4H-3,1-BENZOXAZINES.

2.* SYNTHESIS OF 2,4-SUBSTITUTED 1,2-DIHYDRO-4H-3,1-BENZOXAZINES

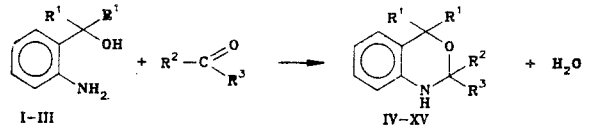
E. V. Gromachevskaya, V. G. Kul'nevich,
T. P. Kosulina and V. S. Pustovarov

UDC 547.867.1.07:543.422

The reactions of o-aminophenylcarbinols with carbonyl compounds have been studied. Optimum conditions have been developed for the synthesis of 2-(5-X-2-furyl)-1,2-dihydro-4H-3,1-benzoxazines. It was found that 2,2-disubstituted 1,2-dihydro-4H-3,1-benzoxazines are unstable and are converted upon heating in the presence of acylating agents to 4H-3,1-benzoxazines.

The condensation products of o-aminobenzylic alcohols with carbonyl compounds were initially assigned azomethine structures [1]. However, based upon spectroscopic studies, these products were later assigned cyclic structures, namely 1,2-dihydro-4H-3,1-benzoxazines [2]. In addition to this method, which appears to be the principal method for the preparation of 1,2-dihydro-4H-3,1-benzoxazines [3, 4], other methods are also known, involving oxidation of N,N-disubstituted 2-(hydroxymethyl)anilines with manganese dioxide [5], reduction of 4H-3,1-benzoxazines with organolithium and organomagnesium compounds [6], or reaction of phenylmagnesium bromide with an azomethine prepared from o-aminobenzophenone [3]. Interest in the chemistry of these little-studied 4H-3,1-benzoxazines has been stimulated by the potential of obtaining new compounds with biological activity. Within the series of 1,2-dihydro-4H-3,1-benzoxazines, compounds have been identified with herbicidal [7], fungicidal [8], and pharmacological activity [9].

The previously unknown 1,2-dihydro-4H-3,1-benzoxazines IV-XV were obtained upon condensation of o-aminophenylcarbinols I-III with a variety of aldehydes and ketones of different structural types.



I-III IV-XV

I, IV—VIII, XIV, XV $R^1=C_6H_5$; II, IX—XII $R^1=CH_3$; III, XIII $R^1=CH_2CH_2C_6H_5$; IV, IX, XV $R^2=CH_3$; V $R^2=n\text{-}CH_2—CH_2—CH_3$; VI $R^2=$ β-(5-methyl-2-furyl)ethyl; VII, XI R^2 5-bromo-2-furyl XII $R^2=$5-nitro-2-furyl VIII, XIII $R^2=$5-dimethylamino-2-furyl X $R^2=CCl_3$; IV—XIII $R^3=H$; XIV $R^2,R^3=(CH_2)_5$; XV $R^3=CH_2CH_3$

o-Aminophenyldiphenylcarbinol (I) reacts readily with aldehydes under a variety of different conditions: upon refluxing in benzene in the presence of a catalyst (acetic acid [1, 2], KU-2) or without one, in ether with TSK [4], as well as in acetic acid upon cooling or in liquid SO_2. At elevated temperatures dehydration reactions interfere with the synthesis of compounds IX-XIII based on o-aminophenyldialkylcarbinols II and III, decreasing the yields of desired products (Table 1).

Optimum conditions for the preparation of dihydrobenzoxazines from carbinols II and III involve using a minimum amount of acetic acid upon cooling. Acetic acid acts as both the solvent and catalyst (under these conditions). Catalysis by mineral acid was needed only in the case of compound IX.

Acetic acid is unsuitable for the synthesis of 2-(5-dimethylamino-2-furyl)-4,4-diphenyl- and 2-(5-dimethylamino-2-furyl)-4,4-di(2-phenyl-1-ethyl)-1,2-dihydro-4H-3,1-benzoxazines

Krasnodar Polytechnical Institute, Krasnodar. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 842-847, June, 1988. Original article submitted October 28, 1986; revision submitted November 9, 1987.

