Analysis of SO_3-Sulfonation Products of 1-Alkenes by Spectrometric Methods

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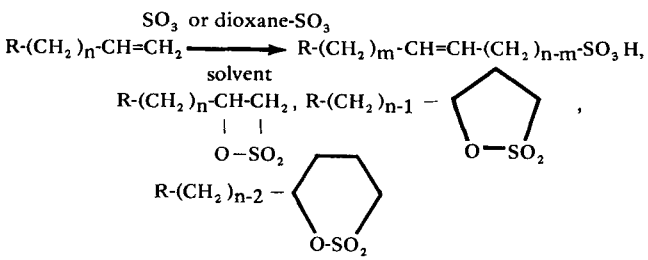
ABSTRACT

The preparation and identification of four types of SO_3-sulfonated products of 1-alkenes are described. ^{13}C and, to a lesser extent, ^1H nuclear magnetic resonance spectra are used to ascertain the structures of 2-alkenesulfonic acids, β-sultones (as 2-methoxyalkanesulfonic acids), γ- and δ-sultones. The mass spectra of some methyl 2-methoxyalkanesulfonates and 4-alkyl-δ-sultones are also studied. Sufficiently volatile mixtures are separated by gas liquid chromatography after methylation of the sulfonic groups.

INTRODUCTION

The SO_3-sulfonation of 1-alkenes was developed on a commercial scale about 15 years ago. This reaction, however, always gives complex mixtures containing mainly alkenesulfonic acids and sultones (1,2), and, despite the numerous studies effected in the laboratory since the earlier work by Suter et al. (3-7), the separation, identification and determination of these types of products are sometimes difficult.

Several publications (8-20) describe results on this subject. We report here the analytical part of a study concerning the SO_3-sulfonation of some linear and branched 1-alkenes (C_5 to C_{14}) in liquid phase according to the general scheme:



In addition to chemical methods, e.g., degradative oxidation, the principal analytical techniques used in this work are gas liquid chromatography (GLC), mass spectrometry (MS), ^1H and ^{13}C nuclear magnetic resonance (NMR).

MATERIALS AND METHODS

Reagents and Solvents

Sulfur trioxide was used in 1,2-dichloroethane solution, alone or as its 1,4-dioxane 1:1 complex. It was prepared from sulfur dioxide and oxygen by the contact process (catalyst: V_2O_5) and distilled before being dissolved. No stabilizer was added.

Dioxane (analytical grade) was stored over sodium wire. The absence of peroxide was checked. Methanol was distilled over anhydrous barium oxide; its purity was greater than 99.5%. 1-Alkenes and 1,2-dichloroethane were reagent grade compounds.

Sulfonations

A double-jacketed reaction vessel (allowing the circulation of cold methanol) was fitted with a mechanical stirrer, a silica gel tubing and a thermometer. In order to avoid any contact with air moisture, SO_3 was mixed with the solvent (on occasion with dioxane), then transferred to the reaction vessel by means of a device consisting of two bulbs and allowing pressure equilibration through silica gel tubing. Moreover, the apparatus was cautiously swept by dry nitrogen before being filled.

In a typical preparative experiment, a solution of 0.23 mol SO_3 in 150 mL 1,2-dichloroethane was added by drops during a few minutes at room temperature to 0.23 mol 1,4-dioxane dissolved in 300 mL of the same solvent. The solution of complex so obtained was then poured rapidly (15-20 sec) into a cooled solution of 1-alkene (e.g., 0.24 mol 1-hexene in 400 mL 1,2-dichloroethane). Just after this addition, a temperature rise of ca. 10 C was observed followed by a rapid decrease to its initial value (~0 C). Analytical preparations were conducted in a similar manner but on a smaller scale (ratio 1:10).

Treatment of Sulfonated Products

Alkenesulfonic acids. Mixtures of these acids were obtained either directly by evaporation of the solvent or after isomerization of the corresponding β-sultone (21). In the second case, the reaction medium was allowed to stand at room temperature for 4-5 days. Alkenesulfonic acids were either analyzed as such or converted to their methyl esters or sodium salts, which were easier to purify. Quantitative methylation was achieved by diazomethane prepared from *p*-tolylsulfonylmethylnitrosamide (Diazald® [22-24]). Methyl esters with no more than seven carbon atoms in the chain could be purified by distillation (p ~ 1 mm Hg). Sodium salts were prepared by mixing the acid with a stoichiometric amount of sodium methanolate dissolved in methanol. The mixture was refluxed 30 min, filtered on sintered glass while hot, concentrated until the salt began to precipitate, and allowed to stand for 4 hr or more at -15 C. The solid was filtered off and dried at 70 C under reduced pressure (20 mm Hg).

