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PHOTO- AND THERMOCHROMIC SPIRANS.

16.* 2-OXO-3-PHENYL-5,5-DIMETHYLSPIRO(1,3-OXAZOLIDINE-4,2'-[2H]CHROMENES)

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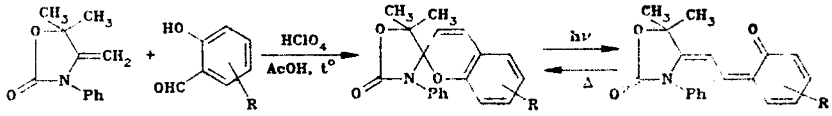
New spirans of the 5,5-dimethyl-3-phenyl-2-oxazolidone series that display photochromic properties in alcohol solutions at $\sim$−80°C were synthesized. The photoinduced forms are characterized by the presence of two long-wave absorption bands at 350-420 nm and 500-650 nm. The ^{1}H and ^{13}C NMR spectra were studied. Anisochronicity of the diastereotopic methyl groups of the oxazolidone ring shows up only in the ^{13}C NMR spectra.

Calculation of the energy of anionic localization of the conjugate acid of 4-methylene-5,5-dimethyl-3-phenyl-2-oxazolidone (I) gives L^{-} = 3.51 eV. This is considerably lower than the critical value of 6.2 eV, below which it is expected [2] that the equilibrium of the spiran (II) and merocyanine (III) forms of spiro[2H]benzopyrans should be shifted to favor II in solutions and in the solid phase. On the basis of this prediction we undertook the synthesis of a new series of spiropyrans II via the scheme



I IIa-p IIIa-p

Spiropyrans of the 5,5-dimethyl-3-phenyl-2-oxazolidone series of the II general type were obtained in 60-70% yields by condensation of methylene base I with the corresponding o-hydroxy aromatic aldehydes in the presence of catalytic amounts of perchloric acid (Table 1). The IR spectra of the spirans obtained contain an intense absorption band at 1730-1750 cm^{-1} (Table 2), which is typical for the carbonyl group of the oxazolidone ring (1750 cm^{-1} for methylene base I), and an absorption band of medium intensity at 1630-1665 cm^{-1} ($\nu_{C=C}$ of the pyran ring).

In the case of irradiation with UV light with λ_{max} 313 nm under steady-state conditions in ethanol solutions at −100°C the spiropyrans undergo II $\rightleftarrows$ III valence isomerization and display photochromic properties. The long-wave absorption bands of the III form lie at 350-420 nm and 500-650 nm (Table 2). The typical pattern of the spectral photochromic transformations is presented in Fig. 1. Calculations of the electronic spectra of the open forms of the spirans by the SCF PPP MO (self-consistent field Pariser–Parr–Pople molecular orbital) method correctly predict the presence of two long-wave absorption bands in the visible region; however, the bands of the calculated electron transitions are shifted hypsochromically 0.3-0.4 eV as compared with the experimental values when the usual parametrization [2] is used.

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*See [1] for communication 15.

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TABLE 1. R-2-Oxo-3-phenyl-5,5-dimethylspiro(1,3-oxazolidine-4,2'-[2H]chromenes)