 0009-3127/88/2406-0692$12.50

TABLE 1. Physical Characteristics and Conditions for the Synthesis of Substituted 1,2-Dihydro-4H-3,1-benzoxazines IV-XV

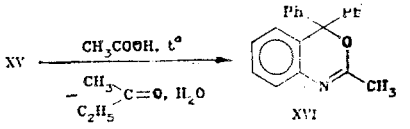
Compound	Reaction conditions			mp, °C	R_f	Found, %			Molecular formula	Calculated, %			Yield, %
	T_{reac}, °C	solvent	catalyst			C	H	N		C	H	N	
IV	5	CH_3COOH	CH_3COOH	137—139	0,32	83,5	6,5	4,5	$C_{21}H_{19}NO$	83,8	6,3	4,6	85
	80	C_6H_6	CH_3COOH										70
V	5	CH_3COOH	CH_3COOH	128	0,48	83,5	6,9	4,4	$C_{23}H_{29}NO$	83,9	7,0	4,2	91
	80	C_6H_6	KU-2										68
	80	C_6H_6	—										58
VI	5	CH_3COOH	CH_3COOH	127—128	0,55	82,1	6,2	3,7	$C_{27}H_{25}NO_2$	82,0	6,3	3,5	92
VII	5	CH_3COOH	CH_3COOH	167—168	0,68	66,5	4,2	3,1	$C_{24}H_{18}BrNO_2$	66,7	4,2	3,2	93
	80	C_6H_6	CH_3COOH										73
VIII	5	CH_3COOH	CH_3COOH	111—112	0,04	78,0	6,0	6,8	$C_{26}H_{24}N_2O_2$	78,8	6,1	7,1	25
	—20	SO_2	—										65
IX	5	CH_3COOH	H_2SO_4	60—61	0,18	74,6	8,3	7,6	$C_{11}H_{15}NO$	74,5	8,5	7,9	50
	—20	SO_2	—										35
X	5	CH_3COOH	CH_3COOH	122—123	0,74	46,7	4,3	5,1	$C_{11}H_{12}Cl_3NO$	47,0	4,3	5,0	89
XI	5	CH_3COOH	CH_3COOH	121—122	0,85	54,3	4,7	4,4	$C_{14}H_{14}BrNO_2$	54,5	4,5	4,5	75
XII	5	CH_3COOH	CH_3COOH	141—142	0,65	69,2	5,2	11,4	$C_{14}H_{14}N_2O_4$	69,4	5,8	11,6	83
XIII	—20	SO_2	—	134—135	0,03	79,2	7,4	7,0	$C_{30}H_{32}N_2O_2$	79,6	7,1	6,2	70
XIV	20—40	CH_3COOH	CH_3COOH	164—165	0,87	84,3	7,3	4,1	$C_{23}H_{25}NO$	84,6	7,1	3,9	84
XV	20—40	CH_3COOH	CH_3COOH	141	0,87	84,2	7,3	4,3	$C_{23}H_{25}NO$	83,9	7,0	4,2	72
	80	C_6H_6	CH_3COOH										44
	34	$(C_2H_5)_2O$	$CH_3C_6H_4SO_3H$										55

*For Communication No. 1, see Ref. [10].

(VIII and XIII), due to resinification of the products. It was found, however, that compounds VIII and XIII could be prepared by using liquid SO_2. The difficulty (associated with resin formation) is corrected under these conditions by the ease of isolation of the compounds in crystalline form after removal of the SO_2 by evaporation.

