ORGANIC SULFUR COMPOUNDS CONTAINING FUNCTIONAL GROUPS COMMUNICATION 5. SYNTHESIS OF α , β -EPOXYALKYL SULFONES

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Lately interest in the chemical conversions of α,β -epoxy sulfones has increased in connection with the synthesis from them of aldehydes and ketones that contain functional groups (Br, SR, SO₂R, N₃, etc.) in the α position [1-3]. The α,β -epoxy sulfones have been synthesized by epoxidation of α,β -unsaturated sulfones [4,5], Darzens condensation of α -chloromethylsulfones with aldehydes and ketones in the presence of potassium tert-butylate [3, 6] or by interphase catalysis [1, 7, 8], and condensation of organolithium derivatives of α -chloromethylsulfones [2].

Before our investigation, only α -chloromethylaryl sulfones were used to synthesize α, β -epoxy sulfones by the Darzens condensation, because it was believed [6] that in the presence of base α -chloromethylalkyl sulfones would have to undergo a competitive Ramberg-Becklund reaction to form episulfones, which under the reaction conditions are converted to olefins. But the formation of olefins in the presence of a carbonyl addend (aldehyde or ketone) was not confirmed experimentally in [6]. It seemed advisable to verify this assumption, and to clarify the possible synthesis of α, β -epoxyalkyl sulfones by the condensation of α -chloromethylalkyl sulfones with various aldehydes and ketones in the presence of t-BuOK.

Model experiments showed that in the absence of a carbonyl addend, α -chloromethylalkyl sulfones (I) are indeed converted to olefins (III) in the presence of t-BuOK over a wide temperature range (-10 to 20°C):



just as under the standard conditions for the Ramberg-Becklund reaction [9]; but episulfone (II) could not be detected.

According to the generally accepted mechanism of the Ramberg-Becklund reaction [9] and the Darzens condensation [10], the sulfone (I) undergoes deprotonization under the action of base, which ought to form the carbanions A and B. Consequently in the presence of a carbonyl addend the formation of episulfone (II) or epoxysulfone (IV) ought to be determined by the difference in the formation rates of A and B, and by the electrophilicity of the C atom in the SO₂CH₂Cl and C=O groups.

To confirm this hypothesis, we measured the rates of formation of carbanions A and B in a model experiment, using PMR spectroscopy, with partial inclusion of a deuterium tracer from a CD₃OD medium in the α , α -methylene groups of sulfones (I) (R = C₃H₇ or C₇H₁₅), under the action of a weak base (Na₂CO₃) at room temperature.

* The R and R^1 groups in (IV) and (V) are identified in Table 1.

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RCH₂SO₂HC-CHR¹ (IV) and RCH₂SO₂HC-C (V)

