REACTION OF BENZOYLACETALDEHYDE TETRAETHYLACETAL WITH QUATERNARY SALTS OF NITROGEN-CONTAINING HETEROCYCLIC BASES

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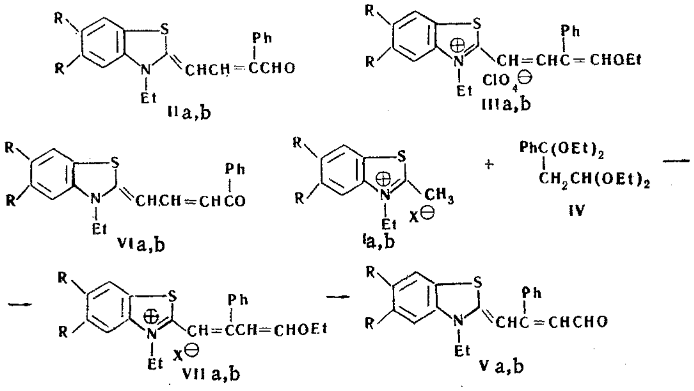
δ-Alkoxy-β-phenylbutadienyl salts of heterocyclic bases were synthesized by the reaction of of benzoylacetaldehyde tetraethylacetal with quaternary salts of nitrogen-containing heterocyclic bases in acetic anhydride.

We have previously established that 2-phenylmalonic dialdehyde tetraethylacetal reacts with the tosylates of nitrogen-containing heterocyclic bases (Ia, b) in acetic anhydride to form compounds with a free aldehyde group (IIa, b) [1] and with their perchlorates to form δ-alkoxybutadienyl salts (IIIa,b) [2].

In this connection, a similar reaction to form Va,b or VIa,b or a mixture of them might have been expected for the interaction of benzoylacetaldehyde tetraethylacetal (IV) [3] with tosylates Ia,b:



X = TsO; ClO$_4$; I; a R = H; b R = Me

However, we found that substances of a salt-like nature that, according to the IR spectra, do not contain a free aldehyde group are isolated from the reaction mixture, and, in accordance with the results of elementary analysis, can be assigned structure VIIa,b or the isomeric structure with a phenyl group attached to the δ-carbon atom [4]. Similar compounds were also isolated in all of the remaining cases that we studied (Table 1). We also found that the reaction proceeds to form a δ-alkoxybutadienyl salt regardless of the nature of the anion of the quaternary salt (I).

To determine the position of the phenyl group, the salts obtained from Ia and IV and from Ib and IV were dequaternized with an aqueous alcoholic solution of potassium carbonate. The dequaternization products were compared with VIa and VIb, obtained either by condensation of quaternary salts of heterocyclic bases with the sodium salt of hydroxymethyleneacetophenone [5] or by the method proposed for acetyl derivatives [6]. It turned out that the physical constants of the dequaternization products do not agree with the physical constants of VIa and VIb, and the ν_{CO} values in the IR spectra of the latter are shifted by 25-30 cm^{-1} to lower frequencies relative to the corresponding vibrations in the IR spectra of the dequaternization products.

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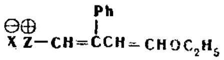
TABLE 1