Compound	R	mp, deg C (from ethanol)	Found, %			Empirical formula*	Calculated, %			Yield, %
			C	H	N		C	H	N	
IIa	H	125—126	74,7	5,5	4,2	$C_{19}H_{17}NO_3$	74,3	5,6	4,6	65
IIb	7'-CH_3	151—152	74,5	6,3	4,1	$C_{20}H_{19}NO_3$	74,7	6,0	4,4	70
IIc	5', 6'-Benzo	155—156	76,9	5,7	3,7	$C_{23}H_{19}NO_3$	77,3	5,4	3,9	75
IId	6', 7'-Benzo	189—190	77,6	5,1	4,2	$C_{23}H_{19}NO_3$	77,3	5,4	3,9	55
IIe	7', 8'-Benzo	136—137	77,0	5,6	3,6	$C_{23}H_{19}NO_3$	77,3	5,4	3,9	60
IIf	6'-Cl	167—168	66,6	4,8	3,8	$C_{19}H_{16}ClNO_3$	66,8	4,7	4,1	70
IIg	6',8'-Cl_2	157—158	60,4	3,8	3,9	$C_{19}H_{15}Cl_2NO_3$	60,7	4,0	3,7	75
IIh	6'-Br	165—165,5	58,8	4,4	3,9	$C_{19}H_{16}BrNO_3$	59,1	4,2	3,6	85
IIi	6',8'-Br_2	161—162	48,8	3,6	2,8	$C_{19}H_{15}Br_2NO_3$	49,1	3,3	3,0	60
IIj	8'-OCH_3	120—121	71,5	5,5	3,9	$C_{20}H_{19}NO_4$	71,2	5,7	4,2	60
IIk	7'-$OCH_2C_6H_5$	119—120	75,8	5,3	3,7	$C_{26}H_{23}NO_4$	75,5	5,6	3,4	60
IIl	6'-NO_2	110—110,5	65,0	4,3	8,2	$C_{19}H_{16}N_2O_5$	64,8	4,6	8,0	50
IIm	8'-NO_2	126—127	65,1	4,8	7,7	$C_{19}H_{16}N_2O_5$	64,8	4,6	8,0	65
IIn	6',8'-$(NO_2)_2$	161—162	57,1	4,1	10,1	$C_{19}H_{15}N_3O_7$	57,7	3,8	10,6	65
IIo	6'-Cl-8'-NO_2	152—153	58,8	4,2	6,9	$C_{19}H_{15}ClN_2O_5$	59,0	3,9	7,2	65
IIp	6'-Br-8'-NO_2	170—171	53,1	3,3	6,7	$C_{19}H_{15}BrN_2O_5$	52,9	3,5	6,5	70

*The compositions of IIf-i,o,p were confirmed by determination of the amount of halogen present in them.

TABLE 2. Spectral Characteristics of Spirans IIa-p and the Photoinduced Forms (IIIa-p) in Alcohol

Compound	IR spectrum, ν, cm^{-1}	λ_{max}, nm (lg ε)	λ_{max}, photoinduced forms, nm
IIa	1750, 1645, 1600	265 (4,14); 273 (4,07); 305 (3,88); 317 sh (3,84)	383, 505 sh, 535, 575, 650 sh
IIb	1747, 1642, 1592	265 (3,55); 272 (3,53); 315 (3,21)	362 sh, 370, 505 sh, 540, 580 sh, 620 sh
IIc	1747, 1632, 1587	262 (4,12); 277 (3,72); 290 (3,85); 307 (4,07); 340 (3,87); 357 (3,95)	420 sh, 480, 640 sh
IId	1754, 1637, 1585	267 (4,64); 280 (4,30); 290 (4,39); 303 (4,46); 345 (3,25); 365 (3,15)	461
IIe	1738, 1665, 1580	260 (4,68); 270 (4,79); 283 (3,65); 313 (3,63); 324 (3,60); 338 (3,73); 358 (3,66)	375, 480, 515 sh
IIf	1747, 1640, 1592	265 (3,89); 270 (3,82); 276 (3,77); 317 (3,50); 325 (3,41)	320 sh, 380, 510 sh, 535, 585, 635
IIg	1742, 1646, 1580	268 (4,15); 274 (4,08); 278 (4,02); 318 (3,77); 331 (3,69)	380, 520 sh, 580, 620, 650 sh
IIh	1740, 1632, 1585	263 (4,03); 273 sh (3,96); 316 (3,63); 330 (3,49)	353 sh, 380, 500 sh 540, 580, 625
IIi	1735, 1632, 1577	268 (4,19); 280 sh (4,08); 320 (3,57); 383 (3,50)	393, 526 sh, 560, 605, 640
IIj	1750, 1537, 1587	260 sh (4,03); 270 (4,10); 280 (4,01); 303 (3,73)	400, 585, 620 sh
IIk	1730, 1660, 1592	282 (3,92); 305 (3,46)	400, 450 sh, 485, 520 sh.
IIl	1728, 1638, 1600	267 (4,38); 273 (4,30); 314 (3,98); 330 (3,95)	555, 583
IIm	1730, 1628, 1582	270 sh (4,22); 340 (3,88)	525 sh, 575, 620
IIn	1740, 1632, 1580	303 (4,05); 338 (4,02)	550
IIo	1718, 1628, 1590	254 (4,25); 263 sh (4,12); 350 (3,71)	600
IIp	1715, 1625, 1572	258 (4,40); 269 (4,29); 347 (3,76)	550, 625

