EFFECT OF THE STRUCTURE OF CONJUGATED TRIENONES AND δ-PHENYL DIENONES ON THEIR ABILITY TO UNDERGO CYCLIZATION TO 2H-PYRANS

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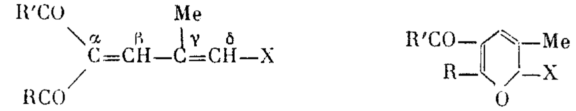
In a continuation of research on dienone ⇄ 2H-pyran valence isomerization [1-4], in the present study γ-methyl-α-functionally substituted trienones and δ-phenyl dienones were synthesized for the first time in order to study the effect of lengthening of the polymethine chain or the introduction of a Ph group in the δ position on valence isomerization to 2H-pyrans.



R and R' = Me, OMe; X = CH=CHNMe$_2$, CH=CMe$_2$, Ph.

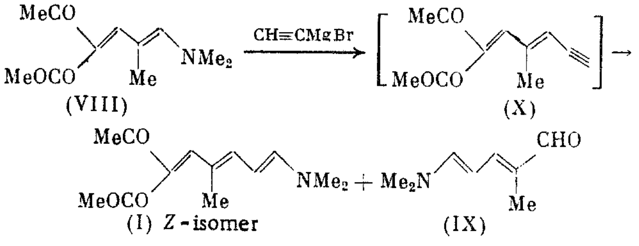
Substances that display solvatochromic, thermochromic, and photochromic properties as a result of δ-amino dienone ⇄ 2-amino-2H-pyran valence isomerization were detected in series of γ-substituted δ-dimethylamino dienones, which were previously sysnthesized [4-6]. In this connection the synthesis of ξ-dimethylamino-γ-methyl trienones (X = CH=CHNMe$_2$) also seemed of practical interest, since a substantial shift to the long-wave region of the absorption maximum of the strongly conjugated open form as compared with the cyclic form, in which the enamine fragment is removed from the conjugation chain, was expected in the electronic spectrum in the case of the existence of an equilibrium between the trienone and 2H-pyran forms in these compounds.

A pyran form was not detected in previously studied [7] unsubstituted ξ-amino trienones and δ-amino dienones.

However, we have shown [1, 4, 6] that a dynamic equilibrium between the dienone and 2H-pyran forms was established in δ-amino dienones in view of the strong steric interaction between one of the substituents attached to the C$_\alpha$ atom and the γ proton when Me, Ph, and Cl substituents are introduced in the γ position.

Considering these data, we assumed that the introduction of an Me group in the γ position of ξ-dimethylamino trienones would lead to the formation of both valence isomers.

Trienone I was obtained in 38% yield in the reaction of keto ester VIII with CH≡CMgBr, as in [7].*



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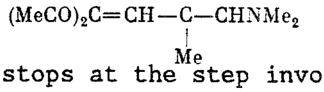
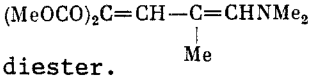
*We were unable to obtain a trienone from  $(MeCO)_2C{=}CH{-}\underset{Me}{C}{-}CHNMe_2$ and CH≡CMgBr, since, according to the UV spectral data, the reaction stops at the step involving the formation of a butadienyl acetylenic diketone, to the C≡CH bond of which NHMe$_2$ did not add. Since  $(MeOCO)_2C{=}CH{-}\underset{Me}{C}{=}CHNMe_2$ did not react with CH≡CMgBr, we were unable to obtain the trienic diester.

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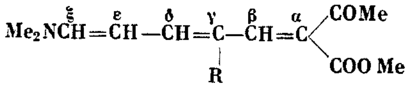
TABLE 1. Data from the UV and IR Spectra of



$$Me_2N\overset{\xi}{C}H=\overset{\varepsilon}{C}H-\overset{\delta}{C}H=\underset{R}{\overset{\gamma}{C}}-\overset{\beta}{C}H=\overset{\alpha}{C}\begin{matrix}COMe\\COOMe\end{matrix}$$

UV spectrum, λ_{max}, nm (EtOH)		IR spectrum, ν, cm^{-1}, with KBr (in CHCl$_3$)	
R=H *	R=Me (I)	R=H *	R=Me (I)
499	460	1690, 1635 (sh), 1615, 1575 (1695, 1630, 1575)	1710, 1630, 1480 (1715, 1630, 1545)

*A mixture of the Z and E isomers (2:1) [7].

