8. M. I. Rybinskaya, A. N. Nesmeyanov, and N. K. Kochetkov, Usp. Khim., 38, 978 (1969).
9. K. K. Babievskii, V. M. Belikov, and É. V. Zaporozhets, Zh. Organ. Khim., 9, 1063 (1973).

GENERATION AND PROPERTIES OF EPISULFONIUM INTERMEDIATES

COMMUNICATION 5*. STEREOCHEMISTRY OF FORMATION AND OPENING OF EPISULFONIUM COMPLEXES OBTAINED FROM cis- AND trans-BUTENES

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Methods for the generation of episulfonium intermediates and some of their reactions were described in previous communications [1-5]. In particular, the reactions of the S-alkyl- and S-arylepisulfonium complexes, obtained from cyclohexane, with nucleophiles of variable nature lead to the exclusive formation of the trans-1,2-derivatives of cyclohexane [6, 7].

The purpose of the present paper was to study the stereochemistry of the formation and opening of the analogous intermediates for the case of the acyclic alkenes, and specifically of the cis-(Ia) and trans-2-butenes (Ib).

The simplest path for obtaining episulfonium intermediates is the direct reaction of the alkene with the cationoid reagent ArS^+Y^- (path A) [4]; this method proved to be quite efficient for the case Ar = $p\text{-}ClC_6H_4$. However, in the case Ar = $2,4\text{-}(O_2N)_2C_6H_3$ the reaction with (I) proceeded with complications, and consequently for this case the episulfonium complex was generated by an alternate method (path B + C) [5] via the step of obtaining the covalent adducts (IIIa) and (IIIb), which were synthesized by a modification of the method given in [8].

The thus-obtained complexes (IIa, b) and (IVa, b) are quite stable in solution, and in the absence of nucleophiles they can be stored without change at −20°C for several hours (IV) or several days (II). They react with bases in the same manner as was described previously for the complexes that were obtained by analogous routes from other olefins [1, 5], and lead to adducts of general formula $ArS{\cdot}C_4H_8{\cdot}Z$, where Z is the nucleophilic group of the added base. (See Scheme at top of following page.)

The stereochemistry of the formation and opening of the episulfonium complexes was studied in detail for the case of their reaction with AcOH, which proceeds quite easily even at −20° and gives the corresponding acetoxy adducts (V) and (VI) in high yield. Based on the TLC analysis data for (VIa) or (VIb) and the GLC analysis data for (Va) or (Vb), and also the NMR spectral data, the formed acetoxy adducts are pure compounds and are not contaminated with the stereoisomers. Adducts (VIa) and (VIb) were identified as respectively being the threo and erythro isomers by comparison with authentic specimens [9]. The configuration of (Va) and (Vb) was adopted by analogy, based on the fact that the reactions for their respective formation from (IIa) and (IIb) are unambiguous.

The exclusive formation of the threo acetates from the complex obtained from cis-butene, and of the erythro acetates from trans-butene, shows that the reaction of intermediates (II) and (IV) with AcOH proceeds as stereospecific trans-opening of the episulfonium ring.

*See [1] for Communication 4.

