6. E. Fahr, Annalen, 638, 1 (1960).
7. L. A. Tolochko, A. M. Sipyagin, and V. G. Kartsev, Khim. Geterotsikl. Soedin., No. 2, 276 (1986).
8. E. Piers, M. B. Geraghty, R. D. Smillie, and M. Soucy, Can. J. Chem., 53, 2849 (1975).
9. V. I. Andrianov, Z. M. Safina, and B. L. Tarnopol'skii, Rentgen-75 Programs [in Russian], Chernogolovka (1975).

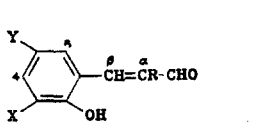
INTRAMOLECULAR CYCLIZATION OF 2-HYDROXYCINNAMALDEHYDES

Yu. M. Chunaev, N. M. Przhiyalgovskaya, and L. N. Kurkovskaya

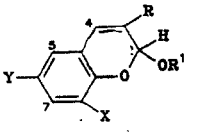
UDC 547.576'814.1.07

The effect of substituents on the intramolecular cyclization of 2-hydroxycinnamaldehydes was studied. It was established that aldehydes that contain bulky groups in the side chain and in the 3 position of the benzene ring are readily converted to intramolecular hemiacetals or bimolecular acetals either spontaneously at the moment of isolation or in solutions in DMF or DMSO, as well as on heating. An increase in the lability of the phenolic proton favors the cyclization.

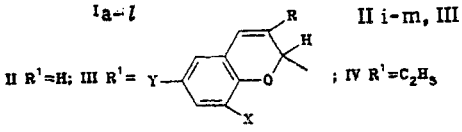
It has been reported that 2-hydroxycinnamaldehydes Ia-c are not capable of intramolecular cyclization and the formation of 2H-chromene form II [1-4]. At the same time, this form of isomerism is known for 2-hydroxybenzocinnamaldehydes [3-6]. In order to study the effect of structural factors on the relative stabilities of linear (I) and ring (II) isomers we obtained 2-hydroxycinnamaldehydes containing various substituents in the side chain and in the benzene ring. Their synthesis was accomplished by condensation of salicylaldehydes with aldehydes of the aliphatic series in an alkaline medium.



Ia–l



II i–m, III i, j, n, IVj



II R^1=H; III R^1= ; IV R^1=C_2H_5

I—IVa, b, d, g, h X=H, c, e, i, j, m X=Br, f, l X=NO_2, k X=OCH_3; n X=CH_3; a, k, l Y=H, b, c, f, h, j, n Y=NO_2, d, e, g, i, m Y=Br; a-f R=H, g, h, k-n R=C_2H_5, i, j R=CH_3

It was established that the majority of 2-hydroxycinnamaldehydes Id-l have a linear structure. α-Ethyl-3,5-dibromo-2-hydroxycinnamaldehyde (IIm) was isolated in cyclic form. Acetal IIIn was formed in the synthesis of α-ethyl-3-methyl-5-nitro-2-hydroxycinnamaldehyde (In), evidently as a consequence of intermolecular dehydration of intermediate hemiacetal IIn. A comparison of aldehydes Im, n, which exist in the form of 2H-chromenes, with Ie, g, h, which have linear structures, makes it possible to conclude that the introduction of bulky substituents into the side chain and the 3 position of the benzene ring promotes cyclization. Similar facts are known in the literature. Thus, according to the data in [7], the stability of ring isomers increases in the presence of alkyl substituents attached to the sp^3-carbon atoms in the chain between the interreacting groups. Alkyl groups or halogen atoms in the ortho position relative to the reaction group (hydroxy) exert "steric pressure" on it and thereby also promote cyclization.

Compounds Ii-l, like aldehydes Im, n, contain bulky substituents stimultaneously in both the side chain and the 3 position of the benzene ring. However, despite this, they exist primarily in the open form. The greater stability of the linear isomer of α-methyl-3,5-dibromo-2-hydroxycinnamaldehyde (Ii) as compared with α-ethyl-substituted aldehyde Im can be explained by the decrease in the volume of the substituent in the side chain. An im-

D. I. Mendeleev Moscow Institute of Chemical Technology, Moscow 125047. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 460-465, April, 1988. Original article submitted December 1, 1986.