Spiropyran IId with linearly annelated rings is a special case. According to the calculations, the long-wave absorption band of the colored form should be found at ~750 nm [2]. However, for the synthesized spiran the longest-wave absorption band is observed at 461 nm, i.e., the experimental transition energy differs from the calculated value by 1 eV.

Model benzochromene V was synthesized by the scheme proposed by Hlubeck and co-workers [3].

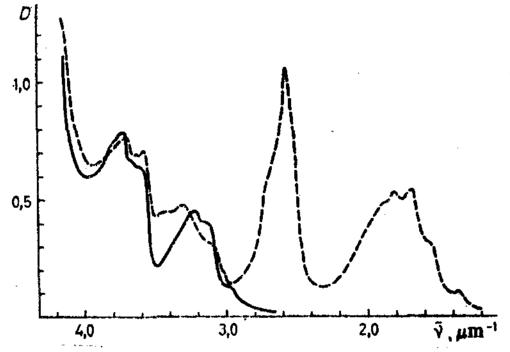


Fig. 1. Electronic absorption spectra of 2-oxo-3-phenyl-5,5-dimethylspiro(1,3-oxazolidine-4,2'-[2H]-chromene) in ethanol at –100°C (c $5.7 \cdot 10^{-5}$ mole/liter; l = 1 cm) before (——) and after (---) irradiation.

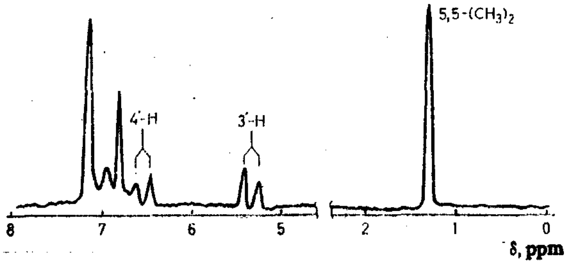
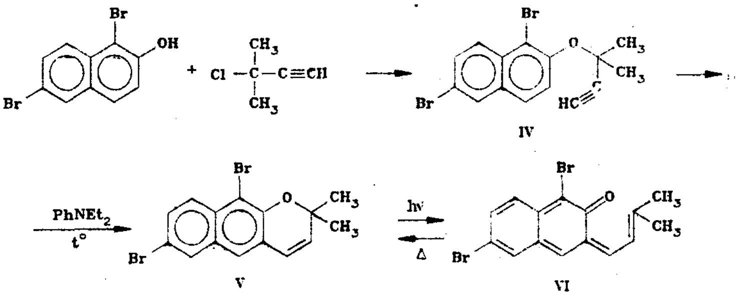


Fig. 2. PMR spectrum of IIa in CCl_4.



However, a long-wave absorption band with a maximum at 461 nm, which also is not in agreement with the calculated value, is observed experimentally for its photoinduced form IV.

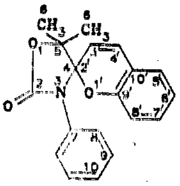
The typical PMR spectrum is presented in Fig. 2 (IIa). The signals of the 3' and 4' protons are represented by an AB spectrum with $\delta_{(3')}$ = 5.34 ppm and $\delta_{(4')}$ = 6.52 ppm ($J_{3'4'}$ = 9.75 Kz). Despite the noncoplanarity of the structures of spirans IIa-p, the protons of the diastereotopic methyl groups in the 5 position of the oxazolidone ring are virtually isochronic in the PMR spectra: a singlet at 1.28 ppm is observed in the spectra of solutions in CCl . Two signals of methyl groups with $\Delta\delta$ = 0.05 ppm are observed in the spectra of solutions in chlorobenzene at 20°C, and $\Delta\delta$ = 0.02 ppm in the spectra of solutions in methylene chloride at 0°C (a singlet is observed at room temperature). The introduction of a benzyloxy group in the 7' position of the benzopyran part of the molecule (IIk) also did not lead to the expected diastereotopic splitting in the spectra of the signals of the methylene group of the benzyl residue.

