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SYNTHESIS AND PROPERTIES OF FURAN DERIVATIVES.

1. SYNTHESIS OF 3,5-DISUBSTITUTED Δ^2-ISOXAZOLINES CONTAINING FURFURYL FRAGMENTS

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3,5-Disubstituted Δ^2-isoxazolines containing furan fragments have been synthesized by 1,3-dipolar cycloaddition reactions.

Substituted Δ^2-isoxazolines are convenient synthons for the synthesis of polyfunctional compounds (α,β-unsaturated ketones, β-hydroxyketones, etc.) [1], 2-substituted furans, bisheteroaromatic compounds, and others [2]. However, until recently only limited reports have appeared in the literature concerning the preparation and properties of Δ^2-isoxazolines containing furan fragment substituents. In this regard the only example which has been published is the synthesis of Δ^2-isoxazolines via 1,3-dipolar cycloaddition reactions involving 2-furancarbonitrile-N-oxide and 5-nitro-2-furancarbonitrile-N-oxide [3, 4].

We now report the synthesis of 3,5-disubstituted Δ^2-isoxazolines containing furfuryl radicals in the 3-position. These compounds are of potential interest as biologically active compounds and as intermediates for the preparation of 2-substituted furans containing a functional group in the β-position of the side chain.

In order to pursue the preparation of these compounds we have studied the 1,3-dipolar cycloaddition reactions of monosubstituted ethylenes with 1,3-dipoles generated in situ from 2-(2-nitroethyl)-5-R-furans Ia, b via treatment with phenylisocyanate in the presence of triethylamine. According to the literature data, the 1,3-dipoles formed from the aci form of primary nitro compounds upon treatment with phenylisocyanate in the presence of catalytic amounts of tertiary amines represent either nitrone esters (A) [5] or their further transformation products, namely nitrile-N-oxides (B) [6].

We have found that the most favorable conditions for carrying out the reactions are in absolute benzene at a mole ratio for nitroalkane Ia, b to dipolarophile to phenylisocyanate equal to 1:5:2, for a period of 6-8 h at room temperature, followed by refluxing the reaction mixture for an additional 2 h. Under these conditions the desired 3,5-disubstituted Δ^2-isoxazolines are obtained in satisfactory yields (Table 1). However, when allyl chloride and

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TABLE 1. Physical Characteristics of Compounds I and II

