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PREPARATION OF 1,3-DIOXANIUM PERCHLORATES

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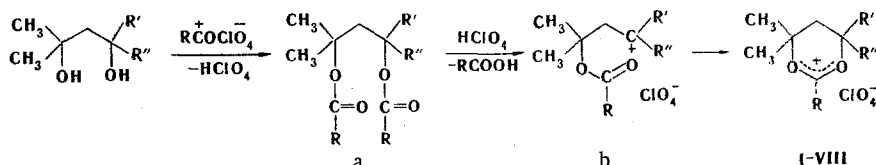
2,4,4,6,6-Substituted 1,3-dioxanium perchlorates were obtained by acylation of ditertiary 1,3-diols with carboxylic acid anhydrides in the presence of 70% perchloric acid.

1,3-Dioxanium salts contain a stabilized $\text{--}\overset{+}{\text{O}}\text{--}\overset{+}{\text{C}}\text{--}\overset{+}{\text{O}}\text{--}$ carboxonium ion, and this makes them extremely reactive and makes it possible to obtain valuable organic compounds from them.

We have previously reported [1] a method for the synthesis of 1,3-dioxanium salts by cyclization of primary 1,3-diols by means of an acylating mixture of acetic anhydride and perchloric acid.

However, the possibility of the extensive study and, especially, the application in organic synthesis of 1,3-dioxanium salts have been limited by the low yields of final products.

It is well known [2] that the stability of salts containing the $\text{--}\overset{+}{\text{O}}\text{--}\overset{+}{\text{C}}\text{--}\overset{+}{\text{O}}\text{--}$ fragment is determined by the presence in the ring of a substituent with donor character. We therefore used primary-tertiary and ditertiary 1,3-diols, synthesized by the method in [3], as starting compounds in the present research. In selecting the optimum reaction conditions we varied the component ratios, the temperature conditions, and the conditions used to isolate the products. The best yields (see Table 1) were obtained when the reaction was carried out by slow addition of 70% perchloric acid to a cooled (to 0 to -5°) mixture of the acid anhydride and 1,3-diol. The ratio of the starting materials was 1:5:1, respectively (method A). The evolution of a large amount of heat is observed during the reaction.



In refining the reaction scheme [1] we established that intermediate diacylate a is preferably formed in the first step and in acidic media splits out an acid molecule to give

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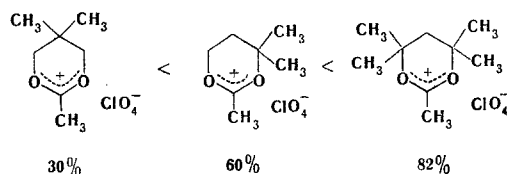
TABLE 1. 1,3-Dioxanium Perchlorates

Compound	R	R'	R''	mp, °C (dec.)	Empirical formula	Found, %			Calc., %			Yield, %
						C	H	Cl	C	H	Cl	
I	CH ₃	H	H	54	C ₇ H ₁₃ ClO ₆	36,0	5,2	16,1	36,8	5,7	15,5	66
II	C ₂ H ₅	H	H	53	C ₈ H ₁₅ ClO ₆	39,7	5,7	15,0	39,6	6,2	14,6	60
III	CH ₃	CH ₃	CH ₃	72—73	C ₉ H ₁₇ ClO ₆	41,5	6,8	13,2	42,2	6,6	13,8	82
IV	C ₂ H ₅	CH ₃	CH ₃	90—91	C ₁₀ H ₁₉ ClO ₆	43,8	7,5	12,8	44,3	7,0	13,0	67,5
V	CH ₃	CH ₃	C ₂ H ₅	109—110	C ₁₀ H ₁₉ ClO ₆	43,4	6,9	13,2	44,3	7,0	13,0	50
VI	C ₂ H ₅	CH ₃	C ₂ H ₅	133—134	C ₁₁ H ₂₁ ClO ₆	46,0	7,0	12,5	46,4	7,4	12,5	54
VII	CH ₃	CH ₃	C ₃ H ₇	73—74	C ₁₁ H ₂₁ ClO ₆	46,1	7,0	12,6	46,4	7,4	12,5	40
VIII	C ₂ H ₅	CH ₃	C ₃ H ₇	85—86	C ₁₂ H ₂₃ ClO ₆	47,5	7,0	12,5	48,2	7,7	11,9	45

carbonium ion b. The latter attacks the nucleophilic oxygen atom of the ester grouping to give the dioxanium salts (I-VIII).

