AN ENE-TYPE REACTION BETWEEN AN UNACTIVATED OLEFIN AND AN "ACTIVATED" SULFOXIDE, AND SOME PROPERTIES OF THE RESULTING SULFONIUM SALTS

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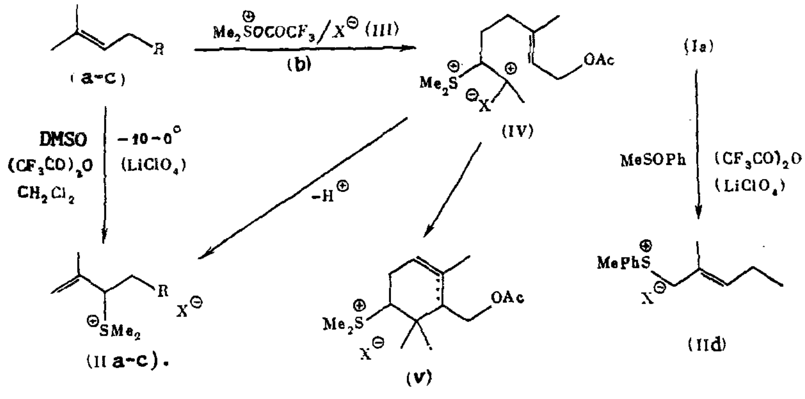
Hyroxysulfonium cations substituted at oxygen ("activated" sulfoxides [1]) are weakly electrophilic species, which have been reported to react with (cyclo)aliphatic and (hetero)aromatic C-nucleophiles, CH-acids [2, 3], cyclopentadienes and fulvenes [4] to give the sulfonium salts. We now report for the first time the use of unactivated, trisubstituted olefins in this reaction, together with some of the properties of the allylsulfonium salts thus obtained, the formation of which was postulated by us in the reaction of the same olefins with sulfoxide halohydrates [5].

Methylpentene (Ia), citronellyl acetate (Ib), and geranyl acetate (Ic) react at —10-0°C with 3 mole-equiv. of a 1:1 mixture of DMSO and $(CF_3CO)_2O$ in dichloromethane to give after 7-8 h nearly quantitative yields of the corresponding trifluoroacetates (IIa-c; A). The structures of these novel sulfonium salts are shown by their spectral data, and confirmed in the case of (IIb, c) by the chemical reactions described below.

The formation of the salts (IIA) is clearly due to attack of the weakly nucleophilic olefin (I) on the S—O bond in the weakly electrophilic acyloxysulfonium ion (III) formed from DMSO and $(CF_3CO)_2O$ [1] via the biscation (IV) in the case of geranyl acetate (Ic). The existence of such intermediates had been postulated in interpreting the results of a formal ene reaction of olefins (Ib, c) with the hydroxyl- and (or) halosulfonium ions (X = Cl, Br) generated from the DMSO·HX complexes [5], and indirectly confirmed by the appearance in the PMR spectrum of the overall product of the reaction under discussion (Ic) of single signals for the gem-dimethyl group (VA) at $\delta \simeq 1.0-1.3$ ppm. The relative integral intensity (RII) of these signals indicates the formation under the conditions described of ~5% of the α-salt(VA), in agreement with the isolation of saffranol (see below) from the mixed perchlorates (IIc)/(V).



R = Me (a), $CH_2CHMe(CH_2)_2OAc$ b), E-$CH_2CMe{=}CHCH_2OAc$ (c), X = CF_3CO_2 (A), ClO_4 (B).

Considering these results in terms of an Ad_E reaction between the starting materials (I) and (III) at the key step, it would be logical to expect, as in related cases [5, 6], that it would be considerably accelerated by the doping effect of added $LiClO_4$ [6, 7]. In fact, treatment of the trisubstituted olefins (I) at —10-0°C in dichloromethane with an

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equimolar mixture of 1.2 mole-equiv. of (III) and $LiClO_4$ results in almost complete conversion, after approximately one hour, into the perchlorates (IIB), the PMR spectra of which are virtually identical with those of the corresponding trifluoroacetates (IIA), and with geranyl acetate (Ic) the impurity (VB), according to these findings for the total product, reaches 10%.