Compound	Molecular formula	bp, °C (mm Hg)	n_D^{20}	PMR spectrum, δ, ppm, SSCC, Hz										yield, %
				furan ring protons	H_A, ddt	H_B, ddt	H_X, dd	$-CH_2-$ m	R¹	$^2J_{AB}$	$^3J_{AX}$	$^3J_{BX}$	$^4J_{A,CH_2}$ (B, HC_2)	
Ia	$C_6H_7NO_3$	62(2)	1,4848											47
Ib	$C_7H_9NO_3$	98(7)	1,1510											37
IIa	$C_{11}H_{17}NO_2$	106(3)	1,4971	6,21 (ddt, 1H, 3-H, $^3J_{3,4}=3,2$); 6,36 (dd, 1H, 4-H, $^3J_{4,5}=2,0$); 7,44 (dd 1H, 5-H, $^4J_{3,5}=0,9$)	3,07	2,70	3,89	3,74	0,05 (s, 9H)	16,1	15,3	11,0	1,0 (0,7)	16
IIb	$C_{10}H_{13}NO_3$	120 ... 121(3)	1,4879	6,13 (ddt 1H, 3-H, $^3J_{3,4}=3,2$); 6,29 (dd, 1H, 4-H, $^3J_{4,5}=1,9$); 7,31 (dd 1H, 5-H, $^4J_{3,5}=0,8$)	3,02	2,69	5,49	3,75	1,17 (t, 3H); 3,57 (dq 2H)	17,9	6,1	2,3	1,1 (0,5)	73
IIc	$C_9H_{10}NO_2Cl$	117(3)	1,5171	6,14 (ddt, 1H, 3-H, $^3J_{3,4}=3,2$); 6,30 (dd, 1H, 4-H, $^3J_{4,5}=1,9$); 7,33 (dd 1H, 5-H, $^4J_{3,5}=0,9$)	3,10	2,82	4,79	3,71	3,52 (dd, 2H)	17,5	9,5	7,3	0,9 (0,9)	15
IId	$C_9H_7N_2O_2$	134(3)	1,5111	6,18 (ddt, 1H, 3-H, $^3J_{3,4}=3,2$); 6,32 (dd 1H, 4-H, $^3J_{4,5}=1,9$); 7,34 (dd 1H, 5-H, $^4J_{3,5}=0,9$)	3,40	3,17	5,16	3,78	—	19,2	9,2	7,8	0,9 (0,9)	47
IIe	$C_{10}H_{11}NO_4$	152(3)	1,5005	5,87 (ddt, 1H, 3-H, $^3J_{3,4}=3,2$); 6,02 (dd, 1H, 4-H, $^3J_{4,5}=1,9$); 7,01 (dd 1H, 5-H, $^4J_{3,5}=0,9$)	2,91	2,43	4,57	3,33	3,26 (m, 3H)	17,2	11,4	6,7	0,9 (0,9)	65
IIf	$C_{11}H_{15}NO_2$	129 ... 130(3)	1,4846	6,14 (ddt, 1H, 3-H, $^3J_{3,4}=3,2$); 6,31 (dd 1H, 4-H, $^3J_{4,5}=2,0$); 7,33 (dd 1H, 5-H, $^4J_{3,5}=0,9$)	2,97	2,48	4,62	3,70	0,92 (br.s, 3H); 1,48 (m, 4H)	17,0	9,9	8,0	0,9 (0,9)	49
IIg	$C_{14}H_{13}NO_2$	163(3)	1,5555	6,22 (ddt, 1H, 3-H, $^3J_{3,4}=3,2$); 6,35 (dd, 1H, 4-H, $^3J_{4,5}=1,8$); 7,44 (dd 1H, 5-H, $^4J_{3,5}=0,9$)	3,44	2,87	5,56	3,78	7,32 (s, 5H)	17,2	10,7	8,4	1,0 (1,0)	42
IIh	$C_{11}H_{15}NO_3$	122 ... 123(3)	1,5261	6,01 (ddt, 1H, 3-H, $^3J_{3,4}=3,1$); 5,87 (d. q, 1H, 4-H, $^4J_{4,CH_3}=1,0$); 2,24 (dd, 3H, 5-CH_3, $^5J_{3,CH_3}=0,4$)	3,08	2,71	5,52	3,72	1,20 (t, 3H); 3,60 (dq, 2H)	18,0	6,0	2,3	1,0 (1,0)	37
IIi	$C_{10}H_{12}NO_2Cl$	131(2)	1,5120	6,02 (ddt, 1H, 3-H, $^3J_{3,4}=3,1$); 5,88 (d q, 1H, 4-H, $^4J_{4,CH_3}=1,0$); 2,25 (dd 3H, 5-CH_3, $^5J_{3,CH_3}=0,4$)	3,07	2,94	4,80	3,67	3,51 (dd, 2H)	17,4	9,3	7,2	0,9 (0,9)	15
IIj	$C_{10}H_{10}N_2O_2$	153 ... 154(3)	1,5102	6,07 (ddt, 1H, 3-H, $^3J_{3,4}=3,1$); 5,90 (d q, 1H, 4-H, $^4J_{4,CH_3}=1,1$); 2,25 (dd 3H, 5-CH_3, $^5J_{3,CH_3}=0,4$)	3,35	3,25	5,17	3,73	—	19,0	9,0	7,6	0,9 (0,9)	49
IIk	$C_{12}H_{17}NO_2$	124 ... 125(2)	1,4874	5,97 (ddt, 1H, 3-H, $^3J_{3,4}=3,1$); 5,83 d. q, 1H, 4-H, $^4J_{4,CH_3}=1,0$); 2,25 (dd 3H, 5-CH_3, $^5J_{3,CH_3}=0,4$)	2,94	2,46	4,57	3,63	0,94 (br.s, 3H); 1,49 (m, 4H)	16,9	10,3	8,4	1,0 (1,0)	44
IIl	$C_{15}H_{15}NO_2$	183(4)	1,5491	6,0 (ddt, 1H, 3-H, $^3J_{3,4}=3,1$); 5,86 (d q, 1H, 4-H, $^4J_{4,CH_3}=1,0$); 2,23 (dq 3H, 5-CH_3, $^5J_{3,CH_3}=0,4$)	3,37	2,92	5,55	3,71	7,31 (s, 5H)	17,2	10,5	8,3	1,0 (1,0)	33
IIm	$C_{11}H_{13}NO_4$	174(3)	1,4990	—	—	—	—	—	—	—	—	—	—	40