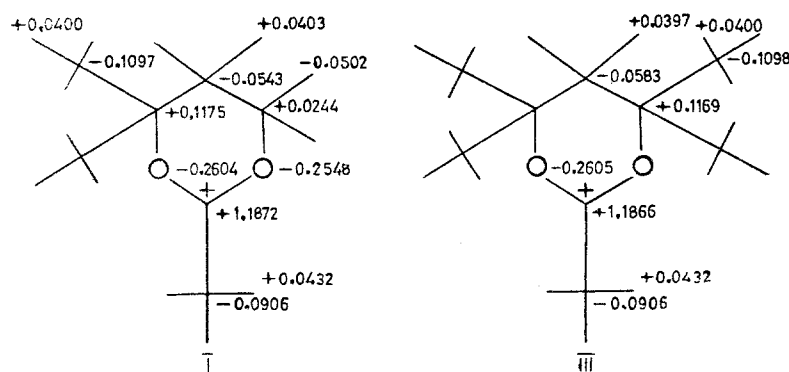
Proof of the proposed scheme is provided by the isolation of 2,4-dimethyl-2,4-pentane-diol diacetate (in 90% yield) under the conditions of synthesis of the 1,3-dioxanium salt in the presence of catalytic amounts of perchloric acid. Perchlorate III (method B) was synthesized from the diacetate with equivalent amounts of perchloric acid in acetic acid.

The yields of salts obtained from diprimary, primary-tertiary, and ditertiary alcohols increase in the order



When a bulky substituent is introduced in the 6 position of the ring, a definite tendency toward a decrease in the yield in the order III, V, VII is observed, and this is probably associated with steric hindrance.

The stability of the 1,3-dioxanium salts corresponds to the number, location, and donor strength of the substituents, which may be explained both by steric hindrance to attack by the nucleophile and to the more effective delocalization of the positive charge. Calculations of the total charges on the atoms (as seen from the molecular diagrams*) by the Del Re method of induction parameters show that the positive charge on the meso carbon atom in I is somewhat higher than in III.



1,3-Dioxanium perchlorates are hygroscopic compounds and are hydrolyzed by air moisture to give the monoacylate of the corresponding 1,3-diol. For example, hydrolysis of perchlorate III gives 2,4-dimethyl-2,4-pentanediol monoacetate. Some of the perchlorates (for example, I) were therefore isolated in a dry box in a stream of dry nitrogen.

*The calculations were performed in the Ufimskii Petroleum Institute. We thank S. S. Zlotskii for his assistance.

The IR spectra contain intense bands at 1537-1584 and 1490-1510 cm^{-1} , which are not characteristic for dioxane derivatives and can be assigned to vibrations of the $\begin{array}{c} + \\ -\text{O}-\text{C}-\text{O}- \end{array}$ fragment in analogy with [4]; the spectra also contain the absorption of a ClO_4^- ion (1100 cm^{-1}).

It might have been expected that according to the data in [3], under the conditions of acylation of 1,3-diols acid cleavage of the pinacol to a ketone and a tertiary alcohol would be observed, which, under the influence of acetyl perchlorate at high temperatures, would give pyrylium salts [5, 6]. However, we did not observe this but obtained only 1,3-dioxanium perchlorates. By carefully observing the conditions for the synthesis of 1,3-dioxanium salts (with a small excess of acid anhydride and a temperature below 0°), we were able to avoid side reactions. We isolated 2,6-dimethyl-4-ethylpyrylium perchlorate, identical to that described in [7], in only about 0.5% yield only in the synthesis of V. The rate of acid cleavage under the indicated conditions is probably considerably lower than the rate of acylation of the hydroxyl group of the acyl cation.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in acetic anhydride-acetic acid (1:3), in which only one band with a maximum at 286 nm is observed for perchlorates I-VIII, were measured with an SF-4 spectrophotometer. The ditertiary 1,3-diols were obtained by the method in [3].

2,4-Dimethyl-2,4-pentanediol Diacetate. One drop of 70% HClO_4 was added to a cooled (to 0°) mixture of 1.32 g (0.01 mole) of 2,4-dimethyl-2,4-pentanediol and 4 ml of acetic anhydride, and the mixture was allowed to stand at room temperature for 2 h. It was then diluted with ether and neutralized with 5% sodium carbonate solution. The ether layer was dried with anhydrous sodium sulfate, the ether was removed by distillation, and the diacetate crystals were isolated to give 1.94 g (90%) of a product with mp $45-46^\circ$. Found, %: C 61.8; H 9.3. $\text{C}_{11}\text{H}_{20}\text{O}_4$. Calculated, %: C 61.1; H 9.3. IR spectrum: 1727 ($\text{C}=\text{O}$) and 1240 cm^{-1} ($\text{O}-\text{C}-\text{O}$).