 0009-3122/88/2404-0376$12.50

portant factor that affects the intramolecular cyclization process is the lability of the phenolic proton, which should increase with an increase in the electron-acceptor properties of the ortho and para substituents. The I → II conversion is therefore hindered in Ik, which contains a bulky but electron-donor OCH_3 substituent. The open form of 3-nitro-substituted aldehyde Il is stabilized by an intramolecular hydrogen bond (IMHB) between the hydroxy and nitro groups [7], which also hinders transfer of the phenolic proton to the aldehyde group.

Linear aldehydes Ii-l are quite readily converted to hemiacetals IIi-l by heating in DMSO or DMF. The formation of the cyclic form also occurs in the cold, although the process takes place much more slowly. According to NMR data, the rates of the I → II conversion differ for substituted aldehydes. Thus heating Il, which is stabilized by an IMHB, in d_6-DMSO at 90°C leads to its complete conversion to cyclic isomer IIl only after 2.5 h; this is determined by the requirement of additional energy for cleavage of the IMHB. In the case of Ik, which contains an electron-donor substituent, the I → III conversion is slower by a factor of two than even for aldehyde Il. In other words, in addition to favorable geometry, which is determined by substituents R and X, an increase in the lability of the phenolic proton promotes cyclization. Either the basic medium or the carbonyl group itself acts as the proton acceptor.

In addition to DMF and DMSO, we also tested other solvents for carrying out the cyclization. The isomerization proceeds very slowly in refluxing acetonitrile. Treatment of aldehyde Ij with hot ethanol leads to acetal IVj, whereas acetals IIIi, j are formed when Ii, j are heated without a solvent. In the latter case intermediate chromenes IIi, j evidently undergo spontaneous intermolecular dehydration. The coincidence or closeness of the melting points of Ij and IIIj and Ii and IIi (Table 1) is explained by the occurrence of this reaction, as are the dual melting points of some of the substances obtained. For example, it was noted that aldehyde Ii melts at 141-146°C. If it is heated to 220°C and then cooled, the melt crystallizes at 170°C. On reheating the compound melts at 257-259°C, which corresponds to the melting point of acetal IIIi. Aldehyde Ij and hemiacetals IIi, j behave similarly (Table 1).

The compositions and structures of the substances obtained were confirmed by the results of elementary analysis and mass-spectral data (Table 1), as well as by data from the IR spectra (see the experimental section) and the PMR spectra (Tables 2 and 3).

The IR spectra of aldehydes I contain an intense absorption band of a carbonyl group at 1655-1695 cm^{-1} and a broad band of an associated hydroxy group at 3050-3400 cm^{-1}. The band of a carbonyl group vanishes in the spectra of hemiacetals II, while the absorption band of the hydroxy group is shifted to 3520 cm^{-1} (in KBr) and becomes considerably narrower. As compared with the spectra of hemiacetals II, the absorption band of a hydroxy group is absent in the spectra of III and IV.

The PMR spectra of 2-hydroxycinnamaldehydes I contain the signal of an aldehyde proton at ∿9.6 ppm in the form of a doublet (for Id, e) with spin-spin coupling constant (SSCC) $J_{\alpha,CHO}$ = 7.5 Hz or in the form of a singlet (for α-substituted aldehydes Ig-l). The proton of the hydroxy group gives, in $CDCl_3$, a signal at ∿6 ppm (Id-k) or at 11.16 ppm (Il with an IMHB between the hydroxy and nitro groups) (Table 2). A transoid E configuration was previously established for aldehydes Ia-c by PMR spectroscopy [1-4]. The Id, e synthesized by us have a similar structure. Thus SSCC $J_{\alpha,\beta}$ ∿ 16 Hz constitutes evidence for trans orientation of the protons attached to the double bond, while SSCC $J_{\alpha,CHO}$ = 7.5 Hz attests to an s-trans configuration of these molecules [1]. In contrast to the spectra of I, the signal of an aldehyde proton is absent in the PMR spectra of hemiacetals II. A doublet of the 2-H proton with SSCC $J_{2,OH}$ ∿ 6 Hz appears at ∿6 ppm. The signal of the hydroxy proton is shifted to ∿3-4 ppm (in $CDCl_3$), while the 4-H proton gives a doublet with SSCC $J_{R,4}$ ∿ 1.2 Hz at ∿6.4 ppm. The spectra of acetals III are similar to the spectra of hemiacetals II (Table 3). In contrast to the spectra of II, the spectra of III do not contain signals of hydroxy protons, while the 2-H protons appear in the form of singlets.

