REGIOSPECIFIC MARKOVNIKOV OPENING OF 1,1-DIMETHYL-S-ARYLEPISULFONIUM IONS BY NUCLEOPHILES

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It is known [1] that the Ad_E reaction of sulfenyl halides with terminal alkenes leads to the predominant formation of anti-Markovnikov adducts, in which connection this regioselectivity is increased when going from propylene to isobutylene [2]. In order to reconcile this anomaly (for the Ad_E process) with the generally accepted mechanism of the reaction, which postulates the intermediate formation of a bridge cationoid intermediate, the episulfonium ion (ESI), it was postulated in [3] that the direction of opening the latter is controlled mainly by steric, and not by electronic factors, i.e., by the presence of CH_3 groups, which block the approach of the nucleophile to the more substituted center. However, recently it was found [4] that the opening of S-arylepisulfonium ions that represent propylene derivatives is accomplished chiefly as the result of the nucleophile attacking the methine C atom, i.e., it is controlled by the usual electronic effects.

The purpose of the present paper * was to study the regioselectivity of the reactions of nucleophiles with ESI that represent isobutylene derivatives, for which, on the basis of [1, 2], it could be expected that steric factors will play an important role in controlling the regioselectivity of the process.

The ESI were obtained by standard methods in harmony with Scheme 1.

Scheme 1 † $Me_{2}C = CH_{2} + ArSHal \rightarrow Me_{2}C(Hal)CH_{2}SAr + Me_{2}C(SAr)CH_{2}Hal$ (I) (III (IIIa-c) M (IIIa-c) aM (IIIa-c) M + aM $\xrightarrow{AgSbF_{4}} Me_{2}C - \overset{2}{C}H_{2}$ $\overset{+}{S}SbF_{6}^{-}$ (IVa-c) $\overset{-}{Ar}$ Ar = Ph (a), 4-ClC₆H₄(j, 2, 4, 6-Me_{3}C₆H₂(c)

In liquid SO₂ solutions the precipitation of AgCl from (IIIa, b) (Hal = Cl) was quite complete at -70 to -50°C in 30-40 min, while in the case of (IIIc) it was slow at the indicated temperatures and consequently (IVc) was obtained from the bromo adduct (IIIc) (Hal=Br).

Compounds (IVa-c) proved to be less stable in concentrated solutions than their propylene analogs, and consequently only (IVc) could be characterized via the ¹³C NMR spectrum (δ , ppm, relative to HMDS): 91.7 (¹³C₁), 54.9 (¹³C₂), 19.0 (¹³CH₃ at C₁); the noticeable ($\Delta \delta \simeq 22$) paramagnetic shift for C₁ when compared with the signal of this center in the propylene analogs [4] is evidently explained by the presence of an additional CH₃ group in (IVc) (cf. with the data for halonium ions [6]).

Compounds (IVa-c) proved to be quite stable in more dilute solutions (0.1-0.3 M), which made it possible to study their reaction with nucleophiles. Thus, the reaction of (IVa-c) with a MeCOOH – MeCOOK mixture in liquid SO₂ leads to the formation of acetoxy adducts (Va-c) in 72-91% yields.



* See [5] for preliminary communication.

 $\dagger M$ and $\mathbf{a}M$ are the addition products of the electrophile (ArS^{\oplus}) and nucleophile in harmony with the Markovnikov rule and contrary to it.

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The structure of (Va-c) as being aryl (2-methyl-2-acetoxy)-1-propyl sulfides was proved via the PMR spectra: singlets of Me₂ (1.41-1.43 ppm), MeCOO (1.65-1.74 ppm), and CH₂S (2.98-3.27 ppm) groups. The signals of the CH₂OCOMe fragment in the 3.9-4.2 ppm region are absent in the PMR spectra, and consequently the obtained acetoxy adducts (Va-c) are practically not contaminated (within the accuracy limits of the PMR) with the aryl (1.1-dimethyl-2-acetoxy)ethyl sulfides. As a result, the reaction of ESI (IVa-c) with acetate ion proceeds with a high degree (95%) of regioselectivity and leads to the formation of adducts that correspond to opening of the episulfonium ring in harmony with the Markovnikov rule. Here, on the example of the conversion (IVa) - (Va) it was shown that the exclusive formation of Markovnikov adducts is also observed in less polar media, for example, in a $C_2H_4Cl_2 - CH_2Cl_2$ mixture.

