RESEARCH ON 4H-3,1-BENZOXAZINES.
9.* 2-ALKYL(ARYL, FURYL)-4H-3,1-BENZOXAZINIUM PERCHLORATES AND THEIR TRANSFORMATIONS

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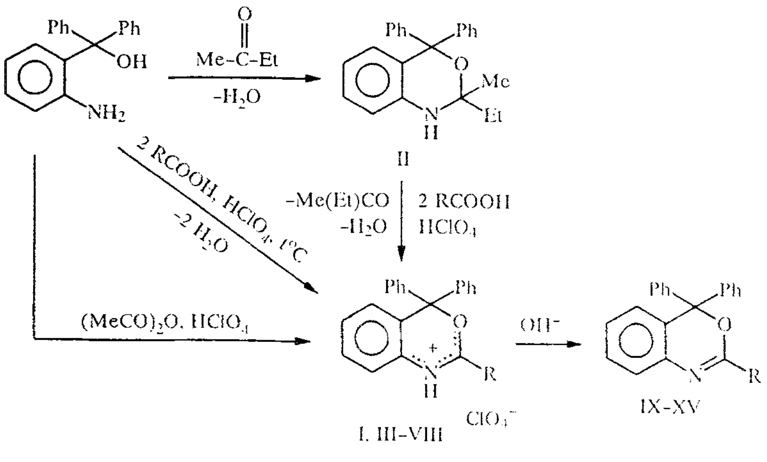
A new method was developed for obtaining 4,4-diphenyl-4H-3,1-benzoxazinium perchlorates by acylation of o-aminophenyldiphenylcarbinol with organic acids in the presence of perchloric acid. Weak CH acidity of the exocyclic methyl group of the corresponding perchlorate was observed.

The acylation of o-aminophenyldiphenylcarbinol with acid halides by heating [1] or in the cold in the presence of antimony pentahalides (Lewis acids) [2] leads to 4H-3,1-benzoxazinium chlorides or hexahaloantimonates, which made it possible to obtain previously undescribed 4H-3,1-benzoxazines. It is known that the latter are obtained using o-aminobenzyl alcohols, o-aminobenzyl halides, or their N-acyl derivatives by heating with carboxylic acid anhydrides [3, 4] or by the reaction of 4H-3,1-benzoxazinones with Grignard reagents [5]. The conversion of substituted 2,2-dialkyldihydrobenzoxazines to 2-methyl-4,4-diphenyl-4H-3,1-benzoxazine by refluxing in acetic acid was described in [6]. Among compounds of this class there are substances with pharmacological properties [7]; some of them have been proposed as herbicides [8].

We have continued our research on the synthesis of 4H-3,1-benzoxazinium salts and bases obtained from them. 2-Methyl-4,4-diphenyl-4H-3,1-benzoxazinium perchlorate (I) is formed in up to 85% yields in the reaction of o-aminophenyldiphenylcarbinol with excess acetic anhydride in the cold in the presence of an equimolar amount of $HClO_4$.



I, IX R = Me; III, X R = $CH_2CH_2CH_3$; IV, XI R = 2-nitrophenyl V, XII R = 3-nitrophenyl; VI, XIII R = β-(2-furyl)vinyl VII, XIV R = 5-chloro-2-furyl; VIII, XV R = 5-nitro-2-furyl

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*For communication 8 see [1].

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In order to synthesize the desired compounds by a more convenient method that makes it possible to significantly increase the number of them available we studied the behavior of this carbinol and 2-methyl-2-ethyl-4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazine (II) under the influence of carboxylic acids with various structures. As a result, we found a method for obtaining 4H-3,1-benzoxazinium perchlorates I and III-VII by the action on o-aminophenyldiphenylcarbinol of a twofold amount of carboxylic acids of the aliphatic, aromatic, and furan series in refluxing chloroform with the stepwise addition of an equimolar amount of $HClO_4$.* Perchlorates I and III-VIII are isolated by precipitation with absolute ether.

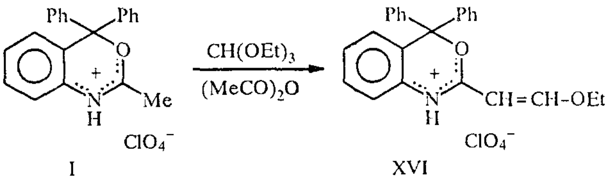
Under the conditions described above 2,2-dialkyldihydrobenzoxazine II is also converted to 2-alkyl(aryl, furyl)-4H-3,1-benzoxazinium perchlorates I, III, IV, and VII but in considerably lower yields (Table 1).

We assume that the 4H-1,3-benzoxazinium perchlorates are formed from the carbinol through the intermediately formed N-acylamino derivatives [1]. The latter are dehydrated under the influence of perchloric acid and undergo heterocyclization to the corresponding perchlorates.

Perchlorates I and III-V were decomposed with ammonium hydroxide to give bases IX-XII (Table 2). The physicochemical constants of IX are in agreement with those described in [1]. Furan-containing benzoxazines XIII-XV were obtained by decomposition of the corresponding perchlorates in a layer of silica gel (by column chromatography), since furan salts VI-VIII underwent destruction of the heterocyclic part of the molecule under the influence of ammonia.

