and washed with water to give 1.15 g (3.9 mmole) of product VIIa. Diaminothiazole VIIb was similarly synthesized from amide VIb.

LITERATURE CITED

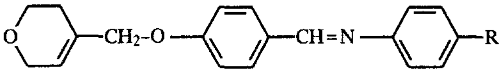
1. U. G. Ibatullin, Kh. F. Sagitdinova, G. R. Talipova, M. G. Safarov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 12, 2753 (1985).
2. K. K. Kuznetsova, N. G. Ostroumova, and N. M. Kukina, *Zh. Obshch. Khim.*, **32**, 10 (1962).
3. R. L. Nevill and J. McLee, *Canad. J. Chem.*, **41**, 2123 (1963).
4. Yu. V. Svetkin and A. N. Minlibaeva, *Zh. Obshch. Khim.*, **44**, 44 (1988).
5. G. R. Talipova, Kh. F. Sagitdinova, U. G. Ibatullin, and M. G. Safarov, Summaries of Papers Presented at the Scientific-Technical Conference on the Chemistry of Reagents [in Russian], Ufa (1986), p. 82.
6. V. A. Mnatsakyan, S. A. Vartanyan, S. O. Vartanyan, É. A. Markaryan, S. L. Mndzhoyan, and G. A. Panayan (eds.), *Syntheses of Heterocyclic Compounds* [in Russian], Vol. 14, Izd. Akad. Nauk Armyansk. SSR, Yerevan (1984), p. 33.

SYNTHESIS AND INVESTIGATION OF THE MESOMORPHIC PROPERTIES OF PYRAN DERIVATIVES

M. M. Murza and V. I. Kopelev

4′-[(5,6-Dihydro-2H-pyran-4-yl)methoxy]benzylidene-4″-alkoxyanilines, which have the properties of smectic liquid crystals, were synthesized. The effect of the pyran ring in the benzylidene component and the length of the aliphatic radical in the aniline component on the type and thermal stability of the meso phase was ascertained.

Continuing our investigation of the effect of the molecular structure on mesomorphism in azomethines [1] we synthesized 4′-[(5,6-dihydro-2H-pyran-4-yl)methoxy]benzylidene-4″-alkoxyanilines.



I - XI

I R=H, II R=OCH_3, III R=OC_2H_5, IV R=OC_3H_7; V R=OC_4H_9, VI R=OC_5H_{11}, VII R=OC_6H_{13},
VIII R=OC_7H_{15}, IX R=OC_8H_{17}, X R=OC_9H_{19}, XI R=$OC_{10}H_{21}$

4-Methylenetetrahydropyran (XII), which is a high-tonnage waste product in the manufacture of isoprene via the dioxane method [2], was used as the starting compound. Compound XII reacts quantitatively with bromine in CCl_4, and the resulting 4-bromo-4-bromomethyltetrahydropyran (XIII) reacts with p-hydroxybenzaldehyde in methyl ethyl ketone in the presence of potassium carbonate to give 4′-[(5,6-dihydro-2H-pyran-4-yl)methoxy]benzaldehyde (XIV). Condensation of XIV with p-alkoxyanilines gave I-XI.

Bashkir State University, Ufa 450074. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 327-328, March, 1992. Original article submitted June 15, 1990; revision submitted January 8, 1991.

0009-3122/92/2803-0272 $12.50

TABLE 1. Characteristics of the Synthesized I-XI*

Compound	Empirical formula	mp, °C	T_s, °C	T_i, °C	Yield, %
I	$C_{19}H_{19}NO_2$	113...115	—	115	71
II	$C_{20}H_{21}NO_3$	132...134	—	134	70
III	$C_{21}H_{23}NO_3$	129...130	—	126	66
IV	$C_{22}H_{25}NO_3$	125...126	126	135	60
V	$C_{23}H_{27}NO_3$	129...130	113	129	56
VI	$C_{24}H_{29}NO_3$	120...121	118	128	63
VII	$C_{25}H_{31}NO_3$	117...118	116	127	70
VIII	$C_{26}H_{33}NO_3$	115...116	114	126	72
IX	$C_{27}H_{35}NO_3$	113...114	113	126	75
X	$C_{28}H_{37}NO_3$	115...115,5	111	124	80
XI	$C_{29}H_{39}NO_3$	119...121	109	122	85

---

*T_s and T_i are the temperatures of existence of the smectic and isotropic modifications, respectively.

Signals of protons of a methylene group bonded to a pyran ring at 2.0-2.2 ppm and of protons of the methylene group in the 5 position at 2.6-8.2 ppm are present in the PMR spectra of I-XI; the methylene groups in the 2 and 6 positions of the pyran ring resonate at 3.5-4.5 ppm, the methylidyne proton of the CH=C bond of the pyran ring gives a signal at 5.6-5.9 ppm, the aromatic protons form multiplets at 6.5-7.9 ppm, and the proton of the azomethine group gives a singlet at 7.9-8.2 ppm.

A study of the liquid-crystal properties of I-XI showed that mesomorphism of the smectic type at 109-135°C is characteristic for them.

An increase in the length of the hydrocarbon chain in the aniline component leads to broadening of the range of the meso phase. The introduction of a pyran ring into the benzylidene component of I-XI increases the thermal stability of the meso phase as compared with similar mesogens that have an aliphatic radical in the benzylidene component [3]; the pyran ring increases side interaction, which leads to the formation of a smectic meso phase.