β-Sultones. Sulfonation mixtures were treated with a large excess of methanol 30 min after the addition of SO_3, allowed to stand overnight and concentrated. Thus, β-sultones were analyzed as the corresponding 2-methoxyalkanesulfonic acids or their derivatives (sodium salts or methyl esters).

TABLE I

Long-Chain Alkenesulfonic Acids: Distribution of Positional Isomers (in percent)

Chain length (number of C atoms)	n= 0	1	2	3
11	17	80	3	<0.5
12	2	93	4	1
13	9	87	4	<0.5
14	6	85	8	1

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TABLE II

^{13}C Chemical Shifts in Linear 2-Alkenesulfonic Acids (I H:R ≡ *n*-alkyl, R_2, R_3 ≡ H)

	Chemical shifts δ (ppm relative to TMS)[a]									
	C_1		C_2		C_3		C_4		C_5	
R	E	Z	E	Z	E	Z	E	Z	E	Z
C_2H_5	55.4	50.3	115.5	115.0	142.8	141.0	25.6	20.9	12.9	13.6
n-C_3H_7	55.4	50.5	116.7	115.9	141.1	139.2	34.6	29.5	22.0	22.4
n-C_4H_9	55.5	50.5	116.3	115.5	141.4	139.5	32.3	27.3	30.9	31.2
n-C_8H_{17}	55.4	50.3	116.9	116.2	140.7	138.9	32.7	28.9	29.4	29.4
n-C_9H_{19}	55.5	50.5	116.7	116.0	141.1	139.2	32.7	28.9	29.7	29.7
n-$C_{10}H_{21}$	55.4	50.5	116.8	116.0	141.0	139.1	32.7	28.9	29.7	29.7
n-$C_{11}H_{23}$	55.4	50.8	117.1	116.4	140.5	138.8	32.7	28.9	29.8	29.8

[a] ^{13}C Nuclei farther from the sulfonic group show standard chemical shifts.

TABLE III

^{13}C Chemical Shifts in Methyl 2-Alkenesulfonates (I Me)

Compound			δ (ppm) relative to TMS													
			C_1		C_2		C_3		C_4		C_5		C_6	C_7	R_2		R_3
R	R_2	R_3	E	Z	E	Z	E	Z	E	Z	E	Z			E	Z	
C_2H_5	H[a]	H	56.7	48.6	115.3	114.6	142.9	141.2	25.8	21.2	13.1	13.1	–	–	–	–	–
n-C_3H_7	H	H	56.3	48.7	116.0	115.1	141.3	139.3	34.6	29.6	21.9	22.3	13.5	–	–	–	–
i-C_3H_7	H	H	56.5	48.4	113.1	112.3	148.0	146.3	31.2	27.2	21.8	21.8	–	–	–	–	–
n-C_4H_9	H	H	56.2	48.8	115.7	114.8	141.6	139.7	32.3	30.9	27.2	27.2	22.4	13.8	–	–	–
i-C_4H_9	H	H	56.2	48.8	116.8	115.6	140.3	138.3	41.8	36.6	28.1	28.4	22.3	–	–	–	–
C_2H_5	CH_3[b]	H	59.5	56.3	122.6	121.6	137.8	137.0	21.6	21.9	13.5	13.7	–	–	16.1	23.6	
CH_3	CH_3[c]	CH_3	55.9		115.4		136.1		21.2						19.2		21.2

[a] If R_2 ≡ H, δ_{OCH_3} = 53.6 ± 0.2 ppm.
[b] δ_{OCH_3} = 52.4 ppm.
[c] δ_{OCH_3} = 55.1 ppm.

TABLE IV

^{13}C Chemical Shifts in Sodium 2-Alkenesulfonates (I Na; R_3 ≡ H)

Compound		δ (ppm) relative to TMS											
		C_1		C_2		C_3		C_4		C_5		C_6	C_7
R	R_2	E	Z	E	Z	E	Z	E	Z	E	Z		
CH_3	H	56.5	–	121.8	–	136.1	–	19.5	–	–	–	–	–
C_2H_5	H	56.0	50.9	119.0	119.0	142.1	140.5	26.4	21.7	13.8	14.6	–	–
n-C_3H_7	H	56.2	51.2	120.3	119.6	140.5	138.7	35.5	30.4	23.0	23.5	14.6	–
n-C_4H_9	H	56.4	51.3	120.9	120.3	140.2	138.3	33.5	32.5	28.4	28.4	23.5	15.2
t-C_4H_9	CH_3[a]	49.5	60.4	126.7	122.0	145.0	139.8	32.3		30.6			

[a] δ = 31.5 ppm.

