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# GENERATION AND CHEMICAL REACTIONS OF EPISULFONIUM IONS

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Episulfonium ions have been long considered to be important species in electrophilic addition of sulfenyl halides /1/. Until recently only indirect evidence was available about the chemical properties of these intermediates. Here we report what seems to be the general procedure for the generation of episulfonium complexes /2/ and the data on their chemical reactions /3/.

Preparation. We have shown that stable solutions of complexes could be prepared either by direct reaction (route A) of alkene with cationoid reagent $RS^+Y^-$($Y^-$-$BF_4^-$ or $SbF_6^-$, generated in situ by the reaction of RSHal with corresponding silver salt) or by the stepwise procedure (route B+C) via the preparation of β-haloalkyl thioethers which are further treated with the same silver salts. Both procedures proved to be generally useful as shown by the representative examples given in Charts 1-5. The structures of episulfonium ions $I_1$-$I_6$ suggested for these complexes are supported by the following chemical evidence /4/.

Stability. The complexes $I_1$-$I_6$ were stable for at least several hours at-30°C in the non-nucleophilic solvents ($CH_2Cl_2$, $C_2H_4Cl_2$, $SO_2$, $CH_3NO_2$) /5/.

Reactions of $I_1$-$I_6$ with nucleophiles proceeded smoothly within several minutes even at-30°C÷0°C after the addition of corresponding base. All the nucleophiles studied, irrespective of their nature, reacted with $I_1$-$I_6$ in a similar fashion giving the corresponding β-substituted thioethers as the major products /6/.

Regioselectivity of the nucleophile attack proved to be quite sensitive both to the structure of the intermediate and to the nature of the quencher. Thus $I_2$ was converted to Markovnikov's adducts V (a-d) upon the action of all the nucleophiles studied. On the contrary, the exclusive formation of anti-Markovnikov's adducts, XI (a-f), was observed for the quenching of $I_4$ with all the nucleophiles but nitriles: the latter gave Markovnikov's adducts X (a,b). A rather peculiar pattern of regioselectivity was observed for the reactions of $I_3$: its quenching with $H_2O$ or $CH_3OH$ afforded adducts VII ( a or b) while the anti-Markovnikov's adduct VIIIa was formed in the reaction with $CH_3COOH$.

Stereoselectivity. The exclusive formation of trans-adducts has been observed for the transformations of $I_1$ into II or III; the trans-configuration of the products was supported by PMR data ($J_{AB} \cong$ 9-12Hz, determined for 3,3,6,6-$d_4$-

II(a-c,h,i) or III(a-d) /7/). The interaction of acyclic episulfonium complexes with nucleophiles should be described as a trans-stereospecific process since the quenching of the solutions of $I_5$ or $I_6$ (prepared at -40°C from XIII or XIV respectively) with $CH_3COOH$ produces pure acetates XV or XVI /8/. However, it has also been found that both $I_5$ and $I_6$ while being configurationally stable at -40°C (at least for 4 hours) could be made to equilibrate on warming up to +20°C. The subsequent quenching of the equilibrated complex with $CH_3COOH$ afforded the mixture of XV and XVI, the ratio of products being independent on the geometry of olefin used for the preparation of original intermediate.

Rearrangements. It was shown that although $I_4$ is sufficiently stable at -30°C, allowing the preparation of unrearranged products X or XI, it could undergo the irreversible conversion into the covalent product XII upon heating to +20°C. The structure of XII suggested the reaction pathway shown on the Chart 4. Similar rearrangements were also observed for norbornene derivatives /9/.

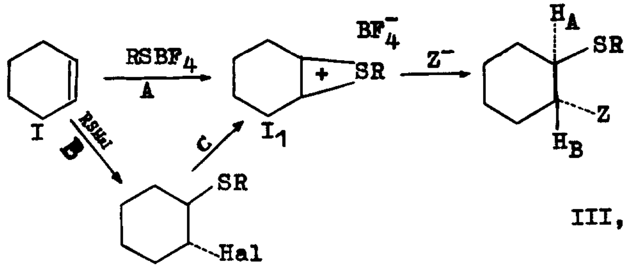
Typical experimental procedures are as follows. Formation of $I_4$: Route B+C. The solution of $XI_f$(2.1 mmoles prepared as in /1b/) in $C_2H_4Cl_2$-$CH_2CL_2$(5ml,1:4) was treated at -40°C with $AgBF_4$(5 mmoles) in $CH_3NO_2$(3ml). The precipitation of AgCl was observed. To ensure the completeness of the reaction the mixture was additionally kept for 10 min at -15°C. Route A. The solution of $AgBF_4$(5.0 mmoles) in $CH_3NO_2$(3 ml) was added at -55°C to the solution of $C_6H_5SCl$ (4.2 mmoles) in $C_2H_4Cl_2$-$CH_2Cl_2$(6 ml, 1:2). After the complete precipitation of AgCl (5 min) the solution of IX (2.1 mmoles) in $CH_2Cl_2$(4 ml) was added at -55°C. The formation of $I_4$ is complete in 5-10 min.

