STEREOCHEMISTRY OF REACTION OF EPISULFONIUM

SALTS WITH π -DONORS

M. A. Ibragimov, O. V. Lyubinskaya, and V. A. Smit

UDC 541.63:542.91: 547.379.2-38

It was found that the reaction of episulfonium ions (ESI) with π -donors, which are active aromatic compounds [1], and trimethylsilyl enol ethers [2] proceeds strictly stereospecifically according to a trans-ring opening scheme. Thus ESI salts (Ia, b) obtained from cis- and trans-butene [3], in a reaction with mesitylene (MsH) or 2-trimethylsiloxypropene (II) give stereoisomeric individual (GLC, PMR data, 250 MHz) adducts (IIIa, b) and (IVa, b), in yields of 50-70%.

$$MeCH=CHMe \rightarrow MeHC-CHMe \rightarrow MrS Ms (III)$$

$$Ar=S BF_4 (I a, b) (III) MeCH-CHMe \rightarrow ArS CH_2COMe (IV)$$

$$cis \rightarrow cis - (Ia) \rightarrow 95\% threo - (IIIa), (IVa)$$

$$trans \rightarrow trans - (Ib) \rightarrow 95\% erythro - (IIIb), (IVB)$$

From the literature data on the stereochemistry of the ring opening of ESI by π -donors [3] and the value of the spin-spin coupling constant, a three configuration was assigned to adducts (IIIa) and (IVa), and an erythro configuration to (IIIb) and (IVb). In the reaction of ESI of cyclic alkenes, trans-disubstituted derivatives (V) and (VI) are formed stereoselectively in yields of 30-60%.

$$\begin{array}{c|c} & SAr \\ \hline & X = CH_r \end{array} & \begin{array}{c} & & \\ & &$$

The above examples are the first cases of the stereospecific opening of ESI by the action of weak nucleophiles which are π -donors.

The structure of all the products was confirmed by data of elemental analysis, mass- and $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra.

LITERATURE CITED

- 1. M. A. Ibragimov, V. A. Smit, A. S. Gybin, and M. Z. Krimer, Izv. Akad. Nauk SSSR, Ser. Khim., 1929 (1981).
- 2. M. A. Ibragimov and V. A. Smit, Izv. Akad. Nauk SSSR, Ser. Khim., 2177 (1982).
- 3. W. A. Smit, M. Z. Krimer, and E. A. Vorob'eva, Tetrahedron Lett., 2451 (1975).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, p. 1204, May, 1983. Original article submitted November 22, 1982.