Alkoxyalkyl-Substituted Glycerol Acetals: New Hydrophobic Intermediates for Surfactant Synthesis[1]

Andrzej Piasecki
Institute of Organic and Polymer Technology, Technical University of Wrocław, 50-370 Wrocław, Poland

In acid-catalyzed, one-step reactions of monofunctional alcohol (I) and glycerol mixture with a simple α,β-unsaturated carbonyl compound (acrolein, crotonaldehyde or methylvinyl ketone), four component glycerol acetals [mixtures of *cis*- + *trans*-2-(2-alkoxyalkyl)-substituted derivatives of 4-hydroxymethyl-1,3-dioxolanes and 5-hydroxy-1,3-dioxanes] or two component glycerol ketals [mixtures of *cis*- + *trans*-2-(2-alkoxyethyl)-2-methyl-4-hydroxymethyl-1,3-dioxolanes] were obtained, respectively. These compounds may be used as a new group of hydrophobic intermediates for synthesis of chemodegradable surfactants, which rapidly hydrolyze to nonsurfactant compounds in acidic aqueous solutions. Methods of synthesis, yields, compositions and chemical structures of components of reaction products, and products of their chemical degradation have been discussed.

KEY WORDS: 2-(2-Alkoxyalkyl)-1,3-dioxacyclane, chemical structure, 1,3-dioxacyclane derivative, hydrophobic intermediate, synthesis.

In 1969, cyclic acetals and ketals of glycerol with a long hydrocarbon chain at the C-2 carbon atom of 1,3-dioxacyclane rings were proposed as hydrophobic intermediates for synthesis of surfactants (1). They were obtained from reactions of long-chain aldehydes or ketones with glycerol, and were mixtures of 2-alkyl-4-hydroxymethyl-1,3-dioxolanes with 2-alkyl-5-hydroxy-1,3-dioxanes or 2,2-dialkyl-4-hydroxymethyl-1,3-dioxolanes, respectively. Nonionic (1–5) or ionic surfactants (6–9) obtained from these hydrophobic intermediates show good surface activity.

Because of high stability of acetal groups in neutral or alkaline water solutions, and because of usually rapid hydrolysis under acidic conditions (7–18) and susceptibility to oxidation (19,20), terms such as cleavable, destructible or chemodegradable surfactants have been used in many papers when acetal surfactants were investigated. Acetal-type chemodegradable surfactants constitute most often 1,3-dioxolane derivatives with carboxylate (9), phosphate (6), quaternary ammonium (7–9,11–14,16,17), sulfate (6), alkoxysulfonate (8,15) or oligooxyethylene nonionic (1–5) polar groupings and one or two hydrophobic alkyl chains located at C-2, C-4 or C-5 carbon atoms of the 1,3-dioxolane ring. Nonionic (18,21) and ionic (18,22) 1,3-dioxane derivatives and derivatives of noncyclic acetals also have been investigated as cleavable surfactants. Some of the acetal-type surfactants are effective as catalysts in micellar or emulsion media (7,9,11,12,14,15,17) or are able to form vesicles (8,13–15). After fulfilling their original functions, they can be converted to nonsurfactant species by simple acidification. This is especially suitable for the isolation of neutral organic reaction products from micellar/emulsion or vesicular media by straightforward extractive workup procedures. However, in spite of interesting surface properties and chemodegradability, acetal-type surfactants have not been manufactured in large (industrial) scale until now, probably due to the low supply of the long-chain carbonyl substrates.

In earlier papers we have stated that, under appropriate conditions, the α,β-unsaturated carbonyl compound (acrolein, crotonaldehyde) reacts with a mixture of aliphatic alcohol and diol to obtain, in moderate or high yield, the product of nucleophilic addition of the aliphatic alcohol molecule to the -CH=CH- bond and simultaneous acetalization of the aldehyde carbonyl group with the diol molecule (23,24) (Scheme 1).