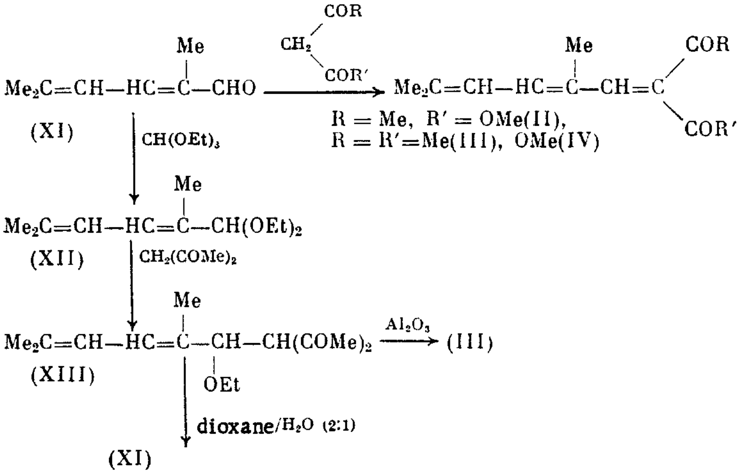
We unexpectedly isolated aldehyde IX as a side product.

According to the ^1H and ^{13}C NMR and UV spectral data, trienone I exists only in the open form, regardless of the solvent. In conformity with the data in [8, 9], it follows from the chemical shift of the carbonyl carbon atom in MeCO (194.14 ppm) and the constant of spin–spin coupling of this carbon atom with the H_β proton ($^3J_{C=O,H_\beta}$ = 6.07 Hz) obtained in the ^{13}C NMR spectrum that I is the Z isomer with respect to the α, β double bond, in which COMe and H_β have a cis configuration. Strong steric interaction between COMe and the Me group attached to the C_γ atom in the E isomer evidently does not lead to its cyclization to a 2H-pyran, as occurred in substituted δ-amino dienones, but rather to isomerization to the Z isomer.

The significant (39 nm) hypsochromic shift of λ_{max} and the 20 cm^{-1} increase in $\nu C{=}O$ in substituted trienones as compared with unsubstituted trienones (Table 1) constitute evidence for substantial disruption of the conjugation when an Me group is introduced in the γ position.

It subsequently seemed of interest to study γ-methyl-substituted trienones II and III, which do not contain an NMe_2 group, especially since the analogous γ-methyl-substituted dienones were converted completely to 2H-pyrans [1, 3].

Trienones II and III and, for comparison, IV* were obtained on the basis of aldehyde XI or its acetal XII via the following scheme:



Trienones II and III are formed via the Knoevenagel reaction (with piperidine as the catalyst) in yields no higher than 15% and contain a difficult-to-separate admixture (~7-10%) of starting aldehyde XI. Compounds II and IV were obtained in 30 and 49% yields by the method in [10] (with $TiCl_4$ as the catalyst). Since III could not be obtained by this

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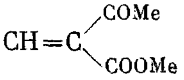
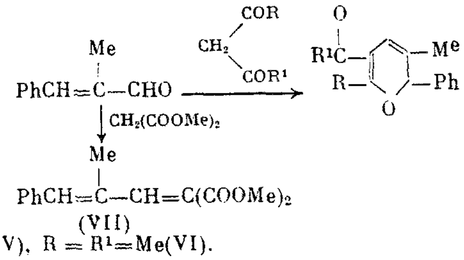
*The dienic diesters always exist in the open form [1, 3].

method or by the action of Al_2O_3 and $MgSO_4$ in refluxing pyridine, we checked its preparation from ethoxy diketone XIII. Compound III was obtained in 10% yield by splitting out of EtOH from XIII by means of Al_2O_3. Other methods for splitting out EtOH did not give positive results: Heating a toluene solution of XIII with traces of $p\text{-}CH_3C_6H_4SO_3H$ led to complete resinification, while heating an aqueous dioxane solution of XIII by the method in [11] led to the formation of aldehyde XI as a result of cleavage of the C–C bond.