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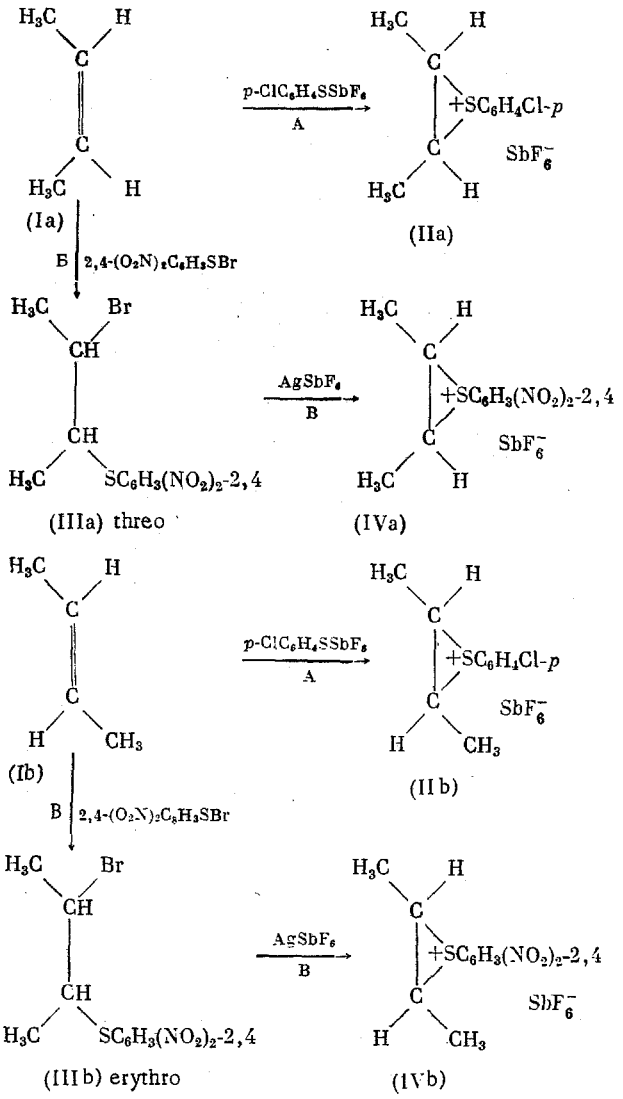
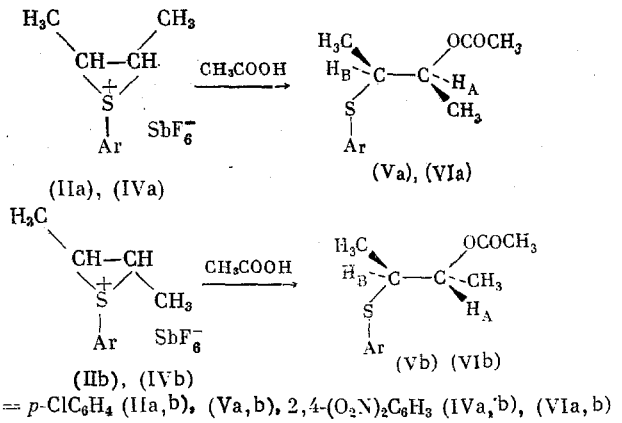
Scheme 1



Scheme 2

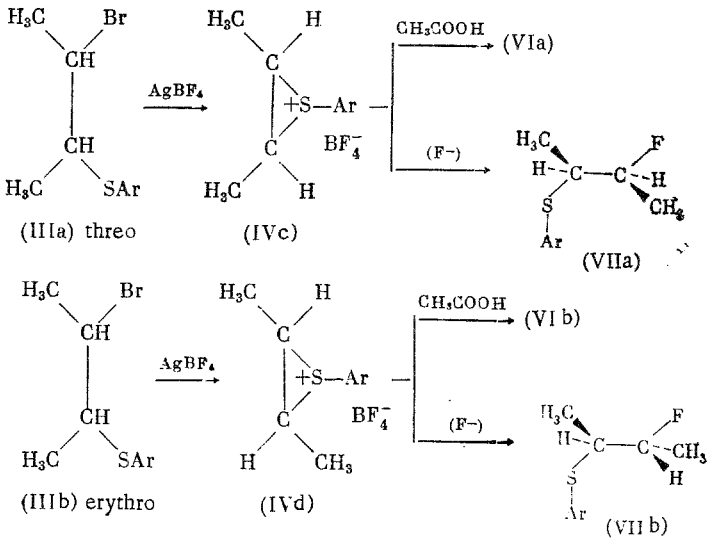


Ar = p-ClC_6H_4 (IIa,b), (Va,b), 2,4-$(O_2N)_2C_6H_3$ (IVa,b), (VIa,b)

The stereochemistry of forming acetates (V) and (VI) is independent of whether the corresponding intermediates (II) and (IV) were obtained by the direct path or by the step scheme (see Scheme 1). In particular, it follows from this that the formation of the episulfonium complex from covalent adducts of the (III) type is a stereospecific process of trans-anti elimination.