According to the investigations of acrolein and crotonaldehyde reactions with mixtures of *n*-butanol and ethylene glycol or trimethylene glycol [$R^1 = n\text{-}C_4H_9$, $R^2 = H$ or CH_3, $R^3 = H$, $R^4 = CH_2CH_2$ or $(CH_2)_3$], the optimal conditions for preparation of 2-(2-alkoxyalkyl)-substituted 1,3-dioxolanes and 1,3-dioxanes were determined (23,24).

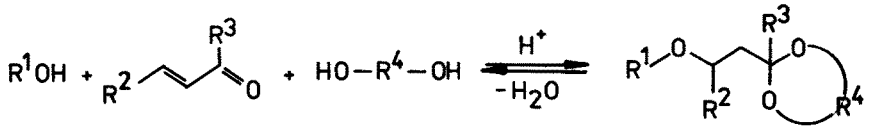
In this report we describe the properties of reaction products of three simple α,β-unsaturated carbonyl compounds, *i.e.* acrolein, crotonaldehyde and methylvinyl ketone, with mixtures of aliphatic alcohol and glycerol. They may be useful as new hydrophobic intermediates for the synthesis of acetal-type surfactants.

EXPERIMENTAL PROCEDURES

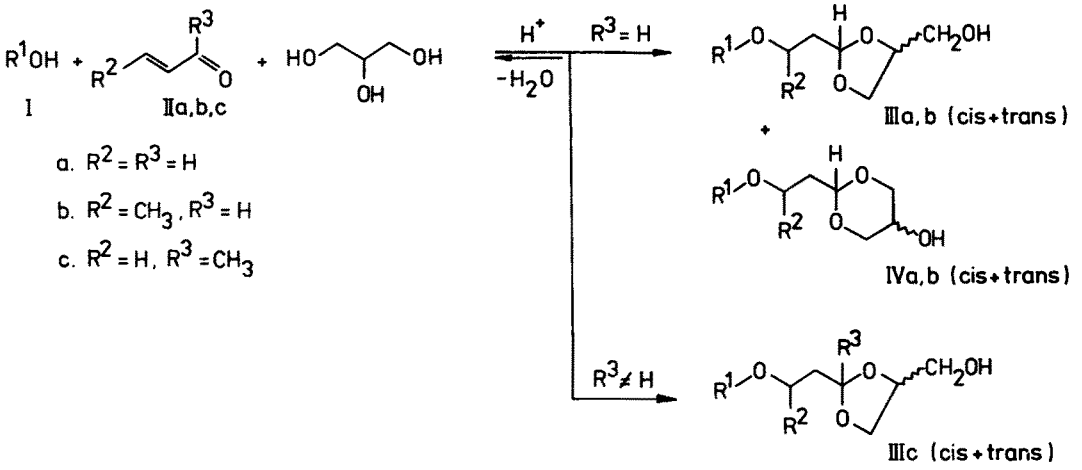
Materials. α,β-Unsaturated carbonyl compounds: acrolein (**IIa**), crotonaldehyde (**IIb**) and methylvinyl ketone (**IIc**) were purified by repeated fractional distillation and stabilized with 0.1 wt% of hydroquinone. Monofunctional alcohols were purified by vacuum fractional distillation. Glycerol (88 wt% water solution) was dried azeotropically and then purified by vacuum fractional distillation.