At the same time, significant anisochronicity of the carbon atoms of the methyl groups in the 5 position of the oxazolidone ring of the corresponding noncoplanar structures IIa-p is observed in the ^{13}C NMR spectra (Table 3). The assignment of the signals in the ^{13}C NMR spectra of the synthesized spiropyrans was made in analogy with the data in [4, 5].

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord IR-71 spectrometer. The PMR spectra were obtained with Tesla BS 467 (60 MHz) and Tesla BS

TABLE 3. Chemical Shifts of the ^{13}C Nuclei (δ, ppm) of I and II



Compound	2	4	5	6	7	8	9	10	3′	4′	5′	6′	7′	8′	9′	10′
I	151,0	78,3	80,8	26,0	133,5	126,0	128,0	126,8	—	—	—	—	—	—	—	—
IIa	152,9	95,1	85,3	21,7 19,5	134,4	125,7	127,2	126,0	110,8	128,5	125,8	120,2	129,2	115,8	150,7	116,8
IIf	152,6	95,4	85,8	21,7 19,5	134,2	125,9	127,4	126,0	115,6	128,7	125,9	124,5	127,6	117,3	149,5	118,4
IIg	152,8	96,3	85,6	21,8 19,4	133,9	126,4	127,5	126,0	118,4	128,4	124,3	124,4	127,3	119,7	145,2	119,5
IIh	152,2	95,4	85,4	21,7 19,5	134,2	125,9	127,4	126,1	116,0	128,3	127,5	111,7	131,6	117,2	150,0	118,9
IIj	153,0	95,2	85,8	21,6 19,2	134,5	125,6	127,2	125,8	117,8	128,7	112,3	120,0	116,2	146,1	139,8	117,6
IIl	152,7	96,4	85,9	21,8 19,5	133,8	126,3	127,5	126,5	114,9	127,4	121,6	140,9	124,8	118,0	155,7	117,2
IIm	152,8	96,4	85,6	21,9 19,3	133,7	126,4	127,5	126,8	117,4	127,8	130,6	119,9	124,2	136,2	143,8	119,4

487 S (80 MHz) spectrometers with hexamethyldisiloxane as the internal standard. The ^{13}C NMR spectra of solutions in acetone were recorded with a Varian XL-100 (100 MHz) spectrometer with complete spin decoupling of the protons under pulse Fourier conditions. The electronic spectra were recorded with a Specord UV-vis spectrophotometer equipped with a special cryostat for recording of the spectra of the photocolored forms of the spiropyrans at low temperatures. Irradiation with UV light was carried out with a DRSh-250 mercury lamp with a light filter that isolated the light with λ_{max} 313 nm.

The characteristics of the compounds are presented in Tables 1-3.

2-Oxo-3-phenyl-5,5-dimethylspiro(1,3-oxazolidine-4,2'-[2H]-chromenes) (IIa-p). A mixture of 2.01 g (10 mmole) of methylene base I [6] and 11 mmole of the corresponding o-hydroxy aromatic aldehyde in a mixture of 20 ml of glacial acetic acid and three drops of 70% $HClO_4$ was refluxed for 1 h, after which it was poured into 80 ml of water. The aqueous mixture was extracted with four 20-ml portions of benzene, and the benzene extracts were washed with 5% sodium bicarbonate solution and water and dried with sodium sulfate. The residue obtained after removal of the solvent on a water bath *in vacuo* (water aspirator) was recrystallized from ethanol with the addition of activated charcoal. The yields of the spiropyrans can be increased 5-10% when the acetals of the corresponding o-hydroxy aromatic aldehydes are used as the aldehyde components.