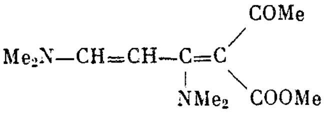
According to ^1H and ^{13}C NMR and UV spectral data, trienones II-IV exist only in the open form. Trienone II is a mixture of the E and Z isomers (3:1) with respect to the $C_\alpha{=}C_\beta$ bond.

In contrast to II and III, γ-methyl-substituted δ-phenyl dienones V and VI, which were synthesized via the Knoevenagel reaction from α-methylcinnamaldehyde (with piperdine as the catalyst), exist only in the cyclic form. It should be noted that unsubstituted PhCH=CH–

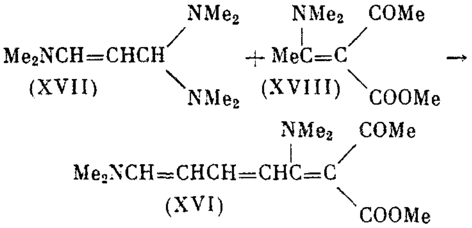

$CH{=}C\begin{smallmatrix}COMe\\COOMe\end{smallmatrix}$ (XIV) [2], just like diesters VII and $PhCH{=}CH{-}CH{=}C(COOMe)_2$ (XV), which were obtained for comparison, exist only in the open form.


R = Me, R^1 = OMe(V), R = R^1=Me(VI).

In this research we obtained the first representative of β-substituted trienones (XVI), which, like the β-substituted dienone


$Me_2N{-}CH{=}CH{-}C(NMe_2){=}C(COMe)(COOMe)$

[12], did not contain the isomeric 2H-pyran



EXPERIMENTAL

The UV spectra were recorded with a Specord UV-VIS spectrophotometer. The PMR spectra were recorded with Bruker WM-250 and Tesla BS-467 spectrometers with ^1H operating frequencies of 250 and 60 MHz, respectively. The high-resolution ^{13}C NMR and $^{13}C\text{-}\{H\}$ NMR spectra were recorded with a Bruker WM-250 spectrometer with a ^{13}C operating frequency of 62.89 MHz. The chemical shifts are the values relative to tetramethylsilane (δ ± 0.03 ppm, $J_{^{13}C,^{1}H} = \pm 1$ Hz).

The ^1H and ^{13}C NMR spectra of I-IV and XVI are presented in Tables 2 and 3.

3-Carbomethoxy-5-methyl-8-dimethylaminoocta-3,5,7-trien-2-one (I). A 3.6-g (0.017 mole) sample of methyl 5-dimethylamino-2-acetylpenta-2,4-dienoate (VIII) was added gradually at 0°C in a stream of acetylene to CH≡CMgBr, obtained from 0.82 g (0.034 mole) of Mg in 60 ml of absolute THF. The reaction mass was stirred for 30 min at 20°C and for 15 min at 50°C, after which it was cooled to 0°C and treated with 3 ml of a benzene solution of $NHMe_2$ (1:1) and 20 ml of a saturated solution of NH_4Cl. The mixture was then extracted with ether and $CHCl_3$, and 2 ml of a benzene solution of $NHMe_2$ and $MgSO_4$ were added to the combined extract, the UV spectrum of which contained a λ_{max} band at 295 nm, which is characteristic for a butadienyl acetylenic ester [7]. After 24 h, the light-yellow extract turned dark red, and λ_{max} bands appeared at 375 and 465 nm (optical density ratio 2:3) in place of the λ_{max} band at 295 nm in the UV spectrum.