2-(2-Alkoxyalkyl)-substituted glycerol acetals and ketals. These compounds were synthesized according to the procedures presented elsewhere (25,26). One mole of freshly distilled unsaturated carbonyl compound [acrolein (**IIa**), crotonaldehyde (**IIb**) or methylvinyl ketone (**IIc**)] stabilized with 0.1 wt% of hydroquinone, 3 moles of an appropriate monofunctional alcohol (I), 1.5 moles of anhydrous glycerol and 2 g of *p*-toluenesulfonic acid monohydrate were boiled for about 20 h in the solution of 300 mL of hexane or chloroform, with continuous separation of reaction water in the azeotropic trap. After cooling to room temperature, the reaction mixture was alkalized with 3-fold excess of K_2CO_3 and then shaken four times with 100-mL portions of slightly alkalized water to remove unreacted glycerol. The water layers were separated and the organic layer was dried with anhydrous $MgSO_4$. After filtration and evaporation of the solvent on a rotary evaporator, the residue was subjected to vacuum fractional distillation. After removal of the unreacted monofunctional alcohol, which was used in excess, the fraction of an appropriate mixture of *cis*- + *trans*-2-(2-alkoxyethyl)-4-hydroxymethyl-1,3-dioxolane (**IIIa**) with *cis*- + *trans*-2-(2-alkoxyethyl)-5-hydroxy-1,3-dioxane (**IVa**), or *cis*- + *trans*-2-(2-alkoxypropyl)-4-hydroxymethyl-1,3-dioxolane (**IIIb**) with *cis*- + *trans*-2-(2-alkoxypropyl)-5-hydroxy-1,3-dioxane (**IVb**), or *cis*- + *trans*-2-(2-alkoxyethyl)-2-

[1]Part XX in the series: Acetals and Ethers. Part XIX, A. Piasecki, *Polish J. Chem.* 62:579 (1988).



SCHEME 1



SCHEME 2

methyl-4-hydroxymethyl-1,3-dioxolane (**IIIc**) was separated as colorless and viscous liquid. The yield of products was in the range 55–75 mol%. Their physical constants are listed in Tables 1 and 3.

Analytical methods. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Tesla BS497 (Tesla, Brno, Czechoslovakia) apparatus at 100 MHz. Tetramethylsilane (TMS) was used as internal standard and 10% solutions of compounds in $CDCl_3$ or CCl_4 were measured. Gas-liquid chromatography (GLC) analysis on a Giede G.CH.F.18.3 (Chromatron, Berlin, Germany) apparatus equipped with flame ionization detector (FID) was used to check the purity of substrates and the composition of reaction products. A metallic column (3 mm i.d. and 1 m long) packed with 15% Silicon XE60 on Chromosorb G AW DMCS 60/80 mesh (nitrogen as carrier gas) was used.

RESULTS AND DISCUSSION

Mixtures of monofunctional alcohol and glycerol, in the reaction with unsaturated carbonyl compound, lead to the 2-(2-alkoxyalkyl)-substituted 1,3-dioxacyclanes with a primary or secondary hydroxy group in the 1,3-dioxacyclane rings (25,26) (Scheme 2). These compounds with appropriate substituents $R^1 \div R^3$ may be useful as new hydrophobic intermediates for synthesis of chemodegradable acetal-type surfactants.

The reaction products of acrolein (**IIa**, $R^2 = R^3 = H$) or crotonaldehyde (**IIb**, $R^2 = CH_3$, $R^3 = H$) with mixtures of monofunctional alcohol R^1OH (**I**) and glycerol constitute the four component mixtures of *cis-* + *trans*-2-(2-alkoxyalkyl)-4-hydroxymethyl-1,3-dioxolanes [*cis-* + *trans*-(**IIIa**) or *cis-* + *trans*-(**IIIb**)] and *cis-* + *trans*-2-(2-alkoxyalkyl)-5-hydroxy-1,3-dioxanes [*cis-* + *trans*-(**IVa**) or *cis-* + *trans*-(**IVb**)]. Physical constants of these products, with the R^1 substituent varied from $n\text{-}C_4H_9$ to $n\text{-}C_{12}H_{25}$, are presented in Table 1. In each case, the gas-liquid chromatography (GLC) analyses of these products proved the presence of four well-separated chromatographic peaks with constant ratios of their retention times $[R_{t(i)}]:R_{t(1)}:R_{t(4)} = 0.355$ and $R_{t(2)}:R_{t(3)} = 0.790$ when $R^2 = H$ or 0.380 and 0.850, respectively, when $R^2 = CH_3$ (peak numbers are ordered with increasing retention times). The individual components with shorter and longer retention times were separated from some four-component mixtures of acrolein acetals by repeated fractional distillation (followed by crystallization from hexane when $R^1 = n\text{-}C_{10}H_{21}$ or $n\text{-}C_{12}H_{25}$) as the lower and the higher boiling fractions, respectively. Chemical structures and conformations of separated components were determined by analysis of their ^1H NMR spectra (Table 2).

