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THE GENERATION AND PROPERTIES OF EPISULFONIUM INTERMEDIATES. 8.* REGIOSELECTIVITY IN THE NUCLEOPHILIC RING OPENING OF EPISULFONIUM ION DERIVATIVES OF SOME UNSYMMETRICAL ALKYL- AND ARYLOLEFINS

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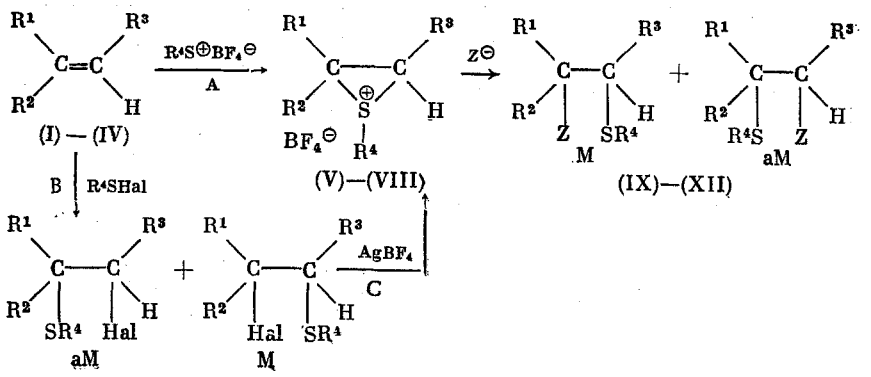
Episulfonium ion (ESI) derivatives of propylene and isobutylene are converted upon reaction with nucleophiles ($Z^{\ominus}$) to β-substituted thioethers, and M adducts greatly predominate in the mixture of M and aM adducts† formed [2, 3]. In order to determine whether this behavior is general, we studied the possible generation and regioselectivity of ring opening of ESI obtained from unsymmetrical alkenes: trimethylethylene (I), isopropylethylene (II), styrene (III), and 2,3,4,5,6-pentafluorophenylethylene (IV).

The conversion of these alkenes to ESI was carried out in accord with our previous methods [4]: by the reaction of the alkene with $RS^+BF_4^-$ (obtained in solution by the reaction of RSCl with $AgBF_4$) (path A) or through a step of the corresponding β-halothioethers with their subsequent treatment with a solution of $AgBF_4$ (path B + C) (see Scheme 1)

Scheme 1



$R^1 = R^2 = R^3 = Me$; $R^4 = Ar$ (I), (V), (IX); $R^1 = i\text{-}Pr$, $R^2 = R^3 = H$; $R^4 = Ar$ (II), (VI), (X); $R^1 = Ph$, $R^2 = R^3 = H$; $R^4 = Me$ (III), (VII), (XI); $R^1 = C_6F_5$, $R^2 = R^3 = H$; $R^4 = Me$ (IV), (VIII), (XII).

For the case of formation of the ESI of (V), $R^4 = 4\text{-}ClC_6H_4$, the ^{13}C NMR spectra support the structure presented for this complex (the chemical shifts of the bridge ^{13}C nuclei are 72.97 (^{13}CH) and 88.76 ($^{13}CR^1R^2$), compare with values for the derivatives of propylene, isobutylene [3], and di-tert-butylethylene [5]). The structures of the remaining ESI were taken by analogy.

The solutions of the ESI of (V)-(VIII) obtained were then reacted with various nucleophiles $Z^{\ominus}$ ($Z^{\ominus} = OCOMe^{\ominus}, MeO^{\ominus}, HO^{\ominus}, H^{\ominus}$), leading to the formation of the corresponding cova-

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†Here and subsequently, the terms M and aM refer to products of addition according and opposite to the Markownikoff rule (RS^+ is the electrophile).

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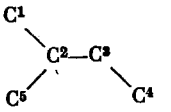
TABLE 1. Data on Reactions of Episulfonium Ions