γ- and δ-Sultones. These were analyzed and studied as such.

Syntheses

Sodium (E)-2-butenesulfonate was prepared by the reaction of 0.4 mol Na_2SO_3 on 0.21 mol(E)- crotyl chloride for two days (Strecker reaction [25]).

δ-Sultones. Truce's method (26) was adapted to alkenesulfonic acids to give δ-sultones. The acid mixture was carefully distilled (~1 mm Hg) to afford pure 4-alkyl-δ-sultones.

γ-Sultones. We applied Willems' method (27) to alkenesulfonic acids. After purification, a mixture of γ- and δ-sultones was always obtained with δ-sultone as the major product. Unsubstituted γ- and δ-sultones were available commercially.

Analyses

Degradation. Linear sodium alkenesulfonates from C_{11} to C_{14} were oxidized at the double bond according to Lemieux and Von Rudloff (28,29).

GLC separations. The carboxylic acids obtained from sodium alkenesulfonates were chromatographed isothermally as their methyl esters at 110 C (stationary phase: SE 30, 10% on Chromosorb W NAW; 1=2 m; Ø= 1/8"; flow rate of the carrier gas (He) : 50 mL min^{-1}; temperature of the injection port: 250 C, thermal conductivity detector thermostated at 230 C).

Sulfonated products with up to seven carbon atoms in the chain were chromatographed isothermally at 130 C (stationary phase: DC-QF 1, 10% on Chromosorb W AW; 1= 1.5

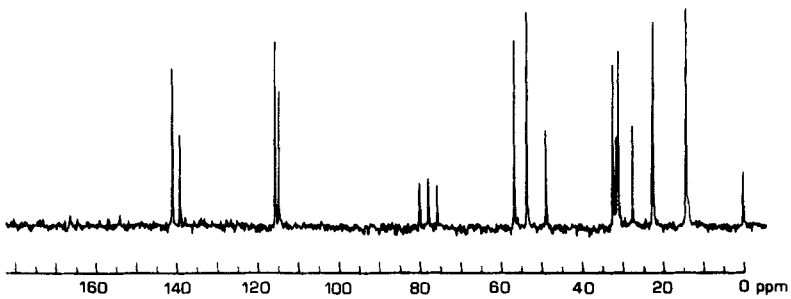


FIG. 1. ^{13}C NMR spectrum of methyl 2-heptenesulfonate.

TABLE V

Quantitative Analysis by ^{13}C NMR (I Me; R_2, $R_3 \equiv H$)

R	(E)-isomer percentages[a]		
	Normal mode	Repolarization (pulse delay)	$Cr(acac)_3$
C_2H_5	70 ± 2	66 ± 2	70 ± 3
n-C_3H_7	64 ± 2	64 ± 1	65 ± 3
n-C_4H_9	67 ± 2	63 ± 1	67 ± 2

[a]From surfaces of C_1 to C_5 signals.

m; Ø = 1/8"; temperature of the injection port: 235 C; other conditions as already cited). To avoid too much degradation of the substances during the analysis, the sample must be diluted with 1,2-dichloroethane. To ensure good separation of the peaks analysis sometimes took up to 1 hr. Peak assignment according to functional groups was made easier by performing some analyses on sulfonation media before methylation and adding a precolumn adsorbing all free sulfonic acids.

Mass spectrometry. Mass spectra were taken on a Riber spectrometer (Model QSM) with an ionization energy of 70 eV. Liquid samples were introduced at 60 C. The pressure in the ionization chamber was 10^{-5} mm Hg; perfluorotributylamine was used as a calibration standard.

^{13}C and ^1H NMR. Proton decoupled ^{13}C NMR spectra were taken at 15.08 MHz on a Bruker (WP 60) PFT spectrometer. Sulfonic acids, methyl sulfonates and sultones were analyzed in $CDCl_3$ with TMS as internal standard. Sodium sulfonates were analyzed in D_2O with dimethylsulfoxide (DMSO) as internal standard (δ_{DMSO} = 40.5 ppm).

^1H NMR spectra were taken at 90 MHz on a Bruker (WH 90) PFT spectrometer or at 60 MHz on a Varian T 60 spectrometer in the solvent systems already described. However, in D_2O, tetramethylphosphosilane (TMPS) was used as internal standard.