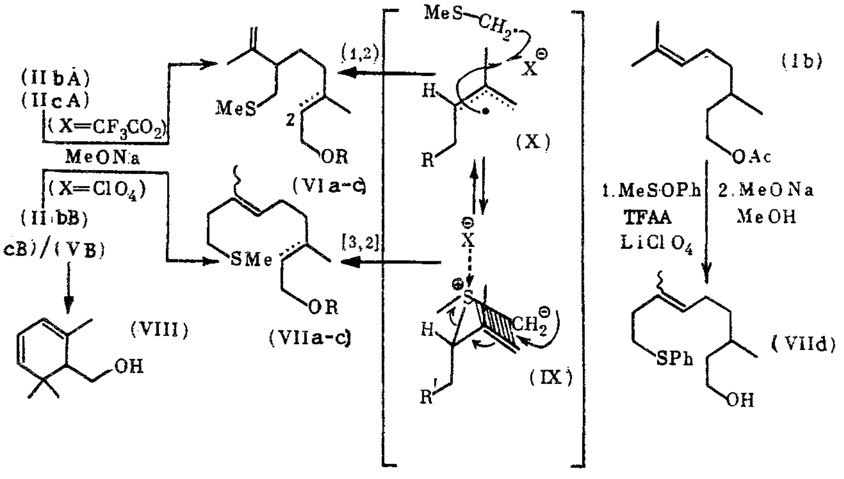
Attempts to carry out both versions of the reaction were unsuccessful with Ph_2SO. However, MeSOPh and (Ia) reacted smoothly to give the oily primary salts (IId; A, B), apparently formed by allyl isomerization of the secondary salts (IIa), which proceeds readily in this instance. The structures of (IId; A, B) were established by their PMR spectra, which in particular showed signals for the methyl (br. s) and vinyl (br. t) protons at $\delta \simeq 1.7$ and 5.4 ppm respectively corresponding to the fragment E-MeC=CH.

The allyldimethylsulfonium salts (II; A, B) which have thus become readily accessible were then examined in some of the known reactions for compounds of this type [8, 9], of greatest synthetic interest being their rearrangement and nucleophilic substitution at the C—S bond.

Treatment of the salts (IIb, c) with strong bases in order to initiate [3, 2]-sigmatropic rearrangement and (or) the Stevens S-ylid rearrangement resulted in all cases in competitive S-demethylation and β-elimination. Maximum suppression of these reactions was achieved using ~3 mol.equiv. of MeONa in boiling methanol. Under these conditions, the trifluoroacetates (IIb, c; A) unexpectedly gave 55-60% yieles of the Stevens rearrangement product (VIa) and (VIc), the first of these being characterized as its acetate (VIb), while according to the PMR spectrum of the reaction mixture the [3, 2] reaction products (VIIa, c) were virtually absent. In contrast, under the same conditions the perchlorate (IIb; B) gave >80% of the alcohol (VIIa), which was also characterized as the acetate (VIIb). Similarly, the mixture of perchlorates (IIc; B)/(VB) reacted smoothly to give a chromatographically readily separable mixture of the allyl alcohols (VIIc) and saffranol (VIII) [10]. In neither case did the amounts of the regioisomers of (VIIa, c), i.e. (VIa, c), exceed 5% (PMR), even when the MeONa was replaced by n-BuLi or $NaNH_2$.

In contrast to the dimethyl suflides (IIa-c; A, B), the thioanisyl derivatives (IId; A, B) were more labile, so that it was not possible to characterize the chromatographically located salts (IIa, d) corresponding to the terpenyl acetates (Ib, c). The most stable of these was the perchlorate (obtained from (Ib)) which was convertible without further purification (by treatment with MeONa) into the hydroxysulfide (VIId) free from contamination by the branched regioisomer (VI).

The structures of the novel sulfides (VI) and (VII) were confirmed by their PMR spectra, which in the case of (VI) showed three characteristic broadened single signals for the isopropenyl residue at $\delta \simeq 4.85$, 4.75, and 1.65 ppm. The E/Z—MeC=CH fragment which is common to the open-chain compounds (VII) appears as a broadened triplet and two singlets, $\delta \simeq 5.2$, 1.7, and 1.6 ppm, assigned respectively to the vinyl and methyl protons, the RII of the latter two signals indicating an E/Z isomer ratio of $\simeq$ 4:1.