Preparation of XIa. Glacial $CH_3COOH$ (25 ml) was added to the solution of $I_4$ at -50°C. The mixture is warmed up to 0°C, treated with aq.$NaHCO_3$ and extracted with ether. Ethereal layer was washed with aq.$NaHCO_3$, $H_2O$ and dried over $Na_2SO_4$. Distillation afforded 0.8 gr of pure (g.l.c., PMR) XIa (77%). Other adducts were prepared in the similar fashion with following bases as quenchers: $CH_3CN$ (or $C_6H_5CN$) and $H_2O$ for X, and $CH_3OH$, $HNEt_2$, $NaCH(COOCH_3)_2$, $NaBH_4$, $Bu_4NCl$ for XI (b-f, respectively).

Preparation of XII. The solution of $I_4$ was warmed up to +20°C, kept for 1,5h at this temperature, then cooled down to -50°C and quenched with $CH_3COOH$. Usual work-up (see above) and t.l.c. separation ($Al_2O_3$) afforded 3,4,4-trimethyl - [5,6]-benzthiochromane (XII, 0,62 gr, 77%) and XIa (0.24 gr, 22%).

Discussion. We believe that the above data taken together leave no reasonable alternative to the suggested episulfonium ion formulation of the structures of the complexes $I_1$-$I_6$. The existence of bridging in these intermediates is strongly supported by (i) their ability to form both Markovnikov's and anti-Markovnikov's adducts on quenching and (ii) the strong preference for the rear-side nucleophile attack. The chemical behaviour of the $I_1$-$I_6$ in several aspects patterns that of the open carbonium ion. Especially relevant is their ability to undergo: (i) the exclusive (or predominant) attack at carbon atom /10/ for

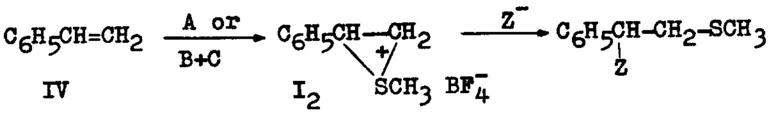
Chart 1



II, R = $CH_3$, Z = OH(a,53)[x]; $OCH_3$(b,63); Cl(c,85); $NHCOC_6H_5$(d,62); H(e,42); $CH(COOC_2H_5)_2$(f,56); $N(C_2H_5)_2$(g,42); $OCOCH_3$(h,54); $C_6H_5S$(i,44)

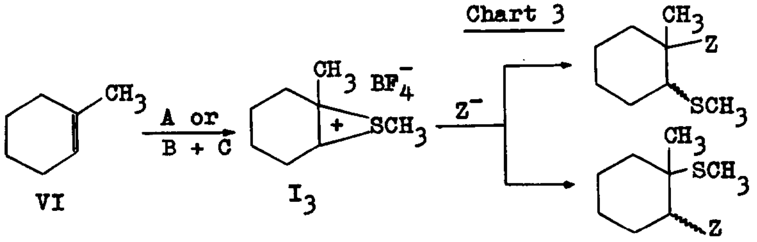
III, R = $C_6H_5$, Z = OH(a,75); $OCOCH_3$(b,70); $OCH_3$(c,97); Cl(d,88)

Chart 2



V, Z=OH(a,42); $OCH_3$(b,67); $OCOCH_3$(c,52); $NHCOCH_3$(d,20)

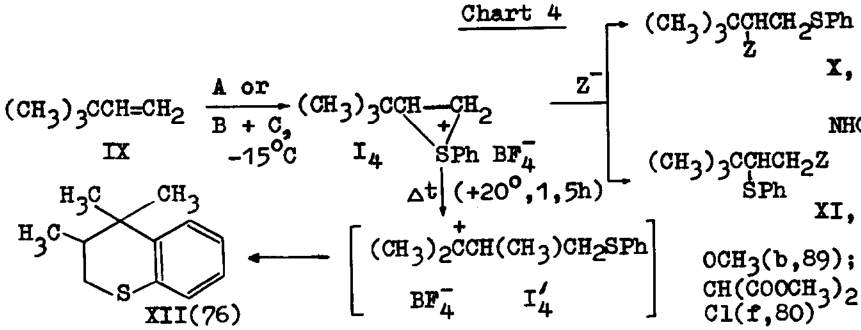
Chart 3



VII, Z = OH(a,40); $OCH_3$(b,50)

VIII, Z=$OCOCH_3$(28)