The IR spectra of 4H-3,1-benzoxazinium perchlorates I and III-VIII are characterized by vibrations of the OC^+NH fragment and the ClO_4^- anion, while their bases X-XV are characterized by vibrations of the C=N bond (see Tables 1 and 2).

Signals of protons of gem-diphenyl groups attached to the $C_{(4)}$ atom of the heteroring at 7.18-7.25 ppm in the form of one or two singlets are present in the PMR spectra of benzoxazines X-XV. Proceeding from the structure of 4H-3,1-benzoxazines X-XV it is legitimate to assert that these groups are symmetrically oriented relative to the plane of the heterocyclic and aromatic rings and that they are equivalent. The nonequivalence of the gem-diphenyl groups for X and XV can be explained as being a consequence of their different degrees of rotation about the $C_{(sp^3)}$—$C_{(sp^2)}$ bond.



The signals of the protons of the benzene ring annelated with the heteroring are recorded in the form of a multiplet at 6.46-7.50 ppm. The protons in the 4 and 3 positions of the furan ring are nonequivalent for furan compounds XIII-XV. In the spectra of XIV and XV, in which the 5 position of the ring is substituted, these protons are present in the form of a quartet (an AB system). For XIII the unsaturated α,β protons in the side chain exhibit spin-spin coupling constants (SSCC) ($^3J_{\alpha,\beta}$ = 6.0 Hz) that are characteristic for cis interactions [9] (see Table 2).

In addition to the principal absorption peak [1] at 227-270 nm, the UV spectra of benzoxazines XI-XV contain yet another intense absorption maximum associated with the introduction of donor-acceptor groups (halo, nitro, and vinyl groups) into the furyl and phenyl substituents in the 2 position of the heteroring.

It seemed of interest to investigate the lability of the hydrogen atoms in the exocyclic methyl group. However, 2-methyl-4,4-diphenyl-4H-3,1-benzoxazinium perchlorate (I) does not undergo crotonic condensation with aromatic aldehydes [10]. A yellow compound, the spectral characteristics and results of elementary analysis of which make it possible to assign the 2-(β-ethoxyvinyl)-4,4-diphenyl-4H-3,1-benzoxazinium perchlorate (XVI) structure to it, was obtained only when perchlorate I was refluxed with ethyl orthoformate in acetic anhydride [11].

The low yield of product XVI (see the experimental section) constitutes evidence for the extremely weak CH acidity of the methyl group of starting perchlorate I.

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*2,4,4-Triphenyl-4H-3,1-benzoxazinium perchlorate is not formed; the carbinol reacts with benzoic acid to give 2,4,4-triphenyl-4H-3,1-benzoxazine only in the presence of catalytic amounts of $HClO_4$.

TABLE 1. Characteristics and Conditions for the Synthesis of 4,4-Diphenyl-4H-3,1-benzoxazinium Perchlorates I and III-VIII

Compound	Reagent	Empirical formula	mp, °C	IR spectrum, ν, cm^{-1}			Yield, %
				$O^-—C^+—N^-$	ClO_4^-	NO_2	
I	APC P	$C_{21}H_{18}ClNO_5$	250...251	2715, 1665	1130, 1050	—	85 60
III	APC P	$C_{23}H_{22}ClNO_5$	188...189	2725, 1650	1120, 1050	—	70 55
IV	APC P	$C_{26}H_{19}ClN_2O_7$	194...195	2710, 1660	1100, 1080	1520, 1335	74 48
V	APC	$C_{26}H_{19}ClN_2O_7$	202...204	2710, 1660	1110, 1090	1510, 1330	76
VI	APC	$C_{26}H_{20}ClNO_6$	150 dec.	2750, 1630	1110, 1080	—	45
VII	APC P	$C_{24}H_{17}Cl_2NO_6$	131...132	2720, 1660	1140, 1100	—	72 45
VIII	APC	$C_{24}H_{17}ClN_2O_8$	137...138	2750, 1660	1130, 1100	1500, 1340	58

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*Abbreviations: APC is o-aminophenyldiphenylcarbinol, and P is perchloric acid.

TABLE 2. Physicochemical Characteristics of 2-Alkyl(aryl, furyl)-4,4-diphenyl-4H-3,1-benzoxazines X-XV