RESULTS AND DISCUSSION

The main products formed during the SO_3-sulfonation of 16 1-alkenes in liquid phase below room temperature were identified. The substrates studied include linear hydrocarbons from C_5 to C_8 and from C_{11} to C_{14} and some branched ones with no more than eight carbon atoms: 2-, 3- and 4-methyl 1-pentenes, 2,3- and 3,3-dimethyl 1-butenes, 5-methyl 1-hexene, 2,3,3-trimethyl 1-butene and 2,4,4-trimethyl 1-pentene. The products are alkenesulfonic acids, β-, γ- and δ-sultones.

Alkenesulfonic Acids

Position of the double bond. The carboxylic acids produced by the degradative oxidation of long-chain linear alkenesulfonic acids (C_{11} to C_{14}) were analyzed by GLC as their methyl esters. Four positional isomers may be considered as the precursors, the general formula of which is:

$$R\text{-}CH = CH\text{-}(CH_2)_n - SO_3H \qquad (n = 0,1,2,3).$$

The peak areas (in percentages) relative to these isomers are shown in Table I. Under the chosen reaction conditions (SO_3-dioxane complex), 2-alkenesulfonic acid is by far the major product. This remains true without dioxane, though a somewhat lower selectivity is observed in this case (21).

^{13}C NMR spectra. Alkenesulfonic acids were studied either directly (H) or as their methyl esters (Me) or sodium salts (Na). The only detectable carbon resonances were those associated with (E)- and (Z)-2-alkenesulfonic derivatives I-(E) and I-(Z).

TABLE VI

^1H Chemical Shifts in Sodium 2-Alkenesulfonates (I Na; $R_3 \equiv H$)

Compound		δ (ppm) relative to TMPS					
		H-C_1					
R	R_2	E	Z	H-C_2=C_3-H	H-C_4	$(CH_2)_n$	CH_3 (in R)
-CH_3	H	3.54 (d)	–	5.67 (c)	–	–	1.71
-C_2H_5	H	3.58 (d)	3.68 (d)	5.69 (c)	2.11 (m)	–	0.98 (t)
n-C_3H_7	H	3.51 (d)	3.62 (d)	5.62 (c)	2.04 (m)	1.38 (m)	0.87 (t)
i-C_3H_7	H	3.53 (d)	3.64 (d)	5.56 (c)	2.38 (sep)	–	0.98 (d)
n-C_4H_9	H	3.49 (d)	3.60 (d)	5.58 (c)	2.04 (m)	1.31 (c)	0.84 (prt)
n-C_8H_{17} to n-$C_{11}H_{23}$	H	3.48 (d)	3.57 (d)	5.56 (c)	2.05 (m)	1.27 (c)	0.84 (prt)
C_2H_5	CH_3[a]	3.51 (s)	3.62 (s)	5.41 (prt)	2.03 (m)	–	0.93 (t)

[a]δ = 1.79 ppm (s); s = singlet; d = doublet; sd = split doublet; t = triplet; prt = poorly resolved triplet; sep = septet; m = multiplet; c = clump.

TABLE VII

^{13}C Chemical Shifts in 2-Methoxyalkanesulfonic Acids (III H)

R	δ (ppm) relative to TMS[a]				
	C_1	C_2	C_3	C_4	C_5
n-C_3H_7	55.3	76.8	35.7	18.1	14.0
n-C_4H_9	55.4	77.1	33.0	26.9	22.5
n-C_5H_{11}	55.1	77.4	33.7	24.5	31.8
i-C_5H_{11}	55.0	77.1	31.1	33.5	28.0
n-C_9H_{19}	55.4	77.0	32.0	29.7	29.7
n-$C_{10}H_{21}$	55.7	77.9	32.2	29.9	29.9
n-$C_{11}H_{23}$	55.4	77.1	32.1	29.8	29.8
n-$C_{12}H_{25}$	55.4	77.1	32.1	29.8	29.8

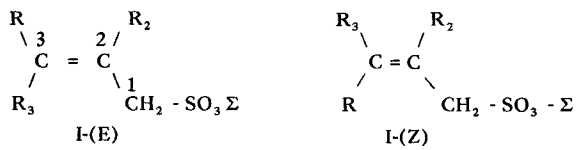
[a]^{13}C nuclei farther from the sulfonic group show standard chemical shifts; δ_{OCH_3} = 56.8 ± 0.1 ppm.