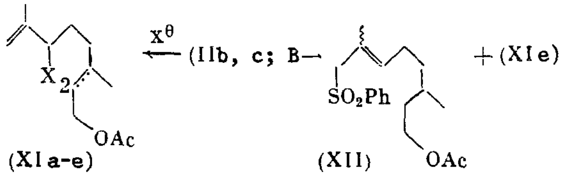
R = H (VIa), (VIIa); Ac(VIb),(VIIb), H, Δ^2(VIc),(VIIc).

On treatment with strong bases, therefore, the dimethylallylsulfonium salts (II) undergo, depending on the counterion present, conversion into the homallyl sulfides (VI) or (VII), the first of which must clearly arise by homolytic dissociation of the C—S bond in the common precursor (IX), followed by recombination of the stabilized radical pair (X) (cf. [8, 9]). It is however known that the contribution of the 1,2-shift is thermodynamically less favored than the converted [3,2]-sigmatropic reaction leading to (VII), which is usually small in the aliphatic, but dominant in the acyclic series in the presence of unfavorable steric and (or) conformational factors which prevent the formation of a five-centered 6π-electron transition state corresponding to the ylid (IX) [9, 11]. Such limitations are clearly absent in (IX), so that the reason for suppression of [3,2]-rearrangement in favor of the Stevens rearrangement, which has no precedent in the chemistry of sulfonium compounds, must obviously be sought in the structural features of this intermediate.

The ylid (IX), obtained from the perchlorate (IIB) and the trifluoroacetate (IIA) probably exists as a correspondingly separated and close ion pair (or even a tetracoordinated sulfurane. It would therefore be reasonable to expect that partial (or even complete) compensation by the trifluoroacetate ion of the effective positive charge on the tricoordinated sulfur atom would increase the activation energy of the [3,2]-sigmatropic rearrangement, thus facilitating the competitive 1,2-shift. In addition, examination of a molecular model of the sulfurane-like structure (IX) (hindered conformation) shows the spatial proximity of the trifluoroacetate group to the methyl group of the isopropenyl residue, hindering the coplanarity of this with the S-ylidene fragment, which is essential for the [3, 2] reaction to proceed. Finally, assuming that the perchlorate corresponding to MeSOPh and the olefin (Ib) has the very likely structure (IId), the observed conversion of this compound into the 1,2-reaction products (VIId) is also explicable in terms of partial intramolecular "extinction" of the charge in the intermediate sulfonium cation by the π-electrons of the phenyl substitutent.

Of the possible reactions of the salts (IIb, c; A, B) with nucleophiles, there were formerly investigated the reaction of the relatively more stable perchorates with appropriate ammonium halides, which as expected proceeded smoothly to give the allyl chlorides (XIa, b) and the bromide (XIc). The latter have also been obtained previously by us from the olefins (Ib, c) and DMSO hydrochloride or hydrobromide in the presence of $LiClO_4$ resulting from partial occurrence of this reaction via the unidentified stage of salts (IIb, c) [5].

Acetolysis of the salt (IIb; B) gives ~35% of the diacetate (XId) [12] with concurrent S-demethylation to give the hitherto unreported acetoxysulfide (XIe). The structures of these compounds, which were mixtures of diastereomers, were confirmed spectroscopically, the presence in the PMR spectrum of (XId) of a signal for the allyl CH_2OAc group (br.s, 4.43 ppm) and its RII indicating the formation of ~10% of the competing S_N2' reaction product. The latter becomes predominant with this salt on treatment with $PhSO_2Na$, to give >75% of a chromatographically readily separable mixture of (XII) and (XIe) ($\approx$2:1).



(XIa-e) (XII)

X = Cl (XIa); X = Cl, Δ^2(XIb); X = Br, Δ^2(XIc); X = OAc(XId); X = SMe(XIe).

The structures of the E/Z-acetoxysulfones (XII) were confirmed by their PMR spectra, and the method used in the case of the related stereoisomers of (VII) showed the E/Z ratio to be $\approx$10:1.

