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FUNCTIONALLY SUBSTITUTED SULFUR-CONTAINING COMPOUNDS.

9.* REACTIONS OF 2-[(ORGANYLTHIO)METHYL]OXIRANES WITH ACETIC ANHYDRIDE AND ACETYL CHLORIDE

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Reaction of 2-[(organylthio)methyl]oxiranes with acetic anhydride gives a mixture of 3-(organylthio)-1,2-diacetoxypropane and 2-(organylthio)-1,3-diacetoxypropane, and with acetyl chloride a mixture of 2-chloro-3-(organylthio)l-acetoxypropane and 3-chloro-2-(organylthio)-l-acetoxypropane. In both cases, the ratio of the isomers depends on the nature of the organylthio group and on the nature of the electrophile.

In the course of a study of the reactivity of 2-[(organylthio)methyl]oxiranes [2, 3], their reaction with electrophiles - acetic anhydride and acetyl chloride - was examined.

It is well known that acetic anhydride and acetyl chloride react with epoxycompounds to form the corresponding diacetoxy and chloroacetoxy derivatives [4]



X -- AcO, CI.

A reaction of this type has not been reported for sulfur-containing epoxides. We have established that the reaction of 2-[(organylthio)methyl]oxiranes (I) with acetic anhydride for 4 h at 130°C and molar ratio 1:1.5 gives a mixture of 3-(organylthio)-1,2-diacetoxypropane (II) and 2-(organylthio)-1,3-diacetoxypropane (III) (Table 1).



It follows that 1,2-migration of the organylthic group takes place in the course of the reaction in a similar way to the reaction of 2-[(alkylthic)methyl]oxiranes with carboxylic acids [5].

*For previous communication, see [1].

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Product	Ratio (II) : (III)	Yield, %	Bp, °C (p, mm Hg)	F Ca	ound lculate	Empirical	
				С	н	s	formula
(Ha)+(HIa)	2 : 3	84	80-82(0.7)	$\frac{49,01}{49,07}$	$\frac{7.37}{7.32}$	$\frac{14.31}{14.56}$	C ₉ H ₁₆ O ₄ S
$(\Pi p) + (\Pi p)$	2:3	87	100(0,5)	$\frac{53,41}{53,20}$	<u>8,09</u> 8,12	$\frac{12,96}{12,91}$	$\mathrm{C_{11}H_{20}O_4S}$
(IIc)+(IIIc)	1:2	80	102-104(2)	$\frac{53,45}{53,20}$	<u>-8,26</u> 	$\frac{12.81}{12,91}$	$\mathrm{C_{51}H_{20}O_4S}$
(IId)+(IIId)	2:3	73	14114 2 (0,5)	<u>59,38</u> 59,18	<u>9,15</u> 9,27	<u>10,72</u> 10,53	$C_{15}H_{28}O_4S$
(IIe)+(IIIe)	2:3	70	162-164(0,5)	$\frac{61.63}{61,41}$	$\frac{9,87}{9,70}$	<u>9,55</u> 9,64	$\mathrm{C}_{17}\mathrm{H}_{32}\mathrm{O}_4\mathrm{S}$
(IIf)+(IIIf)	2:3	72	158-160(3)	$\frac{59,70}{59,55}$	$\frac{-6,55}{-6,43}$	<u>11.61</u> 11.35	$\mathrm{C}_{14}\mathrm{H}_{18}\mathrm{O}_4\mathrm{S}$
(IIg)+(IIIg)	2:3	75	108-110(3)	$\frac{51,58}{51,70}$	$\frac{6.87}{6.64}$	<u>13,95</u> 13,80	$C_{10}H_{16}O_4S$
(IIh)+(IIIh)	1:1	75	148- 150(3)	$\frac{58,08}{58,19}$	<u>-5,93</u> 6,01	$\tfrac{12,21}{11.95}$	$C_{13}H_{16}O_4S$

TABLE 1. Physicochemical Characteristics of Products of Reaction of Epoxysulfides (I) with Ac₂0

TABLE 2. Physicochemical Characteristics of Diols (IV) and (V)