Hemiacetals IIk, l were unstable compounds: they decomposed readily during isolation and storage to give complex mixtures of products. The conversion of aldehydes Ik, l to chromenes IIk, l was detected by PMR spectroscopy (d_6-DMSO, 90°C). The structure of IIk was also confirmed by means of the PMR spectra (in $CDCl_3$) and IR spectra recorded immediately after isolation of the substances.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	Found, %				M*	Empirical formula	Calculated, %				Yield, %
		C	H	N	Br			C	H	N	Br	
Id	153—154	47,2	3,3	—	35,0	226	$C_9H_7BrO_2$	47,6	3,1	—	35,2	30
Ie	169—171	35,0	1,7	—	51,9	304	$C_9H_6Br_2O_2$	35,4	2,0	—	52,1	17
If	169—172	45,0	2,3	11,6	—	238	$C_9H_6N_2O_6$	45,4	2,5	11,8	—	34
Ig	128—130	51,4	4,3	—	31,6	254	$C_{11}H_{11}BrO_2$	51,8	4,4	—	31,3	25
Ih	151—152	59,9	5,0	6,2	—	221	$C_{11}H_{11}NO_4$	59,7	5,0	6,3	—	32
Ii	141—146	38,0	2,4	—	49,7	318	$C_{10}H_8Br_2O_2$	37,5	2,5	—	50,0	44
Ij	249—252** (dec.)	42,2	3,1	4,7	28,1	285	$C_{10}H_8BrNO_4$	42,0	2,8	4,9	27,9	40
Ik	112—113	69,8	6,8	—	—	206	$C_{12}H_{14}O_3$	69,9	6,8	—	—	20
Il	118—120	59,9	5,0	6,0	—	221	$C_{11}H_{11}NO_4$	59,7	5,0	6,3	—	53
IIf	139—141**	37,7	2,4	—	49,6	318	$C_{10}H_8Br_2O_2$	37,5	2,5	—	50,0	90
IIj	160—162**	41,8	2,8	4,6	27,7	285	$C_{10}H_8BrNO_4$	42,0	2,8	4,9	27,9	60
IIm	97—99	40,0	3,1	—	47,4	332	$C_{11}H_{10}Br_2O_2$	39,6	3,0	—	47,9	19
IIIi	257—259	38,8	2,4	—	51,4	618	$C_{20}H_{12}Br_4O_3$	38,7	2,0	—	51,6	88
IIIj	249—252 (dec.)	43,3	2,8	5,1	28,9	552	$C_{20}H_{14}Br_2N_2O_7$	43.3	2,6	5,1	28,8	93
IIIn	243—245	63,6	5,0	5,8	—	452	$C_{24}H_{24}N_2O_7$	63,7	5,4	6,2	—	29
IVj	106—108	46,0	4,0	4,5	25,1	313	$C_{12}H_{12}BrNO_4$	45,9	3,9	4,5	25,4	85

*Determined with an MKh-1303 mass spectrometer in the case of I, II, and IV and with a Varian MAT-112 mass spectrometer in the case of III.

**Aldehyde Ij melts at 185-186°C and solidifies again at temperatures above 186°C. Melted hemiacetal IIi, heated to 250°C, solidifies on cooling to 200°C, whereas on reheating it melts at 255-256°C. Melted hemiacetal IIj crystallizes at 174°C and melts again with decomposition at 245-252°C.

TABLE 2. PMR Spectra of 2-Hydroxycinnamaldehydes in $CDCl_3$

Compound	PMR spectrum, δ, ppm								J, Hz						
	CHO	OH	R	8-H	X	4-H	Y	6-H	R, CHO	R, β	3,4	4,5	5,6	4,6	CH_2, CH_3
Id	9,67	5,94	6,94	7,66	6,79	7,34	—	7,61	7,5	16,1	8,8	—	—	2,5	—
Ie	9,66	~6,0	6,73	7,64	—	7,54	—	7,63	7,5	16,0	—	—	—	2,3	—
If	9,59	5,60	2,50 (CH_2); 1,12 (CH_3)	7,41	6,79	7,38	—	7,51	—	—	8,8	—	—	2,4	7,4
Ih	9,58	~6,1	2,49 (CH_2); 1,13 (CH_3)	7,34	6,94	8,13	—	8,26	—	—	8,4	—	—	2,4	7,4
Ii	9,56	5,83	1,98	7,38	—	7,58	—	7,43	—	1,2	—	—	—	2,3	—
Ij	9,61	6,40	2,03	7,41	—	8,39	—	8,26	—	1,4	—	—	—	2,4	—
Ik	9,59	6,09	2,53 (CH_2); 1,12 (CH_3)	7,55	3,93		6,91—7,09		—	—	—	—	—	—	7,3
Ik*	9,53	—	2,40 (CH_2); 1,02 (CH_3)	7,61	3,84		6,83—7,05		—	—	—	—	—	—	7,4
Il	9,64	11,16	2,48 (CH_2); 1,13 (CH_3)	7,52	—	8,18	7,10	7,73	—	—	—	8,5	7,6	1,5	7,6
Il*	9,62	—	2,37 (CH_2); 1,00 (CH_3)	7,54	—	8,02	7,12	7,69	—	—	—	8,2	7,4	1,5	7,5