These results therefore show that it is possible to carry out an $LiClO_4$ catalyzed ene reaction between trisubstituted olefins and activated sulfoxides, opening up another route for the termainal functionalization of open-chain isoprenoids.

EXPERIMENTAL

The IR spectra of solutions in CCl_4 were recorded on a UR-20 instrument, and UV spectra (in ethanol) on a Specord UV-VIS spectrophotometer. The PMR spectra of $CDCl_3$ solutions were measured on a Bruker WM-250 (δ, ppm; J, Hz), and mass spectra on a Varian MAT CH-6 spectrometer at 70 eV. R_f values are given for bound layers of Silufol silica.

Dimethyl(2-methylpent-1-en-3-yl)sulfonium Trifluoroacetate (IIa; A), Dimethyl-(8-acetoxy-2,6-dimethyloct-1-en-3-yl)sulfonium Trifluoroacetate (IIb; A), Dimethyl(8-acetoxy-2,6-dimethyloct-1,6E-dien-3-yl)sulfonium Trifluoroacetate (IIc; A) and the Corresponding Perchlorates (IIa-c; B). To a stirred solution at −10°C under argon of 0.36 g (4.3 mmoles) of (Ia) and 1.02 g (13 mmoles) of DMSO in 3 ml of dichloromethane was added over ~1 h 2.73 g (13 mmoles) of $(CF_3CO)_2O$. The mixture was kept for ~6 h at 0°C (followed by TLC), then diluted with pentane and the oily product which separated was purified by threefold precipitation with pentane from a solution in dichloromethane and dried in vacuo to give 0.92 g (87%) of (IIa; A). PMR spectrum: 1.02 t (3H, CH_3, J = 7), 1.80 br. s (3H, CH_3), 1.8 − 2.0 m (2H, CH_2), 2.78 and 2.93 s (6H, CH_3S), 3.87 br. d.d (1H, CHS, J = 4 and 12), 5.33 and 5.43 br. s (2H, $C{=}CH_2$).

To a stirred suspension of 0.4 g (4.75 mmoles) of (Ia), 0.44 g (5.63 mmoles) of DMSO and 0.6 g (5.64 mmoles) of $LiClO_4$ in 3 ml of dichloromethane was added with stirring under argon at —10°C, 1.99 g (9.47 mmoles) of $(CF_3CO)_2O$ over ~5 min. The mixture was kept for ~1 h at 0°C, then diluted with ether. The oily product which separated was purified by freezing out at 0°C from solution in $CHCl_3$, and dried in vacuo to give 1.08 g (93%) of (IIa; B). PMR spectrum: 1.00 t (3H, CH_3, J = 7), 1.80 br. s (3H, CH_3), 1.8—2.0 m (2H, CH_2), 2.86 and 3.02 s (6H, CH_3S), 4.12 br. d.d (1H, CHS, J = 4 and 12), 5.39 and 5.41 br. s (2H, $C{=}CH_2$).

Similarly, from (Ib) there was obtained 90-95% of the trifluoroacetate (IIb; A) and the Perchlorate (IIb; B) as colorless, viscous oils. PMR spectrum of the mixture of isomers (IIb; B): 0.75 br. d(3H, CH_3, J = 6.5), 1.70 br. s (3H, CH_3), 1.92 s (3H, CH_3CO), 0.8-2.0 m (7H, CH, CH_2), 2.76 and 2.94 br. s (6H, CH_3S), 3.95 m (2H, CH_2O), 4.12 m (1H, CHS), 5.27 and 5.33 br. s (2H, $C{=}CH_2$).

Similarly, from (Ic) there were obtained ~90% of the trifluoroacetate (IIc; A) and the perchlorate (IIc, B) admixed with ~5-10% of (VA) and (VB) (PMR), as colorless, viscous oils.

PMR spectrum of (IIc; B): 1.72 and 1.83 br. s (6H, CH_3), 2.05 s (3H, CH_3CO), 1.8-2.1 m (4H, CH_2), 2.90 and 3.08 s (6H, CH_3S), 4.26 br. d.d (1H, CHS, J = 4.5 and 13), 4.58 d (2H, CH_2O, J = 6.5), 5.37 br. t (1H, HC^7, J = 6.5), 5.44 and 5.46 br. s (2H, $C{=}CH_2$).