Com	в	PI	Yield,	mp, °C	F	ound	-	
Com-					Calculated			Empirical
Pound	1	1	⁰ /0 .	Î	С	н	s	Torritura
	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	
(177.0)		CU	40	28 20	40,13	6,95	21,20	CHOR
$(\mathbf{I}\mathbf{V}\mathbf{A})$		0113	40	20-30	39,98	6,71	21,75	051110035
(IVb)	C ₃ H ₇	CH ₃	51	16-17	47,32	8.14	17,71	$C_7H_{14}O_3S$
(137)	CII	CT	54	245 22	56,29	9,44	13.80	CHOC
(\mathbf{IVC})	67H15		51	01,0-00	56,37	9,46	13,68	0111122035
(IVd)	C_9H_{19}	CH_3	51	35-36	59,64	10,06	12,42	$C_{13}H_{26}O_3S$
	CH.	C ₂ H-	75	145-155	47,29	7,95	17,72	C.H.O.S
(ive)	Cars	03117	15	11,0 10,0	47,17	7,92	17,99	071114030
(IVf)	C ₃ H ₇	C ₃ H ₇	83	19,5-20,5	$\frac{52,30}{52,40}$	8,87	15,39 15,54	$C_9H_{18}O_3S$
(IV g)	C ₇ H ₁₅	C_3H_7	85	34-35	59,38	9,96	12,33	C13H26O3S
(- , 5)					59,50	9,98	12,22	
(IVh)	C_9H_{18}	C _s H ₇	85	39,5-40	62,03	10,37 10,41	11.04	$C_{15}H_{30}O_{3}S$
(IV i)	CH ₃	C ₆ H ₅	85	105,5106,5	56,91	5,74	15,24	C10H12O3S
			[56,68	5,70	15,08	
(IVj)	$C_{3}H_{7}$	C_6H_5	85	9394	59,98	6,71	13,32	$C_{12}H_{16}O_{3}S$
(IVk)	<i>t</i> -C4H9*	C ₆ H ₅	73	99,5100,5	60,23	6,88	13,23	C12H16O3S
					63 45	6,71	13,32	
(IV l)	C_5H_{11}	C ₆ H ₅	85	80,581,5	62,78	7,51	11,92	$C_{14}H_{20}O_{3}S$
(IVm)	C_7H_{15}	$C_{\theta}H_{5}$	88	8889	64,81	8.08	10.84	$C_{16}H_{24}O_{3}S$
(177.)	a			00.00	64,78	8,14	10,82	
(1vn)	G9H19	G6H5	90	88-89	66,62	8,69	9.87	G18H28U35
(IVo)	C_6H_5	C_8H_5 [†]	83	103 - 105	-	-	-	$C_{14}H_{12}O_3S$
(IV n)	C.H.	o-ClCoH	35	46-47	52,65	5.73	11,47	C ₁₂ H ₁₅ ClO ₂ S
(1 • P)	03117	0 0106114		TT OF	52,45	5,50	11,67	-1013 04 0 50
(IV q)	C_7H_{15}	o-ClC6H4	35	72 - 73	58.24	7.22	9.65	$C_{16}H_{23}CIO_3S$
(IVr)	C ₀ H ₁₀	o-ClC ₆ H	40	79-80	60,23	7.55	8,92	C18H27ClO3S
(-018				60,23	7,58	8,93	~ ~ ~
(Vb)	C_3H_7	CH ₃	85	Oil	49.92	8.30	16.65	$C_8H_{16}O_3S$
(Vc)	C7H15	CH3	85	22 - 24	58,03	9,75	13.06	$C_{12}H_{24}O_3S$
					58,03	9,74	12,96	C II O C
(V d)	C_9H_{19}	CH₃	90	35,5-36,5	60,83	10,37	11,60	$G_{14}\pi_{28}G_{3}S$
(V _s)	C_3H_7	C_2H_5	85	Oil	52,18	8,63	15,75	$C_9H_{18}O_3S$
))		52,40	8,79	15,54	
(V t)	C_9H_{19}	C_2H_5	87	15 - 16	$\frac{61,97}{62.03}$	$\frac{10,26}{10.41}$	$\frac{10,94}{11.04}$	$\mathrm{C}_{15}\mathrm{H}_{30}\mathrm{O}_3\mathrm{S}$
(77)	C II	сu	88	01	56,53	9,26	13,55	C14H22O3S
(v [.] u)	U ₃ H ₇	<u>64П9</u>	00	011	56,37	9,46	13,68	-11-12-01
(V ₩)	C_9H_{19}	C_4H_9	88	16-17	$\frac{63,93}{64,10}$	10,75	10,07	$C_{17}H_{34}O_3S$
(V·v)	C ₂ H ₂	CeHea	82	Oi1	59,33	10,17	12,06	$C_{13}H_{26}O_3S$
(* X)	03117	Q4*13			59,50 60.94	9,98 7.54	12,22 12.66	a u o o
(Vj)	C_3H_7	C_6H_5	65	Oil	61,39	7,13	12,61	$G_{13}H_{18}O_3S$
(V n)	C ₉ H ₁₉	C_6H_5	70	36-37	67,60	8,82	9,33	$C_{19}H_{30}O_3S$
		ou o	<u></u>		63,02	0,93 7,39	9,41 11,98	Cu Hach-S
(V z)	$C_{3}H_{7}$	p-CH₃C6H₄	85	Oil	62,78	7,51	11,92	G141120€3©

TABLE 1 (continued)

Com-	_	R1	Yield, %	mp, °C	Found Calculated, %			Empirical formula
pound	к				С	Ħ.	s	
(V z ₁)	C_3H_7	p-CH ₃ OC ₆ H ₄	80	Oil	58.84 59,13	7,24 7,09	<u>11,15</u> 11,28	$C_{14}H_{20}O_{4}S$
(V_{Z_2})	$\mathrm{C_7H_{15}}$	p-NO ₂ C ₆ H ₄	65	76-77	57,73 57,44	7,17 7,09	8,81 9,02	$\mathrm{C_{17}H_{25}NO_5S}$

* $\operatorname{RCH}_2 = t - C_4 H_9$.