TABLE VIII

^{13}C Chemical Shifts in Methyl 2-Methoxyalkanesulfonates (III Me)

R	δ (ppm) relative to TMS[a]						
	C_1	C_2	C_3	C_4	C_5	C_6	C_7
n-C_3H_7	56.1	76.2	36.0	18.2	14.7	–	–
n-C_4H_9	55.9	76.1	33.3	26.8	23.4	14.8	–
n-C_5H_{11}	55.9	76.2	33.6	24.3	33.1	23.8	15.2
i-C_5H_{11}	55.8	76.4	31.5	33.6	28.0	22.5	–

[a]Ester group: δ_{OCH_3} = 53.8 ppm; ether group: δ_{OCH_3} = 57.3 ± 0.1 ppm.



I-(E)

I-(Z)

R ≡ alkyl group
R_2, R_3 ≡ H or CH_3
Σ ≡ H, Na or CH_3.

Precise assignment of the C_1, C_2, C_3 signals was done by comparison of the spectra of sodium salts with that of sodium (E)-2-butenesulfonate (I-[E] Na; R ≡ CH_3; R_2, R_3 ≡ H) prepared from (E)-crotylchloride by the Strecker reaction. It then appears that the (E)-isomer is nearly always produced in larger amount than the (Z)-isomer and this fact helped with the remaining assignments. The corresponding chemical shifts are shown in Tables II-IV. A typical spectrum, that of methyl 2-heptenesulfonate (I Me; R ≡ n-C_4H_9; R_2, R_3 ≡ H; mixture of [E] and [Z] isomers), is presented in Figure 1. Attempts at preparing alkenesulfonic acids from 3-methyl 1-pentene, and 2,3,3-trimethyl 1 butene (16) were unsuccessful.

It should be noticed that 3,3-dimethyl-1 butene gives, after rearrangement, the same acid as 2,3-dimethyl 1-butene (I; R, R_2, R_3 ≡ CH_3), whereas in the former case, only a γ-sultone was mentioned by Robbins (16). In addition, the main product of the sulfonation of 2,4,4-trimethyl 1-pentene seems to be the (Z)-isomer of the 2-alkene sulfonic acid, rather than the 1-alkenesulfonic acid proposed by Bordwell and Osborne (11).

Quantitative analysis of (E)-and (Z)-isomers was achieved in three ways: (a) direct determination of peak areas, (b) integration with delay time (10 sec between two pulses), (c) addition of a paramagnetic substance $Cr(acac)_3$ at various concentrations. Table V shows that the E:Z ratio is always near 2:1. This may be explained by overcrowding of the (Z) forms with respect to the (E)-forms, at least when R_3 ≡ H. Furthermore, all three approaches give the same results (up to Cr[acac]$_3$ concentrations of 0.05 m); so it is apparent that spin lattice relaxation times and NOE can be assumed to be similar enough to allow integration to be used as a method of determining E:Z ratios.

^1H *NMR spectra.* Only sodium sulfonates (I Na) were studied by ^1H NMR (Table VI). In fact, salts were found to be more convenient for two reasons. They can be purified by recrystallization and they do not possess $\underline{CH_3}$-O signal which would make the $\underline{CH_2}$-SO_3-region more complex. The signals of the methylene groups $\underline{CH_2}$-SO_3Na were assigned after the quantitative ^{13}C NMR analysis and after the simpler spectra of sodium (E) 2-butenesulfonate (I-[E]Na; R ≡ CH_3; R_2, R_3 ≡ H) and sodium 2-methyl 2-pentenesulfonates (I Na; R ≡ C_2H_5; R_2 ≡ CH_3; R_3 ≡ H) were measured.

TABLE IX

^{13}C Chemical Shifts in Sodium 2-Methoxyalkanesulfonates (III Na)

R	δ (ppm) relative to TMS[a]						
	C_1	C_2	C_3	C_4	C_5	C_6	C_7
n-C_3H_7	55.8	78.5	36.7	18.9	14.7	–	–
n-C_4H_9	56.0	78.9	34.3	27.8	23.4	14.8	–
n-C_5H_{11}	56.4	78.9	34.9	25.6	33.1	23.8	15.2

[a]δ_{OCH_3} = 57.6 ± 0.2 ppm.