1,1-Dimethyl-2-propynyl 1,6-Dibromo-2-naphthyl (Ether (IV). A mixture of 18.12 g (50 mmole) of 1,6-dibromo-2-naphthol [7], 7.25 g (75 mmole) of 3-chloro-3-methyl-1-butyne [8], 13 g (78 mmole), of KI and 8 g (58 mmole) of potassium carbonate in 75 ml of absolute acetone was refluxed with stirring for 20 h, after which the precipitate was removed by filtration and washed with acetone. The filtrates were evaporated, and the residue was dissolved in 80 ml of ether. The ether solution was washed with 10% NaOH solution and water and dried with sodium sulfate. The either was removed by distillation, and the product was distilled *in vacuo* in a stream of argon to give 14.7 g (67%) of a yellow oil with bp 194°C (6 mm). Found: C 50.1; H 3.0; Br 43.2%. $C_{15}H_{12}Br_2O$. Calculated: C 48.9; H 3.2; Br 43.5%.

2,2-Dimethyl-7,10-dibromo-2H-benzo[g]chromene (V). A 14-g (37 mmole) sample of ether IV was refluxed in 50 ml of diethylaniline for 8 h, after which 100 ml of ether was added, and the mixture was washed with 10% sulfuric acid solution, water, and a saturated solution of salt and dried with sodium sulfate. The ether was removed by distillation, and the resulting oil was purified with a column packed with aluminum oxide (activity II) by elution with petroleum ether—benzene (1:4). The solvent was removed by distillation, and the residue was recrystallized from hexane to give 4.5 g (30%) of white needles with mp 85°C. PMR spectrum: 1.35 (6H, s, CH_3), 5.47 (1H, d, J = 10 Hz, 3-H), 6.7 (1H, d, J = 10 Hz, 4-H), and 6.85-7.6 ppm (4H, m, 5,6,8,9-H). Found: C 48.9; H 3.5; Br 43.5%. $C_{15}H_{12}Br_2O$. Calculated: C 48.9; H 3.2; Br 43.5%.

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REGIOSPECIFIC CLEAVAGE OF 1,3-DIOXANES BY ORGANOALUMINUM COMPOUNDS

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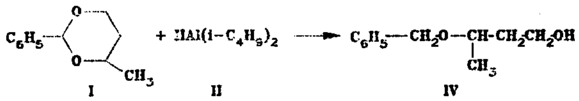
Organoaluminum compounds react with 4-methyl-2-phenyl-1,3-dioxane with cleavage of the O_1-C_2 bond to give monoethers with a primary alcohol group.

The reduction of cyclic acetals and ketals by alkylaluminum hydrides leads to monoethers of glycols [1], whereas tetrasubstituted 1,3-dioxolanes are selectively reduced to monoethers with a tertiary hydroxy group [2]. Information regarding the specificity of the cleavage of unsymmetrically substituted 1,3-dioxanes is not available.

In the present research we studied the transformations of 2-phenyl-4-methyl-1,3-dioxane (I), which exists in the cis-E, E conformation, under the influence of diisobutylaluminum hydride (II) and triethylaluminum (III). Compound I is reduced to 3-benzyloxy-1-butanol (IV) in virtually quantitative yield under the influence of reagent II. The isomeric 4-benzyloxy-2-butanol is not formed.

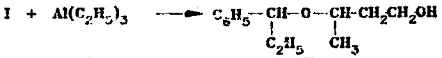


I II IV

$$\mathrm{I} + HAl(i\text{-}C_4H_9)_2 \longrightarrow C_6H_5-CH_2O-\underset{\displaystyle CH_3}{CH}-CH_2CH_2OH$$

In the ^{13}C NMR spectrum of IV the doublet of the $-O-CH(CH_3)-$group is located at weaker field (73.1 ppm) than the signal of the $-CH_2OH$ fragment (59.3 ppm, t).

Under the influence of triethylalumunum (III) acetal I forms only 3-(α-phenylpropoxy)-1-butanol (V):



III V

$$\mathrm{I} + Al(C_2H_5)_3 \longrightarrow C_6H_5-\underset{\displaystyle C_2H_5}{CH}-O-\underset{\displaystyle CH_3}{CH}-CH_2CH_2OH$$

The structure of ether V also follows unambiguously from its ^{13}C NMR spectrum (Table 1).

Steric shielding of the adjacent oxygen atom by the methyl group in acetal molecule I apparently does not make it possible for the aluminum atoms to realize coordination at the

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