TABLE 2. Parameters of the PMR Spectra of I-IV and XVI

Compound	Isomer	δ, ppm									J, Hz			Solvent
		Me	MeCO	MeOCO	NMe_2	H_β	H_γ	H_δ	H_ε	H_ξ	δ, ε	ε, ξ	γ, δ	
(I)		1,60 1,64	2,20 2,21	3,78 3,72	2,88 2,94	7,15 7,25		6,66 6,97	5,1 5,27	6,60 6,82	12,0 12,0	12,0 12,0		$CDCl_3$ CD_3OD
(II)	*E* *	1,85–1,95	2,33	3,85		7,18		6,76	6,19		11,7			$CDCl_3$
(II)	*Z*	1,85–1,95	2,36	3,85		7,72		6,56	6,34		11,7			
(III)		1,82, 1,87, 1,93	2,36, 2,40			7,03		6,68	6,15		11,6			The same
(IV)		1,82, 1,87, 1,93		3,80, 3,85		7,38		6,75	6,17		11,6			»
†			2,47	3,55	3,25 (6H) 2,98 (6H)		5,95	7,46	5,38	6,87	12,0	12,0	12,0	»
(XVI)			2,32	3,52	3,18 (3H), 3,27 (3H), 3,03 br. s (6H)		6,0	7,37	5,64	7,26	12,0	12,0	12,0	CD_3OD

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*The assignment of the signals to the isomers was made in analogy with [2].

†The assignment of the signals to methylidyne protons was made taking into account double-resonance data.

TABLE 3. Parameters of the ^{13}C NMR Spectra of I-IV and XVI in $CDCl_3$, δ, ppm ($J_{^{13}C,^{1}H}$, Hz)

Compound	Isomer	C_α	C_β	C_γ	C_δ	C_ε	C_ξ	MeCO		MeOCO		NMe_2	Me	Me>Me
								Me	CO	MeO	CO			
(I)[a]		120,09	148,8 (149,8)	124,21	149,49 (148,0)	96,38 (152,6)	150,98 (164,6)	26,25	194,14	51,67	170,46	40,77 (137,8)	12,69 (125,8)	
(II)[b,c]	*E*	130,66	146,75 (151,4)	129,54	138,50 (151,4)	121,71 (153,8)	144,76	27,03 (129,4)	194,73	52,12 (146,5)	169,07		12,88 (129,4)	18,69 (124,5) 26,31 (124,5)
(II)	*Z*	127,2	137,65 (148,9)	127,2	137,32 (148,9)	120,42 (161,1)	144,0	26,83	194,80	52,12 (146,5)	168,2		18,55	20,66 26,52
(III)		129,64	145,89	121,41	138,22	121,77	144,95	32,57	195,15				14,77	18,91 26,25
(IV)[c]		121,31	147,79 (155,0)	129,33	138,93 (150,6)	121,60 (151,1)	144,28			52,28 (52,24)	167,9 165,4		12,81 (126,75)	18,85 (122,6) 27,00 (126)
(XVI)		91,86	177,36	110,36 (154,4)	155,74 (150,8)	99,45 (155,0)	154,46 (163,6)	26,73 (127,0)	189,32	49,70 (144,0)	168,78	41,96 s 40,86 br.s (139,2)		

[a] The spin–spin coupling constants (SSCC) for the carbonyl carbon atoms were obtained at −10°C: $^{3}J_{CO,H_\beta} = 6.07$, $^{2}J_{CO,CH_3} = 6.07$, $^{3}J_{COOMe,H_\beta} = 12.13$, $^{3}J_{COOCH_3,OCH_3} = 3.91$ Hz.

[b] The assignment of the signals to the C_α and C_γ atoms was arbitrary.

[c] The assignment of the signals to the C_ε, C_β, and C_δ atoms was made taking into account heteronuclear double-resonance data; the assignment of the signals to the E and Z isomers was made taking into account the integral intensities and the data in Table 2.

A 5-ml sample of absolute ether was added to the evaporated residue, the mixture was cooled to 0°C, and 1.5 g (38%) of a bright-red precipitate, which was identified as I with λ_{max} 460 nm and a small shoulder at 375 nm, was separated. Recrystallization from absolute MeOH gave a product with mp 110-111°C. UV spectrum (λ_{max}, nm) in EtOH: 460 (ε 47,400); in $CHCl_3$: 440 (ε 45,400); in hexane: 396 (ε 31,600). Mass spectrum (m/z): 237 (M^+). Found, %: C 65.68; H 8.15; N 5.96. $C_{13}H_{19}NO_3$. Calculated, %: C 65.80; H 8.07; N 5.90.

According to the UV spectral data, I remained unchanged in H_2O in the course of 24 h; however, after 3-4 h in $CHCl_3$, MeOH, and EtOH the ε value at λ_{max} 460 nm decreased, and a new λ_{max} appeared at 235 nm.