Previously it was reported [7] that the result of reacting (IVa) with MeO⁻ in liquid SO₂ is the formation of the M adduct, which, in the opinion of the authors, is associated with the specific solvation in this solvent. Since the generation of (IVa) by the method described in this paper requires the use of a substantial excess of SbCl₅, we deemed it necessary to repeat this reaction under "pure" conditions. It proved that the reaction of the (IVa), obtained under standard conditions, with MeO⁻ is highly selective and gives adduct (VIa), which, based on the PMR data, is not contaminated with the regioisomer.

Scheme 3 (IV a) $\xrightarrow{MeO^{-}} Me_2C-CH_2SPh$ OMe (VIa)

This reaction is equally selective when run in $C_2H_4Cl_2 - CH_2Cl_2$ medium, and consequently the regioselectivity of forming (VIa), the same as in the case of (Va), is independent of the nature of the solvent.

As a result, the rule for the opening of episulfonium complexes that are isobutylene derivatives by nucleophiles is the formation of the Markovnikov adducts, in which connection the regioselectivity of this process is practically insensitive to variations in the nature of the aryl substituent or nucleophile. A comparison of these data with the data given in [4] on the ESI that are propylene derivatives reveals that the insertion of an additional CH_3 group in the ESI not only fails to create steric hindrance to attack of this center by the nucleophile (as was postulated previously [3]), but, in contrast, facilitates the attack of this center in complete harmony with the hypothesis given in [4] on the determining role of electronic effects in controlling the regioselectivity of the discussed process. Consequently, the generally accepted postulate of the anti-Markovnikov direction of opening ESI [1, 3] is incorrect, at least when it applies to propylene and isobutylene derivatives. In view of the obtained results it is apparently necessary to reexamine the data given in [8] on the theoretical substantiation of this postulate by quantum-chemical calculations.

EXPERIMENTAL

The GLC analysis was run on an LKhM-8-MD instrument, using the phases OV-101 and XE-60 deposited on Chromosorb (3-5%) and a 1-2 m × 4 mm column. The mass spectra were taken on a Varian CH-6 instrument, the PMR spectra were taken on Varian DA-60-IL and Bruker WP-60 instruments (60 MHz), and the ¹³C NMR spectra were taken on a Bruker WP-60 instrument (15.08 MHz). The preparative separation of the products was run on 24×24 cm glass plates covered with a loose SiO₂ layer 2 mm thick. The solvents were purified and dried by standard procedures. All of the operations on the preparation and transformations of the ESI were run in a dry argon stream.

The chloro adducts (IIIa, c) were obtained as described in [3]; the arylsulfenyl bromides (IIa, c) and bromo adducts (IIIa, c) were obtained as described in [4]. The characteristics of the compounds are given in Table 1.

The ESI (IVc) for taking the ¹³C NMR spectra was obtained directly in a 1.5-ml glass insert by adding 1.3 mmoles of freshly prepared (IIIc) to a stirred solution of $AgSbF_6$ (1.5 mmoles) in 1.3 ml of liquid SO_2 , cooled to -70° . After holding at -60 to -50° for 40 min the ampul was sealed and the spectrum was recorded at -70° (using HMDS as the external standard).