$$X^{\ominus} \overset{\oplus}{Z}-CH=\overset{Ph}{\overset{|}{C}}CH=CHOC_2H_5$$

Z	X	Appearance (from ethanol)	Mp, °C	λ_{max}, nm	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	N	C	H	N	
1-Methyl-2-pyrrolinylium	ClO_4	Yellow needles	145	375	$C_{17}H_{22}ClNO_5$			3,7			3,9	62,8
3-Ethyl-4,5-diphenyl-2-thiazolium	ClO_4	Yellow needles	165	430	$C_{29}H_{28}ClNO_5S$	64,5	5,1	2,6	64,7	5,2	2,6	72
3-Ethyl-2-benzoxazolium (VIII)	ClO_4	Brown prisms	200	410	$C_{21}H_{22}ClNO_6$	59,9	5,0	3,6	60,1	5,3	3,3	88
5,6-Dimethyl-VIII	I	Yellow prisms	180	414	$C_{23}H_{26}\ INO_2$	58,3	5,4	3,2	58,1	5,5	3,0	81
5-Phenyl-VIII	ClO_4	Yellow needles	240	420	$C_{27}H_{26}ClNO_6$	65,2	5,2		65,4	5,30		91,3
3-Butyl-2-benzothiazolium	ClO_4	Yellow prisms	180	440	$C_{23}H_{26}ClNO_5S$	59,4	5,7	2,9	59,5	5,6	3,0	91,3
3-Ethyl-2-benzothiazolium (IX)	ClO_4	Yellow prisms	218	434	$C_{21}H_{22}ClNO_5S$	S7,2			S7,4			93*
5-Chloro-IX	TsO	Red needles	161	445	$C_{28}H_{28}ClNO_4S_2$	60,1	4,0	2,5	60,3	4,1	2,5	92,6
5,6-Dimethyl-IX	ClO_4	Yellow prisms	235	440	$C_{23}H_{26}ClNO_5S$	59,4	5,5	3,1	59,5	5,6	3,0	89
3-Ethyl-5-methoxy-2-benzoselenazolium	TsO	Red needles	180	464	$C_{29}H_{31}NO_5SeS$			2,3			2,4	60
1-Ethyl-2-quinolinylium	I	Brown plates	175	440	$C_{23}H_{24}INO$	60,2	5,0	2,9	60,4	5,3	3,0	86,6
1-Ethyl-4-quinolinylium	I	Red prisms	200	450	$C_{23}H_{24}INO$	60,2	5,2	3,0	60,4	5,3	3,0	87

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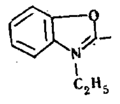
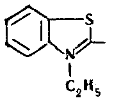
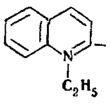
*Obtained from 3-ethyl-2-methylbenzothiazolium perchlorate; obtained in 72% yield from 3-ethyl-2-methylbenzothiazolium tosylate.

TABLE 2. Absorption Maxima of Alcohol Solutions of Alkoxybutadienyl Salts in the Visible Region

$$\overset{\ominus}{X}\,\overset{\oplus}{Z}\text{—CH=CR}_1\text{CR}_2\text{=CHOC}_2\text{H}_5$$

Z	X	R_1	R_2	λ_{max}, nm
	ClO_4	H	H	408
	ClO_4	C_6H_5	H	410
	ClO_4	H	C_6H_5	416
	ClO_4	H	H	408[2]
	I	C_6H_5	H	434
	I	H	C_6H_5	440
	ClO_4	H	H	422[2]
	I	C_6H_5	H	440
	ClO_4	H	C_6H_5	442[2]

Thus it can be assumed that the dequaternization products contain a formyl group, that structure Va or Vb should be assigned to them, and that structure VIIa or VIIb can therefore be assigned to the compounds obtained from Ia,b and IV. The β-phenyl-substituted butadienyl salt structure should apparently also be assigned to the products in the case of salts of other heteroresidues.

We investigated the absorption spectra of alcohol solutions of the synthesized salts. We found that the absorption maxima of the salts are shifted to the long-wave region as compared with the absorption maxima of unsubstituted salts. Thus a phenyl group in the β position has a bathochromic effect, but it is less than in the γ position of the polymethine chain [2] (Table 2). The bathochromic effect in the β position is intensified as the basicity of the heteroresidue increases.

EXPERIMENTAL

2-(δ-Ethoxy-β-phenylbutadienyl)-3-ethylbenzothiazolium Iodide (VIIa, X = I). A mixture of 0.3 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium iodide (Ia, X = I), 0.35 g (1 mmole) of benzoylacetaldehyde tetraethylacetal (IV), and 5 ml of acetic anhydride was heated at 100° for 1 h. The crystals were removed by filtration and washed with ether to give 0.39 g (84.8%) of red needles (from ethanol) with mp 175° and λ_{max} 434 nm.* Found: C 54.4; H 4.90; N 3.2%. $C_{21}H_{22}INOS$. Calculated: C 54.4; H 4.80; N 3.0%.

2-(δ-Ethoxy-β-phenylbutadienyl)-3-ethyl-5-methoxybenzothiazolium Tosylate. A mixture of 0.38 g (1 mmole) of 2-methyl-3-ethyl-5-methoxybenzothiazolium tosylate, 0.35 g (1 mmole) of IV, and 5 ml of acetic anhydride was heated at 70-80° for 5 h. The dye was precipitated with ether, and the crystals were removed by filtration and washed with ether to give 0.44 g (81.5%) of yellow needles (from ethanol) with mp 185° and λ_{max} 446 nm. Found: C 64.6; H 5.7; N 2.6%. $C_{28}H_{31}NO_5S_2$. Calculated: C 64.8; H 5.8; N 2.6%.

