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PREPARATION OF DIASTEREOMETRICALLY PURE SODIUM SALTS OF SULFATED 2-n-ALKYL-5-HYDROXYMETHYL-5-METHYL-1,3--DIOXANES[1]

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Abstract: Sulfur trioxide • pyridine complex has been found to be an excellent reagent for preparation of diastereometrically pure sodium salts of sulfated cis- and trans-2-n-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes.

In connection with our studies on the relation between the polar substituents configuration in alkyl-substituted 1,3-dioxacyclane derivatives and their amphiphilic properties[2,3] we attempted to elaborate a mild and efficient method for introduction of sulfate grouping into pure cis and trans diastereomers of the title compounds. For among numerous and well-known methods of sulfation of hydroxy-substituted organic compounds with gaseous sulfur trioxide[4] (a method widely used in surface active agents industry), chlorosulfonic acid[5,6], methods which use complexes of sulfur trioxide with various usually or-

[1] Part XXI in the series: Acetals and Ethers. For Part XX see Ref. 1.

ganic acceptors are most useful for sensitive compounds. Sulfur trioxide•1,4-dioxane complex reduces to a minimum both the reaction at the double bond and the process of the double bond migration when oleyl alcohol or monoethers of oleyl alcohol and oligooxyethylene glycols are sulfated[7]. Sulfation of equimolar mixture of propanol-2 and propanol-1 with sulfur trioxide•triethyl amine complex leads to the sulfuric ester of only propanol-1 with 77 % yield[8].

2-Alkyl-substituted derivatives of 5-hydroxymethyl-5--methyl-1,3-dioxanes are mixtures of two geometric isomers when obtained in an acid catalyzed reaction of aliphatic aldehydes with 1,1,1-tris(hydroxymethyl)ethane. Similarly, both individual isomers undergo transacetalization reaction to an equilibrium mixture of two isomers under acidic conditions. As we have stated earlier, the hydroxyl group configuration in low soluble in water and forming there only real solutions cis- and trans-2-n-alkyl-5-hydroxy-1,3-dioxanes influences their amphiphilic properties[2,3]. Thus we decided to prove these results for sulfate derivatives of 2-n-alkyl-5-hydroxymethyl-5--methyl-1,3-dioxanes which can form micellar solutions. At first we proved that the title compounds (mixtures of isomers) can be easily obtained by sulfation of an appropriate 1,3-dioxane derivative with chlorosulfonic acid or sulfur trioxide•pyridine complex in almost quantitative yields if the latter sulfation agent is used[9].

Furthermore, we found that the yield of sulfation reaction of cis + trans-2-(4-methylphenyl)-5-hydroxymethyl--5-methyl-1,3-dioxanes (entry 1, 78 : 22 molar ratio, calculated from GLC and ^{1}H NMR analysis) with 10 mol-% excess of sulfur trioxide•pyridine complex was only 74 mol-% but the reaction product constituted pure cis diastereomer (analyzed by ^{1}H NMR spectra).When cis + trans 2-n-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes (average molar ratio 70 : 30,alkyl: n-C_7H_{15}, n-$C_{11}H_{23}$, entries 3, 7) were sulfated to obtain pure cis sulfate derivatives, 50 mol-% equivalents of sulfation agent only were used. Sulfation reactions of isolated pure cis and trans diastereomers of 2-n-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes (with 10 mol-% excess of sulfur trioxide•pyridine complex) led to appropriate diastereometrically pure sulfate derivatives with excellent yields and without cis--trans equilibration process (entries 4 - 6).

Experimental Section.

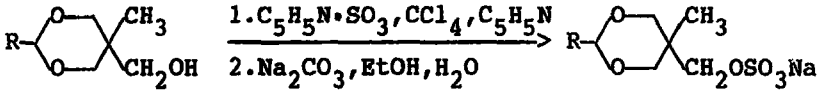
Preparation of sulfur trioxide•pyridine complex. The modification of the method of Baumgarten[10] was elaborated. To a well stirred, cooled with ice bath and protected against moisture, solution of 0.25 mole of dry pyridine in 100 ml of dry carbon tetrachloride,0.11 mole of chlorosulfonic acid was dropped during 0.5 h. After another 15 min. of stirring ice bath was removed and the solution was sucked off over precipitated sulfur trioxide pyridine complex. Then, the precipitate was washed five

times with 100 ml volumes of dry carbon tetrachloride--chloroform (85 : 15 v/v) and immediately used in sulfation reaction.

