ENE-TYPE REACTION OF "ACTIVATED SULFOXIDE" WITH NON-ACTIVATED OLEFIN. COUNTER-ION DEPENDENT $(1, 2) - \underline{vs}$. [3,2] SHIFT DICHOTOMY OF YLIDES DERIVED FROM ALLYLSULFONIUM SALTS

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<u>Summary</u>: Lithium perchlorate-accelerated ene-type reaction of an "activated sulfoxide" with non-activated trisubstituted olefin to give respective allylsulfonium salt and counter-ion dependent (1,2)- <u>vs</u>. [3,2] rearrangement of the ylide generated from this salt are discussed.

"Activated sulfoxides"^{1,2} belong to a category of weak electrophiles which can react with some (cyclo)aliphatic or (hetero)aromatic C-nucleophiles¹⁻³ as well as with cyclopentadienes and (benzo)fulvenes⁴ to afford respective sulfonium salts. Here we demonstrate the possibility to involve O-acylated sulfonium cations into an ene-type reaction with non-activated olefins and discuss some unique properties of the compounds thus obtained.

Treatment of geranyl acetate (<u>1</u>) with the reagent <u>3</u> /produced <u>in situ</u> from Me₂SO and (CF₃CO)₂O, 3 mol equiv. each% in CH₂Cl₂ at -10° C for 7h yields <u>ca</u>. 90% of the sulfonium salt <u>2a</u>.⁵ Its formation can be explained within Ad_E-type ligand exchange process between <u>3</u> and <u>1 via</u> an intermediate biscation <u>4</u> at a key step (Scheme 1). From this viewpoint, it was reasonable to



expect, in our case, a promotive effect of LiClo_4 found for related electrophilic reactions.⁶ In fact, treatment of <u>1</u> with 1:1 mixture of the reagent <u>3</u> and LiClo_4 (1.2 mol equiv. each) in CH_2Cl_2 at -10°C for lh leads regiospecifically to the perchlorate salt $2b^{5,7}$ in the same isolated yield.

Inspection of PMR spectra of the total reaction product revealed in both cases that the ene process leading to $\underline{2a}, \underline{b}$ is accompanied by a cationic cyclization of the incipient intermediate $\underline{4}$ into cyclogeranyl derivatives $\underline{5a}, \underline{b}$ in up to 10% yield. This conclusion follows from the integral intensity of additional, \underline{cf} .⁷, singlet signals at $\underline{3} \simeq 1.0-1.3$ ppm attributed to <u>gem</u>-dimethyl group protons of $\underline{5}$ and was confirmed by its conversion to safranol (<u>vide infra</u>).

Synthetically most promising reactions of allylsulfonium salts generally involve Stevens and/or [3,2] sigmatropic rearrangements of respective sulfur ylides, <u>cf</u>.^{8,9} The latter were generated in our case under the action of MeONa (3 mol equiv.) in boiling MeOH (3h).¹⁰

Under these conditions, the <u>trifluoroacetates</u> 2a/5a = 95:5 unexpectedly furnished in 60% yield the branched homoallylic sulfide $\underline{6}^{5,11}$ (Scheme 2) contaminated¹² with the traces of its regioisomer $\underline{7}$ and $\leq 5\%$ of (\pm) -safranol ($\underline{8}$),^{5,13} the latter being readily separable by flash chromatography on silica gel. Surprisingly, the <u>perchlorates</u> $\underline{2b}/\underline{5b} = 9:1$ under the same conditions yielded (70%) <u>ca</u>. 93:7 mixture of $\underline{7}^{5,14}$ and $\underline{8}$ containing¹² $\leq 5\%$ of $\underline{6}$.