We have also examined for the first time the reactions of o-aminophenylcarbinols containing a tertiary hydroxyl group with ketones. It was found that compounds XIV and XV could be obtained in highest yield from o-aminophenyldiphenylcarbinol (I) and aliphatic ketones in acetic acid medium at temperatures in the range 10-45°C. Compounds XIV and XV are unstable. Upon thin layer chromatography of the pure compounds on Silufol plates two spots were observed, with R_f 0.87 or 0.65, corresponding to dihydrobenzoxazine XIV and XV, respectively, and carbinol I, due to partial decomposition on silica gel. This was verified by complete reversion of compound XV to the starting carbinol I upon column chromatography of a benzene solution on silica gel.

Compound XIV and XV are converted, at the boiling point of acetic acid, to 2-methyl-4,4-diphenyl-4H-3,1-benzoxazine (XVI):



The UV spectra of 1,2-dihydro-4H-3,1-benzoxazines IV-VII, IX-XII, XIV, and XV are characterized by two absorption maxima, in the 233-248 and 282-305 nm regions. With respect to the position of the main absorption bands, the spectra of dihydrobenzoxazines are similar to the spectra of the starting carbinols I-III (Table 2); the nature of these spectra is determined primarily by p,π-conjugation between the nitrogen atom in the NH- or NH_2-group with the aromatic nucleus. Upon formation of the condensed bicyclic 1,2-dihydro-4H-3,1-benzoxazine system the conjugation which is present initially in the aminoalcohol system undergoes only insignificant changes, while the oxo compound which is introduced into the molecule simply intensifies the absorption (extinction coefficients) of compounds VII, XI, and XII relative to the carbinol precursors I and II (λ_{max} 237-238 nm, $\Delta \log \varepsilon_{VII-I} = 0.35$; λ_{max} 236-244 nm, $\Delta \log \varepsilon_{XI-II} = 0.36$; λ_{max} 300-302 nm, $\Delta \log \varepsilon_{XII-II} = 0.63$). In the case of compounds VIII and XIII, which contain a dimethylfuryl radical, a bathochromic shift of the second absorption maximum in the visible region of the spectrum is observed (Table 2).

The absence of an intense absorption band at 320-330 nm, characteristic of Schiff bases [11], in the UV spectra of these compounds provides additional evidence for the cyclic nature of these condensation products.

The IR spectra of compounds IV-XV contain a series of bands, including ones characteristic of an N—C—O fragment, in the region 1180-1020 cm^{-1}, and also $\nu_{C=C}$ and $\nu_{=CH}$, respectively, for the aromatic nucleus, at 1470-1620 and 3040-3160 cm^{-1}. A free NH bond stretching vibration is observed in the form of a narrow absorption band at 3350-3410 cm^{-1} (Table 2). The absence of a broad absorption band in the region 3100-3500 cm^{-1}, associated with an OH group, as well as the lack of C=N bond stretching vibrational absorption bands at 1640-1680 cm^{-1}, in the IR spectra of these condensation products are also indicative of the formation of cyclic structures [11].

The IR spectra of the 1,2-dihydrobenzoxazine furan derivatives VI-VIII, and XI-XIII are complex: they contain $\nu_{=CH}$ absorption bands for the CH bonds in the furan ring at 3160-3130 cm^{-1}, ring stretching and bending vibration bands at 1600-1470 cm^{-1} (either two or three bands), 934-908, and 753-735 cm^{-1}. In addition, the bands due to the ether functional group in the furan ring and the N—C—O fragment in the heterocycle overlap one another in the 1000-1200 cm^{-1} region.

The PMR spectra of compounds IV-XII, XV contain two singlet signals for the protons geminal to the phenyl and methyl groups at $C_{(4)}$ of the ring, at 7.25-7.03 and 1.40-1.60 ppm, respectively. The protons for the benzene ring which is annelated with the heterocycle resonate at 7.10-6.50 ppm in the form of a multiplet. In the case of the furan derivatives VII, VIII, XI, and XII, the protons in positions β to the furan ring are nonequivalent, as indicated by their appearance as AB quartets in the range 6.20-7.25 ppm (Table 2).

