3. A. I. Kiprianov and A. I. Tolmachev, Zh. Obshch. Khim., 29, 2868 (1959).
4. A. I. Tolmachev, Zh. Obshch. Khim., 30, 2884 (1960).
5. J. Degani, R. Fochi, and C. Vinzenci, Gass. Chim. Ital., 94, 451 (1964).
6. A. I. Tolmachev, V. P. Sribnaya, and I. K. Ushenko, Khim. Geterotsikl. Soedin., No. 3, 459 (1968).
7. B. Tilak and Z. Mulyiani, Tetrahedron, 24, 949 (1968).
8. H. Larive, D. Collet, and R. Dennilauler, Bull. Soc. Chim. France, 1449 (1956).

SYNTHESIS, STRUCTURE, AND STEREOCHEMISTRY OF 2-ALKYL-4,4,5-TRIMETHYL- AND 2-ALKYL-4,4,6,6-TETRAMETHYL-1,3-DIOXANIUM PERCHLORATES

Yu. Yu. Samitov, Z. I. Zelikman,
T. P. Kosulina, and V. G. Kul'nevich

UDC 547.841.07:541.63:542.951:
543.422.25

A number of 2-alkyl-4,4,5-trimethyl- and 2-alkyl-4,4,6,6-tetramethyl-1,3-dioxanium perchlorates were obtained by acylation of 1,3-diols in the presence of 70% perchloric acid. Acid-catalytic cleavage of the heteroring with subsequent cyclization to 2-alkyl-1,3-dioxanium perchlorates occur in the reaction of 2-aryl(alkyl)-substituted and 2-unsubstituted 1,3-dioxanes with carboxylic acid anhydrides and 70% $HClO_4$. Hypothetical detachment of a hydride ion by means of the acceptor acylium cation does not occur under the investigated conditions. The structures of the synthesized perchlorates were studied by PMR spectroscopy and it was shown that 1,3-dioxanium cations at room temperature exist in a state of rapid conformational isomerization of the "chair—chair" form. The rate of interconversion of the 2,4,4-trimethyl-1,3-dioxanium cation decreases appreciably as the temperature is reduced to −90°, as evidenced by marked broadening of the lines of the protons of the gem-dimethyl groupings.

At present little study has been devoted to the synthesis and stereochemistry of nonaromatic carbonium systems. Up until now most attention has been directed to synthesis of 1,3-dioxolanium cations [1, 2]. There are only several communications [3, 4] in the literature regarding 1,3-dioxanium cations; synthesis without a detailed analysis of the structure is illustrated in these communications. Continuing our studies of the stereochemistry of 1,3-dioxanes [5] we studied methods for the synthesis of alkyl-substituted 1,3-dioxanium perchlorates and some of the problems involved in their dynamic stereochemistry.

For this, we obtained 1,3-dioxanium perchlorates by acylation of 1,3-diols in the presence of 70% perchloric acid by the method in [6]; the physical constants of some of these compounds are presented in Table 1. The structures of the salts were confirmed by their IR spectra and were studied in detail by PMR spectroscopy.

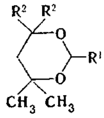
To obtain more proof for the structure of the perchlorates we hoped to obtain them by "alternative" synthesis of the corresponding 1,3-dioxanes using a reaction involving detachment of a hydride ion from the 2 position in analogy with the research previously accomplished for dioxolanium salts [7]. For this, a number of 1,3-dioxanes (Table 2) were obtained by condensation of carbonyl-containing compounds with 1,3-diols. Acyl perchlorates were used as the hydride-ion acceptor. Crystalline 1,3-dioxanium perchlorates were isolated after treatment of the 1,3-dioxanes with a mixture of carboxylic acid anhydrides with 70% perchloric acid. Absorption bands at 1537-1585 and 1490-1510 cm^{-1}, which are peculiar to the vibrations of the $O-\overset{+}{C}-O-$

Krasnodar Polytechnic Institute, Krasnodar 350006. V. I. Ul'yanov-Lenin Kazan State University, Kazan 420008. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 182-186, February, 1977. Original article submitted June 15, 1976.