For the case Ar = 2,4-$(O_2N)_2C_6H_3$ we studied the possibility of obtaining the episulfonium complexes with the BF_4^- anion by reacting (III) with $AgBF_4$. Also in this case the AgBr was precipitated easily and quickly; however, after treating the reaction mixture with AcOH the main products proved to be the fluoro adducts (VIIa) or (VIIb) (in respective yields of 71 and 50%), and not the acetoxy adducts (VIa) or (VIb) (in respective yields of 22 and 28%). The formation of the former is apparently caused by the lower stability of the BF_4^- anion when compared with the SbF_6^- anion, as a result of which the obtained intermediates (IVc) or (IVd) are potentially capable of being stabilized via the addition of the nucleophile F^-, which is contained in the counterion, "without waiting" for the addition of the nucleophile from the outside (AcOH). Adducts (VIIa) and (VIIb) were isolated as the pure compounds and are characterized completely by the elemental analysis and IR, ^1H, and ^{19}H, NMR spectral data. Based on the values of the vicinal spin–spin coupling constants of protons A and B, which are respectively equal to 6.5 and 4.5 Hz, it may be assumed that VIIa) is the threo, and (VIIb) is the erythro isomer [10]. From this it is clear that the trans-stereospecificity of the reaction for forming and opening spisulfonium complexes is retained both with change in the character of the counterion when the complex is obtained, and of the leaving nucleophile when it is opened.

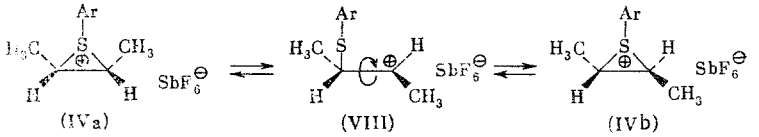
Scheme 3



Ar = 2,4-$(O_2N)_2C_6H_3$

The fact that stable solutions of complexes (II) and (IV) could be obtained made it possible to raise the question of studying their heat stability and the possibility of cis-trans interconversions in this series.

We found that if solutions of (IVa) or (IVb), obtained at −20 to −40°, are heated to room temperature and kept under these conditions for 1-1.5 h, then, as the result of subsequent treatment with glacial AcOH under the usual conditions for the stereospecific formation of (VIa) and (VIb) (i.e., after cooling the mixture to −40°), a mixture of the threo and erythro acetates is formed in a 1:3 ratio,* in which connection this ratio is independent of whether the starting complex is (IVa) or (IVb). This result shows that equilibrium is established between (IVa) and (IVb) when the temperature is raised, in which connection the less-hindered trans-isomer predominates in the mixture. It is obvious that the transformation (IVa) ⇄ (IVb) should proceed via the step of opening the bridge and forming the configuration-loose carbonium ion (VIII).



Ar = 2,4-$(O_2N)_2C_6H_3$

*Determined on the basis of integrating the signals of the methyl and acetate groups in the NMR spectra, and confirmed by the data of preparative separation by TLC.

A similar picture was also observed for complexes (IIa) and (IIb), with the difference that these intermediates proved to be more stable than (IVa) and (IVb). It was found that keeping (IIa) or (IIb) at 20° for 3-5 h does not lead to noticeable interconversion, since after treatment with AcOH the GLC data disclosed the formation of the nearly pure threo isomer (Va) from (IIa) (less than 5% of (Vb) as impurity) and the pure erythro acetate (Vb) from (IIb). However, if the time of keeping a solution of (IIa) or (IIb) at ~20° is increased to 24 h, then the subsequent treatment with AcOH leads to the formation of a mixture of acetates (Va) and (Vb). In this case the composition of the mixture under equilibrium conditions could not be established, since, together with the stereoconversion (Va) ⇄ (Vb), the progress of condensation reactions was observed and the total yield of mixed acetates dropped to 30-40% on long keeping. The mixture (Va):(Vb) = 3:2 was obtained from complex (IIa) under the optimum conditions, and the mixture (Va):(Vb) = 1:4 from complex (IIb).