Alkene	Electrophile $R'S^+$	Nucleophile, Z^- (base)	Product	Yield, %	Comp. M	Comp. aM	Found/calculated, % C	H	S	Hal
$Me_2C{=}CHMe$ (I)	$4\text{-}ClC_6H_4S^+$	MeCOO⁻ (MeCOONa+MeCOOH)	(IXa)	88	90	10	–	–	11,63 11,75	12,86 12,99
	The same	H⁻ [$(n\text{-}C_4H_9)_4NBH_4$]	(IXb)	75	90	10	61,21 61,52	7,21 7,04	14,97 14,92	16,54 16,50
$Me_2CHCH{=}CH_2$ (II)	»	MeCOO⁻ (MeCOONa+MeCOOH)	(Xa)	80	30	70	57,29 57,24	6,41 6,28	11,72 11,75	12,86 12,99
	$4\text{-}CF_3C_6H_4S^+$	The same	(Xb)	79	47	53	54,90 54,89	5,94 5,60	10,38 10,47	17,71 18,60
$PhCH{=}CH_2$ (III)	MeS⁺	MeCOO⁻ (MeCOOH)	(XIa)	52	95		62,86 62,86	7,04 6,67	15,53 15,24	–
	MeS⁺	MeO⁻ (MeOH)	(XIb)	67	95		65,98 65,93	7,81 7,69	17,25 17,58	–
	MeS⁺	HO⁻ (HOH)	(XIc)	42	95		64,57 64,29	7,36 7,14	18,47 18,05	–
	MeS⁺	HCOMe⁻ [MeCN(a), HOH(b)]	(XId)	20*	95		63,43 63,16	7,45 7,18	14,91 15,31	–
$C_6F_5CH{=}CH_2$ (IV)	MeS⁺	MeCOO⁻ (MeCOOH)	(XIIa)	54	95		41,61 41,86	2,60 2,71	–	–
	MeS⁺	MeO⁻ (MeOH)	(XIIb)	76	95		43,27 43,38	3,53 3,31	–	–
	MeS⁺	HO⁻ (HOH)	(XIIc)	48	95		41,95 41,67	3,53 3,12	–	–

*In addition to (XId), 20% hydroxy product (XIc) was isolated.

TABLE 2. PMR Spectral Data for Adducts (IX) and (X)*



R⁴	Adduct	M/aM	Signal of protons at carbon atoms, J, Hz			
			C¹, ⁵	C²	C³	C⁴
SAr; OAc	(IXa)	M	1,52 s	–	3,96 q, J=7	1,27 d, J=7
		aM	1,20 s	–	4,81 q, J=7	1,21 d, J=7
SAr; H	(IXb)	M	0,99 d, J=7	1,81 m	3,04 m	1,19 d, J=7
		aM	1,19 s	–	1,45 m	†
			†	2,05 m	4,7 m	2,9 d, J=6
ArS; AcO	(Xa)	M	1,05 d } J=6–7†	2,05 m	3,1 d.t, J_{HCH}=7, J_{HCH_2}=4	4,08 d, J=7
		aM	0,99 d }			
ArS; AcO	(Xb)	M	1,11 d } J=9	2,06 m	4,78 m	3,06 m
			1,03 d }			
		aM	0,93 d } J=7	2,06 m	3,36 m	4,16 m
			0,92 d }			

*The spectra were taken for 20% solutions in CCl_4 and the chemical shifts are given in the δ scale from TMS, coupling constants (J), Hz. Aromatic proton signals are found in the spectra of all adducts at 7.2 ppm and, in the spectra of (IXa), (Xa), and (Xb), MeCOO group singlets are found at 1.88-1.94 ppm.
†The signals of the two isomers overlap.

lent adducts (IX)-(XII) (see Scheme 1 and Table 1). The structures of the adducts were found on the basis of analytical and spectral data (Tables 1-3).

The isomeric composition (Table 1) was determined by the relative integral intensities of the nonoverlapping signals of the isomers in the PMR spectra of the mixtures formed.

It was of interest to compare the regioselectivity of the formation of adducts (IX)-(XII) of the addition of RSHal to the same alkenes according to literature data. Such a comparison is even more justified since it has been specially shown in this work (as in our previous work [3]) that the regioselectivity of ring opening of the ESI [for example, (V)] is only slightly sensitive to changes in the nature of the solvent (liquid SO_2, CH_2Cl_2 – $C_2H_4Cl_2$, and $MeNO_2$) or the nucleophile [compare the M:aM ratio for (IXa) and (IXb)].