TABLE 1. Alkyl-Substituted 1,3-Dioxanium Salts I-VIII

Compound	R^2	R^3	R^4	mp (dec.), °C	$\nu_{O-\overset{+}{C}-O}$, cm^{-1}	$\nu_{ClO_4^-}$, cm^{-1}	Yield, %
I	H	H	CH_3	52—54	1570, 1510	1100	75
II	H	H	C_2H_5	53—55	1570, 1510	1080	78
III	H	H	C_3H_7	55—56	1550, 1510	1100	60
IV	CH_3	H	CH_3	72—73	1570, 1515	1090	82
V	CH_3	H	C_3H_7	75—76	1575, 1510	1178	60
VI	H	CH_3	CH_3	52—53	1570, 1515	1100	50
VII	H	CH_3	C_2H_5	55—56	1580, 1510	1100	45
VIII	H	CH_3	C_3H_7	58—60	1570, 1515	1100	42

TABLE 2



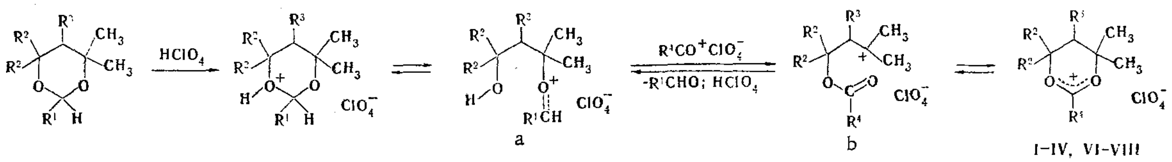
Compound	R^1	R^2	bp, °C (mm)	n_D^{20}	Found, %		Empirical formula	Calc., %		Yield, %
					C	H		C	H	
IX[a]	CH_3	H	143	1,4230	64,5	10,9	$C_7H_{14}O_2$	64,6	10,8	50
X	2-Furyl	H	121—122 (10)	1,4800	65,9	7,1	$C_{10}H_{14}O_3$	65,9	7,7	20
XI	C_6H_5	H	120—122 (5)	1,5135	75,4	8,2	$C_{12}H_{16}O_2$	75,0	8,3	25
XII	p-$CH_3OC_6H_4$	H	179 (10)	1,5140	70,7	8,3	$C_{13}H_{18}O_3$	70,3	8,1	30
XIII[b]	CH_3	CH_3	53 (7)	1,4320	68,8	12,0	$C_9H_{18}O_2$	68,4	11,4	40
XIV	C_6H_5	CH_3	140—142 (10)	1,5150	76,9	9,4	$C_{14}H_{20}O_2$	76,4	9,1	20
XV	p-$CH_3OC_6H_4$	CH_3	135 (5)	1,5160	77,6	9,8	$C_{15}H_{22}O_2$	77,2	9,4	30
XVI	2-Furyl	CH_3	107 (5)	1,4890	69,0	8,8	$C_{12}H_{18}O_3$	68,6	8,6	25

---

[a] bp 143° (30 mm) [8].

[b] bp 150° [9].

fragment [2, 6], and a broad intense band of a ClO_4^- ion at 1100 cm^{-1} were observed in their IR spectra. The spectra of the salts obtained on the basis of 2-furyl- or 2-aryldioxanes X-XII and XIV-XVI do not have characteristic absorption bands of aromatic rings and therefore do not confirm the proposed structure. In addition, the IR spectra of salts synthesized by this method from 2,4,4,6,6-pentamethyl- and 4,4,6,6-tetramethyl-2-phenyl-1,3-dioxanes are absolutely identical. Since it is difficult to form a judgment regarding the structure of the 4,4-dimethyl- and 2,4,4-trimethyl-1,3-dioxanium cations, which differ from one another only with respect to the substituent in the 2 position, from the IR spectra, we used PMR spectroscopy, which made it possible to solve this problem. The spectrum of a salt obtained from 4,4-dimethyl-1,3-dioxane completely clearly shows (see below) that this salt corresponds to the structure of I. The latter fact proves that detachment of a hydride ion from the 2 position of the dioxane ring does not occur under the influence of an acyl perchlorate. Acid-catalytic cleavage of the 1,3-dioxane ring to give intermediate cation *a*, which is converted to carbonium ion b by splitting out the corresponding aldehyde under the influence of the acylating mixture, probably takes place initially under the reaction conditions. Carbonium ion b undergoes cyclization to the salt. The development of an aldehyde in the presence of catalytic amounts of perchloric acid was proved by gas–liquid chromatography (GLC).



Thus the reaction of 1,3-dioxane with an acylating mixture may be a simple method for the synthesis of 2-aklyl-substituted 1,3-dioxanium salts; this is of definite interest for the use of industrial fractions of 1,3-dioxanes. We obtained perchlorates I-IV and VI-VIII by means of this method. Advantages of this method as compared with the methods used in [6] are exclusion of the step involving isolation of the pure 1,3-diol and a 10-15% increase in the yield of the salt.