 $\dagger RCH_2 = C_8H_5$. Compound has been described; see [4].

TABLE 2. Chemical Shifts and Spin-Spin Coupling Constants in Epoxide Ring of Epoxysulfones

			δ,	J. o Hz		
Compound	К	R'	Ηα	Η _β	,°α, p, τ	
(IVb) (IVd) (IVf) (IVh) (VIIIg) (IVm) (IVj) (IVk) (IVn) (IVp) (IVq) (VIIIq)	$\begin{array}{c} C_4 H_9 \\ C_{10} H_{21} \\ C_4 H_9 \\ C_{10} H_{21} \\ CH_3 (CH_2)_6 CD_2 \\ C_2 H_3 \\ C_4 H_9 \\ t-C_4 H_9 \\ t-C_4 H_9 \\ C_{10} H_{21} \\ C_4 H_9 \\ C_{10} H_{21} \\ C_8 H_{17} \\ CH_3 (CH_2)_6 CD_2 \end{array}$	$\begin{array}{c} CH_{3}\\ CH_{3}\\ C_{3}H_{7}\\ C_{3}H_{7}\\ C_{5}H_{7}\\ C_{6}H_{5}\\ c_{6}H_$	$\begin{array}{c} 3,88\\ 3,90\\ 3,88\\ 3,92\\\\ 4,20\\ 4,15\\ 4,25\\ 4,25\\ 4,11\\ 4,05\\ 4,05\\\end{array}$	$\begin{array}{c} 3,65\\ 3,62\\ 3,67\\ 3,60\\ 3,65\\ 4,50\\ 4,47\\ 4,45\\ 4,47\\ 4,80\\ 4,80\\ 4,80\\ 4,80\\ 4,80\\ \end{array}$	1,5 1,55 1,55 1,5 1,5 1,5 1,5 1,5 1,5 1,	

$$RSO_2HC - CHR^1$$
 (IV)

TABLE 3.	PMR Spectra of Epoxysulfones	RCH ₂ SO ₂ HC – C	(V)
		\sim_0	, ,

 CH_3

Com- pound		ð, ppm			Com-	δ, ppin			
	H_{α}	CH3 (E)	CH3 (Z)	E:Z	pound	Hα	$\operatorname{CH}_3(E)$	$\operatorname{CH}_{\mathfrak{z}}(Z)$	E:Z
(Vb) (Vc) (Vd) (Vs) (Vt) (Vu) (Vu) (Vw)	3,70 3,65 3,70 3,77 3,75 3,73 3,73 3,72	1,70 1,67 1,70 1,62 1,65 1,64 1,62	$1,42 \\ 1,41 \\ 1,42 \\ 1,37 \\ 1,37 \\ 1,38 \\ 1,36$	- 7:3 7:3 7:3 7:3 7:3	$ \begin{vmatrix} (V & x) \\ (Vj) \\ (Vn) \\ (Vz) \\ (Vz_1) \\ (Vz_2) \end{vmatrix} $	$\begin{vmatrix} 3,71 \\ 4,23 \\ 4,25 \\ 4,22 \\ 4,35 \\ 4,19 \end{vmatrix}$	1,63 1,84 1,86 1,85 1,83 1,78	1,36 1,50 1,51 1,50 1,49	7:3 96:4 96:4 95:5 7:3 100:0

The integrated intensity of the proton signals of the α , α '-methylene groups of (I) (R = C₃H₇, C₇H₁₅) during the reaction showed that in the presence of weak base, exchange of the chloromethyl protons is relatively fast (85-90% in 30 min). The exchange of the α -methylene protons of the hydrocarbon radical is about 76-81% in 3 days. It follows that the formation of carbanion B is very much faster than that of carbanion A. This circumstance, combined with the high electrophilicity of the C = O bond of the carbonyl addend, must be responsible for the predominant formation of epoxysulfones (IV) in the reaction of aldehydes and ketones with sulfones (I).