^1H NMR data from Table 2 clearly show that the separated components are derivatives of 2-(2-alkoxyethyl)-5-hydroxy-1,3-dioxane (**IVa**). The chemical shifts of the $H_{a\text{-}2}$ proton and of the $H_{e\text{-}4,6}$ and $H_{a\text{-}4,6}$ protons, with their characteristic coupling constants observed for the lower-boiling isomers, show that they are *cis*-(**IVa**) isomers with 2-(2-alkoxyethyl)-substituents at the C-2 carbon atom in equatorial position and the hydroxy group at the C-5 carbon atom in axial position. Analogously, the ^1H NMR data observed for the higher-boiling isomers are characteristic for *trans*-(**IVa**) isomers with the hydroxy group located in equatorial position. The same relationships were observed for the four-component 2-alkyl-substituted glycerol acetals (27–29). Based on the observations made earlier (28), we accepted that the remaining components of glycerol acetals located at the second and third positions in the GLC analysis are *cis-* and *trans*-2-(2-alkoxyalkyl)-4-hydroxymethyl-1,3-dioxolanes, respectively. An

TABLE 1

Physical Constants of Four-Component Mixtures of *cis* + *trans*-2-(2-Alkoxyalkyl)-4-hydroxymethyl-1,3-dioxolanes and *cis* + *trans*-2-(2-Alkoxyalkyl)-5-hydroxy-1,3-dioxanes (IIIa + IVa, R^2 = H; IIIb + IVb, R^2 = CH_3)

Number	R^1	R^3	Boiling point (°C/mmHg)	n_D^{20}	d_4^{20}
1	n-C_4H_9	H	103.5–114.0/0.7	1.4524	1.0635
2	n-C_5H_{11}	H	110.5–120.0/0.5	1.4529	—
3	n-C_6H_{13}	H	109–115/0.1	1.4530	1.0135
4	n-C_7H_{15}	H	113–124/0.1	1.4543	0.9995
5	n-C_8H_{17}	H	132–143/0.5	1.4564	—
6	n-C_9H_{19}	H	140–151/0.3	1.4579	0.9889
7	n-$C_{10}H_{21}$	H	151–165/0.2	1.4596	0.9875
8	n-$C_{12}H_{25}$	H	162–169/0.1	solid	
9	$C_6H_5CH_2$	H	140–155/0.3	1.5205	1.1515
10	n-C_6H_{13}	CH_3	109–125/0.2	1.4514	0.9925
11	n-C_8H_{17}	CH_3	128–142/0.15	1.4541	0.9787
12	n-$C_{10}H_{21}$	CH_3	157–169/0.3	1.4556	0.9697
13	cyclo-C_6H_{11}	CH_3	119–137/0.2	1.4760	1.0742

TABLE 2

^{1}H NMR Data of *cis* and *trans*-2-(2-Alkoxyethyl)-5-hydroxyl-1,3-dioxanes (IVa, R^2 = H)

Number	Configuration	R^1	Chemical shifts, δ [ppm][a]						Coupling constants, J [Hz]		
			$H_{a\text{-}2}$[b]	CH_2 (α)	CH_2 (β)	CH_2 (γ)	$H_{e\text{-}4,6}$	$H_{a\text{-}4,6}$	$J_{5,4e}$	$J_{5,4a}$	$J_{4gem}=J_{6gem}$
1	*cis*[c]	C_2H_5	4.63	1.82	3.44	3.37	3.92	3.80	1.5	1.5	11.5
2	*cis*[d]	n-$C_{12}H_{25}$	4.74	1.90	3.52	3.40	4.00	3.90	1.5	1.5	11.3
3	*trans*[c]	n-C_3H_7	4.48	1.77	3.49	3.30	4.04	3.26	5	10	≈10
4	*trans*[d]	n-$C_{10}H_{21}$	4.57	1.87	3.50	3.40	4.12	3.34	5	10	≈10
5	*trans*[d]	n-$C_{12}H_{25}$	4.57	1.87	3.49	3.39	4.15	3.34	5	10	≈10

[a]Cnemical shifts downfield from TMS.
[b]Triplet, J = 5.2 Hz.
[c]Spectrum in $CDCl_3$ solution.
[d]Spectrum in CCl_4 solution.