The PMR spectra of 2,4,4-trimethyl-1,3-dioxane (IX) and its salt (I) are presented in Fig. 1. The vicinal constants ($^3J_{Aa}$ = 11.0, $^3J_{Ba}$ = 5.5 and $^3J_{Be}$ = 1.6 Hz), the fact of inversion of the chemical shifts of the 5-H*a* and

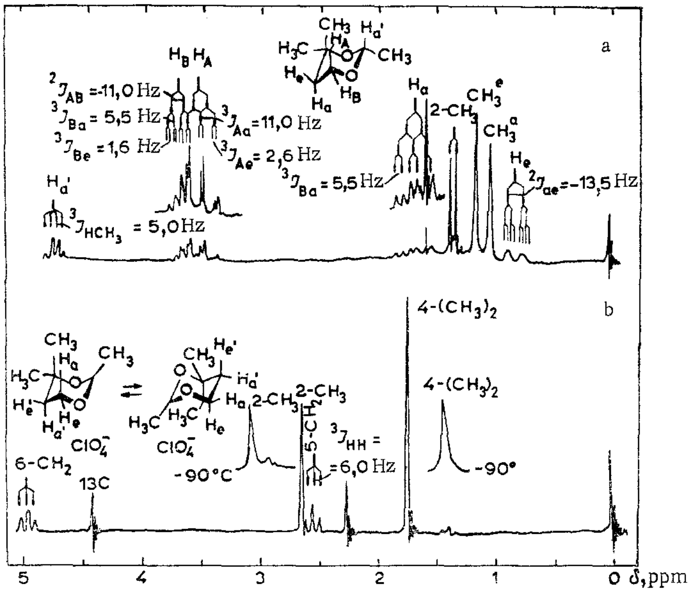


Fig. 1. PMR spectra of 2,4,4-trimethyl-1,3-dioxane (IX, spectrum a) and 2,4,4-trimethyl-1,3-dioxanium perchlorate (I, spectrum b). The line designated by ^{13}C is a satellite from the solvent (methylene chloride). The line designated by an asterisk corresponds to an impurity. The spectral lines at −90° are presented without reference to the chemical shift scale. The operating frequency was 100 MHz.

5-H$_e$ protons, the position of the doublet line of the 2-CH$_3$ protons (δ 1.35 ppm), and the nonequivalence of the protons of the gem-dimethyl grouping make it possible to assert for IX (spectrum a) that its molecules reside primarily in a chair conformation with an equatorial 2-CH$_3$ group. The chemical shift of the methylidyne quartet at δ 4.78 ppm with allowance for the magnetic anisotropic shift under the influence of an axial 4-CH$_3$ group indicates the equatorial character of the methyl group. Structures with 1,4-twist and 2,5-twist conformations [10] are excluded here, since inversion of the nuclear magnetic shielding constants of the H$_A$ and H$_B$ protons develops in these forms.* The PMR spectrum of salt I (spectrum b) shows the singlet character of the resonance signal of the methyl protons in the 2 position and a strong shift of the positions of all of the signals to lower field as compared with the corresponding signals of IX. All of this proves the cationic nature of I (see the numerical estimates of $\Delta\sigma$ below). The fact that the protons of the gem-dimethyl group resonate in the form of a singlet at δ 1.75 ppm, whereas the 5-H and 6-H protons resonate in the form of triplets at δ 2.58 and 4.97 ppm with average spin−spin coupling constants $^3J = 6.0$ Hz constitutes evidence for rapid (on the PMR time scale) interconversion of the six-membered heteroring either of the chair ⇄ chair form or in a set of conformations of "flexible" forms [10]. In fact, a study of 4,4-dimethyl-1,3-dioxane [11], the molecules of which at room temperature reside in a state of rapid conformational transitions, showed that the 5- and 6-H methylene protons give a spectrum of the A_2B_2 type, which, within a first-order approximation, as in our case, consists of two triplets. However, as the temperature of the sample is lowered to −60° all of the spectral lines begin to undergo pronounced broadening. The character of the broadening of the lines of the 2-CH$_3$ and 4-(CH$_3$)$_2$ protons at −90° is shown in Fig. 1. This fact, first, confirms the presence of interconversion at both −90° and at higher temperatures, and, second, serves as proof that in the absence of interconversion the methyl protons of the gem-dimethyl grouping should prove to be nonequivalent.