Sulfones (I) were condensed with aldehydes and ketones at -5 to $+10^{\circ}$ C in medium of t-BuOH and ether in the presence of an equimolar amount of t-BuOK. Formation of olefins (III) was monitored by GLC. In most cases epoxysulfones (IV) were obtained in good yield (Table 1); the Ramberg-Becklund reaction, which yields olefins (III), practically does not occur at all.

Epoxysulfone (IV) formation is affected substantially by the reaction time, the structure of the carbonyl addend, and the stability of the final product. Thus, condensation of sulfones (I) with benzaldehyde for 15-20 min yields epoxysulfones IVi-IVn with average yields of 80-90%. If the reaction time is prolonged to 3-4 h, the yield falls to $\sim 60\%$

In reactions with aliphatic and aromatic aldehydes the yield of epoxysulfone decreases in the sequence $C_{3}H_{7}CHO > CH_{3}CHO \gg CH_{2}O$ and $p-CH_{3}OC_{6}H_{4}CHO \approx C_{6}H_{5}CHO > o-ClC_{6}H_{4}CHO \gg p-NO_{2}C_{6}H_{4}CHO$ (see Table 1). The relatively high yield of epoxysulfones IVp-r is apparently related to the higher degree of conversion, since unconverted starting compounds and olefins (III) are practically absent from the reaction mixture. The condensation of sulfone (I, $R = C_{7}H_{15}$) with p-nitrobenzaldehyde or formaldehyde stops at the substituted acid chloride stage, VIa and VIb, respectively.

 $\begin{array}{ccc} C_{s}H_{1;}SO_{2}CH_{2}Cl & \xrightarrow{\mathbf{R}^{*}CHO} & C_{s}H_{1;}SO_{2}CH-CHR^{1} \xrightarrow{\mathbf{C}H_{2}O/l-\mathbf{Bu}OK} & C_{s}H_{1;}SO_{2}C(CH_{2}OH)_{2} \\ & & & | & & | \\ (VIa,b) & Cl & OH & & Cl \\ & & & (VII) \\ R^{1} & = p-NO_{2}C_{s}H_{4}(a); H(b). \end{array}$

The acid chloride VIb then condenses with a second molecule of formaldehyde to form diol VII.

In most cases the epoxysulfones IV are crystalline materials, which when pure can be kept for a long time under ordinary conditions without substantial change. But in some cases they cannot be isolated because of their low stability. Thus in the condensation of I, $R=C_7H_{15}$, with p-methoxybenzaldehyde, a 73% yield of 2-octylsul-fonyl-3-(p-methoxyphenyl)oxirane is obtained, which quickly decomposes to a complex mixture of materials of undetermined structure.

The condensation of sulfones I with ketones goes much more smoothly. Here the yields of epoxysulfones V are 85-90% for aliphatic ketones, and 70-80% for aliphatic aromatic ketones. As with the aromatic aldehydes, the epoxy-sulfore stability depends on the nature of the substituent in the aromatic ring of the carbonyl addend. For p-substituted acetophenones the stability increases in the sequence $NO_2 > H > CH_3 > CH_3O$. However epoxide Vn, obtained from acetophenone, is more stable then epoxide IVj, whereas epoxide V z_1) from p-methoxyacetophenone is more stable then the epoxide obtained from p-methoxybenzaldehyde.

Substitution of alkylsulfonyl for arylsulfonyl in sulfones I yields epoxysulfones of significantly lower stability (see [6]).

The structures of epoxysulfones IV and V were confirmed by elemental analysis and IR and PMR spectra. The IR spectra show the absorption bands typical of the SO₂ group (1320-1330 and 1130-1147 cm⁻¹) and the epoxide ring in the 910-930 cm⁻¹ region. For epoxysulfones IVa-d the epoxide band is near 873 cm⁻¹.

For epoxides IV the values of the chemical shifts (CS) of the epoxide ring protons were established by comparing the PMR spectra of IVg, q with their deuteroanalogs VIIIg, q.