Methylphenyl(2-methylpent-2E-en-1-yl)sulfonium Trifluoroacetate(IId; A) and the Corresponding Perchlorate (IId; B). Under the conditions described above for (IIa; A), from 0.36 g (4.3 mmoles) of (Ia), 1.47 g (10.5 mmoles) of MeSOPh, and 2.73 g (13 mmoles) of $(CF_3CO)_2O$ there was obtained 1.12 g (85%) of (IId; A) as a colorless, viscous oil. PMR spectrum: 0.68 t (3H, CH_3, J = 7), 1.67 br. s (3H, CH_3), 1.86 d.q (2H, CH_2, J = 6.5 and 7), 3.23 s (3H, CH_3S), 4.21 AB (2H, CH_2S, J_{AB} = 11 Hz, $\Delta\delta$ = 0.26), 5.37 br. t (1H, CH^3, J = 6.5), 7.4-7.9 m (5H, C_6H_5).

As described above for (IIa; B), from 0.4 g (4.75 mmoles) of (Ia), 0.8 g (5.7 mmoles) of MeSOPh, 2 g (9.5 mmoles) of $(CF_3CO)_2O$ and 0.61 g (5.7 mmoles) of $LiClO_4$ there was obtained 1.1 g (75%) of (IId; B) as a colorless, viscous oil, the PMR spectrum of which was the same as that gave above for (IId; A).

3,7-Dimethyl-6-methylthiometyloct-7-en-1-ol (VIa). A solution of 1.8 g of the trifluoracetate (IIb; A) in 10 ml of methanol and 16.1 ml of 3M MeONa in methanol was boiled for 3 h under argon, then diluted with ether, neutralized with 50% sulfuric acid, washed with water, and dried over $MgSO_4$. The residue (0.75 g) after removal of the solvents was chromatographed on 40 g of silica. Gradient elution from hexane to ether (up to 30% of the latter) gave 0.61 g (59%) of the hydroxysulfide (VIa) as a colorless oil, R_f 0.60 (ether—hexane, 1:2). PMR spectrum of the mixture of diastereomers of (VIa): 0.90 br. d (3H, CH_3, J = 5.5), 1.1-1.8 m (7H, CH, CH_2), 1.60 br. s (3H, CH_3), 2.05 s (3H, CH_3S), 2.20 m (1H, HC^6), 2.45 br. d (2H, CH_2S, J = 7), 3.55 m (2H, CH_2O), 4.70 m (2H, $C{=}CH_2$).

Acetate (VIb). Colorless liquid, bp 99-100°C (0.08 mm), n_D^{20} 1.4815. IR spectrum (ν, cm^{-1}): 900, 965, 1040, 1055, 1260, 1370, 1440, 1465, 1730, 2875, 2925, 2965, 3025.

PMR spectrum of the mixture of diastereomers of (VIb): 0.89 and 0.91 d (3H, CH_3, J = 5.5), 1.1-1.8 m (7H, CH, CH_2), br. s (3H, CH_3), 2.02 and 2.07 s (6H, CH_3S, CH_3CO), 2.23 m (1H, HC^6), 2.51 br. d (2H, CH_2S, J = 7), 4.08 m (2H, CH_2O), 4.74 and 4.82 br. s (2H, $C{=}CH_2$). Found: C 64.57; H 10.19; S 12.79%; M^+ 258. $C_{14}H_{26}O_2S$. Calculated: C 65.07; H 10.14; S 12.40%; molec. wt. 258.4.

3,7-Dimethyl-6-methylthiomethylocta-2E-7-diene-1-ol (VIc). Obtained similarly from 1.4 g of the trifluoroacetate (IIc; A) was 0.46 g (57%) of (VIc) as a colorless oil, bp 105-107°C (6.10^{-2} mm), n_D^{20} 1.5115. IR spectrum (ν, cm^{-1}): 900, 990, 1100, 1170, 1240, 1380, 1440, 1645, 1665, 2865, 2925, 2945, 2990, 3080, 3450, 3615. PMR spectrum: 1.4-2.0 m (4H, CH_2), 1.65 and 1.67 br. s (6H, CH_3), 2.08 s (3H, CH_3S), 2.25 m (1H, HC^6), 2.53 d (2H, CH_2S, J = 6.5), 4.14 d (2H, CH_2O, J = 7), 4.78 and 4.85 br. s (2H, $C{=}CH_2$), 5.40 t (1H, $C{=}CH$, J = 7). Found: C 67.26; H 10.49; S 14.78%; (M^+—Me) 199. $C_{12}H_{22}OS$. Calculated: C 67.24; H 10.34; S 14.96%; molec. wt. 214.4.

