXVc with the keto ester XXVIa gives a 40:60 mixture of the (*E*)- and (*Z*)-isomers of the keto ester XXVIIIe, which undergoes cyclization when heated to the ylidene pyran XXXc.



(*Z*)-XXVIIIe (*E*)-XXVIIIe

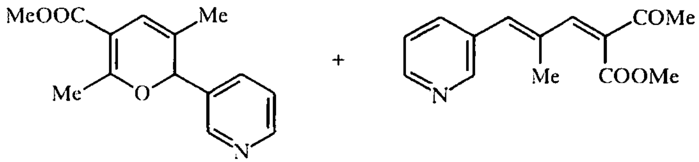
XXIXc XXXc

The condensation of β-(3-pyridyl)acrolein XXV with the keto ester XXVIa gives the keto ester XXVIIIf in the form of a 55:45 equilibrium mixture of (*Z*)- and (*E*)-isomers.



(*Z*)-XXVIIIf (*E*)-XXVIIIf

In contrast to the aldehyde XXVd the reaction of its α-methyl-substituted derivative XXVi with the keto ester XXVIa leads to 3,6-dimethyl-5-methoxycarbonyl-2-(3-pyridyl)pyran XXIXf, containing 14% of the dienone (*Z*)-XXVIIIg.



XXIXf XXVIIIg

The product obtained by the condensation of β-(4-pyridyl)acrolein XXVe with the keto ester XXVIa, as also with the keto ester XXVIIIf, represents a 3:2 mixture of the (*Z*)- and (*E*)-isomers of XXVIIIh not containing the corresponding pyran as impurity.

(*Z*)-XXVIIIh (*E*)-XXVIIIh

It should be noted that of the pyridyl-containing dienones and 2H-pyrans only those containing a 2-pyridyl ring are converted into ylidene pyrans of the XXX type.

As in the series of dienones containing an alkyl, phenyl, or dimethylamino group at the δ-position, the introduction of a substituent at the γ-position of δ-heteroaryldienones has a significant effect on the position of the equilibrium between the valence isomers.

With the introduction of a methyl substituent at the γ-position of δ-furyl(thienyl)dienones the formation of a three-component mixture of the (*E*)- and (*Z*)-isomers and the corresponding 2H-pyran is observed, while in γ-methyl-δ-pyridyldienes the equilibrium is shifted completely toward the 2H-pyran form.

In all cases where the (*E*)- and (*Z*)-isomers of the diene keto esters or their mixtures with the corresponding 2H-pyrans are formed as a result of the reaction of β-heteroaryl- and β-heteroaryl-α-methylacroleins with the ketoester XXVIa it was possible to isolate the individual crystalline (*Z*)-isomers, which were converted after several days in solution in deuterochloroform, deuteromethanol, or other solvents into an equilibrium mixture of the same composition, from which they were isolated.

The condensation of β-hetoaryl- and β-heteroaryl-α-methylacroleins XXVa-i with the malonates XXVIIa,b gave the diene diesters, which exist only in the open form and do not contain the 2H-pyrans.

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