TABLE X

^1H Chemical Shifts in 2-Methoxyalkanesulfonic Acids and Derivatives

Compound R	Σ	δ (ppm) relative to TMS (III H; III Me) or TMPS (I Na)						
		OCH_3[a]	SO_3-$\underline{\Sigma}$	$\underline{CH_2}SO_3$	>$\underline{CH}$-O-CH_3	-$\underline{CH_2}$-CH-OCH_3	$(\underline{CH_2})_n$	$\underline{CH_3}$-CH_2-
n-C_3H_7	H	3.43 (s)	10.98 (s)	3.24 (m)	–	1.47 (c)	1.47 (c)	0.96 (t)
	Me	3.38 (s)	3.89 (s)	3.23 (m)	3.71 (q)	1.47 (c)	1.47 (c)	0.94 (t)
n-C_4H_9	H	3.47 (s)	11.04 (s)	3.29 (m)	–	1.64 (c)	1.36 (c)	0.91 (t)
	Me	3.39 (s)	3.90 (s)	3.22 (m)	3.73 (q)	1.58 (c)	1.38 (c)	0.91 (t)
	Na	3.31 (s)	–	3.00 (m)	3.56 (m)	2.00 (c)	1.56; 1.28 (c)	0.84 (t)
n-C_5H_{11}	H	3.49 (s)	9.24 (s)	3.10 (m)	3.73 (m)	1.56 (c)	1.31 (c)	0.89 (t)
	Me	3.40 (s)	3.90 (s)	3.24 (m)	3.74 (q)	1.58 (c)	1.30 (c)	0.89 (t)
	Na	3.29 (s)	–	2.96 (m)	3.51 (m)	2.02 (c)	1.49; 1.27 (c)	0.84 (t)
n-C_9H_{19} n-$C_{11}H_{23}$	H	3.42 (s)	10.82 (s)	3.26 (m)	3.80 (m)	1.61 (c)	1.27 (c)	0.89 (t)

[a]Ether group. s = singlet; t = triplet; q = quintet; m = multiplet; c = clump.

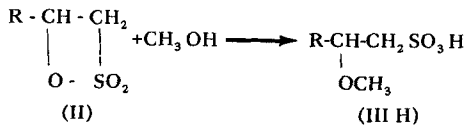
TABLE XI

^{13}C Chemical Shifts in δ-Sultones (IV)

R	δ (ppm) relative to TMS							
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
H	48.7	22.9	23.6	74.4	–	–	–	–
CH_3	47.0	22.3	30.7	83.2	21.2	–	–	–
C_2H_5	47.3	22.2	28.6	88.1	28.2	9.2	–	–
n-C_3H_7	47.3	22.3	29.2	86.6	37.2	18.0	13.6	–
n-C_4H_9	47.3	22.3	29.2	86.9	34.8	26.9	22.3	13.9

β-Sultones

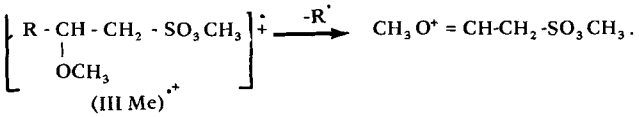
Occurrence of β-sultones (II) in sulfonation mixtures was evidenced by methanolysis of these compounds giving 2-methoxyalkanesulfonic acids (III).



(II) (III H)

The structure of the substances of general formula III were confirmed by MS and ^{13}C and ^{1}H NMR.

Mass spectra. Four methyl esters (III Me; R ≡ n-C_3H_7, n-C_4H_9, n-C_5H_{11}, i-C_5H_{11}) were studied. The parent ion peak is not detectable, as previously described (30) for methyl alkanesulfonates. The base peak, always situated at m/e 153, results from the loss of the alkyl group R:



(III Me)$^{\cdot+}$

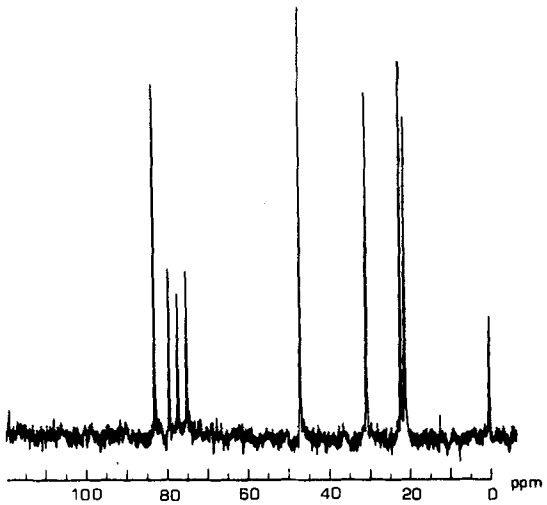
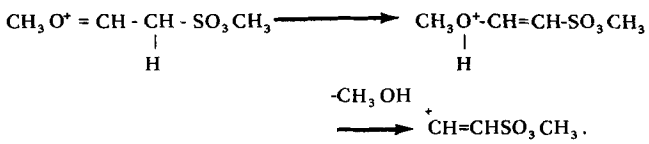
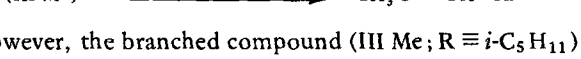


FIG. 2. ^{13}C NMR spectrum of 4-methyl-δ-sultone.