Preparative TLC of the ether mother liquor obtained after separation of I on SiO_2 in an acetone—hexane system (2:3) with elution with $CHCl_3$ gave 0.3 g of aldehyde IX. UV spectrum (λ_{max}, nm, in EtOH): 375 (ε 17,300). PMR spectrum ($CDCl_3$, δ, ppm): 1.7 (CH_3), 2.91 (NMe_2), 5.2 (H_γ), 6.75 (H_δ), 6.82 (H_β), 9.1 (CHO); $J_{\beta,\gamma}$ = 11.5 Hz, $J_{\gamma,\delta}$ = 12.5 Hz. The data from the UV and PMR spectra of IX were identical to the data indicated in [13]. The picrate of IX had mp 155-157°C (mp 157°C [13]).

2,5-Dimethylhexa-2,4-dienal (XI). A) A 37-ml sample of propenyl ether was added with stirring at 35-40°C in the course of 1.5 h to a mixture of 51 g of β,β-dimethylacrolein diethylacetal and 9.2 ml of a 10% solution of $ZnCl_2$ in ethyl acetate, after which the mixture was maintained for 0.5 h at 20°C and then for 1.5 h at 50°C. The mixture was then cooled and treated with 50 ml of 5% NaOH and 50 ml of ether. The ether layer was separated, washed with water, dried with K_2CO_3, and evaporated to give 74 g (94%) of 1,1,3-triethoxy-2,5-dimethyl-4-hexene (XVII) in the form of a dark-yellow oil with bp 120-125°C (20 mm) and n_D^{20} 1.4300.

B) A mixture of 74 g of undistilled XVII, 65 g of $MeCOONa\cdot 3H_2O$, and 144 ml of AcOH was heated at 80-85°C for 1 h in a stream of N_2, after which it was cooled and poured into 200 ml of ice water. The aqueous mixture was extracted thoroughly with ether, and the ether and AcOH were removed with a rotary evaporator. The residue was neutralized with $NaHCO_3$ solution and extracted thoroughly with ether, and the extract was dried with $MgSO_4$. This procedure gave 24.4 g (75%) of XI with bp 82-85°C (10 mm) and n_D^{20} 1.5250. UV spectrum (λ_{max}, nm, EtOH): 292 (ε 15,670). PMR spectrum ($CDCl_3$, δ, ppm): 1.8 (CH_3), 1.98 (Me_2C), 6.3 d (H^4), 7.1 d (H^3), 9.45 (CHO); $J_{3,4}$ = 12 Hz. The assignment of the signals to the H^3 and H^4 protons was made on the basis of heteronuclear-resonance data. ^{13}C NMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 8.92 (CH_3), 18.71 and 26.80 (Me_2C), 121.10 (C^4, ^{13}C, ^1H, J = 153.6), 135.29 (C^2), 144.56 (C^3, ^{13}C, ^1H, J = 149.6), 147.18 (C^5), 194.59 (CHO).

2,5-Dimethylhexa-2,4-dienal Acetal (XII). One drop of 60% $HClO_4$ [14] was added at 20°C with stirring to a mixture of 12.4 g of aldehyde XI, 14.8 g of $CH(OEt)_3$, and 4 ml of absolute EtOH. The temperature rose to 35°C, after which the mixture was cooled to 20°C and stirred for another 0.5 h. A 1.5-ml sample of a 10% solution of KOH in alcohol was then added, and the mixture was distilled to give 14 g (71%) of XII with bp 120-122°C (20 mm) and n_D^{20} 1.4680.

3-Carbomethoxy-5,8-dimethylnona-3,5,7-trien-2-one (II). A solution of 6 ml of $TiCl_4$ in 10 ml of absolute CCl_4 was added dropwise at 0°C to 150 ml of absolute THF, after which a mixture of 3 g of aldehyde XI and 3 ml of acetoacetic ester in 50 ml of absolute THF was then added rapidly. After 40 min, a solution of 9 ml of absolute pyridine in 50 ml of absolute THF was added, and the mixture was stirred for 30 min at 0°C and for 30 min at 10°C. It was then cooled to 0°C and treated with 30 ml of water and 30 ml of ether. The ether layer was separated, and the aqueous layer was extracted thoroughly with ether. The combined ether extracts were dried with $MgSO_4$ and distilled to give 1.55 g (30%) of II with bp 112-115°C (0.3 mm) and n_D^{20} 1.5820 (an individual product according to GLC data). The addition of 0.5 ml of absolute MeOH and cooling to −70°C gave II in the form of pale-yellow crystals with mp 55-59°C. UV spectrum (λ_{max}, nm, in EtOH): 345 (ε 31,714). Mass spectrum (m/z): 222 (M^+). Compound II was labile at 20°C but stable in the cold.