Compound	Empirical formula	mp, °C	R_f	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, ν, cm^{-1}	PMR spectrum		Yield, %
						δ, ppm	KCCB, Hz	
X	$C_{23}H_{21}NO$	89...90	0,64	262(3,88)	1630	7,20 and 7,16 (10H, 2c, Ph_2); 6,46(4H, m C_6H_4; 2,32(2H, t, α-CH_2); 1,36(2H, m, β-CH_2); 0,75(3H, t, γ-CH_3)	—	80
XI	$C_{26}H_{18}N_2O_3$	198...199	0,82	263(3,95), 305(3,81)	1640, 1520, 1330	7,20 (10H, s, Ph_2); 6,75 (4H, m, C_6H_4); 7,40 (4H, m, 2-Ar)	—	75
XII	$C_{26}H_{18}N_2O_3$	218	0,80	270(4,17), 309(4,19)	1635, 1520, 1340	7,21 (10H, s Ph2); 6,80 (4H, m, C_6H_4); 7,45 (4H, m, 2-Ar)	—	72
XIII	$C_{26}H_{19}NO_2$	158...160	0,47	2,35(3,97) 341(4,46)	1620	7,25(10H, s, Ph2); 6,80(4H, m, C_6H_4); 6,96(1H, d, α-H); 6,55(1H, d, β-H); 6,66(1H, d, 5-H); 6,46(1H, d, 3-H); 6,35(1H, d, 4-H)	$^3J_{\alpha\beta}$=6,0 $^3J_{45}$=3,0 $^3J_{34}$=1,5	42
XIV	$C_{24}H_{16}ClNO_2$	143...144	0,59	228(4,11) 315(4,25)	1630	7,18(10H, s, Ph2); 6,68(4H, m, C_6H_4); 7,03(1H, d, 4-H); 6,22(1H, d, 3-H)	$^3J_{34}$=3,5	70
XV	$C_{24}H_{16}N_2O_4$	174...175	0,81	253(4,02) 353(4,00)	1635, 1510, 1330	7,22 and 7,19 (10H, 2s Ph2); 6,70(4H, m, C_6H_4); 7,30(1H, d, 4H); 7,11(1H, d, 3-H)	$^3J_{34}$=3,0	55

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*C=N, NO_2.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a Specord IR-75 spectrometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Tesla B3-467 spectrometer (60 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The electronic spectra of solutions in ethanol were recorded with a Specord UV-vis spectrophotometer. Thin-layer chromatography was carried out in a benzene—ether system (8:2) on Silufol UV-254 plates with development by iodine vapors.

The results of elemental analysis of the synthesized compounds for C, H, Cl, and N were in agreement with the calculated values.

2-Methyl-4,4-diphenyl-4H-3,1-benzoxazinium Perchlorate (I). A 2.75-g (0.01 mole) sample of o-aminophenyldiphenylcarbinol was added in portions with stirring to a cooled (to 0°C) mixture of 4.3 g (0.042 mole) of acetic anhydride and 1.0 g (0.01 mole) of 70% $HClO_4$, during which the solution took on a blue-green coloration. The mixture was diluted with absolute ether, and the resulting precipitate was removed by filtration and washed with ether. The yield was 3.37 g.

2-Propyl-4,4-diphenyl-4H-3,1-benzoxazinium Perchlorate (III). A. A 0.31-g (0.0031 mole) sample of 70% $HClO_4$ was added dropwise in the course of 30 min to a mixture of 0.86 g (0.0031 mole) of the carbinol and 0.54 g (0.0062 mole) of butyric acid in 10 ml of chloroform at the boiling point of the solvent, after which the mixture was refluxed for another 2 h. It was then cooled, and the product was precipitated with absolute ether. The yield was 0.93 g (70%). Compounds I and IV-VIII were similarly obtained.

B. A 0.21-g (0.0021 mole) sample of 70% $HClO_4$ was added dropwise in the course of 1 h to a mixture of 0.68 g (0.0021 mole) of benzoxazine II and 0.37 g (0.0042 mole) of butyric acid in 7 ml of chloroform at the boiling point of the solvent, after which stirring was continued until the green color of the reaction mixture vanished. The product was isolated by precipitation with absolute ether. The yield was 0.5 g.

2-Propyl-4,4-diphenyl-4H-3,1-benzoxazine (X). A 1-g (0.0023 mole) sample of salt III was mixed with excess (10 ml) 25% ammonium hydroxide, and the mixture was stirred for 5 min at room temperature. The precipitate was removed by filtration and washed with water. The yield was 0.6 g.

Bases XI and XII were similarly obtained.

Bases XIII-XV were obtained from the corresponding salts by elution through a layer of silica gel (40/100) with benzene—ether (8:2).

2-(β-Ethoxyvinyl)-4,4-diphenyl-4H-3,1-benzoxazinium Perchlorate (XVI, $C_{24}H_{22}ClNO_6$). A mixture of 0.5 g (0.0012 mole) of perchlorate I, 0.27 g (0.0018 mole) of ethyl orthoformate, and 2 ml of acetic anhydride was refluxed for 5 min, during which it took on a red-yellow coloration. It was then cooled, and the product was isolated by precipitation with ether and purified by reprecipitation from acetone by the addition of ether. The yield of the product, which had mp 198-199°C, was 0.15 g (26%). IR spectrum: 2750, 1630 (OC^+N); 1110, 1050 cm^{-1} (ClO_4^-). PMR spectrum (in $CDCl_3$): 0.85 (3H, t, CH_3), 5.05 (2H, q, CH_2), 6.65 (1H, d, =CH—), 6.80 (1H, d, —CH=), 7.18 ppm (14H, m, Ar).

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