CS of the H_{α} protons is 3.89-3.92 ppm for aliphatic derivatives and 4.05-4.25 ppm for aromatic, while that of the H_{β} protons is 3.60-3.67 ppm for aliphatic and 4.45-4.85 ppm for aromatic, respectively (Table 2), which must be taken into account in determining the epoxide structures. The spin-spin coupling constants of H_{α} and H_{β} for all these compounds were 1.5 Hz, which corresponds to a trans configuration for the epoxide (see [6]). Thus the condensation of sulfones I with aldehydes is stereospecific and forms the E isomers of the epoxysulfones IV exclusively.

Epoxide V configuration was determined from the CS of the epoxide methyl, which is 1.62-1.86 ppm for E isomers and 1.36-1.51 for Z isomers (see [8]). In the condensation with unsymmetrical aliphatic ketones and p-methoxyacetophenone, a 7:3 mixture of E and Z isomers was formed (Table 3). Condensation with the other substituted acetophenones is stereoselective to form E isomers predominantly (Vn, z, z₂).

Thus, the features of the condensation of α -chloromethyl alkyl sulfones with aldehydes and ketones are the absence of a competitive Ramberg-Becklund reaction, the stereoselective formation of the E isomers of the α , β -epoxysulfones in the condensations with aldehydes and substituted acetophenones, the formation of E and Z isomer mixtures of the epoxysulfones V in condensations with unsymmetrical aliphatic ketones and p-methoxyacetophenone, and the formation of acid chlorides in the condensations with formaldehyde and p-nitrobenzaldehyde.

EXPERIMENTAL

IR spectra were obtained on a UR-10 spectrometer with KBr for solids and in a thin layer for liquids. PMR spectra were obtained on Varian DA-60-IL and Tesla BS-497 (100 MHz) apparatus in CDCl₃ solution with TMS internal standard. Mass spectra were obtained on a Varian MAT CH-6 apparatus. α -Chloromethylalkyl sulfides were obtained by a modification of the procedure of [11].

 α -Chloromethyl Decyl Sulfide. To a solution of 52.4 g (0.3 mole) of decyl mercaptan in 120 ml of CH₂Cl₂ were added 18 g (0.6 mole) of paraformaldehyde and 30 g of calcined CaCl₂; then at -10 °C a stream of dry HCl was passed in to saturation so that the temperature of the mixture did not exceed -3°C. The mixture was held for 12 h at ~20°C and filtered; the solvent was evaporated and the residue was vacuum distilled. There was obtained 46 g (68.5%) of α -chloromethyl decyl sulfide, bp 115-118°C (2 mm) (see [11]).

The other α -chloromethyl alkyl sulfides were obtained analogously in 70-80% yield; their physical and chemical properties agreed with published values [11-15].

 α -Chloromethyl Decyl Sulfone (I, $R = C_9H_{19}$). To a solution of 5 g (0.022 mole) of α -chloromethyl decyl sulfide in 90 ml of ether at -10° C was added cautiously a solution of 12.4 g (0.066 mole) of monoperphthalic acid in 120 ml of ether so that the temperature did not exceed -5° C, and the mixture was held for 2 days at -3° C. The phthalic acid precipitate was filtered off. The filtrate was washed with NaHCO₃ solution and dried over MgSO₄. The solvent was evaporated and the product was crystallized from hexane. There was obtained 5.4 g (93%) of α -chloromethyl decyl sulfone, mp, 68-68.5°C. Found: C 51.93; H 9.28; S 12.62; Cl 13.95%. C₁₁H₂₃ClO₂S. Calculated: C 51.85; H 9.10; S 12.58; Cl 13.91%.

The other α -chloromethyl alkyl sulfones (I) were obtained analogously. Their physical constants agreed with the published values [12, 13, 15-18].

<u>Non-1-ene</u>. To a solution of 0.68 g (0.003 mole) of α -chloromethyl octyl sulfone in a mixture of 5 ml of t-BuOH and 3 ml of dry ether was added dropwise with stirring a solution of 0.34 g (0.003 mole) of t-BuOK in 3 ml of t-BuOH. The mixture was stirred for 2.5 h at ~20°C and was poured into 50 ml of water, and the product was extracted with ether. The ether extract was washed with water, dried over MgSO₄, and evaporated. From the residue (0.52 g) was isolated 0.27 g of starting material and 0.25 g of non-1-ene (GLC).