Compounds (IVa-c) for the reactions with the nucleophiles were obtained the same as described above from 1.1 mmoles of $AgSbF_6$ and 1.0 mmole of the appropriate Hal adduct (III) in either 5-7 ml of liquid SO₂ or 10-15 ml of a 2:5 $C_2H_4Cl_2 - CH_2Cl_2$ mixture. The reaction mass was stirred for 30-40 min at -50 to -40° [in the case of (IIIa) (Hal = Br), the stirring was done in $C_2H_4Cl_2 - CH_2Cl_2$ for 40 min at -20°], in which connection the AgHal precipitated. The extent to which the (III) compounds (Hal = Cl) reacted in the indicated time was 80-90%. In the case of (IIIa, c) (Hal = Br), due to their instability, partial decomposition occurred

	-		ie ld	۵۵, °C	,	PMR spe	ectrum [*]		Found, %		Ű	ilculated 🦏	
Adduct	(M/aM)	. 8		(p. mm Hg)	m/e	Mea	CH	υ	Ħ	თ	IJ	н	80
(IIIa) (Hal=	=Br) A		84	105(2)†	245	1,75	3,48	1	1	1	I	I	÷ŧ
	aA	M				1,79	3,76						
(IIIc) (Hal-		X X	95	130(1,5)	1	1,53 1,25	3,25 3,42	64,34	2,66	14,49	64,30	7,88	14,60
(IIIc) (Hal:	= Br) 1	¥	85	140(2) +	275	1,80	3,14	i	1	1	1	ł	++
(Va)		W	91	115(2)	224	1,43	3,27	64,20	7,09	14,25	64,25	7,19	14,29
(AV)	1	W	76	140(2)	258	1,41	3,26	55,60	5,50	12,39	55,70	5,84	12,39
(Vc)	1	M	72	120(2)	266	1,43	2,98	67,70	8,39	12,33	67,62	8,34	12,03

(Va-c)	
anc	
(11)	
Adducts	
Characteristics of	
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TABLE	

*The PMR spectra were recorded in CCI₄ solution; the chemical shifts are given relative to HMDS as the internal standard; the given signals appear as singlets: the signals of the protons of the aromatic substituent are present in the spectra of all of the adducts, and also the signals of the MeOCO group in the spectra of (Va-c) (respectively 1.73, 1.74, and 1.65). *Partial decomposition.

#Satisfactory elemental analysis data could not be obtained for the product due to instability.

and up to 10-15% of the corresponding diaryl disulfide was detected in the reaction mixture. At the end of the indicated time the ESI (IVa-c) were treated with the appropriate nucleophile.

Acetoxy adducts (Va-c) were obtained by adding to a solution of the appropriate ESI at -50° a mixture of 0.5 g of MeCOOK and 0.5 ml of MeCOOH in 5-7 ml of the solvent used to obtain (IV), cooled to -50° . After 10 min the temperature was raised to $\sim 20^{\circ}$ and 30 ml of saturated aqueous NaHCO₃ solution was added, after which the mixture was extracted with 2×100 ml of ether, and the extracts were washed with water and dried over Na₂SO₄. After evaporation of the ether the residue was purified by TLC. The characteristics of (Va-c) are given in Table 1.

Methoxy adduct (VIa) was obtained by treating (IVa) as described in [7]. The PMR spectrum was identical with that described in [7].

CONCLUSIONS

The opening of S-arylepisulfonium complexes that are isobutylene derivatives proceeds with the exclusive formation of the Markovnikov adducts.

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EFFECT OF NATURE OF SUBSTITUENTS ON

PHOTOCHEMICAL BEHAVIOR OF

2,6-DISUBSTITUTED 1,4-BENZOQUINONES

UDC 541.14:547.567

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The effect of the nature of the substituents on the photochemical behavior of the 2,6-dimethyl- (I), 2,6di-tert-butyl- (II), and 2,6-diphenyl-1,4-benzoquinones (III) in protic and aprotic solvents was studied in the present paper. A partial study of the behavior of the given objects in photochemical processes was made previously [1-3], but the inadequacy of the photolysis conditions did not permit making a comparative estimate of the effect of structural factors on the characteristics of the photochemical transformations.

The photolysis of the studied quinones in aliphatic alcohols leads to various reduction products (Table 1).

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