3,7-Dimethyl-1-thiomethylon-3E/Z-en-9-ol (VIIa). A solution of 1.54 g of the percholorate (IIb; B) in 10 ml of methanol and 14.3 ml of 3 M MeONa in methanol was boiled for 2 h under argon, then diluted with ether. The usual workup gave 0.81 g of product, which was chromatographed on 50 g of silica. Gradient elution from hexane to ether (up to 30% of the latter) gave 0.75 g (82%) of the hydroxysulfide (VIIa) as a colorless oil, R_f 0.46 (ether—hexane, 2:1). IR spectrum (ν, cm^{-1}): 965, 1060, 1150, 1225, 1315, 1380, 1440, 2855, 2915, 3300, 3630. PMR spectrum: 0.90 d (3H, CH_3, J = 6), 1.1-1.7 m (5H, CH, CH_2), 1.57 and 1.62 br. s (3H, CH_3), 1.9-2.4 m (4H, $CH_2C{=}C$), 2.09 and 2.12 s (3H, CH_3S), 2.55 m (2H, CH_2S), 3.65 m (2H, CH_2O), 5.17 br. t (1H, $C{=}CH$, J = 7).

Acetate (VIIb). Colorless liquid, bp 104-105°C (0.05 mm), n_D^{20} 1.4829. IR spectrum (ν, cm^{-1}): 960, 1055, 1240, 1365, 1440, 1740, 2850, 2920, 3020. PMR spectrum: 0.90 d (3H, CH_3, J = 6), 1.1-1.7 m (5H, CH, CH_2), 1.61 br. s (3H, CH_3), 1.9-2.3 m (4H, $CH_2C{=}C$), 2.03 s (3H, CH_3CO), 2.09 and 2.12 s (3H, CH_3S), 2.55 m (2H, CH_2S), 4.08 m (2H, CH_2O), 5.15 br. t (1H, $C{=}CH$, J = 6.5). Found: C 64.60; H 9.89; S 12.00%; M^+ 258. $C_{14}H_{26}O_2S$. Calculated: C 65.07; H 10.14; S 12.40%, molec. wt. 258.4.

To a rapidly stirred suspension of sodamide, freshly prepared from 250 mg (10.9 mg-atom) of sodium in 50 ml of ammonia, was added at —60°C under argon a solution of 1.73 g (4.8 mmoles) of the perchorate (IIb; B) in 15 ml of

THF over ~5 min. The mixture was kept for 20 min at —60°C, then decomposed with saturated aqueous ammonium chloride, the ammonia evaporated, and the residue extracted with ether. The usual workup of the organic layer gave 1.1 g of product, which was chromatographed on 80 g of silica. Gradient elution from hexane to ether gave 0.84 g (72%) of the acetate (VIIb) and 0.2 g (20%) of the alcohol (VIIa), identical with samples of these compounds prepared as above.

To a stirred solution of 0.99 g (2.8 mmoles) of the perchlorate (IIb; B) in 20 ml of THF was added at —60°C under argon 3.4 ml of a 2.1 M solution of n-BuLi in hexane (7.1 mmoles). The mixture was kept for 30 min at —60°C, then decomposed with 20 ml of ethyl acetate, the mixture warmed to ~25°C over ~15 min, and after 30 min worked up in the usual way. The product obtained (0.93 g) was chromatographed on 50 g of silica. Gradient elution from hexane to ether (up to 10% of the latter) gave 0.49 g (69%) of the E/Z-acetoxysulfide (VIIb), identical with the sample described above.