2,4,4,6,6-Pentamethyl-1,3-dioxanium Perchlorate (III). Method A. A 1-ml (0.01 mole) sample of 70% HClO_4 was added slowly dropwise at -5° to a mixture of 1.32 g (0.01 mole) of 2,4-dimethyl-2,4-pentanediol and 5 ml of acetic anhydride; and the resulting white crystals were removed by filtration, washed with 120 ml of ether-acetone (3:1), and recrystallized from the same solvent mixture. Dilution of the mother liquor with ether made it possible to raise the yield to 2 g (82%).

Method B. An 0.5-ml (0.005 mole) sample of 70% HClO_4 was added slowly with cooling to a solution of 1.08 g (0.005 mole) of 2,4-dimethyl-2,4-pentanediol diacetate in 1 ml of acetic anhydride and 2 ml of glacial acetic acid. Dilution of the mixture with ether yielded 0.9 g (80%) of crystalline III. Samples obtained by methods A and B were identical with respect to their IR spectra.

Perchlorates I, II, and IV-VIII were similarly obtained.

2,4-Dimethyl-2,4-pentanediol Monoacetate. The addition of 10 ml of water to 2.56 g (0.01 mole) of perchlorate III yielded an oily product, which was extracted with ether. The ether extract was washed with 5% sodium bicarbonate solution and dried with anhydrous sodium sulfate. The ether was removed, and the residue was distilled to give 1.7 g (97%) of the monoacetate with bp 175° and n_D^{20} 1.483. Found, %: C 62.4; H 10.2. $\text{C}_9\text{H}_{18}\text{O}_3$. Calculated, %: C 62.1; H 10.3. IR spectrum: 3500 (OH) and 1720 cm^{-1} ($\text{C}=\text{O}$).

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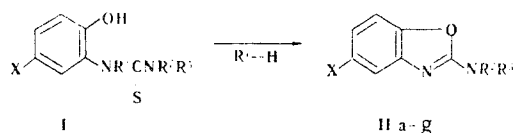
SYNTHESIS OF 2-AMINO BENZOXAZOLES AND 2-IMINO BENZOXAZOLINES

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The cyclization of sulfonamide derivatives of alkylated 2-hydroxyphenylthioureas in the presence of an ammoniacal solution of silver oxide gives 2-alkylamino-benzoxazole-5-sulfonamides or the corresponding 3-alkyl-2-alkyliminobenzoxazolines. Alkyl-substituted 2-aminobenzoxazole-5-sulfonamides were also obtained by the reaction of benzoxazolythione with secondary amines and aniline.

We have previously shown that the corresponding 2-hydroxyphenylthioureas (I) are obtained in the reaction of primary amines with benzoxazolythione derivatives [1]. We have found that sulfonamide derivatives of I ($X = SO_2NH_2$) with alkyl substituents in the 3 position are cyclized by an ammoniacal solution of silver nitrate to give good yields of 2-alkylaminobenzoxazole-5-sulfonamides (IIa-d, $R^3 = H$).



We also obtained 5-sulfonamide derivatives of substituted 2-aminobenzoxazoles (IIe-g) by another method — by substitution of the thiol group of benzoxazolythione by reaction with secondary amines (piperidine and morpholine) and aniline (see Table 1). In this case the opening of the oxazole ring that is observed in the reaction with strong aliphatic amines [2] does not occur.

Cyclization of 1,3-dialkyl-substituted thioureas I and their sulfonamide derivatives ($X = H, SO_2NH_2, R^1 = CH_3$) gives the corresponding 3-methyl-2-alkyliminobenzoxazolines (III). The 2-iminobenzoxazoline derivatives have an exocyclic azomethine group, the stretching vibrations of which have unusually high frequencies — 1700–1740 cm^{-1} (the IR spectra of these compounds were the subject of a separate communication [3]).

TABLE 1. 2-Aminobenzoxazole-5-sulfonamides (IIa-g)

Compound	R^2	R^3	Reaction time, h	mp, °C	Found, %		Calc., %		Yield, %
					N	S	N	S	
IIa	C_2H_5	H	2	209–211		13,2		13,3	75
IIb	C_4H_9	H	2	176–178	15,5		15,9		91
IIc	C_6H_{11}	H	2	212–214	14,5		14,2		82
IId	$CH_2C_6H_5$	H	2	210–212	14,1		13,8		88
IIe	$-(CH_2)_4-$		5	233–235		11,4		11,4	59
IIf	$-(CH_2)_2O(CH_2)_2-$		4	216–218		11,3		11,3	51
IIg	C_6H_5	H	3*	237–239	14,6		14,5		81

*The reaction was carried out at 130–140°C.

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