The fact that intermediates (II) and (IV) are configurationally stable at low temperatures and easily react with nucleophiles to exclusively give the trans-adducts makes it possible to assume that they represent bridge cationoid complexes of the type of episulfonium ions, as is depicted in the above given structures. The observed ability of the stereoisomeric intermediates to undergo the interconversion a ⇄ b testifies to the comparatively low barrier of the transition: bridge ion ⇄ open carbonium ion.

It is interesting to compare the data of the present paper with the described stereochemistry of the reactions for the electrophilic addition of covalent sulfene halides to multiple bonds. It is known that in all cases these reactions practically proceed as trans-addition,* in which connection it was found on the example of adding p-ClC_6H_4SCl to the cis- and trans-butenes that this rule remains in full force when the temperature is varied from −30 to 140° [12]. Since it is customary to assume that episulfonium ions are the intermediate in these reactions, this insensitivity of the reaction course to changes in the temperature (and also in the solvent or nature of the reactant [13]) is usually regarded as being evidence that the episulfonium bridge is highly stable. However, the data of the present paper show that raising the temperature by even 40-50° is sufficient to convert the stereoisomeric episulfonium intermediates. For this reason we assume that the exclusiveness of the trans-stereochemistry of adding RSHal to multiple bonds, mentioned in the literature, should be attributed to the intermediate formation of the covalent bridge sulfuran [14] in this reaction, while the episulfonium ions can no longer be regarded as being intermediates for the electrophilic addition reactions of covalent sulfene halides under the usual conditions.

In conclusion mention should be made of still another interesting trait of the reactivity of episulfonium complexes. It was found that if complexes (II) or (IV) are obtained by the direct path (see Scheme 1, path A) in the presence of excess olefin, then their subsequent treatment with AcOH gives not only acetates (V) or (VI) respectively, but also oligomeric products,† whose composition ($ArS \cdot C_8H_{15}$, mass spectra) corresponds to the reaction of one equivalent of complex (II) or (IV) with one mole of the starting olefin. This fact indicates that the obtained episulfonium intermediates are quite strong electrophiles, which are capable of reacting not only with nucleophiles of the n-donor type, but also with π-donors. The possibility of using a similar reaction as a method of alkylating unsaturated compounds is being studied at the present time.

EXPERIMENTAL

The NMR spectra were taken on a Varian DA-60IL spectrometer (60 MHz), the chemical shifts are given on the δ scale, the standard was HMDS, and the solvent was $CDCl_3$, except for the specified cases. The IR spectra were recorded on a UR-10 instrument, while the mass spectra were taken on a Varian CH-6 instrument. The mixtures of acetates (VIa, b) and F adducts (VIIa, b) were analyzed by TLC on Silufol, while the mixtures of acetates (Va, b) were analyzed by GLC (LKhM-8MD, glass capillary filled with SE-30, length 30 m, 145°). The reaction products were isolated by preparative TLC on 24 × 24 cm plates.

*The sole exception [11] refers to the addition of 2,4-$(O_2N)_2C_6H_5SCl$ to cis-acetol; it is postulated that the reason for this infraction is the high stability of the open carbonium ion in the given system.

†In the case of (IV) the formation of the oligomeric products is observed even at −40°, whereas for (II) this reaction proceeds to substantial degree only at 0°.

GENERATION OF COMPLEXES (IVa) AND (IVb) (PATH B + C)

Preparation of Adducts (IIIa) and (IIIb) (step B). With stirring and cooling to −10°, to a solution of 12 g of 2,4-$(O_2N)_2C_6H_3SBr$ in 350 ml of abs. CH_2Cl_2 was added in 1.5 h a solution of 6.45 g of (Ia) in 5 ml of CH_2Cl_2, after which the mixture was kept at −5° for 2 h, at 0° for 1 h, and then the temperature was raised up to ~20° in 20 min and let stand overnight. After removing the CH_2Cl_2 the residue was dissolved in hot $CHCl_3$ and then precipitated with hexane. We isolated 10.9 g (76%) of (IIIa), mp 135-136° (from CCl_4); cf. [8].

In a similar manner, from 12 g of 2,4-$(O_2N)_2C_6H_3SBr$ in 350 ml of abs. CH_2Cl_2 and 6.3 g of (Ib) in 5 ml of CH_2Cl_2 we obtained 11.34 g (79%) of (IIIb), mp 92-93°; cf. [8].