The occurence of [3,2] reaction of <u>2b</u> derived ylide to <u>7</u> corresponds to the usual pattern of allylic S-ylides rearrangement. On the contrary, Stevens reaction of the, formally, the same ylide (route <u>2a</u> \rightarrow <u>6</u>) looks puzzling in view of the thermodynamic preponderance of [3,2] - over (1,2) shift well documented for aliphatic allylsulfonium ylides.^{8,9} The opposite has been observed mainly in those cases where steric and/or conformational factors prevent the formation of a five-centered 6 π -electronic transition state like <u>9</u>.^{9,15} The absence of such peculiarities for 2a forced us to depict its transformation

Scheme 2



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as a process involving an intermediacy of generated from the starting tight ion pair carbanion <u>10</u> (or tetracoordinated G-sulfurane species formed due to interaction with nucleophilic trifluoroacetate counter-ion). Homolytic dissociation of the C-S bond in <u>10</u> followed by cage-recombination of the stabilized radical pair, <u>cf</u>.^{8,9} would lead finally to the Stevens rearrangement product 6.

Preliminary data demonstrate that the reactions of other trisubstituted olefins (2-methylpentene-2, neryl, linalyl, and citronellyl acetates) with sulfoxides $/Me_2SO$, $(CH_2)_4SO$, PhSOMe/ and transformations of the respective allylsulfonium salts follow the regularities found for the pair $\underline{1}/Me_2SO$.

References and Notes

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- 5. Satisfactory analytical data were obtained for this compound.
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- 7. PMR spectra of <u>2a</u>,<u>b</u> are practically identical \$ ^{CDC1}_{TMS} 3: 1.72 and 1.83 (bs, 6H, CH₃), 2.05 (s, 3H, CH₃CO), 1.8 2.1 (m, 4H, CH₂), 2.90 and 3.08 (s, 6H, CH₃S), 4.26 (bdd, J 4.5 and 13 Hz, 1H, CHS), 4.58 (d, J 6.5 Hz, 2H, CH₂O), 5.37 (bt, J 6.5, 1H, HC⁷), 5.44 and 5.46 ppm (bs, 2H, H₂C=C).
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- 10. The use of such agents as <u>n</u>-BuLi, <u>t</u>-BuOK, NaNH₂, etc. led to a noticeble formation of S-demethylation and *b*-elimination products.
- 11. Colourless oil, b.p. $105-7^{\circ}C/0.06 \text{ mm Hg}$, n_D^{20} 1.5115. PMR spectrum, $\$ TMS^{CDC1}3$: 1.4 - 2.0 (m, 4H, CH₂), 1.65 and 1.67 (bs, 6H, CH₃), 2.08 (s, 3H, CH₃S), 2.25 (m, 1H, HC⁶), 2.53 (d, J 6.5 Hz, 2H, CH₂S), 4.14 (d, J 7 Hz, 2H, CH₂O), 4.78 and 4.85 (bs, 2H, H₂C=C), 5.40 ppm (t, J 7 Hz, 1H, HC=C).
- 12. According to PMR, GLC, and HPLC data.
- 13. Colourless liquid, b.p. 39-40^oC/2 mm Hg, n_D²⁰ 1.4955; A ^{EtOH}_{max} 267 nm (£ 5000). <u>Cf</u>. T. Kametani, K. Suzuki, H. Kurobe, H. Nemoto, Chem. Pharm. Bull. <u>29</u>, 105 (1981).
- 14. Colourless oil, b.p. $108-10^{\circ}$ C/0.05 mm Hg, n_D^{20} 1.5140. PMR spectrum, **8** $_{\text{TMS}}^{\text{CDC1}}$ 3: 1.62, 1.69 and 1.71 (bs, 6H, CH₃), 2.0 - 2.4 (m, 6H, CH₂), 2.11 and 2.14 (s, 3H, CH₃S), 2.55 (m, 2H, CH₂S), 4.15 (bd, J 7 Hz, 2H, CH₂O), 5.18 (m, 1H, Hc⁴), 5.42 ppm (bt, J 7 Hz, 1H, Hc⁸).
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