Deuterium Exchange between α -Chloromethyl Octyl Sulfone and Deuteromethanol. To a solution of 0.8 g of α -chloromethyl octyl sulfone in 8 ml of deuteromethanol was added 0.2 g of anhydrous Na₂CO₃. The suspension was stirred at ~20°C, and 1 ml portions of solution were removed at specified time intervals. The sample was filtered, the deuteromethanol was evaporated in vacuum, the residue was dissolved in 0.4 ml of deutero-chloroform, 2-3 drops of Cf₃COOH were added, and the PMR spectrum was taken. The course of the deuterium exchange was monitored by PMR from the change in the signals of the RCH₂SO₂ and the SO₂CH₂Cl groups, which have CS (δ , ppm) of 3.23 and 4.57 respectively.

Deuterium exchange between α -chloromethyl butyl sulfone and deuteromethanol was carried out analogously.

<u>2-Octylsulfonyl-3-(o-chlorophenyl)oxirane (IVq).</u> To a solution of 0.45 g (0.002 mole) of α -chloromethyl octyl sulfone and 0.28 g (0.002 mole) of o-chlorobenzaldehyde in a mixture of 6 ml of t-BuOH and 4 ml of dry ether was added dropwise at 0-3°C a solution of 0.28 g of t-BuOK in 2 ml of t-BuOH. The mixture was allowed to warm up to ~20°C and stirred for another 20 min; then 40 ml of water was added and the mixture was extracted with ether. The ether extract was washed with water and dried over MgSO₄, and the solvent was evaporated and the product was crystallized from methanol. There was obtained 0.24 g (35%) of IVq, mp 72-73°C. Found: C 58.24; H 7.22; S 9.65%. C₁₆H₂₃ClO₃S. Calculated: C 58.08; H 7.01; S 9.69%. IR (ν , cm⁻¹): 2960 (CH₃), 2927 (CH₂), 1335, 1138 (SO₂), 920 (epoxy), 760 (CCl). PMR (δ , ppm): 0.88 t (3 H, CH₃), 1.16-2.10 m (12 H, (CH₂)₆), 3.13 t (2 H, CH₂SO₂), 4.05 d (1 H, H_{\alpha}, J = 1.5 Hz), 4.80 d (1 H, H_{\beta}, J = 1.5 Hz), 7.30 m (4 H, C₆H₄).

The other α,β -epoxysulfones were synthesized by the method described; their physical and chemical properties are presented in Table 1.

<u>2-Octylsulfonyl-3-propyloxirane, IV g.</u> From 0.45 g (0.002 mole) of α -chloromethyl octyl sulfone, 0.145 g (0.002 mole) of butyraldehyde, 0.23 g (0.002 mole) of t-BuOK, 8 ml of t-BuOH, and 4 ml of dry ether there was isolated, by the method described for IVq, 0.445 g (85%) of IVg, mp 34-35°C. Found: C 59.38; H 9.96; S 12.33%. C₁₃H₂₆O₃S. Calculated: C 59.50; H 9.98; S 12.22%. IR (ν , cm⁻¹), 2973 (CH₃), 2930 (CH₂), 1323, 1148 (SO₂), 922 (epoxy). PMR (δ , ppm): 0.88 t (3 H, CH₃), 0.93 t (3 H, CH₃), 1.16-2.10 m (18 H, (CH₂)₆ and (CH₂)₃), 3.09 t (2 H, CH₂SO₂), 3.65 m (1 H, H_{\beta}), 3.90 d (1 H, H_{\alpha}, J=1.5 Hz).