Preparation of (IVa) and (IVb) (step C). To a solution of 0.3 g of (IIIa) in 6 ml of CH_2Cl_2, cooled to −30 to −40° was added in 1 min a solution of 0.36 g of $AgSbF_6$ in 0.9 ml of CH_3NO_2, and the mixture was kept at −40 to −20° for 10 min in order to assure complete precipitation of the AgBr. In the same manner, we obtained intermediate (IVb) from 0.3 g of (IIIb) in 6 ml of CH_2Cl_2 and 0.36 g of $AgSbF_6$ in 0.9 ml of CH_3NO_2.

REACTION OF (IVa) AND (IVb) WITH AcOH

Preparation of (VIa). With stirring, to a solution of (IVa) at −40° was added 10 ml of glacial AcOH in 5 min, and then the temperature of the stirred mixture was raised to 0° in 20 min. After treating the mixture with aqueous $NaHCO_3$ solution, extraction with $CHCl_3$, and removal of the solvent we isolated (Al_2O_3, benzene–petroleum ether–AcOEt = 10:7:3) 0.21 g (78%) of (VIa), mp 119-120.5°; cf. [9]. Infrared spectrum (ν, cm^{-1}): 1165, 1205, 1740 ($OCOCH_3$). NMR spectrum (δ, ppm): 1.33 d and 1.42 d (6H, $\underline{CH_3} - CH_A - CH_B - \underline{CH_3}$, $J_{CH_3,H}$ = 6.5 Hz); 208 s (3H, $OCOCH_3$); 3.80 m (1H, CH_B, J_{AB} = 4 Hz); 5.08 m (1H, CH_A); the aromatic protons form an XYZ system: 8.10 d (1H, H_X, J_{XY} = 9, J_{XZ} = 1 Hz); 8.43 d (1H, H_Y, J_{YZ} = 3 Hz); 9.00 d (1H, H_Z).

Preparation of (VIb). The treatment of (IVb) was done in the same manner. Here we isolated (Al_2O_3, benzene–petroleum ether–AcOEt = 10:2:1) 0.22 g (82%) of (VIb), mp 97-98°, cf. [9]. Infrared spectrum (ν, cm^{-1}): 1165, 1205, 1740 ($OCOCH_3$). NMR spectrum (δ, ppm): 1.37 d and 1.47 d (6H, $\underline{CH_3} - CH_A - CH_B - \underline{CH_3}$, $J_{CH_3,H}$ = 6.5 Hz); 2.00 s (3H, $OCOCH_3$); 3.77 m (1H, CH_B, J_{AB} = 3.6 Hz); 5.15 m (1H, CH_A); the aromatic protons form an XYZ system: 7.53 d (1H, H_X, J_{XY} = 9, J_{XZ} = 1 Hz); 8.25 double d. (1H, H_Y, J_{YZ} = 2.5 Hz); 8.72 d (1H, H_Z).

STEREOCONVERSION OF (IVa) AND (IVb)

1) A solution of (IVa), obtained from 0.3 g of (IIIa) at −40° as described above, was kept at 20° for 1 h, after which it was recooled to −40° and treated with AcOH under the usual conditions for the preparation of (VIa). Based on the NMR spectrum, the obtained product is a mixture of (VIa) and (VIb) (1:3) (based on determining the relative intensity of the signals of the CH_3COO groups in (VIb) and (VIa) with chemical shifts of 1.87 and 2.01 ppm respectively; solvent = CD_3NO_2). We isolated (Al_2O_3, benzene–petroleum ether–AcOEt = 10:2:1) 0.11 g (24%) of (VIa) and 0.22 g (48%) of (VIb).

2) In a similar manner, from (IVb) (from 0.3 g of (IIIb)) we obtained 0.2 g of mixed acetates (VIa) and (VIb) (1:3). The NMR spectrum was taken in CD_3NO_2.