3-Ethyl-2-(β-phenyl-γ-formylallylidene)benzothiazoline (Va). Tosylate VIIa [1.2 g (2.5 mmole)] was dissolved by boiling in 30 ml of alcohol. A solution of 1 g of potassium carbonate in 20 ml of water was added, and the mixture was refluxed for 2 h. The reaction mixture was extracted with benzene, and the extract was dried with potassium carbonate and chromatographed on aluminum oxide. The product was crystallized from benzene to give 0.56 g (72.7%) of orange plates with mp 87°, λ_{max} 486 nm, and ν_{CO} 1656 cm^{-1} (KBr). Found: C 74.3; H 5.7; N 4.3%. $C_{19}H_{17}NOS$. Calculated: C 74.2; H 5.6; N 4.5%.

3-Ethyl-2-(β-phenyl-γ-formylallylidene)-5,6-dimethylbenzothiazoline (Vb). This compound was obtained in 53.7% yield as orange needles with mp 93° (from benzene), λ_{max} 500 nm, and ν_{CO} 1660 cm^{-1} (KBr). Found: N 3.9%. $C_{21}H_{21}NOS$. Calculated: N 4.2%.

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*The λ_{max} values of alcohol solutions are presented for all of the compounds.

α-(3'-Ethyl-5',6'-dimethylbenzothiazolinylidene-2'-ethylidene)benzoylacetone. A 1.1-g (3 mmole) sample of 3-ethyl-2-(β-methylthiovinyl)-5,6-dimethylbenzothiazolium methylsulfate and 1.46 g (9 mmole) of benzoylacetone were dissolved by refluxing in 30 ml of absolute ethanol. Triethylamine (0.3 ml) was added, and the mixture was refluxed for 30 min. The crystals were removed by filtration and washed with alcohol to give 1.05 g (93%) of orange plates with mp 179-180° and λ_{max} 476 nm. Found: N 3.6%. $C_{23}H_{23}NO_2S$. Calculated: N 3.7%.

α-(3'-Ethylbenzothiazolinylidene-2'-ethylidene)benzoylacetone. This compound was similarly obtained in 70.7% yield as orange plates with mp 164-165° and λ_{max} 472 nm.

3-Ethyl-2-(γ-benzoylallylidene)benzothiazoline (VIa). A) A mixture of 0.35 g (1 mmole) of tosylate Ia, 0.2 g (1 mmole) of the sodium salt of benzoylacetaldehyde, and 5 ml of pyridine was heated at 70-80° for 4 h. The reaction mixture was diluted with water and extracted with chloroform. The extract was dried with potassium carbonate, and the chloroform was removed by distillation. The reaction product was dissolved in benzene, and the solution was chromatographed on aluminum oxide. The product was recrystallized from benzene to give 0.13 g (43.3%) of orange needles with mp 106°, λ_{max} 490 nm, and ν_{CO} 1631 cm^{-1} (KBr) [7]. Found: N 4.5%. $C_{19}H_{17}NOS$. Calculated: N 4.5%.

B) A 1.33-g (3.8 mole) sample of α-(3'-ethylbenzothiazolinylidene-2'-ethylidene)benzoylacetone in 120 ml of dilute hydrochloric acid (1 : 1) was refluxed for 5 min, diluted with water, and neutralized with sodium bicarbonate. The precipitate was removed by filtration and dissolved in benzene. The benzene solution was chromatographed on aluminum oxide to give 0.8 g (69%) of VIa, which was identical to the product described above.

3-Ethyl-2-(γ-benzoylallylidene)-5,6-dimethylbenzothiazoline (VIb). A 0.56-g (1.5 mmole) sample of α-(3'-ethyl-5',6'-dimethylbenzothiazolinylidene-2'-ethylidene)benzoylacetone was allowed to stand for 24 h with 45 ml of dilute hydrochloric acid (1 : 1). The product was isolated and purified as in the case of VIa to give 0.44 g (88%) of orange prisms of VIb with mp 169-170° (from ligroin), λ_{max} 500 nm, and ν_{CO} 1630 cm^{-1} (KBr). Found: N 4.3%. $C_{21}H_{21}NOS$. Calculated: N 4.20%.

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