Methyl 2-Carbomethoxy-4,7-dimethylocta-2,4,6-trienoate (IV). A solution of 6 ml of $TiCl_4$ in 10 ml of CCl_4 was added dropwise to 100 ml of absolute THF, during which a yellow precipitate formed. Under the same conditions a mixture of 3 g of malonic ester and 3 g of aldehyde XI in 25 ml of absolute THF was added rapidly, after which a solution of 9 ml of absolute pyridine in 50 ml of THF was added in the course of 1 h. The resulting mixture was then stirred for 1 h at 20°C and allowed to stand overnight. Water (20 ml) and ether

TABLE 4. Yields, Constants, and UV and PMR Spectral Data for V-VII and XV

Compound	Reaction temp, °C	Yield,* %	Bp, °C (mm)	n_D^{20}	Molecular mass (mass spectrum), found/calculated, %	UV spectrum, λ_{max}, nm (ε), in EtOH	PMR spectrum, δ, ppm, in $CDCl_3$
(V)	0	18	105–108 (0,3)	1,5650	244/244,27	205 (23400) 223 (15200) 245plateau (8100) 300(8050)	1,62 (CH_3–C^3), 2,22 (CH_3–C^6), 3,72 (OCH_3), 5,56 (H^2), 6,35 (H^4), 7,3 (Ph)
(VI)	0	7	100–102 (0,1)	1,5810	228/228,27	208 (17200) 220plateau (16200) 258 (8550) 322 (7150)	1,63 (CH_3–C^3), 2,18 (CH_3–C^6), 2,25 (CH_3CO), 5,55 (H^2), 6,28 (H^4), 7,29 (Ph)
(VII)	20	14	130–132 (0,3)	1,6000	260/260,27	313 (25200)	2,0 (CH_3), 3,77 and 3,81 (OCH_3), 6,94 (H_β), 7,46 (H_δ), 7,31 (Ph)
(XV)	20	59	†			325 (39000)	3,75 and 3.84 (OCH_3), 6,96–7,71 (H_β, H_γ, H_δ and Ph)

*The yields are based on the amount of α-methylcinnamaldehyde used.

†This compound had mp 68-69°C (mp 67°C [15]).

were then added, the aqueous layer was separated, and the ether layer was dried with $MgSO_4$ and evaporated to give a crystallizing oil, to which 3 ml of absolute MeOH was added, and the resulting mixture was cooled to −70°C to give 2.8 g (49%) of IV with mp 78-80°C (from MeOH). UV spectrum (λ_{max}, nm, in EtOH): 330 (ε 30,640). Mass spectrum (m/z): 238 (M^+).

3-Acetyl-4-ethoxy-5,8-dimethylnona-5,7-dien-2-one (XIII). A 0.35-ml sample of $BF_3 \cdot O(Et)_2$ was added at −10°C to 5 g of acetylacetone, 30 min after which 7 g of acetal II was added, and the mixture was maintained for 15 min at −10°C and for 5 min at 0°C. The mixture was then treated with 20 ml of a 15% solution of MeCOONa and dried with $MgSO_4$. Workup gave 2.5 g (28%) of XIII with bp 90-95°C (0.4 mm) and n_D^{20} 1.4870. Mass spectrum (m/z): 252 (M^+). UV spectrum (λ_{max}, nm, EtOH): 246 (ε 26,185). PMR spectrum ($CDCl_3$, δ, ppm, J, Hz): 1.05 (3H, CH_3CH_2), 1.6 (3H, CH_3), 1.75 br. s (6H, H^9, and CH_3–C^8), 1.98 s and 2.13 s (6H, CH_3CO), 3.26 m (2H, CH_3CH_2), 3.9 d (1H, H^3), 4.34 (1H, H^4), 5.86 d (1H, H^7), 6.24 d (1H, H^6), $J_{3,4}$ = 10.5, $J_{6,7}$ = 12, $J_{CH_2\text{-}CH_3}$ = 7.