TABLE 2. Spectral Characteristics of Substituted 1,2-Dihydro-4H-3,1-Benzoxazines IV-XV and o-Aminophenylcarbinols I-III

Compound	UV spectrum (ethanol) λ_{max}, nm, (log ε)	IR spectrum, vaseline mull (NH, N-C-O, C=CH$_{arom}$), ν, cm^{-1}	PMR spectrum in CCl_4	
			δ, ppm	SSCC, Hz
I	238 (3,85), 295 (3,38)	3600 (OH); 3430, 3370, 1620 (NH_2); 3030, 1605, 1580 (C=CHarom)*	3,50 (2H, br.s, NH_2); 4,90 (1H, br. s, OH); 6,58 (4H, m, C_6H_4); 7,18 [10H, s, $(C_6H_5)_2$]	—
II	244 (3,87), 302 (3,39)	3600 (OH); 3400, 3360, 1620 (NH_2); 3030, 1650, 1585 (C=CHarom)*	1,61 and 1,55 [6H, two s, $(CH_3)_2$]; 3,72 (2H, br. s, NH_2); 5,12 (1H, br. s, OH); 6,78 (4H, m, C_6H_4)	—
III	242 (3,84), 304 (3,33)	3600 (OH); 3440, 2370, 1600 (NH_2); 3030, 1580, 1490 (C=CHarom)*	2,35 [8H, m, $(CH_2)_4$]; 3,64 (2H, br.s, NH_2); 5,42 (1H, br. s, OH); 6,50 (4H, m, C_6H_4); 7,05 [10H, s, $(C_6H_5)_2$]	—
IV	242 (3,80), 287 (3,29)	3350, 1020, 1080, 1150, 3030, 1610, 1580	1,33 (3H, d, 2-CH_3); 3,72 (1H, br.s, NH); 4,45 (1H, q, 2-H); 6,57 (4H, m, C_6H_4); 7,08 and 7,20 [10H, two s, $(C_6H_5)_2$]	$^3J_{HCH_3}$ = 6,0
V	240 (3,82), 291 (3,32)	3410, 1020, 1110, 1150, 3030, 1610, 1590	0,70 (3H, t, γ-CH_3); 1,51 (4H, m, α-, β-CH_2); 3,84 (1H, br. s, NH); 4,38 (1H, t, 2-H); 6,54 (4H, m, C_6H_4); 7,06 and 7,20 [10H, two s, $(C_6H_5)_2$]	$^3J_{CH_3CH_2}$ = 6,0, $^3J_{HCH_2}$ = 6,0
VI	240 (3,98), 298 (3,52)	3360, 1020, 1100, 1120, 1160, 3130, 3030, 1600, 1580	1,86 (2H, m, α-CH_2); 2,03 (3H, s, α-CH_3); 2,60 (2H, t, β-CH_2); 3,72 (1H, br s, NH); 4,47 (1H, t, 2-H); 5,58 (2H, s, H_{fur}); 6,57 (4H, m, C_6H_4); 7,10 and 7,22 [10H, two s, $(C_6H_5)_2$]	$^3J_{CH_2CH_2}$ = 6,5, $^3J_{HCH_2}$ = 5,0
VII	237 (4,20), 298 (3,41)	3400, 1010, 1040, 1100, 1120, 3140, 3030, 1610, 1590	4,20 (1H, br. s, NH); 5,50 (1H, s, 2-H); 6,20; 6,36 (2H, d.d, H_{fur}); 6,65 (4H, m, C_6H_4); 7,09 and 7,25 [10H, two s, $(C_6H_5)_2$]	$^3J_{3,4}$ = 3,5