*In d_6-DMSO.

TABLE 3. PMR Spectra of Hemiacetals II and Acetals III and IV in $CDCl_3$

Compound	PMR spectrum, δ, ppm								J, Hz					
	OR^1	2-H	R	4-H	5-H	Y	7-H	X	OH, 2	R, 4	5,6	6,7	5,7	CH_2, CH_3
IIi	3,13	5,89	2,02	6,28	7,10	—	7,47	—	6,4	1,2	—	—	2,2	—
IIj	3,31	6,04	2,07	6,43	7,90	—	8,27	—	6,7	1,5	—	—	2,4	—
IIk	3,78	5,96	2,35 (CH_2); 1,19 (CH_3)	6,39		6,74—6,94		3,88	5,85	—	—	—	—	7,3
IIk*	8,85	5,83	2,30 (CH_2); 1,13 (CH_3)	6,40		6,89—6,94		3,89	—	—	—	—	—	7,4
IIl*	7,48	5,92	2,28 (CH_2); 1,14 (CH_3)	6,54	7,50	7,07	7,73	—	6,6	1,5	7,3	8,0	1,8	7,4
IIm	3,06	5,91	2,35 (CH_2); 1,18 (CH_3)	6,27	7,14	—	7,47	—	6,0	—	—	—	2,2	7,3
IIIi	—	6,15	1,83	6,27	7,09	—	7,48	—	—	1,5	—	—	2,3	—
IIIj	—	6,35	1,91	6,48	7,95	—	8,36	—	—	1,5	—	—	2,5	—
IIIn	—	6,25	2,09 (CH_2); 1,05 (CH_3)	6,44	8,00	—	7,88	2,42	—	1,6	—	—	3,1	7,3
IVj	3,98 (CH_2); 1,32 (CH_3)	5,77	2,12	6,52	8,00	—	8,38	—	—	1,4	—	—	2,4	7,3

*In d_6-DMSO.

EXPERIMENTAL

The PMR spectra of Id, e, g-j, IIi, j, m, and IVj were recorded with a Varian CFT-20 spectrometer (80 MHz), while the PMR spectra of Ik, l, IIk, l, and III were recorded with a Bruker WP-200-SY spectrometer (200 MHz) with tetramethylsilane as the internal standard. The IR spectra of mineral oil suspensions of Id-f, h, KBr pellets of Ig, i-l, IIi, j, IIIj, n, and IVj, and solutions of hemiacetals IIk, m in CCl_4 were recorded with a UR-20 spectrometer. The R_f values were determined on Silufol UV-254 plates.

5-Bromo-2-hydroxycinnamaldehyde (Id). A 10.0-g (50 mmole) sample of 5-bromosalicylaldehyde was dissolved by heating in 400 ml of water containing 2.80 g (70 mmole) of sodium hydroxide, after which the solution was cooled and treated with 7.20 g (160 mmole) of acetaldehyde. The mixture was allowed to stand at 20°C for 21 h and extracted with ether. The aqueous layer was cooled to 0°C and neutralized with 20% hydrochloric acid, and the resulting precipitate was separated and chromatographed with a column packed with silica gel by elution with chloroform to give 3.40 g of aldehyde Id (Rf 0.08) in the form of shiny yellow crystals (from benzene), IR spectrum: 1655 (C=O), 3100-3400 cm^{-1} (OH).