PREPARATION OF F ADDUCTS

Preparation of (VIIa). To a solution of 1 g of (IIIa) in 15 ml of CH_2Cl_2, cooled to −15 to −20°, was added in 15 min a solution of 0.702 g of $AgBF_4$ in 2.16 ml of CH_3NO_2, and the mixture was kept at this temperature for 5 min. The obtained complex (VIc) was treated at −50 to −2° with 40 ml of AcOH and then stirred for 30 min at 0-20°. We isolated (SiO_2, benzene–petroleum ether–AcOEt = 10:2:1) 0.2 g (21%) of (VIa), mp 119-120.5°, and 0.58 g (71%) of (VII), mp 83-84° (from CCl_4). Found: C 44.14; H 4.45; N 9.58%. $C_{10}H_{11}N_2O_4SF$. Calculated: C 43.78; H 4.04; N 10.22%. NMR spectrum (δ, ppm): 1.42 double d (3H, $\underline{CH_3} - \underset{F}{\underset{|}{CH_A}}$, J_{CH_3}, H_A = 6 Hz, $J_{CH_3,F}$ = 23 Hz); 1.5 d (3H, $\underline{CH_3}$–CH_B, J_{CH_3,H_B} = 7 Hz); 3.54 m (1H, CH_B, J_{AB} = 6.5 Hz; $J_{H_B,F}$ = 18 Hz); 4.72 double m (1H, CH_A, $J_{H_A,F}$ = 46 Hz); the aromatic protons form an XYZ system; 7.67 d (1H, H_X, J_{XY} = 9, J_{XZ} = 1 Hz); 8.30 double d (1H, H_Y, J_{YZ} = 3 Hz); 8.90 d (1H, H_Z). Mass spectrum: M^+ with m/e 274.

Preparation of (VIIb). Analogous to (VIIa), we isolated (Al_2O_3, benzene–petroleum ether–AcOEt = 10:2:1) 0.26 g (28%) of (VIb), mp 98-99° (from CCl_4) and 0.41 g (50%) of (VIIb), mp 92-93° (from CCl_4). Found: C 43.46; H 4.25 N 10.00%. $C_{10}H_{11}N_2O_4SF$. Calculated: C 43.78; H 4.04; N 10.22%. NMR spectrum (δ, ppm): 1.38 d (3H, $\underline{CH_3}$–CH_B–J_{CH_3,H_B} = 7 Hz); 1.42 double d (3H, $\underline{CH_3}$–CH_A, J_{CH_3,H_A} = 6, $J_{CH_3,F}$ = 24 Hz); 3.73 m (1H, CH_B, J_{AB} = 4.5 Hz); 4.85

F

double m (1H, CH_A, $J_{H_A,F}$ = 47 Hz); the aromatic protons form an XYZ system: 7.67 d (1H, CH_X, J_{XY} = 9, J_{XZ} = 1 Hz); 8.28 double d (1H, CH_Y, J_{YZ} = 2.5 Hz); 8.90 d (1H, H_Z). Mass spectrum: M^+ with m/e 274.

GENERATION OF INTERMEDIATES (IIa) AND (IIb)

Generation of (IIa) (path A). To a solution of 0.27 g (1.5 mmoles) of p-ClC_6H_4SCl in 1.2 ml of dichloroethane (DCE) and 5 ml of CH_2Cl_2, cooled to –50°, were added in 1 min 0.618 g (1.8 mmoles) of $AgSbF_6$ in 1.54 ml of CH_3NO_2 and 0.65 g (11 mmoles) of (Ia); the obtained complex (IIa) was kept at –50° to –20° for 15 min, which was sufficient to complete the reaction.

Generation of (IIa) (path B + C). To a solution of 0.69 g (3.9 mmoles) of p-ClC_6H_4SCl in 2 ml of CH_2Cl_6, cooled to –30°, was added 1.29 g (23 mmoles) of (Ia), and then the temperature was raised to ~20° in 30 min. After distilling off the solvent we obtained 0.755 g (3.2 mmoles) of the Cl adduct, which was dissolved in 6 ml of CH_2Cl_2 at –40°, after which 1.37 g (3.9 mmoles) of $AgSbF_6$ in 3.4 ml of DCE was added, and the obtained complex (IIa) was kept at –15 to –20° for 20 min.