VIII	246 (3,94), 425 (4,42)	3360, 1050, 1070, 1120, 3140, 3030, 1610, 1580	2,71 and 2,77 [6H, two s, $N(CH_3)_2$]; 5,48 (1H, s, 2-H); 6,58 and 7,95 (2H, d.d, H_{fur}); 7,10 and 7,06 [10H, two s, $(C_6H_5)_2$]; 7,11 (4H, m, C_6H_4)**	$^3J_{3,4}$ = 6,0
IX	241 (3,85), 285 (3,35)	3360, 1030, 1080, 1100, 1125, 3030, 1610, 1580	1,31 (3H, d, 2-CH_3); 1,40 and 1,45 [6H, two s, 4-$CH_3)_2$]; 3,56 (1H, br. s NH); 4,70 (1H, q, 2-H); 6,50 (4H, m C_6H_4)	$^3J_{HCH_3}$ = 6,0
X	235 (3,99), 282 (3,41)	3370, 1025, 1080, 1110, 3030, 1605, 1580	1,51 and 1,56 [6H, two s $(CH_3)_2$]; 4,36 (1H, br. s, NH); 4,96 (1H, s 2-H); 6,75 (4H, m, C_6H_4)	—
XI	236 (4,23), 287 (3,63)	3400, 1030, 1070, 1120, 3130, 3030, 1610, 1590	1,49 and 1,53 [6H, two s, $(CH_3)_2$]; 4,60 (1H, br. s, NH); 5,60 (1H, s, 2-H); 6,21 and 6,45 (2H, d.d H_{fur}); 6,82 (4H, m, C_6H_4)***	$^3J_{3,4}$ = 3,5
XII	233 (3,85), 300 (4,02)	3350, 1020, 1100, 1120, 3110, 3030, 1600, 1580	1,52 and 1,60 [6H, two s, $(CH_3)_2$]; 4,12 (1H, br.s, NH); 5,72 (1H, d, 2-H); 6,70 and 7,28 (2H, d.d, H_{fur}); 6,97 (4H, m, C_6H_4)***	$^3J_{HNH}$ = 1,5, $^3J_{3,4}$ = 4,0
XIII	239 (3,99), 425 (3,82)	3350, 1030, 1060, 1180, 3150, 3030, 1610, 1580	1,48 [8H, m, 4-$(CH_2)_4$]; 2,98 and 3,08 [6H, two s, $N(CH_3)_2$]; 4,22 (1H, br.s, NH); 5,00 (1H, m, 2-H); 7,10 (6H, m, C_6H_4, H_{fur}); 7,18 and 7,22 [10H, two s, $(C_6H_5)_2$]***	—
XIV	245 (3,95), 298 (3,35)	3370, 1020, 1070, 1120, 1140, 3030, 1600, 1580	1,40 [10H, s, 2-$(CH_2)_5$]; 4,27 (1H, br. s, NH); 6,59 (4H, m, C_6H_4); 7,18 [10H, s, $(C_6H_5)_2$]***	—
XV	248 (3,89), 305 (3,42)	3350, 1020, 1060, 1090, 1120, 3030, 1610, 1590	0,88 (3H, t, β-CH_3); 1,10 (3H, s, 2-CH_3); 1,57 (2H, q, α-CH_2); 3,80 (1H, br. s, NH); 6,66 (4H, m, C_6H_4); 7,14 and 7.20 [10H, two s $(C_6H_5)_2$]***	—