Compound	mp or bp, °C(p, mm Hg)		Empirical		
		С	11	S	formula
(IVb)	120-121(2)	$\frac{50.97}{51,18}$	$\frac{9.93}{9.82}$	$\frac{19,61}{19,52}$	C7H16O2S
(1Vc)	104-105(3)	51.25	9.97	<u>19.76</u>	$C_7 H_{16} O_2 S$
(IVd) * (IVe) †	30-31 42-43	31.10	9.82	19,52	
(I\f) ,	162-165(2)	$\frac{60.68}{60.57}$	7.20	<u>16,09</u> <u>16,17</u>	$C_{10}H_{14}O_2S$
(IVh)∓ (\`b)	71-72 12-14	51.38	$\frac{9.71}{9.82}$	$\frac{19,72}{19.52}$	$C_7 H_{16}O_2 S$
(Vc)	78-79	51.28 51.18	9,08	<u>19.32</u> <u>19.52</u>	$C_7H_{16}O_2S$
(Vd)	4243	$\frac{60,31}{59,95}$	$\frac{10,87}{10,98}$	<u>14,40</u> <u>14,55</u>	$\mathrm{C_{11}H_{24}O_2S}$
(Ve)	54-55	$\frac{63.03}{62.85}$	$\frac{\underline{11,38}}{\underline{11,36}}$	<u>12,83</u> 12,91	$\mathrm{C}_{13}\mathrm{H}_{28}\mathrm{O}_2\mathrm{S}$
$(V_{\mathbf{f}})$	84-85	60.71	7.01	16,37	$\mathrm{C_{10}H_{14}O_2S}$
(Vg) [‡]	.47	60,57	7,12	16.17	

*cf. [6].

[†]cf. [7]. [†]cf. [8].

Deacylation of the mixture of diacetates (II) and (III) with alcoholic alkali solution yields a mixture of the corresponding diols (IV) and (V) from which one or both isomers can be isolated by fractional crystallization (Table 2). It is characteristic for the 1,3-diols (Vb-f) to have higher melting points than the corresponding 1,2-diols (IV), but for (Vh) the reverse is the case.

The ratio of the isomers (II) and (III) in the reaction mixtures was determined from their PMR spectra and is almost independent of the nature of the substituent R (Table 1).

Product	Ratio (VI): (VII)	Yield, %	Bp, °C (p, mm Hg)	Found Calculated				Empirical
				С	н	s	CI	formula
(Vla)+(VIIa)	1:1	80	85-86(3)	$\frac{42.70}{42.74}$	6.62	16.56	18,33	C7H13ClO2S
(VIb) + (VIIb)	1:1	77	108-110(3)	$\frac{48,04}{48,10}$	$\frac{7.56}{7.62}$	14.37 14.26	15,88	$C_9H_{17}ClO_2S$
(VIc) + (VIIc)	2:3	75	91-92(2)	$\frac{48.27}{48.10}$	7,85	14.24	<u>15.77</u> 15.77	C ₉ H ₁₇ ClO ₂ S
(VId) + (VIId)	1:1	70	128-130 (0,8)	$\frac{55.72}{55,59}$	9,13	$\frac{11.27}{11.42}$	$\frac{12,45}{12,62}$	$\mathrm{C_{13}H_{25}ClO_2S}$
$(VI_e) + (VIIe)$	1:1	72	148150(0,7)	$\frac{58,41}{58,32}$	<u>9,38</u> 9,46	10,29	<u>11,37</u> 11,48	$C_{15}\mathrm{H}_{29}\mathrm{ClO}_2\mathrm{S}$
(VIf) + (VIIf)	1:1	65	125 127 (1)	$\frac{55,92}{55,70}$	$\frac{6.01}{5.84}$	$\frac{12.30}{12.39}$	$\frac{13,58}{13,70}$	$\mathrm{C}_{12}\mathrm{H}_{15}\mathrm{ClO}_2\mathrm{S}$
(VIg)+(VIIg)	1:3	70	104-105(2)	$\frac{46,01}{46,04}$	$\frac{-6.20}{-6.27}$	$\frac{15.23}{15,36}$	$\frac{16,91}{16,98}$	$\mathrm{C}_{5}\mathrm{H}_{13}\mathrm{ClO}_{2}\mathrm{S}$
(Vlh) + (Vllh)	2:3	75	117-118(1)	$\frac{54,19}{53.98}$	$\frac{5,46}{5,35}$	<u>12.97</u> 13.10	<u>14,33</u> 14,48	$\mathrm{C}_{44}\mathrm{H}_{43}\mathrm{ClO}_2\mathbf{S}$

TABLE 3. Physicochemical Characteristics of Products of Reaction of Epoxysulfides (I) with AcCl

A mixture of two isomers - 2-chloro-3-(organylthio)-1-acetoxypropane (VI) and 3-chloro-2-(organylthio)-1-acetoxypropane (VII) - is also formed in the reaction of the epoxysulfides (I) with acetyl chloride in molar ratio 1:1.5 at 70-100°C (Table 3).