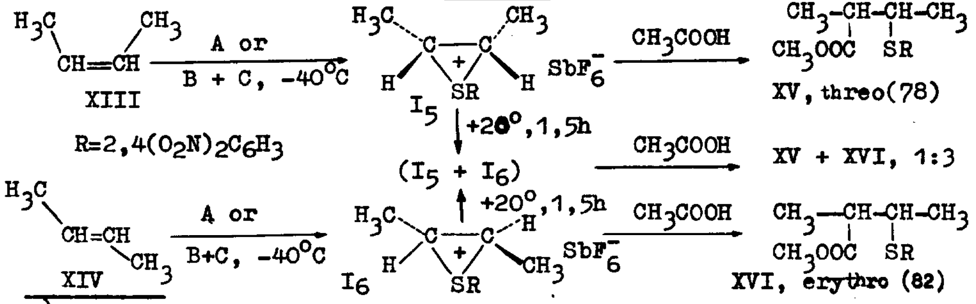
Chart 4



X, Z=$NHCOCH_3$ (a,62); $NHCOC_6H_5$(b,45)

XI, Z=$OCOCH_3$ (a,78); $OCH_3$(b,89); $N(C_2H_5)_2$(c,60); $CH(COOCH_3)_2$(d,50); H(e,34); Cl(f,80)

Chart 5



R=2,4$(O_2N)_2C_6H_3$

XV, threo(78)

XVI, erythro (82)

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[x] Figures in parenthesis refer to yields /6/.

various nucleophiles including $H^-$ (from NaBH or $Et_3SiH$) or RCN /11/ and (ii) stereomutations and sceletal rearrangements. These properties could be accounted for by the assumption of a substantial positive charge localization on carbon and/or by a comparatively low activation barrier for the bridged-ion→open ion transition. Studies on the possible synthetic uses of episulfonium ions as the "masked" equivalents of carbonium ions are under way.

In view of the above results it seems implausible that episulfonium ions similar to $I_1$-$I_6$ could be formed at the rate-determining step of $Ad_E$ reaction of RSHal with alkenes. The latter reaction is well known for its inability to form either rearranged or solvoaddition products /1/ and for the invariancy of its trans-stereospecific course over a wide range of conditions /12/. We believe that the alternative covalent sulfurane structure /13/ should be considered as the more adequate representation of the intermediate involved in RSHal additions to olefin under usually adopted conditions /14/.

## REFERENCES

1. a) W.H.Mueller, Angew.Chem.81, 475 (1969); e.g. b) W.H.Mueller, P.Batler, J.Amer.Chem.Soc.90, 2075 (1968).
2. Stable episulfonium complexes had been previously prepared from: a)cyclooctene, O.J.Pettit, and K.G.Helmkamp, J.Org.Chem.29, 2702(1964); D.Owsley et al. J.Amer.Chem.Soc.91,3606(1969); b)cis-di-tert.-butylethylene, P.Raynolds et al. J.Amer.Chem.Soc.96,3146(1974). Both groups reported the failure to extend the utility of the described procedures to alkenes other than indicated.
3. Preliminary data see, W.A.Smit, A.V.Semenovsky, V.F.Kucherov,M.Z.Krimer, T.N.Chernova and O.V.Lubinskaya, Tetrahedron Letters,1971, 3101.
4. PMR and CMR studies of $I_1$-$I_6$ are under way; results will be reported shortly.
5. The storage of $I_1$-$I_6$ solutions under indicated conditions for several hours did not lead to the decrease in the yields of adduct formed upon quenching.
6. All yields (%) are given for analytically pure samples. The spectral (PMR, IR and MS) and microanalysis date were consistent with the structures shown.
7. E.A.Vorobieva, L.G.Gurvich, N.S.Zefirov, M.Z.Krimer and W.A.Smit,Zh.Org. Khim.10, 883(1974); data on conformations of adducts will be published shortly.
8. Authentic samples of acetates were prepared as described by A.Havlick and N.Kharasch, J.Amer.Chem.Soc.78, 1207 (1956).
9. Thus complex formed from norbornene and $C_6H_5SBF_4$ at-30°C yields unrearranged products upon the quenching,while the warming up of this complex to +20°C afforded mainly 2-fluoro-7-phenylthionorbornane ($^1H$-and $^{19}F$-NMR, MS).
10. Preponderance of attack at sulphure observed in/2a/should be ascribed both to the covalent-like nature of 2,4,6,-trinitrobenzensulphonate complexes and to the transannular hindrance to the rear-side attack in cyclooctane series.
11. $I_5$and $I_6$ were also shown to be reactive toward $\pi$-donor yielding oligomers $C_4H_8.C_4H_7.SC_6H_3(NO_2)_2$(NMR,MS) with the excess of XIII or XIV at 0°C.
12. Thus the temperature changes from -30°C to +140°C did not affected trans-course of p-$ClC_6H_4SCl$ addition to XIII and XIV (G.H.Schmid and V.M.Szismadia. Can.J.Chem.44, 1338 (1966).
13. Similar to the structure originally proposed by D.Owsley, G.Helmkamp and M.Rettig, J.Amer.Chem.Soc. 91, 5239 (1969).
14. Recent data on the formation of rearranged and solvoaddition products for RSHal additions in the presence of perchlorate (I.V.Bodrikov, L.G.Gurvich, N.S. Zefirov, V.R.Kartashov and A.L.Kurtz.Zh.Org.Chim.7, 1545 (1974) disclosed that this reaction could be channeled via the intermediates similar to those described in this paper.