It is well known that the addition of ArSCl to (I) gives primarily aM isomers (M:aM = 35:65, Ar =4-ClC_6H_4 [6]). Almost exclusive formation of aM isomers is also found for the reaction with (II) (M:aM =13:88, Ar =Ph [7]; $\geqslant$ 5:95, Ar =4-ClC_6H_4 [8] or 2,4-$(O_2N)_2C_6H_3$ [9]). According to the generally accepted mechanism for the Ad_E reaction of sulfenechlorides [6-9], the rate-limting step for alkenes (I) and (II) is the formation of the episulfonium ions (V) and (VI) (with chloride counterion). In order to explain the observed regioselectivity in the formation of the chloro adducts, it was previously postulated that the ring opening of these ESI is controlled mainly by substituent steric effects, and, thus, the attack of the chloride nucleophile is directed predominantly toward the least hindered carbon atom.

However, these experimental results on the direction of reactions of (V) and (VI) with nucleophiles indicate the lack of substance of this line of reasoning. Indeed, the presence of two geminal methyl groups in (V) does not pose any steric hindrance for the approach of the nucleophile toward this center, and ring opening in (V) is accomplished according to the generalized Markownikoff rule with the formation of M isomers. The reaction of (VI) proceeds less unequivocally; (VI) contains a bulky isopropyl group but, in this case, the formation of comparable amounts of M and aM adducts (see Table 1) clearly indicates the importance of electronic factors controlling the course of the reaction. Apparently, the role of the steric factor becomes predominant only in the case of the tertiary butyl substituent since, as shown in our earlier work [10], nucleophilic ring opening of the corresponding S–Ph and S–Me of ESI in this case leads to the exclusive formation of aM adducts.

In the case of the ESI of (VII) and (VIII), the regioselectivity in the formation of the corresponding adducts (XI) and (XII) indicates selective attack of the nucleophile on the

TABLE 3. PMR Spectral Data for Adducts $ArCH(Z)CH_2SMe$*

Adduct	CH(Z)	CH_2S	Z	MeS
(XIa)	5,82 d.d , J_{AX}=6, J_{BX}=7,5	2,72 d.q , J_{AB}=14,5	1,97 s (MeCOO)	1,97 s
(XIb)	4,22 d.d, J_{AX}=6, J_{BX}=7,3	2,56 d.q , J_{AB}=14,0	3,17 s (OMe)	1,93 s
(XIc)	4,57 d.d	2,60 m	3,55 s (OH)	1,90 s
(XId)	5,1 q , J=6–7	2,80 d, J=6,5	1,92 s (MeCO)	1,92 s
			6,5 br. d (NH)	
(XIIa)	6,05 d.d , J_{AX}=6, J_{BX}=7,5	2,97 d.q , J_{AB}=13	2,04 s (MeCOO)	2,14 s
(XIIb)	5,06 d.d	2,72 d.q	3,50 s (OH)	2,12 s
(XIIc)	4,74 d.d	2,92 d.q	3,30 s (MeO)	2,12 s

*The PMR spectra were taken for 20% solutions in CCl_4 with TMS as internal standard, except for the spectrum of (XId), which was taken in $CDCl_3$ with HMDS. The integral intensities correspond to the assignments derived and the chemical shifts are given in the δ scale, J, Hz. Aromatic proton signals are also found in the spectra of adducts (XI) at 7.2-7.4 ppm.

more substituted center in accord with the Markownikoff rule. Such a high selectivity is characteristic for the addition of RSCl to these alkenes (M:aM =98:2 for MeSCl [6], ⩾95:5 (Ar =4-ClC_6H_4 and 2,4,6-$Me_3C_6H_2$) for (III), ⩾ 95:5 (Ar = 4-ClC_6H_4), 86:14 (Ar = 2,4,6-$Me_3C_6H_2$) for (IV), present work). Thus, a uniform regioselectivity is found in the case of arylethylenes for the two reactions compared, namely, the ring opening of ESI by the action of nucleophiles and the formation of β-chlorothioethers in the addition of RSCl. Therefore, there is apparent justification for this type of alkenes to consider the mechanism for the latter reaction in terms of the intermediate formation of ESI. An apparent factor facilitating such a mechanism and producing such a high selectivity in the ring opening of the ESI found of (VII) and (VIII) is the presence of an aryl group capable of stabilizing a neighboring carbocation center by direct conjugation.

EXPERIMENTAL

The GLC analysis was carried out on OV-101, OV-17, and GE-XE-60 stationary phases on Chromosorb (3-5% by weight) on a 1-2 m ×4 mm column on an LKhM-8MD chromatograph with flame-ionization detector. The mass spectra were recorded on a Varian CH-6 spectrometer. The PMR spectra were taken on Varian DA-60-IL and Bruker WP-60FT spectrometers at 60 MHz and on a Tesla BS-497 spectrometer at 100 MHz. The ^{13}C NMR spectra were taken on a Bruker WP-60FT spectrometer at 15.08 MHz.