3,5-Dibromo-2-hydroxycinnamaldehyde (Ie), 3,5-dinitro-2-hydroxycinnamaldehyde (If), α-ethyl-5-bromo-2-hydroxycinnamaldehyde (Ig), α-ethyl-5-nitro-2-hydroxycinnamaldehyde (Ih), α-methyl-3,5-dibromo-2-hydroxycinnamaldehyde (Ii), α-methyl-3-bromo-5-nitro-2-hydroxycinnamaldehyde (Ij), α-ethyl-3-methoxy-2-hydroxycinnamaldehyde (Ik), α-ethyl-3-nitro-2-hydroxycinnamaldehyde (Il), 2-hydroxy-3-ethyl-6,8-dibromo-2H-chromene (IIm), and 2,2'-oxybi(3-ethyl-6-nitro-8-methyl-2H-chromene) (IIIn) were similarly obtained from the corresponding substistuted salicylaldehyde and aldehydes of the aliphatic series. Compounds Ie, g-i, l, IIm, and IIIn were purified with a column packed with silica gel. The eluents for the aldehydes were as follows: chloroform for Ie (R_f 0.34), carbon tetrachloride–ether (3:1) for Ig (R_f 0.21), chloroform for Ih (R_f 0.05), chloroform for Ii (R_f 0.36), and carbon tetrachloride–ether (3:1) for Il (R_f 0.67); chloroform for hemiacetal IIm (R_f 0.30), and carbon tetrachloride–ether (5:1) for acetal IIIn (R_f 0.43). The compounds obtained were crystallized from the following solvents: Ie from acetic acid, Ig from carbon tetrachloride–chloroform, Ih from chloroform–acetone, Ii from carbon tetrachloride, Il from hexane, IIm from aqueous isopropyl alcohol, and IIIn from chloroform. Aldehydes If, j, k were precipitated from the reaction masses in the form of crystals of the sodium salts. The salts were removed by filtration, washed with ether, dissolved in water, treated with dilute hydrochloric acid, and recrystallized, respectively, from dilute acetic acid, chloroform, and hexane. IR spectra of Ie-l, IIm, and IIIn: 1675 (C=O), 3100-3380 (O–H); 1680 (C=O), 1535, 1350 (NO_2), 3140-3300 (O–H); 1665 (C=O), 3100-3400 (O–H); 1660 (C=O), 1525, 1343 (NO_2), 3100-3400 (O–H); 1670 (C=O), 3050-3400 (O–H); 1668 (C=O), 1520, 1340 (NO_2), 3050-3400 (O–H); 1670 (C=O), 3100-3400 (O–H); 1690 (C=O), 1540, 1350 (NO_2), 3130-3280 (O–H); 3595 (O–H); 1530, 1350 cm^{-1} (NO_2).

2-Hydroxy-3-methyl-6,8-dibromo-2H-chromene (IIi). A solution of 0.50 g (1.56 mmole) of aldehyde Ii in 4 ml of DMSO was refluxed for 10 min, after which it was cooled and poured into 100 ml of water. The resulting precipitate was removed by filtration and washed with water to give 0.45 g of colorless needles (from hexane). IR spectrum: 3520 cm^{-1} (O–H).

2-Hydroxy-3-methyl-6-nitro-8-bromo-2H-chromene (IIj). A solution of 0.20 g (0.70 mmole) of aldehyde Ij in 5 ml of DMSO was refluxed for 15 min, after which it was cooled and poured into 150 ml of water. The resulting oily product was extracted with benzene, the benzene was evaporated, and the residue was purified with a column packed with silica gel by elution with methylene chloride to give 0.12 g (R_f 0.40) of yellowish needles (from chloroform–carbon tetrachloride). IR spectrum: 1540, 1345 (NO_2), 3520 cm^{-1} (O–H).

2-Hydroxy-3-ethyl-8-methoxy-2H-chromene (IIk). A solution of 0.20 g (0.97 mmole) of aldehyde Ij in 7 ml of DMF was refluxed for 1 h, after which it was cooled and poured into 500 ml of water. The reaction product was extracted with ether. The ether solution was dried and evaporated, and the residue was chromatographed with a column packed with silica gel [elution with carbon tetrachloride–ether (1:1)] to give 0.10 g (50%) of chromene IIk in the form of a colorless oily substance with R_f 0.37. IR spectrum: 3585 cm^{-1} (O–H).

2,2'-Oxybi(3-methyl-6,8-dibromo-2H-chromene) (IIIi). A 0.20-g (0.625 mmole) sample of aldehyde Ii was heated cautiously to 200-210°C and maintained at this temperature for 4 min, after which it was cooled, and the resulting substance was purified with a column packed with silica gel (elution with carbon tetrachloride). The yield of colorless crystals (from chloroform) was 0.17 g (R_f 0.78).