TABLE 3

Physical Constants of Mixtures of *cis* + *trans*-2-(2-Alkoxyethyl)-2-methyl-4-hydroxymethyl-1,3-dioxolanes (IIIc, R^2 = H)

No.	R^1	R^3	Boiling point (°C/mmHg)	n_D^{20}	d_4^{20}
1	n-C_4H_9	CH_3	88/0.1	1.4492	1.0260
2	n-C_5H_{11}	CH_3	109/0.1	1.4498	1.0110
3	n-C_6H_{13}	CH_3	119.5/0.1	1.4505	0.9980
4	n-C_7H_{15}	CH_3	131/0.1	1.4513	0.9810
5	n-C_8H_{17}	CH_3	129/0.2	1.4570	0.9788
6	iso-C_8H_{17}	CH_3	126/0.3	1.4540	0.9844
7	n-$C_{10}H_{21}$	CH_3	155/0.2	1.4579	0.9774

average composition of glycerol acetals (calculated directly from GLC peak areas) was: 1,3-dioxolane:1,3-dioxane derivatives ≈ 53:47; *cis*:*trans* ≈ 60:40 and 65:35 for 1,3-dioxolane and 1,3-dioxane derivatives, respectively.

When the mixtures of monofunctional alcohol (**I**) and glycerol were used in the reaction with methylvinyl ketone (**IIc**, R^2 = H, R^3 = CH_3), only two-component mixtures of *cis* + *trans*-2-(2-alkoxyethyl)-2-methyl-4-hydroxymethyl-1,3-dioxolanes (**IIIc**) were obtained (Scheme 2). Physical constants of these products (R^1 = n-C_4H_9÷n-$C_{10}H_{21}$) are presented in Table 3. In the GLC analysis of (**IIIc**), the presence of two poorly separated peaks in an approximate area ratio of 55:45 was observed. ^{1}H NMR analysis showed, besides the signals due to the protons of 2-(2-alkoxyethyl)-substituent and 1,3-dioxolane ring, the presence of two singlets due to the protons of the methyl group at the C-2 carbon atom of the 1,3-dioxolane ring in the *cis*- and *trans*-(**IIIc**) isomers.

In acidic aqueous solution, 2-(hydroxyalkoxyalkyl)- and 2-(2-alkoxyalkyl)-substituted 1,3-dioxolanes and 1,3-dioxanes undergo hydrolysis as presented elsewhere (30). Investigations made in D_2O/DCl solution (monitored by ^{1}H NMR analysis) suggest that in the first step of the reaction the acetal group hydrolyzes, followed by destruction of the 2-alkoxy-substituted aldehyde to monofunctional alcohol and unsaturated aldehyde. In general, they are more stable than 2-alkyl-substituted 1,3-dioxacyclanes, due to the presence of an ether-oxygen atom in the β-position with respect to the C-2 carbon atom of the 1,3-dioxacyclane ring (30).

Moreover, we have stated earlier that in the 1,3-dioxolane, 1,3-dioxane (31) and 2-methyl-4-hydroxymethyl-1,3-dioxolane derivatives (32), the hydrophobic efficiency of $C_nH_{2n+1}OCH_2CH_2$- and C_nH_{2n+1}-substituents at the C-2 carbon atom of the 1,3-dioxacyclane ring are almost the same.

The reaction of a simple α,β-unsaturated carbonyl compound (acrolein, crotonaldehyde or methylvinyl ketone) with the mixture of monofunctional alcohol and glycerol seems to be a good method for preparing interesting hydrophobic intermediates for the synthesis of chemodegradable acetal-type surfactants. This conclusion will be proven by further work on their synthesis and investigation of their surface properties.

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