<u>1-Octylsulfonyl-1-chloro-2-(p-nitrophenyl)-2-hydroxyethane, VIa.</u> To a solution of 0.68 g (0.003 mole) of α chloromethyl octyl sulfone and 0.45 g (0.003 mole) of p-nitrobenzaldehyde in a mixture of 6 ml of t-BuOH and 4 ml of dry ether was added dropwise at 5°C a solution of 0.34 g (0.003 mole) of t-BuOK in 3 ml of t-BuOH. The mixture was stirred for 30 min at 12-15°C, then was poured into 50 ml of water and acidified weakly with A cOH, and extracted with ether. The ether extract was washed with a small amount of cold water and dried over MgSO₄, and the ether was evaporated. The residue weighed 0.5 g. It was chromatographed on a silica gel column. There was obtained 0.07 g of VIa (6.3%), mp 73-74.5°C. Found: C 50.61; H 6.28; S 8.67; Cl 9.60%. C₁₆H₂₄ClNO₅S. Calculated: C 50.87; H 6.40; S 8.49; Cl 9.39%. IR (ν , cm⁻¹), 2960 (CH₃), 2932 (CH₂), 3510 (OH), 3500-3300 (OH), 1610 (C-C aromatic), 1527 (NO₂), 1350, 1120 (SO₂), 1090 (C-O), 770 (CCl). PMR (δ , ppm): 0.88 t (3 H, CH₃), 1.16-2.10 m (12 H, (CH₂)₆), 3.30 t (2 H, CH₂SO₂), 3.45 s (1 H, OH), 4.72 s (1 H, CH-O), 5.92 s (1 H, CHCl), 7.47-8.25 m (4 H, C₆H₄). Furthermore, 0.25 g of α -chloromethyl octyl sulfone was isolated from the residue.

1-Octylsulfonyl-1-chloro-2-hydroxyethane, VIb, and 2-Octylsulfonyl-2-chloro-1,3-propanediol. VII. A solution of 2.7 g (0.012 mole) of α-chloromethyl octyl sulfone in a mixture of 40 ml of t-BuOH and 26 ml of dry ether was saturated at 5°C with gaseous formaldehyde with simultaneous dropwise addition of a solution of 1.35 g (0.0122 mole) of t-BuOK in 12 ml of t-BuOH over 40 min. The reaction mixture was stirred another 20 min at ~20°C and poured into 300 ml of water. Workup as described above yielded 2.3 g of product which was chromatographed on silica gel. There were obtained 0.4 g of α-chloromethyl octyl sulfone; 0.52 g (17%) of VIb; and 0.8 g (23%) of VII. VIb, mp 47.5-48.5°C. Found: C 46.42; H 8.10; S 12.31; Cl 13.62%, C₁₀H₂₁ClO₃S. Calculated: C 46.77; H 8.24; S 12.49; Cl 13.81%, IR (ν, cm⁻¹): 2962 (CH₃), 2930 (CH₂), 1322, 1143 (SO₂), 1063 (C-O), 3500 (OH), 744 (CCl). PMR (ô, ppm): 0.88 t (3 H, CH₃), 1.16-2.10 m (12 H, (CH₂)₆), 3.14 t (2 H, CH₂SO₂), 3.02 s (1 H, OH), 4.15 d (2 H, CH₂O), 4.51-4.85 m (1 H, CHCl). VII, mp 76.5-77.5°C. Found: C 45.86; H 8.04; S 11.05; Cl 12.21%, C₁₁H₂₃ClO₄S. Calculated: C 46.06; H 8.08; S 11.18; Cl 12.36%, IR (ν, cm⁻¹): 2960 (CH₃), 2930 (CH₂), 1322, 1145 (SO₂), 1072 (C-O), 3500 (OH), 774 (CCl). PMR (ô, ppm): 0.88 t (3 H, CH₃), 1.16-2.10 m (12 H, (CH₂)₆), 1.16-2.10 m (12 H, (CH₂)₆), 3.20 t (2 H, CH₂SO₂), 3.00 s (1 H, OH), 4.15 (2H, CH₂O). The residue consisted of formaldehyde polymers. After prolonged stirring of the reaction mixture at ~20°C, non-1-ene was detected.

 $\frac{2-(1-\text{Dideuterooctyl})\text{sulfonyl-}3-(\text{o-chlorophenyl})-2-\text{deuterooxirane}, \text{VIIIq}.}{\text{of epoxysulfone IVq in 5 ml of deuterated tert-butanol and 1 ml of dry ether was added 20 ml of t-BuOK.}}$ The mixture was stirred for 1 h. 20 ml of hexane was added, and the material was crystallized at -5°C. There was obtained 0.1 g (90%) of VIIIq, mp 72-73°C. IR spectrum was identical with that of the starting epoxide IVq. PMR (ô, ppm): 0.88 t (3H, CH₃), 1.16-2.10 m (12H, (CH₂)₆), 3.13 t (2H, CH₂SO₂), 4.80 s (1H, H_β), 7.30 m (4H, C_eH₄).