Similar ring inversion also occurs in the case of II-V.

From a comparison of the PMR spectrum of salt I with the spectrum of 2,4,4-trimethyl-1,3-dioxane (IX) it may be seen, as pointed out above, that the signals of all of the substituents of I experience a strong shift to weak field. The spectral parameters of 1,3-dioxanium perchlorates I-V are presented in Table 3.

---

*Our next publication, in which the criterion of the inversion of the chemical shifts of the H$_A$ and H$_B$ methylene protons will also be substantiated, will be devoted to a description of the results of a PMR study of the stereochemistry of many previously undescribed substituted 1,3-dioxanes with a 4,4-gem-dimethyl grouping.

TABLE 3. Parameters of the PMR Spectra of 1,3-Dioxanium Perchlorates I-V[a]

Compound	Solvent	δ, ppm							J, Hz		
		2-CH_3 or α-CH_2[b]	β-CH_3[b] or β-CH_2	γ-CH_3	4-CH_3	5-H	6-CH_3	6-H	$^3J_{56}$	$^3J_{\alpha,\beta}$	$^3J_{\beta\gamma}$
I	CH_2Cl_2	2,58 s	—	—	1,75 s	2,51 t	—	5,00 t	6,0	—	—
II	CH_2Cl_2	2,97 q	1,29 t	—	1,75 s	2,58 t	—	5,12 t	6,0	7,3	—
III	CH_2Cl_2	2,93 t	1,70 m	1,0 t	1,77 s	2,60 t	—	5,03 t	5,9	7,2	7,2
IV	CH_2Cl_2	2,67 s	—	—	1,78 s	2,60 s	1,78 s	—	—	—	—
	CF_3COOH	2,59 s	—	—	1,75 s	2,53 s	1,75 s	—	—	—	—
V	CH_2Cl_2	2,90 t	1,50 m	1,0 t	1,73 s	2,67 s	1,73 s	—	—	7,2	7,2

---

[a] The data presented in this table correspond to a sample temperature of +27°C.

[b] The α, β, and γ indexes correspond to the positions of the carbon atom in the R^4 group relative to the 2-C atom.

TABLE 4. Chemical Shifts in the PMR Spectra and Δδ and Δσ Values of I and IX

Compound and Δδ and Δσ values	Recording temperature, °C	Chemical shifts, ppm			
		2-CH_3	4-CH_3	5-H	6-H
I	27	2,66	1,75	2,58	4,97
IX	27	1,35 (e)	1,03 (a) 1,16 (e)	1,68 (a) 0,80 (e)	3,53 (a) 3,65 (e)
IX	120	1,32	1,09	1,24	3,59
Δδ		−1,34	−0,66	−1,34	−1,38
Δσ		—	—	−0,79	−1,16

For the numerical characteristics of the low-field proton shift let us examine the $\Delta\delta = \delta(\text{IX}) - \delta(\text{I})$ value for the proton-containing groups under conditions where the molecules of both compounds exist in a state of rapid conformational isomerization. This condition is realized for IX at 120°, at which point the two lines of the gem-dimethyl grouping merge. The chemical shifts of the protons of I and IX and the Δδ values are summarized in Table 4.

It is apparent from Table 4 that all of the Δδ values are quite high, and Δδ reaches −1.34 ppm in the case of the 2-CH_3 group. Effects of this sort are considered to be very large in PMR spectroscopy. In order to ascertain the nature of these low-field shifts and to confirm the cationic structure of I we made a quantitative evaluation of the effect of a positive charge localized on the 2-C atom on the proton shielding constant σ within a point approximation with allowance for linear and quadratic effects [12] from the formula

$$\Delta\sigma = -9.6\frac{q}{R_i^2}\cdot\cos\theta_i\cdot 10^{-6} - \frac{23q^2}{R_i^4}\cdot 10^{-6},$$

where $q = 1$ is the magnitude of the charge in the electron charges on the 2-C atom, R_i is the distance from the center of the 2-C atom to the H_i protons, and θ_i is the angle formed by the radius vector of R_i with the $C-H_i$ bond. The calculated Δσ values are also presented in Table 4.

By comparing the Δδ and Δσ values (averaged chair ⇄ chair inversions) for the 5-CH_2 and 6-CH_2 groups (Table 4) one may see that satisfactory agreement for the 6-H protons (somewhat less satisfactory agreement for the 5-H protons) between the experimental and calculated Δσ values is obtained within the approximation used. This fact makes it possible, first, to assume that the effect of the electrical field created by the positive charge on the 2-C atom makes the principal contribution to the change in the chemical shifts of the methylene protons, and, second, to consider it to be indirect proof of the cationic structure assigned to I.