The (IIb) complex was generated in a similar manner by path A: from 0.27 g (1.5 mmoles) of p-ClC_6H_4SCl in 1.2 ml of DCE, 0.618 g (1.8 mmoles) of $AgSbF_6$ in 1.54 ml of CH_3NO_2, and 1.25 g (22 mmoles) of (IIb); or by path (B + C): from 0.69 g (3.9 mmoles) of p-ClC_6H_4SCl in 2 ml of DCE and 1.25 g (22 mmoles) of (IIb) was obtained 0.75 g (3.1 mmoles) of the Cl adduct, to which, after dissolving in 6 ml of CH_2Cl_2 and cooling to –40°, was added 1.37 g (3.9 mmoles) of $AgSbF_6$ in 4.0 ml of DCE and the mixture was kept at –15° for 15 min.

REACTION OF (IIa) AND (IIb) WITH AcOH

Preparation of (Va). Complex (IIa) was treated with glacial AcOH (15 ml) at –60° to –30° for 15 min. We isolated (Al_2O_3, petroleum ether:$CHCl_3$ = 1:1) 0.33 g (85%) of (Va); n_D^{18} 1.5419. Found: C 56.01; H 5.86%. $C_{12}H_{15}O_2SCl$. Calculated: C 55.70; H 5.80%. Infrared spectrum (ν, cm^{-1}): 1740 ($OCOCH_3$). NMR spectrum (δ, ppm): 1.12 d and 1.17 d (6H, $\underline{CH_3}$–CH_A–CH_B–$\underline{CH_3}$, $J_{CH_3,H}$ = 7.0 Hz); 1.85 s (3H, $OCOCH_3$); 3.43 m (1H, H_B, J_{AB} = 4.8 Hz); 5.03 m (1H, H_A); 7.31 m (4H, C_6H_4).

Preparation of (Vb). Complex (IIb) was treated the same as above. We isolated (Al_2O_3, petroleum ether–$CHCl_3$ = 1:1) 0.25 g (64%) of (Vb); n_D^{18} 1.5380. Found: C 55.85; H 5.73%. $C_{12}H_{15}O_2SCl$. Calculated: C 55.70; H 5.80%. Infrared spectrum (ν, cm^{-1}): 1740 ($OCOCH_3$). NMR spectrum (δ, ppm): 1.21 d (6H, $\underline{CH_3}$–CH_A–CH_B–CH_3, $J_{CH_3,H}$ = 7 Hz); 1.87 s (3H, $OCOCH_3$); 3.41 m (1H, CH_B, J_{AB} = 4.5 Hz); 5.10 m (1H, CH_A); 7.32 m (4H, C_6H_4).

STEREOCONVERSION OF (IIa) AND (II)

1) A solution of (IIa), prepared at –50° (see above, equimolar ratio of the reactants), was heated up to ~20° and kept at 20°, with the removal of aliquots after 60 min (A), 5 h (B), and 24 h (C), and an additional aliquot after 5 h at 40° (D), which were then treated with glacial AcOH. Sample A represented the pure acetate (Va), in sample B the (Va):(Vb) ratio = 9:1, and in samples C and D the (Va):(Vb) ratio = 3:2 (determined on the basis of the GLC data). Based on the data of separating by TLC the total yield of the acetates decreases with time from 86 (A) to 42% (D).

2) The experiment with a solution of (IIb) was run in a similar manner. Samples A and B represented the pure (Vb), while in sample C the (Va):(Vb) ratio = 1:9, and 1:4 in sample D.

PREPARATION OF OLIGOMERIC PRODUCTS

Generation of (IVa) (path A). To a solution of 0.42 g (1.5 mmoles) of 2,4-$(O_2N)_2C_6H_3SBr$ in 5 ml of CH_2Cl_2, cooled to –50°, were added in 1 min 0.618 g (1.8 mmoles) of $AgSbF_6$ in 1.54

ml of CH_3NO_2 and 0.65 g (11.6 mmoles) of (Ia) in 2 ml of CH_2Cl_2, and the mixture was kept for 10 min at −35 to −45°, then at −55 to −15°, after which it was treated with 20 ml of AcOH and stirred at this temperature for 15 min. After workup we isolated (Al_2O_3, benzene–petroleum ether–AcOEt = 10:5:1) 0.22 g (47%) of (VIa), mp 119-120°, and 0.24 g (52%) of the oligomer. Mass spectrum of oligomer: ($M^+ - 1$) with m/e 309 ($C_{14}H_{18}O_4N_2S$).

