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THE REGIOSELECTIVITY OF EPISULPHONIUM RING OPENING. THE EVIDENCE AGAINST THE INVOLVEMENT OF EPISULPHONIUM INTERMEDIATES IN Ad_E - REACTIONS OF SULPHENYL HALIDES UNDER NON-POLAR CONDITIONS

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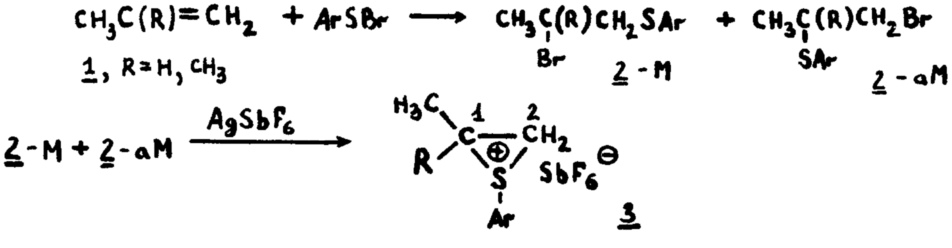
According to the generally held view the Ad_E-reaction of sulfenyl halides with alkenes proceeds via intermediate formation of episulfonium ions /1/. One of the peculiar features of this reaction is the preferential formation of anti-Markovnikov's adducts for the additions to unsymmetrical alkenes. Thus for the addition of RSHal to propene (1, R=H), or 2-methylpropene (1, $R=CH_3$) the ratio of M:aM/2/ was found to be: 32:68 (R=H, $Ar=C_6H_5$, Hal=Cl/3a/); 38:62 (R=H, $Ar=4\text{-}ClC_6H_4$, Hal=Cl/3b/); 23:77 (R=H, $Ar=2,4,6\text{-}(CH_3)_3C_6H_2$, Hal=Br/3c/); 14:86 ($R=CH_3$, $Ar=C_6H_5$, Hal=Cl/3d/); 12:88 ($R=CH_3$, $Ar=4\text{-}ClC_6H_4$, Hal=Cl/3e/).

To reconcile this unusual (for the Ad_E process) regioselectivity with the postulated ionic mechanism it has been assumed /1,3a,b,d,e/ that the positive charge in the episulfonium ions resides mainly at sulfur atom and due to this reason the direction of their opening under nucleophilic attack is controlled not by electronic factors (+ I-effects of CH_3-group(s)) but by the steric hindrance to the nucleophile approach to the more substituted carbon atom.

The purpose of the presented study was to prepare the stable S-arylepisulfonium salts from 1 (R=H or CH_3) in order to check experimentally the validity of the above mentioned argumentation.

Propen (1, R=H) and 2-methylpropene (1, $R=CH_3$) were converted into respective episulfonium salts (3, R=H or CH_3) following the previously described procedure /4/ shown on the Scheme 1.



SCHEME 1

The transformation 2→3 proceeds smoothly at -50° and is essentially complete within 1-2 hours as judged by CMR spectral data and the high yields of the adducts formed upon the quenching of reaction mixtures with appropriate nucleophiles (see below).

The identity of the prepared complexes as episulfonium salts was deduced from CMR data (see Table 1) which revealed the substantial deshielding of $^{13}C_1$ and $^{13}C_2$ ring carbons in comparison to the respective CMR signals of covalent episulfides (for 3, R=H $\Delta\delta_{C_1}$ 27.2-38.7, $\Delta\delta_{C_2}$ 20.1-25.6; cf/5/).

Table 1.

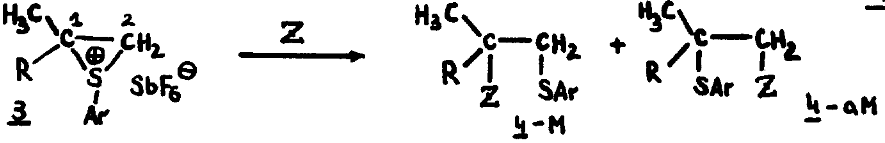
CMR-spectra of 3 /6/

	Ar	CH_3	C_1	C_2
R=H	$4-CH_3C_6H_4$	16.6	62.3	50.6
	$2,4,6-(CH_3)_3C_6H_2$	16.6	69.2	54.4
	$4-ClC_6H_4$	15.0	62.4	49.5
	$4-CF_3C_6H_4$	16.8	66.4	50.9
	C_6F_5	15.9	74.0	54.9
$R=CH_3$	$2.4,6-(CH_3)_3C_6H_2$	19-20	91.6	54.9

The stability of 3 as 1 molar solutions in liquid SO_2, CH_3NO_2 or CH_2Cl_2-$C_2H_4Cl_2$ at-70 ÷ - 30° varies from one hour (for 3, R=H, $Ar=C_6H_5$) up to several weeks (for 3, R=H, $Ar=2,4,6-(CH_3)_3C_6H_2$).