*In CCl_4.
**In CF_3COOD.
***In $CDCl_3$.

The spectra of this series of compounds also exhibit broad peaks for the NH group protons (δ 3.56-4.60 ppm) and singlets for the $C_{(2)}$ protons in the ring (δ 4.38-5.72 ppm). The only spectrum in which the signal due to $C_{(2)}$-H is split into a doublet is that of compound XII, in which a broad, diffuse band due to the NH proton is also present. The NH group resonance is missing in the PMR spectrum of compound VIII in deuterated trifluoroacetic acid solvent, due to exchange with traces of water in the solvent.

The spectral data discussed herein thus confirm the formation of the 1,2-dihydro-4H-3,1-benzoxazine structure in the condensation of o-aminophenyl-carbinols containing tertiary hydroxyl groups. The presence of tautomeric azomethine structures for these compounds was not observed in solution [11].

EXPERIMENTAL

IR spectra were recorded on Specord-71 and UR-20 spectrophotometers using vaseline mulls; PMR spectra were obtained on a Tesla BS-467 spectrometer (at 60 MHz), using solutions in $CDCl_3$, CCl_4, and CF_3COOD, versus HMDS as internal standard. Electronic spectra were measured on a Specord UV-Vis spectrophotometer using solutions in ethanol. TLC analyses were carried out on Silufol UV-254 plates and were visualized using iodine vapor.

o-Aminophenyldiphenylcarbinol (I). To a solution of phenylmagnesium bromide, prepared as in [12] from 12.2 g (500 mmole) Mg and 52.4 ml (500 mmole) bromobenzene in 150 ml absolute ether at 0°C, was added dropwise a solution of 16.15 ml (125 mmole) methyl anthranilate in 20 ml absolute ether. The reaction mixture was refluxed for 1 h, cooled again (in an ice-salt bath), and then decomposed by the addition of a saturated solution of ammonium chloride, until two layers had formed. The ether layer was removed, and the aqueous layer was extracted with ether; the combined ether extracts were washed with 5% $NaHCO_3$ and water, and then dried over anhydrous sodium sulfate. After the ether had been evaporated the residue was crystallized from petroleum ether. Yield 29.2 g (85%), mp 120-121°C (which corresponds to that reported in [13]). Found: C 82.4; H 6.4; N 5.2%. $C_{19}H_{17}NO$. Calculated: C 82.9; H 6.4; N 5.2%.

o-Aminophenyldimethylcarbinol (II) and o-Aminodiphenyldi(2-phenyl-1-ethyl)carbinol (III). These were prepared in an analogous manner, using the corresponding alkylmagnesium halides [12]. Carbinol II. Yield 80%, bp 120-123°C (16 hPa). Found: C 78.8; H 8.8; N 9.0%. $C_9H_{13}NO$. Calculated: C 71.50; H 8.58; N 9.2%. Carbinol III. Yield 61%, bp 92-93°C. Found: C 83.5; H 7.3; N 4.5%. $C_{23}H_{25}NO$. Calculated: C 83.3; H 7.6; N 4.3%.

2-(5-Bromo-2-furyl)-4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazine (VII). To a solution of 1.37 g (5 mmole) o-aminophenyldiphenylcarbinol in 5 ml glacial acetic acid cooled to 0°C was added dropwise 6.87 g (5 mmole) bromofurfural. The mixture was stirred at first while cooled (ice bath), and then at room temperature for 1 h. The resulting precipitate was removed by filtration, washed with a solution of alcohol and water (1:3). Yield 2.02 g (93%).

Compounds IV-VI, IX-XII. These were prepared in an analogous manner. In the case of the synthesis of compound IX, it was necessary to add 0.015 ml concentrated H_2SO_4 to the reaction mixture.

2-(5-Dimethylamino-2-furyl)-4,4-di(2-phenyl-1-ethyl)-1,2-dihydro-4H-3,1-benzoxazine (XIII). To a mixture of 1.42 g (4.3 mmole) compound III in 10 ml liquid SO_2 upon cooling (acetone–liquid nitrogen) was added in portions 0.6 g (4.3 mmole) 5-dimethylaminofurfural. The color of the solution gradually intensified during this time. The mixture was stirred for 40 min. Afterward, 10 ml absolute ether was added gradually, as the cooling bath was removed. As the SO_2 was removed from the reaction mixture a resinous precipitate separated from the reaction mixture, and gradually crystallized. The resulting yellow-red precipitate was purified by reprecipitation from chloroform with ether. Yield 1.37 g (70%).

Compound VIII. Prepared from carbinol I.

2-Methyl-2-ethyl-4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazine (XV). A mixture of 1.37 g (5 mmole) compound I and 0.44 ml (5 mmole) methyl ethyl ketone in 5 ml glacial acetic acid was stirred at room temperature for 30 min, and then at 40°C for an additional 30 min. The resulting precipitate was removed by filtration and washed with acetic acid and petroleum ether. Yield 1.19 g (72%).