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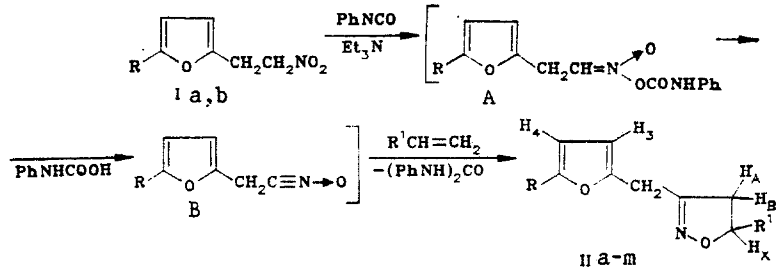
*The spectra of compounds IIa, g were recorded in $(CD_3)_2CO$, that of compound IIe in the C_6D_6. All of the other spectra were measured in $CDCl_3$.



Ia IIa-g $R=H$; Ib IIh-m $R=CH_3$; IIa $R^1=Si(CH_3)_3$, b, h $R^1=OC_2H_5$, c, i $R^1=CH_2Cl$, d, j $R^1=CN$, e, m $R^1=COOCH_3$, f, k $R^1=C_3H_7$-*n*, g, ℓ $R^1=C_6H_5$

trimethylvinylsilane are used as the dipolarophiles the yields of the corresponding adducts are only 15-16%, with significant resin formation observed in the reaction mixture.

The IR spectra of Δ^2-isoxazolines IIa-m exhibit their C=N group absorption bands at 1620-1595 cm^{-1}, which is characteristic of C=N bonds in dihydroazoles [7, 8]. The presence of this type of ring is also supported by the absorption maxima observed at 1435-1420, 1370-1340, and 1080-1070 cm^{-1}, which are assigned to the stretching vibrations of the =N—O—C— fragment in Δ^2-isoxazolines [8, 9]. The IR spectra of all of the newly synthesized compounds also contain variable intensity absorption maxima characteristic of the vibrations of 2-substituted and 2,5-disubstituted furan fragments: 1575-1560, 1505-1495 (ν_{ring}); 1220-1215, 1170-1150 (δ_{CH}), 1020-1015 (ring "breathing" vibrations); 950-910, 885-850, and 820-805 (γ_{CH}); and 750-725 cm^{-1} (β ring) [7].

Rigorous assignments have made for the proton signals in the PMR spectra of compounds IIa-m, based on the fact that the isoxazoline ring protons form an ABX spin system (Table 1). Based on the observed signal multiplicity for these protons, their chemical shift and spin—spin coupling constant values, we conclude that the newly synthesized compounds are, in fact, 3,5-disubstituted Δ^2-isoxazolines, and not their 2,4-disubstituted regioisomers [10, 11].

EXPERIMENTAL

IR spectra were measured on a Specord 75 IR spectrophotometer using a thin (liquid) film. PMR spectra were recorded on a Bruker WP-8-SY (80 MHz) spectrometer versus TMS as internal standard; $CDCl_3$, $(CD_3)_2CO$, and C_6D_6 were used as the solvents.

2-(2-Nitroethyl)-5-R-furans (I). To a solution of 5 mmoles of the appropriate nitroalkane and 0.64 g (6.0 mmoles) benzaldehyde in 25 ml butanol under nitrogen at 20°C was added with stirring 0.65 g (6.0 mmoles) o-phenylenediamine in portions. The reaction mixture was stirred for 2 h at 20°C. The solvent was evaporated at reduced pressure and 15 ml methylene chloride was added to the residue. The mixture was filtered to remove 0.9 g of insoluble 2-phenylbenzimidazole (mp 280°C), and the resulting filtrate was washed with 0.1 N HCl solution; the methylene chloride was also evaporated under reduced pressure. The product was then purified either by column chromatography on silica gel (with chloroform eluent), or by vacuum distillation. The yields and physical constants of the product 2-(2-nitroethyl)-5-R-furans are given in Table 1 [12, 13].