EXPERIMENTAL

1,3-Dioxanes X-XVI were synthesized by the method in [16], and perchlorate V was obtained by the method described in [6].

The PMR spectra of 5-10% solutions of I-V in methylene chloride, of IV in trifluoroacetic acid, and of IX (5% by volume) in benzene were recorded with Varian HA-100 and Varian T-60 spectrometers. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

2,4,4-Trimethyl-1,3-dioxanium Perchlorate (I). A total of 1 ml (0.01 mole) of 70% $HClO_4$ solution was added dropwise to a mixture (prepared at −5°) of 4 ml of acetic anhydride and 1.16 g (0.01 mole) of 4,4-dimethyl-1,3-dioxane. After 10 min, the mixture was diluted with ether, during which an oil was liberated. The oil crystallized rapidly when the mixture was stirred. Workup gave 1.71 g (75%) of a product with mp 52-54° (methylene chloride, ether). Found: C 33.2; H 5.6; Cl 16.0%. $C_6H_{11}ClO_6$. Calculated: C 33.6; H 5.6; Cl 16.6%. Perchlorates I-IV, VII, and VIII were similarly obtained.

LITERATURE CITED

1. C. U. Pittman, S. P. McManus, and J. W. Larsen, Chem. Rev., 72, 357 (1972).
2. L. V. Mezheritskaya and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 8, 1023 (1971).
3. S. Kabiss, Angew. Chem., 2, 81 (1968).
4. G. Schneider, Tetrahedron Lett., No. 47, 5921 (1966).
5. Yu. Yu. Samitov, Z. I. Zelikman, A. I. Shkrebets, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 3, 319 (1974).
6. Z. I. Zelikman, T. P. Kosulina, V. G. Kul'nevich, G. N. Dorofeenko, and L. V. Mezheritskaya, Khim. Geterotsikl. Soedin., No. 2, 169 (1976).
7. Z. I. Zelikman, L. A. Falina, V. G. Kul'nevich, G. N. Dorofeenko, and L. V. Mezheritskaya, Khim. Geterotsikl. Soedin., No. 7, 891 (1973).
8. Z. I. Zelikman, A. I. Shkrebets, V. G. Kul'nevich, and B. A. Tertov, Khim. Geterotsikl. Soedin., No. 4, 438 (1971).
9. G. Kellie and F. Riddell, Chem. Commun., No. 1, 42 (1972).
10. K. Pihlaja, G. M. Kellie, and F. Q. Riddell, J. Chem. Soc., Perkin, No. 2, 252 (1972).
11. J. Delman and C. Barbier, J. Chem. Phys., 41, 1106 (1964).
12. A. D. Buckingham, Can. J. Chem., 38, 300 (1960).
13. Z. I. Zelikman and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., 367 (1969).

SYNTHESIS OF 4-ETHOXYFLAVYLIUM SALTS AND FLAVONES

G. N. Dorofeenko, V. V. Tkachenko,
V. I. Yakovenko, V. V. Mezheritskii,
and É. T. Oganesyan

UDC 547.814.5

4-Ethoxybenzopyrylium salts, which are converted to the corresponding flavones in quantitative yields by refluxing with water, were synthesized by condensation of o-hydroxyacetophenones with aromatic aldehydes in the presence of ethyl orthoformate and 70% perchloric acid.

The previously described methods for the synthesis of 4-alkoxybenzopyrylium salts were based on the reaction of ethyl orthoformate with o-hydroxychalcones [1] or of ethyl orthoformate with (ω-acyl)hydroxyacetophenones [2] in the presence of 70% perchloric acid. We have recently proposed a method for the preparation of 4-ethoxyflavylium salts on the basis of acid condensation of o-hydroxyacetophenones with aromatic aldehydes in the presence of ethyl orthoformate and 70% perchloric acid [3]. As compared with other methods [1, 2], this method for the synthesis of 4-ethoxyflavylium salts is the simplest method, is satisfactorily reproducible, and is convenient for the preparation of natural flavones and their synthetic analogs, which find application as regulators of the nervous system, stimulators of the activity of the heart muscles, and have p-vitamin activity [4].

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don 344711. Pharmaceutical Institute, Pyatigorsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 187-190, February, 1977. Original article submitted January 20, 1976.