Generation of (IVb) (path A). In a similar manner, from 0.42 g (1.5 mmoles of 2,4-$(O_2N)_2C_6H_3SBr$ in 5 ml of CH_2Cl_2, 0.618 g (1.8 mmoles) of $AgSbF_6$ in 1.54 ml of CH_3NO_2, and 0.63 g (11.2 mmoles) of (Ib) in 2 ml of CH_2Cl_2 we obtained 0.18 g (38%) of (VIb), mp 98-99°, and 0.18 g (39%) of the oligomer. Mass spectrum of oligomer: ($M^+ - 1$) with m/e 309 ($C_{14}H_{18}O_4N_2S$).

Generation of (IIa) (path A). A solution of (IIa), obtained as described above at −50°, was heated up to 0°, and after keeping at 0° for 5 min it was treated with AcOH under the conditions of obtaining (Va). We isolated (Al_2O_3, petroleum ether–benzene = 2:1) 0.12 g (31%) of acetate (Va) and 0.14 g (37%) of the oligomer; n_D^{20} 1.5520. When the solution of (IIa) was kept at 0° for 30 min we obtained 0.16 g (41%) of acetate (Va) and 0.18 g (48%) of the oligomer. Mass spectrum: M^+ with m/e 252 and 254 (3:1, $C_{14}H_{17}ClS$).

Generation of (IIb) (path A). In a similar manner, from (IIb) we obtained 0.1 g (26%) of (Vb) and 0.12 g (32%) of the oligomer. Mass spectrum: M^+ with m/e 252 and 254 (3:1, $C_{14}H_{17}ClS$).

CONCLUSIONS

It was shown that stable intermediates of the type of episulfonium ions can be generated by the reaction of the cis- and trans-butenes with the 2,4-dinitrophenylsulfene and p-chlorophenylsulfene hexafluoroantimonates. The stereochemistry of the formation and opening of these intermediates was established, and also the conditions of their cis-trans interconversions.

LITERATURE CITED

1. É. A. Vorob'eva, M. Z. Krimer, and V. A. Smit, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 1318.
2. W. A. Smit, A. V. Semenovsky, V. F. Kucherov, T. N. Chernova, and M. Z. Krimer, Tetrahedron Lett., 1971, 3101.
3. M. Z. Krimer, V. A. Smit, and A. A. Shamshurin, Dokl. Akad. Nauk SSSR, 208, 864 (1973).
4. É. A. Vorob'eva, M. Z. Krimer, and V. A. Smit, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 2832.
5. É. A. Vorob'eva, M. Z. Krimer, and V. A. Smit, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 125.
6. É. A. Vorob'eva, L. G. Gurvich, N. S. Zefirov, M. Z. Krimer, and V. A. Smit, Zh. Organ. Khim., 10, 883 (1974).
7. N. S. Zefirov, L. G. Gurvich, A. S. Shashkov, M. Z. Krimer, and E. A. Vorob'eva, Tetrahedron, 32, 1211 (1976).
8. N. Kharasch and A. Havlik, J. Am. Chem. Soc., 75, 3734 (1953).
9. A. Havlik and N. Kharasch, J. Am. Chem. Soc., 78, 1267 (1956).
10. G. H. Schmid, Can. J. Chem., 46, 3415 (1968).
11. G. H. Schmid and V. J. Nowlan, J. Org. Chem., 37, 3086 (1972).
12. G. H. Schmid and V. M. Csizmadia, Can. J. Chem., 44, 1338 (1966).
13. W. H. Mueller, Angew. Chem., Inter. Ed., 8, 482 (1969).
14. D. Owsley, G. Helmkamp, and M. Rettig, J. Am. Chem. Soc., 91, 5239 (1969).