The peak at m/e 121 may then be interpreted by the loss of methanol from the above fragment, according to the scheme:



The peaks at m/e: 87, 101, 115 (respectively) proceed from the following fragmentation of the molecular peak:



However, the branched compound (III Me; R ≡ i-C_5H_{11})

TABLE XII

^{1}H Chemical Shifts in δ-Sultones (IV)

R	δ (ppm) relative to TMS						
	H-C_1	H-C_2	H-C_3	H-C_4	H-C_5	H-C_6	H-C_7
H	3.17 (t)	1.85	2.27	4.55 (t)	–	–	–
CH_3	3.09	1.82	2.24	4.82	1.43 (d)	–	–
C_2H_5	3.09	1.72	2.23	4.56	1.72	1.01 (t)	–
n-C_3H_7	3.07	1.62	2.20	4.64	1.62	1.62	0.91 (t)

d = doublet; t = triplet; multiplet when unspecified.

TABLE XIII

^{13}C Chemical Shifts in γ-Sultones (V)

Compound				δ (ppm) relative to TMS							
R_1	R_2	R_3	R_4	C_1	C_2	C_3	C_4	C_5	C_6 or R_1	C_7 or R_2	C_8 or R_4
H	H	H	H	44.3	23.7	69.8	–	–	–	–	–
H	H	C_2H_5	H	45.8	29.1	84.3	28.2	9.4	–	–	–
H	H	n-C_3H_7	H	45.8	29.6	82.9	37.1	18.4	13.6	–	–
H	H	n-C_4H_9	H	45.8	29.6	83.1	27.9	34.8	21.7	13.6	–
H	H	n-C_5H_{11}	H	45.8	29.6	83.1	35.1	24.8	31.3	22.3	13.9
H	H	C_2H_5	CH_3	45.8	34.0	91.8	33.9	8.0	–	–	25.2
H	CH_3	C_2H_5	H	42.9	30.6	85.0	29.5	10.0	–	18.1	–
H	CH_3	CH_3	CH_3	52.0	41.8	93.1	27.1	–	–	13.4	21.8
CH_3	CH_3	CH_3	CH_3	59.0	45.4	95.1	23.6	–	23.2	23.2	23.6

TABLE XIV

^{1}H Chemical Shifts in Some γ-Sultones (V)

Compound				δ (ppm) relative to TMS						
R_1	R_2	R_3	R_4	H-C_1	H-C_2	H-C_3	R_1	R_2	R_3	R_4
H	H	H	H	3.24 (t)	2.62 (q)	4.48 (t)	–	–	–	–
H	CH_3	CH_3	CH_3	2.8 –	3.4 (c)	–	–	1.17 (d)	1.53 (s)	1.43 (s)
CH_3	CH_3	CH_3	CH_3	3.13 (s)	–	–	1.23 (s)	1.23 (s)	1.43 (s)	1.43 (s)

s = singlet; d = doublet; t = triplet; q = quintet; c = clump.

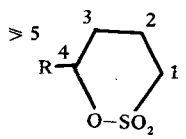
behaves unusually and gives intense peaks at m/e: 87 and 137.

^{13}C and ^1H NMR spectra. The ^{13}C chemical shifts observed on the spectra of some compounds (III H, III Me and III Na) are presented in Tables VII-IX, respectively.

^{13}C NMR analysis was complemented by a study of some proton spectra, the results of which are shown in Table X.

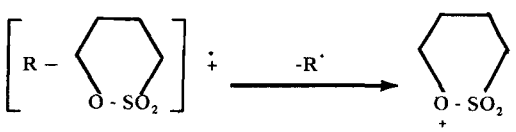
δ-Sultones

Five δ-sultones of general formula IV were studied by MS,

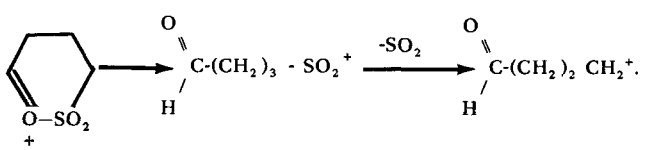
(IV)  R ≡ H, CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9

^{13}C and ^1H NMR. Except for unsubstituted δ-sultone, these substances were prepared pure from linear alkene sulfonation media (in which these sultones are already present).