Compound XIV was prepared in an analogous manner.

2-Methyl-4,4-diphenyl-4H-3,1-benzoxazine (XVI). A mixture of 1.57 g (5 mmole) compound XV in 10 ml acetic acid was refluxed until the precipitate had disappeared. The reaction mixture was then cooled, diluted with water, and the resulting precipitate was recrystallized from alcohol. Yield 1.2 g (76%). The physical chemical properties of benzoxazine XVI corresponded to those reported in [13].

LITERATURE CITED

1. C. Paal and E. Landenheimer, Chem. Ber., 25, 2967 (1892).
2. W. Holly and C. J. Cope, J. Am. Chem. Soc., 66, 1875 (1944).
3. F. Eiden, K. Schnadel, and H. Wiedemann, Arch. Pharm., 307, 204 (1974).
4. F. Eiden, K. Schnadel, and H. Wiedemann, ibid., 308, 622 (1975).
5. F. Kienzle, Tetrahedron Lett., 24, 2213 (1983).
6. R. Rihard Schmidt and B. Reitzke, Chem. Ber., 116, 2115 (1983).
7. W. Stewart Mayers and Homerk Spencer, U.S. Patent No. 4164407; RzhKh, 50437P (1980).
8. U.S. Patent No. 3678046; C07 d 87/14/Huber-Emden, Basel, Switzerland; Priority 29.04.69. Filed 27.04.70.
9. A. Montrup, K. Sehromm, E. Renth, W. Holfke, W. Gaida, I. Streller, and A. Fugner, British Patent No. 3026534; RzhKh 10147P.
10. E. V. Gromachevskaya, I. S. Arustamova, R. B. Valeev, B. A. Bazhenov, A. G. Sakhabutdinov, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 12, 1687 (1985).
11. A. H. Saeed and E. K. Fbraheem, Can. J. Spectr., 28, 169 (1983).
12. V. M. Potapov (ed.), Laboratory Course in Organic Chemistry, Moscow (1979), Vol. 2, p. 193.
13. A. Bayer and V. Williger, Chem. Ber., 37, 3191 (1904).

MESOIONIC COMPOUNDS WITH BRIDGING NITROGEN ATOMS.

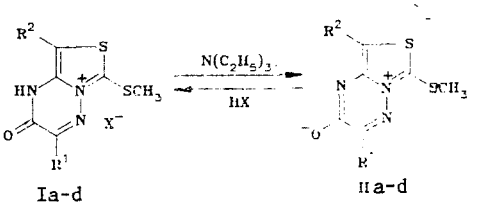
14.* POLYMETHINE DYES CONTAINING A THIOZOLO[3,4-b][1,2,4]TRIAZINIUM OXIDE NUCLEUS

Yu. P. Kovtun and N. N. Romanov

UDC 547.874'789.6:668.819.45

Monomethinecyanine and zeromethinemerocyanine dyes have been synthesized on the basis of mesoionic 6-methylthiothiazolo[3,4-b][1,2,4]triazinium-2-oxides. It was found that these newly synthesized compounds can exist both in mesoionic form and in salt form.

We have previously prepared 6-methylthiosubstituted thiazolo[3,4-b][1,2,4]triazines Ia-d and have investigated their conversion to mesoionic compounds IIa-d [2].



Ia-d IIa-d

I, IIa,c $R^1=CH_3$, b,d $R^1=C_6H_5$; a,b $R^2=H$, c,d $R^2=C_6H_5$

In order to be able to prepare polymethine dyes based on these derivatives of a novel heterocyclic system, it was of interest to us to examine the reaction of these compounds with nucleophilic intermediates, which are generally used for the synthesis of cyanines [3, p. 210, 269].

*For Communication No. 13, see Ref. [1].

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 848-851, June, 1988. Original article submitted December 17, 1986.

0009-3127/88/2406-0697$12.50