2-(1-Dideuterooctyl)sulfonyl-3-propyl-2-deuterooxirane, VIIIg. To a solution of 0.13 g (0.0005 mole) of epoxide IVg in 5 ml of deuteromethanol was added 30 mg of MeONa. The mixture was stirred for 7 h and then treated with dry CO₂. The precipitate was filtered off, the filtrate was evaporated, and the material was crystallized from hexane. There was obtained 0.11 g (85%) of VIIIg, mp 34-35°C. The IR spectrum was identical with that of the starting epoxide IVg. PMR (δ , ppm): 0.88 t (3H, CH₃), 0.93 t (3H, CH₃), 1.16-2.10 m (18H, (CH₂)₆) and (CH₂)₉), 3.09 t (2H, CH₂SO₂), 3.65 t (1H, H_{β}).

CONCLUSIONS

1. The condensation of α -chloromethyl alkyl sulfones with aldehydes and ketones in the presence of potassium tert-butylate forms α , β -epoxysulfones in good yield. Under these conditions the competitive Ramberg-Becklund reaction does not take place.

2. α , β -Epoxysulfones formed from aldehydes and substituted acetophenones have the E configuration, whereas those formed from unsymmetrical aliphatic ketones have a 7:3 mixture of E and Z isomers.

3. The reaction of α -chloromethyl alkyl sulfones with formaldehyde and p-nitrobenzaldehyde stops at the acid chloride stage.

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REACTION OF ALKYLMERCURY AND ALKYLTIN COMPOUNDS WITH DIPHENYLMETHYL SALTS

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Alkyl derivatives of mercury and Group IVB elements containing β hydrogen atoms react with the ionic salts of triarylmethyl to form triarylmethane, an olefin, and the dealkylation product of the organometallic compound (OMC) [1-3]. These reactions are classified as β elimination [4, 5], and it has been shown that they are bimolecular and proceed in a single step, with simultaneous breaking of the β -C-H and C-M bonds (E_E2 elimination). For the reaction of (9-methyl-9-fluorenyl)trimethyltin with triphenylmethyl fluoborate, which also forms triphenylmethane and the corresponding olefin, an oxidation-reduction mechanism that includes a one-electron transfer has been demonstrated [6].

In a continuation of our investigation in a number of transition metal OMC, we have studied the reaction of dialkylmercury and tetraalkyltin compounds with diphenylmethyl salts. Such reactions of tetraalkyltins have not previously been investigated. The reaction of organo-Hg compounds with diphenylbromomethane was studied in [7]. The reaction of the latter with dibutylmercury was carried out under severe conditions, so that the products were butyldiphenylmethane in 35% yield, 1,1,2,2-tetraphenylethane, and the decomposition products of the starting materials.

In the present work, in the reactions with dialkylmercury and tetraalkyltin we used the anionized diphenylmethyl salt, viz., diphenylmethyl fluoborate (DPMF), since it has been shown [4] that in β elimination the reactive molecule is the triarylmethyl cation (or ion pair). DPMF was produced directly in the reaction mixture from Ph₂CHCl and AgBF₄. The solvents were MeCN and nitromethane.

The compounds that we chose: R_2Hg and R_4Sn , Ia-e and IIa-e, (where $R = CH_3$ (a), C_2H_5 (b), $i-C_3H_7$ (c), $i-C_4H_9$ (d), $sec-C_4H_9$ (e) and $n-C_3H_7$ (f)) made it possible to study the effect of the OMC radical on the reaction, in particular the presence of a β hydrogen atom.

I and II were reacted with DPMF at $\sim 20^{\circ}$ C in an Ar atmosphere in the absence of light and moisture (from 20 hto 4 days). The reactions with Ia, b are the slowest. Ha-e react substantially more slowly than do Ia-f. Therefore reaction with II was stopped after a week and the reaction mixture was decomposed by pouring into aqueous KCl. In all cases the starting Ha-e were isolated.

The composition and distribution of the reaction products of I and II depends on the structure of the OMC radical. When there is no β hydrogen in OMC (e.g., in Ia and IIa), the reaction is the slowest and the substitution (metal dealkylation) product, 1,1-diphenylethane, is formed:

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