2,2'-Oxybi(3-methyl-5-nitro-8-bromo-2H-chromene) (IIIj). This compound was similarly obtained from 0.20 g (0.70 mmole) of α-methyl-3-bromo-5-nitro-2-hydroxycinnamaldehyde. The product was purified with a column packed with silica gel by elution with carbon tetrachloride–ether (3:1). The yield of a yellowish crystalline powder (from chloroform–ethanol) was 0.18 g (Rf 0.78). IR spectrum: 1525, 1348 cm^{-1} (NO_2).

2-Ethoxy-3-methyl-6-nitro-8-bromo-2H-chromene (IVj). A 0.15-g (0.52 mmole) sample of aldehyde Ij was refluxed in 30 ml of ethanol for 6 h, after which the solvent was evaporated and 5 ml of hexane was added to the residue. The resulting yellowish crystals were removed by filtration and washed with hexane to give 0.14 g of product. IR spectrum: 1530, 1340 cm^{-1} (NO_2).

LITERATURE CITED

1. E. A. Medyantseva, O. M. Babeshko, and V. I. Minkin, Zh. Org. Khim., 12, 897 (1976).
2. O. M. Babeshko, E. A. Medyantseva, O. T. Lyashik, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 11, 1477 (1982).
3. I. M. Andreeva, O. M. Babeshko, E. A. Medyantseva, and V. I. Minkin, Zh. Org. Khim., 15, 1899 (1979).
4. I. M. Andreeva, O. M. Babeshko, E. M. Bondarenko, I. A. Barchan, O. T. Lyashik, E. A. Medyantseva, and Yu. N. Simkina, Khim.-farm. Zh., 19, 177 (1985).
5. I. M. Andreeva, E. M. Bondarenko, E. A. Medyantseva, R. G. Pudeyan, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 5, 610 (1982).
6. I. M. Andreeva, E. M. Bondarenko, E. A. Medyantseva, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 2, 181 (1983).
7. R. E. Valter, Ring-Chain Isomerism in Organic Chemistry [in Russian], Zinatne, Riga (1978).

BENZENOID-QUINOID TAUTOMERISM OF AZOMETHINES AND THEIR STRUCTURAL ANALOGS.

41.* PHOTO- AND THERMOCHROMIC TRANSFORMATIONS OF ACYLATED N-ALKYLIMINES OF 3-HYDROXYBENZO[b]THIOPHENE-2-CARBALDEHYDE AND 3-HYDROXY-1-METHYLINDOLE-2-CARBALDEHYDE

G. D. Palui, L. M. Sitkina, A. D. Dubonosov, V. I. Minkin, V. A. Bren', O. I. Lantsova, and I. V. Grabchak

UDC 547.735'751:541.623'144

O- and N-Acylated alkylimines of 3-hydroxybenzo[b]thiophene-2-carbaldehyde and 3-hydroxy-1-methylindole-2-carbaldehyde were synthesized. Their Z → E isomerizations and N → O-acyl photo- and thermotransformations were investigated by means of electronic and IR spectroscopy. On irradiation N-acyl-N-methyl(or benzyl)aminomethylene derivatives of benzo[b]thiophen-3-one and 1-methylindol-3-one undergo only Z → E isomerization. The introduction of bulkier alkyl substituents (isopropyl, cyclohexyl) relative to the amino nitrogen atom increases the stability of the O-acyl isomers and their conjugate acids and leads to irreversible photoinitiated or acid-catalyzed N → O-acyl rearrangements. Exclusively the O-acyl isomer is realized for compounds with the most bulky N-tert-butyl substituent.

We have previously observed and investigated photo- and thermochromic rearrangements of acylated N-arylimines of 3-hydroxybenzo[b]thiophene-2-carbaldehyde and 3-hydroxy-1-methylindole-2-carbaldehyde of the IZ ⇄ III and IIZ ⇄ IV type (R = Ar, R^1 = CH_3, OCH_3) [2-4]. The task of the present research was to investigate the effect of replacement of aryl groups R in the I-IV molecules by alkyl radicals on the character of photoinduced and thermal acid-catalyzed acylotropic rearrangements [see schemes (1) and (2)]. For this we synthesized a number of N- and O-acylated I-IV with variable structural fragments: the

*See [1] for Communication 40.

Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344104.

Translated from Khimika Geterotsiklicheskikh Soedinenii, No. 4, pp. 466-471, April, 1988. Original article submitted November 19, 1986.

0009-3122/88/2404-0381$12.50