3-Acetyl-5,8-dimethylnona-3,5,7-trien-2-one (III). A) A mixture of 1.3 g of XIII and 50 ml of activity II Al_2O_3 was maintained for 24 h at 35-40°C, after which it was eluted with $CHCl_3$, and the eluate was evaporated. According to the UV spectrum, the residue consisted of XI and III in a ratio of 2:3. Preparative TLC on SiO_2 with an acetone–hexane system (2:3) with elution with absolute ether gave 0.1 g of III in the form of a crystalline material with mp 53-57°C. UV spectrum (λ_{max}, nm) in EtOH: 341 (ε 26,870); in $CHCl_3$: 345; in hexane: 330 split (ε 30,452). Mass spectrum (m/z): 206 (M^+).

B) A mixture of 2.2 g of XI, 2.2 g of acetylacetone, and 0.1 ml of piperidine was allowed to stand for 3 days at 0°C, after which ether was added, and the mixture was washed with 1% H_2SO_4 and water, dried with $MgSO_4$, and distilled in vacuo to give 0.5 g (13%) of III with bp 103-105°C (0.37 mm) and n_D^{20} 1.5600. According to GLC analysis, III contained 7% aldehyde XI.

Action of Aqueous Dioxane on XIII. A 2.4-g sample of XIII was heated in 65 ml of dioxane H_2O (2:1) in a stream of N_2 at 80°C for 5 h, after which the mixture was cooled and ether was added. Sodium chloride was added to the aqueous layer, and it was extracted with ether. The ether extracts were dried with $MgSO_4$ and distilled to give 0.5 g of aldehyde XI with bp 80-86°C (10 mm) and n_D^{20} 1.5200. UV spectrum (λ_{max}, nm, in EtOH): 290. The GLC data and PMR spectrum were identical to those for the XI described above.

Compounds V-VII. A 0.15-ml sample of piperidine was added to a mixture of 14 mmoles of the β-dicarbonyl compound and 14 mmoles of α-methylcinnamaldehyde, and the mixture was allowed to stand for 6 days. It was then diluted with ether, washed with 1% H_2SO_4 solution, dried, and distilled. The reaction temperatures, constants, yields, and spectral data are presented in Table 4. In the preparation of V-VII 60-65% unconverted α-methylcinnamaldehyde, with bp 50-52°C (0.3 mm) and n_D^{20} 1.6055, was isolated. UV spectrum (λ_{max}, nm, EtOH): 285. PMR spectrum [mixture of the E and Z isomers (1:10)] ($CDCl_3$, δ, ppm): 1.98 and 2.0 (CH_3), 7.15 m and 7.39 m (Ph and CH), 9.83 and 9.50 (CHO).

3-Carbomethoxy-4,8-bis(dimethylamino)octa-3,5,7-trien-2-one (XVI). A mixture of 0.3 g of methyl α-acetyl-β-dimethylamino-β-methylacrylate (XVIII) in 1 ml of absolute ether and 0.4 ml of aminal XVII was allowed to stand for 15 min, after which the resulting precipitate was removed by filtration and washed with absolute ether to give 0.4 g (93%) of XVI with mp 193-195°C [from acetone–ether (3:1)]. UV spectrum (λ_{max}, nm, in absolute MeOH): 270 (ε 17,733), 417 (ε 73,800); in $CHCl_3$: 270 (ε 12,160), 420 (ε 34,960); in hexane: 267 (ε 11,000), 420 (ε 31,800); in H_2O: 270 (ε 17,700), 427 (ε 85,840). Mass spectrum (m/z): 266 (M^+). Found, %: C 62.77; H 8.03. $C_{14}H_{22}N_2O_3$. Calculated, %: C 63.13; H 8.33.

CONCLUSIONS

1. γ-Methyl-α-functionally substituted conjugated trienones and δ-phenyl dienones were synthesized.

2. γ-Methyl-α-functionally substituted trienones exist in the open form, while δ-phenyl dienones exist in the form of 2H-pyrans.

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