Mass spectra. The base peak is found at m/e 135. As with lactones (31), this fragmentation involves the loss of an alkyl radical R:



Ring opening followed by loss of sulfur dioxide gives the m/e 71 fragment:



NMR spectra. The ^{13}C chemical shifts observed in compound IV are shown in Table XI. Assignments were made with reference to the spectrum of butanesultone, already published (32), and by means of ^{13}C-^1H coupling. The spectrum of 4-methyl-δ-sultone (IV; R ≡ CH_3) is also given (Fig. 2).

The results of the ^1H NMR study of compounds IV are presented in Table XII.

γ-Sultones

A series of γ-sultones belonging to type V were analyzed by ^{13}C and ^1H NMR. On one hand, sultones (V; R_3 ≡ *n*-alkyl; R_1, R_2 R_4 ≡ H) were produced in small amounts during the sulfonation of linear alkenes. ^{13}C signals in mixtures of isomeric γ- and δ-sultones were assigned with reference to the spectra of δ-sultones (IV) (see above) and unsubstituted γ-sultone (32). On the other hand, some branched alkenes gave γ-sultones as major products. These latter ones could be studied in the absence of δ-sultones. Thus, sultones (V; R_1, R_2 ≡ H; R_3 ≡ C_2H_5; R_4 ≡ CH_3) and (V; R_1, R_4 ≡ H; R_2 ≡ CH_3; R_3 ≡ C_2H_5) originate from 3-methyl 1-pentene. The relative configuration of this latter sultone was assigned after comparison with the corresponding tetrahydrofuran (33).

With respect to the γ-sultones, (V; R_2, R_3, R_4 ≡ CH_3; R_1 ≡ H or CH_3), they come, respectively, from the sulfonations of 3,3-dimethyl 1-butene and 2,3,3-trimethyl 1-butene. The results of ^{13}C and ^1H NMR of compounds V are shown

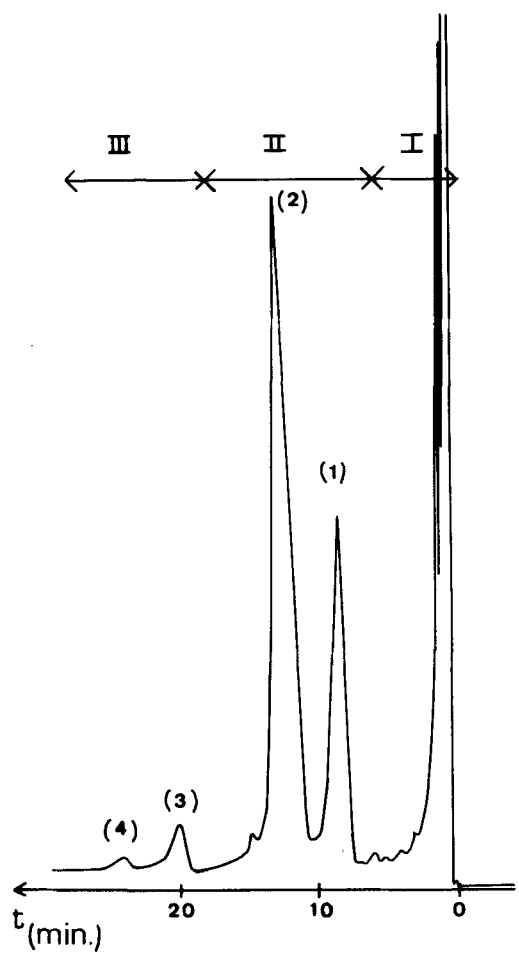
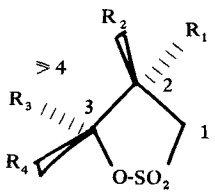


FIG. 3. Gas chromatogram of sulfonated products from 1-hexene (sample methylated by diazomethane): (1) methyl 2-hexenesulfonate; (2) methyl 2-methoxyhexanesulfonate; (3) 4-ethyl-δ-sultone; (4) 3-*n*-propyl-γ-sultone.

in Tables XIII and XIV.



GLC Analysis of Sulfonation Mixtures

A typical gas chromatogram produced by a sample of the sulfonation medium of a low-molecular-weight linear 1-alkene is shown in Figure 3. It can be divided into three regions: region I contains the peaks of volatile compounds: solvent, dioxane and some degradation products; additional peaks are observed after methylation. Region II includes methyl esters of alkenesulfonic acids (I Me and positional isomers) and 2-methoxyalkanesulfonic acid (III Me). Region III contains the peaks of δ- and γ-sultones IV and V.

The compounds isolated during this work were used to assign chromatographic peaks by the overloading method.

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