The preparative separation was carried out on 24 ×24 cm glass plates covered with 2-mm-thick silica layers. The solvents were purified and dried according to standard methods. All the operations for the generation of ESI and their reactions with nucleophiles were carried out in a stream of dry argon.

Arylsulfenechlorides were obtained analogously [7, 11]; β-Cl-thioethers were obtained from (I) and (II) according to Schmid et al. [6, 8].

The ESI of (V) was prepared, for ^{13}C NMR spectroscopy, directly in a 1.5-ml NMR tube by mixing 2.25 mmoles $AgSbF_6$ in 1 ml liquid SO_2 at −70°C with 2.0 mmoles 2-Cl-2-Me-3-(4'-Cl-phenylsulfenyl)butane for 40 min. The tube was sealed and the spectrum was recorded at −70°C with HMDS external standard. The ESI of (V) for reaction with nucleophiles was prepared analogously in 10-15 ml liquid SO_2 or 5:1 CH_2Cl_2 –$C_2H_4Cl_2$ (for 40 min at −40°C for the latter mixture).

The ESI of (VI) was prepared by the reaction of 2.0 mmoles (II) with 2.0 mmoles $ArS^+SbF_6^-$, obtained directly in the reaction medium from 2.0 mmoles ArSCl and 2.2 mmoles $AgSbF_6$ in 15 ml liquid SO_2 for 10 min at −25°C. After the introduction of (II) at −50°C, the ESI was maintained for an additional 10 min at this temperature.

ESI of (VII) and (VIII). Path A. A sample of 2.6 mmoles $(MeS)_2$ was treated with 2.5 mmoles Br_2 in 5 ml CH_2Cl_2 for 10 min at −25°C. The MeSBr formed was treated with 5.0 mmoles $AgBF_4$ for 10 min at −50°C. Then, 5.0 mmoles of the corresponding styrene (III) or (IV) was introduced at −50°C and maintained for 10 min.

Path B + C: A sample of MeSCl was obtained from 2.5 mmoles $(MeS)_2$ and 2.5 mmoles SO_2Cl_2 at −20°C for 10 min, and then we added 5.0 mmoles (III) or (IV) in 5 ml CH_2Cl_2 to this sample. The chloro adduct formed was treated for 10 min with 5.0 mmoles $AgBF_4$ at −50 to −40°C.

The prepared ESI of (V)-(VIII) were treated with a two- to fivefold excess of base (see Table 1). The reaction mass was extracted with ether and the extract was washed with aq. $NaHCO_3$ and dried over Na_2SO_4. The ether was removed to yield a residue which was purified by TLC on silica with 8:2 hexane−ether eluant for (IX) and (X) and 10:1 benzene−ethyl acetate for (XI) and (XII). The characteristics of (IX)-(XII) are given in Tables 1-3.

Addition of ArSCl to (III) and (IV). Equivalent volumes of 1.25 M solutions of the reagents in $CDCl_3$ (+ 1% TMS) were stirred in an NMR tube and the spectrum was taken at −60°C. The reaction with (III) was carried out at −60°C, while the reaction with (IV) was carried out at −20°C. Complex multiplets are found in the PMR spectra of the chloro adducts in addition to the aromatic proton signals:

		$C_6R_5-CH(Cl)-CH_2S$			CH_2Cl	Isomer	%
		CHCl	CH_2S	CHS			
R=H	Ar=4-ClC_6H_4	4,73	3,46	–	–	M	95
R=F	The same	5,07	3,60	–	–	M	95
R=H	Ar=2,4,6-$Me_3C_6H_2$	4,77	3,46	–	–	M	95
R=F	The same	5,15	3,45	–	–	M	86
R=F	»	–	–	4,3*		aM	14

*Overlapping multiplets. The presence of 14% aM isomer is also evident in the appearance of two aromatic proton singlets at 6.73 and 6.86 ppm for M and aM, respectively.

CONCLUSIONS

The ring opening of episulfonium complex derivatives of trimethylethylene, styrene, and 2,3,4,5,6-pentafluorophenylethylene proceeds with the predominant formation of adducts according to the Markownikoff rule, while this reaction yields comparable amounts of the regioisomers for isopropylethylene.

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