The prepared solutions of 3 were treated with different nucleophiles /7/ and the resulting adducts 4 (see scheme 2) were isolated and identified by their analytical and spectral data /8/.

Scheme 2



The high yields of adducts 4 /7/ obtained in these quenching reactions clearly indicate that the nucleophile attack occurs predominantly (if not exclusively) at the carbon atoms of episulfonium ring. The data on the isomeric composition of 4 (M:aM) /9/ given in the Tables 2 and 3 reveal that the preferable site of this attack is methyl(s) bearing carbon of the episulfonium ring /10/.

Table 2

The ratio of M:aM isomers in adducts $4(Z=OCOCH_3)$ for various Ar

	$Ar=C_6H_5$	$4-CH_3C_6H_4$	$2,4,6-(CH_3)_2C_6H_2$	$4-ClC_6H_4$	$4-CF_3C_6H_4$	C_6F_5	$2,4-(O_2N)_2C_6H_3$
R=H	72 : 28	66 : 34	53 : 47	70 : 30	69 : 31	64 : 36	81 : 19
$R=CH_3$	>95:5		>95:5	>95:5			

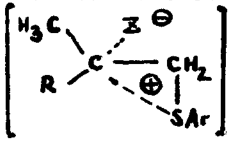
Thus for 3 ($R=CH_3$) the adducts 4 contain more than 95% of Markovnikov's isomers the ratio M:aM being essentially insensitive to the changes of S-aryl substituent or the base used for quenching. Similar pattern is observed for propene derived $\underset{\sim}{3}$ but in this case the regioselectivity of the process was shown to depend to some extent on the nature of aryl substituent and on the nature of attacking nucleophile.

Table 3.

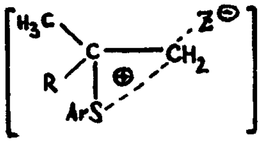
The ratio of M:aM isomers in adducts $\underset{\sim}{4}$ ($Ar=C_6H_5$) for various Z

	Z=$OCOCH_3$	OH	OCH_3	F	$NHCOC_6H_5$	(a)C_6H_5ON(b)H_2O
R=H	72:28	90:10	92:8	>95:5	>95:5	
R=CH_3	95:5		95:5			

These data clearly show that (i) contrary to expectations /1/ the presence of methyl group(s) at the episulfonium ring carbon does not create any substantial steric hindrance to the nucleophilic attack at this center /11/ and (ii) the regioselectivity of this process is controlled by the usual electronic effects (+I-effect of methyl(s) group plus sulfur atom participation) which determine the relative stabilities of the two alternative transition states $M^{\ddagger}$ and a $M^{\ddagger}$.



$M^{\ddagger}$



$aM^{\ddagger}$

The presented results about Markovnikov's regioselectivity of the episulfonium ring opening /12/ show striking difference on comparison with the anti-Markovnikov's course of RSHal addition to the same alkenes. Hence the generally adopted /1,3/ interpretation of the regioselectivity of the latter process (quoted at the beginning of this paper) should be abandoned as incompatible with the experimental facts.

Moreover we belive that an ever-increasing amount of experimental data on the chemical reactivity pattern of episulfonium ions /13/ justifies the general conclusion that these ions are unlikely candidates for the intermediates in Ad_E-reactions of covalent sulfenyl halides under non-polar conditions. The alternative formulation of the structure of this intermediate as the covalent bridged σ-sulfurane /14/ seems to be more compatible both with the presented results and the evidence published earlier /13,15/.