Preparation of sodium salts of sulfated 2-substituted 5--5-hydroxymethyl-5-methyl-1,3-dioxanes. To a well stirred, cooled with ice bath and protected against moisture solution of 0.1 mole of an appropriate mixture of cis + trans diastereomers or individual diastereomer of 2-substituted 5-hydroxymethyl-5-methyl-1,3-dioxane (Ia÷d) in 150 ml of dry carbon tetrachloride and 5 ml of dry pyridine, 0.11 mole or 0.05 mole (see Table) of a wet precipitate of sulfur trioxide•pyridine complex obtained as above was added in small portions during 2 hrs. After another 2-3 hrs of stirring the reaction mixture was left in the room temperature to the next day. Then, the reaction mixture was concentrated under reduced pressure to half of volume and dropped slowly (1-1.5 hrs) to a cooled with ice bath suspension of 0.12 or 0.06 mole of Na_2CO_3 in 200 ml of ethanol and 75 ml of water. After 4 hrs of stirring solvents were evaporated under reduced pressure and residue was washed several times with 100 ml volumes of boiling ethanol and then filtered. After cooling of ethanol filtrate,the obtained sodium salts of sulfated derivative (IIa÷d) was crystallized as long white needles. Mother liquor was evaporated from ethanol and residue dissolved in hot hexane. After cooling an

Table

Preparation of diastereometric sodium salts of sulfated 2-substituted 5-hydroxymethyl-5-methyl-1,3-dioxanes.



cis, trans or cis+trans-Ia÷d — cis or trans-IIa÷d

Entry	Substrate	Reagent ratio[c]	Reaction product: Structure	Yield[d] [mol-%]	mp. [°C][e]
1	4-$CH_3C_6H_4$- cis+trans-Ia (78 : 22)[a]	1.1 : 1	cis-IIa	74.0	235-236
2	4-$CH_3C_6H_4$- cis-IIa	1.1 : 1	cis-IIa	92.7	235-236
3	n-C_7H_{15}- cis+trans-Ib (70 : 30)[a]	0.5 : 1	cis-IIb	28.0	183-184
4	n-C_7H_{15}- cis-Ib	1.1 : 1	cis-IIb	92.0	183-184
5	n-C_9H_{19}- cis-Ic	1.1 : 1	cis-IIc	99.1	177-178
6	n-C_9H_{19}- trans-Ic[b]	1.1 : 1	trans-IIc	89.3	190-191
7	n-$C_{11}H_{23}$- cis+trans-Id (73 : 27)[a]	0.5 : 1	cis-IId	36.0	189-190

[a] cis : trans molar ratio, [b] 97 % of isomer purity, [c] sulfur trioxide•pyridine complex : acetal, [d] in respect to the acetal used, [e] with decomposition

additional amount of sodium salt of sulfated 1,3-dioxane derivative was obtained. Combined crystal fractions were recrystallized from ethanol or ethanol-isopropanol solution. If sulfation reaction product did not contain a considerable amount of unreacted substrate (reaction carried out with 10 mol-% excess of sulfation agent with respect to the acetal used) an additional crystallization from hexane can be omitted. The chemical structure of prepared sodium salts of sulfated 1,3-dioxane derivatives was confirmed by ^{1}H NMR analysis[11] (δ[ppm],J[Hz]):

cis-IIa (R = 4-$CH_3C_6H_4$-, TMS): 0.72(s, 3H); 2.32(s, 3H); 3.61(d, 2H, J = 11.5); 3.92(d, 2H, J = 11.5); 3.97(s, 2H); 5.42(s, 1H); 7.14 - 7.42(m, 4H).

cis-IIb (R = C_7H_{15}-, TMS): 0.78(s, 3H); 0.86(t, 3H, J = 6.5); 1.08 - 1.68(m, 12H); 3.36(d, 2H, J = 11.5); 3.76 (d, 2H, J = 11.5); 3.88(s, 2H); 4.44(t, 1H, J = 4.5).

cis-IIc (R = C_9H_{19}-, HMDS): 0.95(s, 3H); 1.15(t, 3H, J = 6.5); 1.35 - 1.90(m, 16H); 3.64(d, 2H, J = 11.5); 4.06(d, 2H, J = 11.5); 4.20(s, 2H); 4.69(t, 1H, J = 4.5).

trans-IIc (R = C_9H_{19}-, HMDS): 1.12(s, 3H, J = 6.5); 1.37 (s, 3H); 1.40 - 1.90(m, 16H); 3.64(s, 2H); 3.69(d, 4H, J = 10.5); 4.66(t, 1H, J = 4.5).

cis-IId (R = $C_{11}H_{23}$-, HMDS): 0.97(s, 3H); 1.15(t, 3H,J = 6.5); 1.35 - 1.90(m, 20H); 3.64(d, 2H, J = 11.5); 4.09(d, 2H, J = 11.5); 4.24(s, 2H); 4.69(t, 1H, J = 4.5).

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11. ^{1}H NMR spectra were recorded for 10 % solutions in DMSO. Chemical shifts (δ) downfield from TMS (HMDS) standard.

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