3,5-Disubstituted Δ^2-Isoxazolines (II). To a solution of 0.15 moles of monosubstituted ethylene derivative in 50 ml absolute benzene was added 7.14 g (0.06 moles) phenylisocyanate and 4 drops of triethylamine. The resulting mixture was stirred and 0.03 moles of compound Ia, b in 5 ml absolute benzene was added dropwise. The reaction mixture was stirred for 8 h at 20°C, and then heated with stirring for an additional 2 h. The mixture was filtered to remove insoluble diphenylurea, and the solvent was evaporated at reduced pressure; the residue was subjected to vacuum distillation. The isolated products were further purified by column chromatography on silica gel (chloroform eluent). The yields and physical constants of the newly synthesized compounds are summarized in Table 1.

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PHOTOCHEMISTRY OF 2-AMINO-2H-BENZOCHROMENES*

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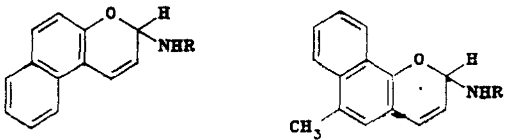
Diabatic photoinduced ring opening of the chromene ring of 2-amino-5,6-benzo-2H-chromenes and 2-amino-6-methyl-7,8-benzo-2H-chromenes leads, in the same way as a thermally induced reaction, to the establishment of ring-chain tautomer equilibrium in the ground electronic state, the position of this equilibrium depending on the polarity of the solvent, the temperature, and structural factors. o-Quinoid tautomers exist as several stable isomeric forms: an acoplanar cis-S-cis-trans-form absorbing in the shortwave region, and S-trans-isomers absorbing in the longwave region of the spectrum. Photoexcitation of the o-quinoid forms in the temperature range 125-190 K initiates mutual conversions of these and the initial 2H-chromene structure. The relative stability of the conformers of the o-quinoid form depends on steric and electronic factors: benzanellation in positions 5,6 leads to stabilization of the cis-S-cis-trans-isomer and in positions 7,8 the S-trans-isomers are more preferred: π-acceptor substituents on the amine component increase the stability of the cis-S-cis-trans isomer and electron-donor substituents stabilize the S-trans-isomer.

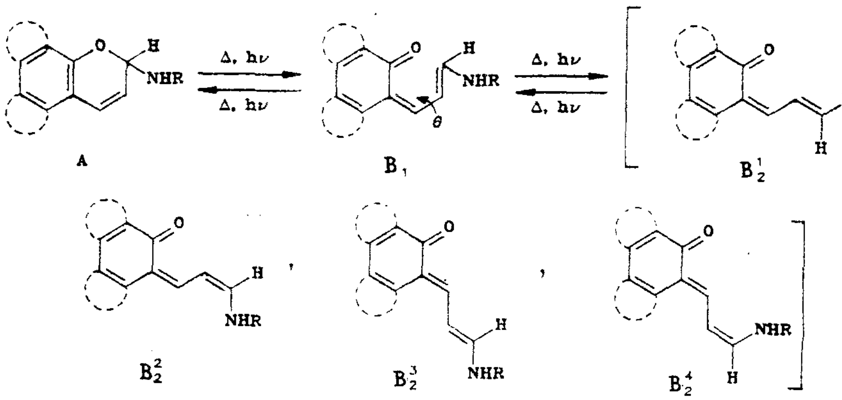
Synthetic methods, structure, and tautomeric equilibria in the ground electronic state for 2-amino-2H-benzochromenes, together with some details of the photochemical properties in solution, have been given in [2-4]. In the present work we consider the influence of the aminogroup substituents and the location of annelation on the spectral and photochemical properties of aminochromenes I-XV (Table 1)



I-X XI-XV

For assignment of radicals, see Table 1

In solutions of the 2H-aminochromenes I-XV ring-chain equilibrium is established involving chromene form (A), the acoplanar (in terms of the angle θ) cis-S-cis-trans-isomer (B_1), and the aggregate of S-trans-isomers $B_2{}^i$ (i = 1, 2, 3, 4) [2-4].



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*Communication 20 from the series "Photo- and thermochromic piranes." See [1] for Communication 19.

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