EXPERIMENTAL

The PMR spectra of solutions of the substances in CCl_4 were recorded with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The temperatures of the phase transitions were measured with an MIN-10 polarization microscope with a heat adapter under heating conditions. The individuality and purity of all of the described compounds were monitored by TLC on aluminum oxide in toluene—chloroform.

The results of elementary analysis of I-XI, XIII, and XIV for C, H, and N were in agreement with the calculated values. The yields and characteristics of the compounds obtained are presented in Table 1.

4-Bromo-4-bromomethyltetrahydropyran was synthesized by the method in [4].

4-[(5,6-Dihydro-2H-pyran-4-yl)methoxy]benzaldehyde (XIV). A mixture of 40 g (0.16 mole) of XIII, 19.4 g (0.16 mole) of p-hydroxybenzaldehyde, and 44 g (0.32 mole) of potassium carbonate in 120 ml of methyl ethyl ketone was refluxed for 24 h, after which the reaction mixture was filtered hot, the methyl ethyl ketone was removed by distillation, and the residue was crystallized from hexane to give 24.42 g (70%) of aldehyde XIV with mp 49-50°C.

4′-[(5,6-Dihydro-2H-pyran-4-yl)methoxy]benzylidene-4″-alkoxyanilines I-XI. A 2.0-g (0.008 mole) sample of XIV and 1.8 g (0.008 mole) of the aromatic amine were refluxed in 60 ml of absolute tetrahydrofuran in the presence of a catalytic amount of piperidine for 2 h, after which the solvent was removed by distillation, and the residue was crystallized from alcohol.

LITERATURE CITED

1. M. M. Murza, I. P. Podlipchuk, and M. G. Safarov, *Zh. Org. Khim.*, **26**, 384 (1990).

2. S. K. Ogorodnikov and G. S. Idlis, *The Manufacture of Isoprene* [in Russian], Khimiya, Leningrad (1973).
3. S. I. Zhdanov, *Liquid Crystals* [in Russian], Khimiya, Moscow (1979).
4. A. A. Gevorkyan, A. S. Arakelyan, and P. I. Kazaryan, *Khim. Geterotsikl. Soedin.*, No. 8, 1025 (1981).

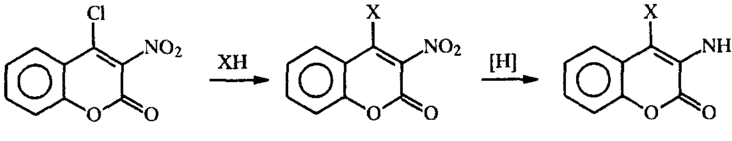
HETEROCYCLIC BIOANTIOXIDANTS.

3.* EFFECT OF A SUBSTITUENT ON THE RESULT OF THE REDUCTION OF 3-NITRO-4-HETERO-SUBSTITUTED COUMARINS WITH SODIUM HYDROSULFITE

É. A. Parfenov and L. D. Smirnov

The effect of a heterosubstituent on the result of the reduction of 3-nitro-4-substituted coumarins with sodium hydrosulfite, which generally leads to a mixture of three compounds, viz., the product of the reduction of the nitro group to an amino group and products of its replacement by hydrogen or a mercapto group, was studied. The result of the transformation is explained by the stabilizing effect of the heterosubstituent on the reaction intermediate.

To synthesize three types of coumarin reductones [2] V-VII, which contain an amino group in the 3 position and an amino, hydroxy, or mercapto group in the 4 position, we used a synthetic scheme based on nucleophilic substitution of the activated halo group in 3-nitro-4-chlorocoumarin (I) [3] and subsequent reduction of the nitro group in intermediates II-IV.



I II-IV V-VII

II, V a $X{=}NH_2$, b $X{=}NHCH_3$, c $X{=}NHCH_2CH{=}CH_2$, d $X{=}NH(CH_2)_2OH$, e $X{=}NHCH_2C_6H_5$, f $X{=}NHC_6H_5$, g $X{=}NHC_6H_4COOH$-*o*, h $X{=}N(C_3H_7)_2$, i $X{=}N(CH_2)_4$, j $X{=}N(C_2H_5)_2$; III, VI a $X{=}OH$, b $X{=}OCH_3$; IV, VII a $X{=}SCH_2C_6H_5$, b $X{=}SC_6H_4COOH$-*o*

Previously, for the synthesis of 3,4-diaminocoumarins V we used catalytic hydrogenation with palladium on carbon [3, 4]; this method has drawbacks, among which are the consumption of a precious metal, as well as the impossibility of introducing of unsaturated groupings and groupings that are sensitive to hydrogenolysis into the composition of the 4-N-substituents in reductones V.

In testing various approaches, we obtained unsatisfactory results in the reduction of 3-nitro-4-aminocoumarins II to the corresponding reductones V with stannous chloride dihydrate in a nonaqueous medium [5] and with sodium borohydride in the presence of hydrogen-transfer catalysts, including Ni(II), Co(II) [6], and Cu(II) [7] salts, as well as nickel and cobalt borides [8]. According to the data in [9], the salt of formic acid with triethylamine reduces the carbon—carbon double bond in 3,6-dinitrocoumarin, whereas it is recommended that the reduction of the nitro group in aromatic compounds be carried out with formic acid or its salts in the presence of a catalyst — palladium on carbon [10]. According to our data, formic acid and its

---

*See [1] for Communication 2.

All-Union Science Center for the Safety of Biologically Active Substances, Kupavna Moscow Region, 142450.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 329-334, March, 1992. Original article submitted February 12, 1990.

0009-3122/92/2803-0274$12.50