REFERENCES

1. W.H.Mueller, Angew.Chem., Int.Ed., $\underline{8}$, 482 (1969).
2. Everywhere in this paper designations M and aM refer to the products resulting from the Markovnikov or anti-Markovnikov addition of RSY (electrophile-RS^+) respectively.
3. a) W.H.Mueller, P.E.Butler, J.Amer.Chem.Soc., $\underline{90}$, 2075 (1968). b) G.H.Schmid, D.Garrat, Can.J.Chem., $\underline{51}$, 2463 (1973); c) W.A.Smit et al., in press; d) M.Oki et al., Chem.Lett., $\underline{1975}$, 1277; e) G.H.Schmid et al., Can.J. Chem., $\underline{54}$, 1253 (1976).
4. E.A.Vorobieva et al., Izvestia Acad.Nauk SSSR, ser.chim., $\underline{1975}$, 125
5. Closely similar $\Delta\delta$ values were reported for S-methylepisulfonium salt of cis-2,3-di-tert-butyl episulfide by P.Raynolds et al., J.Amer.Chem.Soc., $\underline{96}$, 3146 (1974).
6. CMR spectra were recorded with Bruker WP-60 spectrometer at 15.08 MHz for 1 molar solutions in liquid SO_2 at -70° with the use of TMS as internal standart for all $\underset{\sim}{3}$, except $\underset{\sim}{3}$, R=H, $Ar=C_6F_5$ which was registered with external

standart (TMS). For propene derived 3 (R=H) the double set of closely similar ^{13}C-signals was observed evidently due to the presence of both possible syn- and anti-stereoisomers; the figures given in the Table 1 refer to the signals of higher intensity presumably ascribed to the more stable anti-isomer (cf. corresponding data for epi-selenium ions given by G.H.Schmid, D.G. Garrat, Tetrahedron Letters, 1975, 3991). Besides the signals given in the Table 1 all the spectra reveal the presence of the corresponding signals of aromatic residue.

7. The following standart procedure was used for the quenching: the solution of 3 was treated at -50° with the excess of the corresponding nucleophile dissolved or suspended in the same solvent. The mixture was kept for an hour at -50°, then allowed to warm up to ambient temperature and treated with aq. $NaHCO_3$-ether mixture. Ether extracts were washed with water and dried over Na_2SO_4. The removal of the solvent yields essentially pure adducts 4, which could be easily purified (if necessary) by t.l.c. Generally the yields of analytically pure adducts were higher than 85% for 4, R=H and about 80% for 4, $R=CH_3$.

8. Spectral data (PMR, IR, MS) are consistent with the structures shown for adducts 4. Satisfactory combustion analysis were obtained for all the new compounds described in this paper.

9. The ratio of M:aM for adducts 4 was determined by the integration of nonoverlapping signals in PMR spectra recorded at 60 MHz and 100 MHz and additionally substantiated (for several cases) by glc.

10. The data of the Tables 2 and 3 refer to the reactions in liquid SO_2. Control experiments (e.g. for the formation of 4, R=H or CH_3, $Ar=C_6H_5$, $Z=OCOCH_3$ or OCH_3) gave closely similar values for the reactions in CH_3NO_2 or CH_2Cl_2-$C_2H_4Cl_2$ The ratio of M:aM was found to be insensitive to the degree of conversion 3 → 4 (checked for the reaction 3, R=H, $Ar=4\text{-}ClC_6H_4$ with CH_3COOH-CH_3COOK in CH_2Cl_2-$C_2H_4Cl_2$ at -50° stopped by the addition of aq. $NaHCO_3$ after 5, 15 or 60 min intervals). Hence the figures given in the Tables 2 and 3 refer to the kinetically controlled process.

11. The steric factors could affect the regioselectivity of this reaction in case of the bulky substituents and the exclusive formation of aM isomers was observed for nucleophilic opening of 3, $R=C(CH_3)_3$, $Ar=C_6H_5$ (E.Vorobieva et al. Izvestia Acad.Nauk, ser.chim., 1976, 1318.

12. The isolated case of the predominant formation of M isomer was reported for the reaction of 3, $R=CH_3$, $Ar=C_6H_5$ with CH_3ONa in liquid SO_2 (see ref.3d), but this result was considered as abnormal and was ascribed to the effect of specific solvatation.

13. The comparison of other experimental data on the chemical behavior of episulfonium ions with their postulated reactivity pattern was discussed earlier. (W.A.Smit et al. Tetrahedron Letters, 1975, 2451).

14. This structure was originally suggested by G.Helmkamp (J.Amer.Chem.Soc., 91, 5239 (1969); recent ab initio calculations for the model process demonstrated the palatability of this formulation. (V.M.Cizmadia et al., J.Chem.Soc. Perkin II, 1977, 1019).

15. Experimental data of N.S.Zefirov et al. (Intern.J.Sulfur.Chem. 3, 213, 1974). clearly indicates that Ad_E -reaction of covalent RSHaL could be made to proceed via the intermediates closely similar to episulfonium ions when carried out in the presence of perchlorates and in polar solvents (e.g.HCOOH).