The ratio of the isomers (VI) and (VII) was determined from their PMR spectra. In this case, the nature of the substituent R has a greater effect on the isomer composition of the product (Table 3) than in the reaction of the epoxides (I) with acetic anhydride (Table 1).

The most probable mechanism for this reaction is the formation of an episulfonium intermediate (EI) which is decomposed by the anion X- to form a mixture of isomers.



The influence of the organylthic group on the isomer composition of the reaction products can be explained in terms of the different stabilizing effect of R on the epoxysulfonium intermediate (VIII) which determines the equilibrium between EI and the open chain form OCF, the latter giving only the isomers (II) or (VI). Hence, the greater the stabilizing effect of R the greater the relative concentration of isomers (III) or (VII) in the reaction mixture. It is well known that the greatest stabilizing effect for such a system is shown by groups with a positive induction or mesomeric effect. In fact, in both cases the greatest selectivity is shown for R = t-Bu and CH_2 =CHCH₂ (Tables 1 and 3) which have the greatest positive induction and mesomeric effect for this series.

The electrophilic reagent also has some effect on the ratio of the isomers. It is characteristic that for reactions of epoxysulfides (I) with acetic anhydride the selectivity is higher if R = alkyl and for reactions with acetyl chloride the selectivity is higher if $R = CH_2$ -CHCH₂ and Ph.

EXPERIMENTAL

IR spectra were obtained on a UR 20 instrument as thin films for liquids or as KBr disks for solids, and PMR spectra on a Bruker WM 250 in $CDCl_3$.

<u>Reaction of 2-[(Organylthio)methyl]oxirane (I) with Acetic Anhydride.</u> A mixture of 50 mmole epoxide (I) and 75 mmoles Ac_2O was heated 1 h at 130°C (4 h for Ig), cooled, and the product isolated by distillation (Table 1). IR spectra (v, cm⁻¹): 1740 (C=O), 1230 (C=O), 1640 (C=C for CH₂=CHCH₂), 1595 (C=C_{arom} for Ph), 1500, 1460 (C=C_{arom} for PhCH₂). PMR spectra (δ , ppm): for ((IIa-g) + (IIIa-g)): 2.60-2.68 d (CH₂S), 3.00-3.04 m (CHS), 4.25 m (CH₂OAc) and 5.05-5.07 m (CHOAc), for ((IIh) + (IIIh)): 3.15 d (CH₂S), 3.54 m (CHS), 4.25 m (CH₂OAc), 5.06 m (CHOAc).

<u>Deacetylation of Reaction Products.</u> To a solution of 50 mmoles diacetates (II) and (III) in 15 ml MeOH was added a solution of 75 mmoles KOH in 15 ml MeOH and the mixture stirred 20 min at 25-30°C. The solvent was evaporated, the residue diluted with water and the product extracted with ether. The extract was dried over MgSO₄, evaporated, and the residue fractionally crystallized from a hexane-ether mixture to separate the diols (IV) and (V) (Table 2). IR spectra (\vee , cm⁻¹): 3600-3100 (OH), 1050 (C-O); 620 (C-S), 1590 (C-C_{arom} for Ph). PMR spectra (δ , ppm) (IV): 2.67-2.70 d (CH₂S for (IVb-f)), 3.00 d.d (CH₂S for (IVa)), 3.54 d (CH₂O), 3.73-3.80 m (CHO), 3.80-4.00 s (OH); (V): 2.78-2.81 m (CHS), 3.67-3.70 d (CH₂O), 3.35-3.90 s (OH).

<u>Reaction of 2-[(Organylthio)methyl]oxiranes (I) with Acetyl Chloride.</u> A mixture of 50 mmoles of epoxide (I) and 75 mmoles of AcCl was heated from 70 to 100°C and held at this temperature for 15 min (40 min for Ig). It was then cooled and the product separated by distillation (Table 3). IR spectra (ν , cm⁻¹): 1745 (C=O), 1230 (C-O), 750 (C-Cl), 620 (C-S), 1590 (C-C_{arom} for Ph), 1500, 1460 (C-C_{arom} for PhCH₂), 1640 (C=C for CH₂= CHCH₂). PMR spectra (δ , ppm) (VIa-g) + (VIIa-g): 2.80-2.88 d (CH₂S), 3.00-3.08 m (CHS), 3.64-3.72 m (CH₂Cl), 4.05-4.12 m (CH₂OAc), 4.27-4.34 m (CHOAc); ((VIh) + (VIIh)): 3.30 d.d (CH₂S), 3.52 m (CHS), 3.73 d (CH₂Cl), 4.12 m (CH₂OAc), 4.40 m (CHOAc).

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