3,7-Dimethyl-1-thiomethylnona-3E/Z,7E-dien-9-ol (VIIc) and (±)-Saffronol (VIII). As described above for (VIIa), from 2.8 g (7.8 mmoles) of the perchlorates (IIc; B)/(VB) ~ 9:1 in 15 ml of methanol and 26 ml of 3 M MeONa in methanol (78 mmoles) there was obtained 1.4 g of product, which was chromatographed on 50 g of silica. Gradient elution from hexane to ether (up to 30% of the latter) gave 1.04 g (62%) of (VIIc) and 120 mg (10%) of (VIII).

Hydroxysulfide (VIIc). Colorless oil, bp 108-110°C (0.05 mm), n_D^{20} 1.5140. IR spectrum (ν, cm^{-1}): 995, 1095, 1220, 1315, 1440, 1670, 2860, 2970, 3480, 3620. PMR spectrum: 1.62, 1.69, and 1.71 br. s (6H, CH_3), 2.0-2.4 m (6H, CH_2), 2.11 and 2.14 s (3H, CH_3S), 2.55 m (2H, CH_2S), 4.15 br. d (2H, CH_2O, J = 7), 5.18 m (1H, HC^4), 5.42 br. t (1H, HC^8, J = 7). Found: C 67.08; H 10.34; S 14.89%; M^+ 214. $C_{12}H_{22}OS$. Calculated: C 67.24; H 10.34; S 14.95%; molec. wt. 214.4.

(±)-Saffronol (VIII). Colorless liquid, bp 39-40°C (2 mm), n_D^{20} 1.4955. UV spectrum: λ_{max} 267 nm (ε 5000) (EtOH). PMR spectrum: 1.03 and 1.15 s (6H, CH_3), 1.78 br. t (X-region of the ABX spectrum) (1H, HC^1, $J_{AX} \simeq J_{BX} \simeq 4.5$), 1.86 br. s (3H, CH_3), 3.74 AB (2H, CH_2O, $J_{AX} \simeq J_{BX} \simeq 4.5$, $J_{AB} = 11.5$, $\Delta\delta = 0.03$), 5.37 br. d (1H, HC^5, J = 9), 5.71 d.d (1H, HC^4, J = 5.5 and 9), 5.77 br. d (1H, HC^3, J = 5.5), cf. [10]. Found: C 78.56; H 10.50%; M^+ 152. $C_{10}H_{16}O$. Calculated: C 78.90; H 10.59%; molec. wt. 152.2.

3,7-Dimethyl-1-phenylthionon-3E/Z-en-9-ol (VIId). To a suspension of 0.94 g (4.74 mmoles) of (IB), 1 g (7.13 mmoles) of MeSOPh, and 0.76 g (7.14 mmoles) of $LiClO_4$ in 10 ml of dichloromethane was added over ~5 min with stirring at —40°C under argon 2 g (9.52 mmoles) of $(CF_3CO)_2O$. The mixture was kept for ~30 min at —10°C, then diluted with chloroform, and the resulting solution washed with saturated $NaHCO_3$ solution followed by water, and dried over $MgSO_4$. The residue after removal of the solvents under reduced pressure was purified by reprecipitation from dichloromethane with ether, and dried in vacuo. The resulting oily product (1.9 g) was dissolved in 10 ml of methanol, and treated at 0°C with 4.75 ml of 3 M MeONa in methanol (14.25 mmoles). The mixture was kept for 3 h at ~25°C, then diluted with ether, and the organic salt was neutralized with 50% H_2SO_4, washed with water, and dried over $MgSO_4$. The residue (1 g) after removal of the solvents under reduced pressure was chromatographed on 50 g of silica. Gradient elution from hexane to ether (up to 30% of the latter) gave 0.7 g (53% based on citronellyl acetate) of (VIId) as a colorless oil, R_f 0.49 (ether—hexane, 2:1). IR spectrum (ν, cm^{-1}): 960, 1030, 1095, 1380, 1440, 1480, 1585, 2875, 2925, 3360, 3635. PMR spectrum: 0.87 and 0.91 d (3H, CH_3, J = 6), 1.1-1.6 m (5H, CH, CH_2), 1.63 and 1.71 br. s (3H, CH_3), 1.8-2.4 m (4H, $CH_2C{=}C$), 2.95 m (2H, CH_2S), 3.65 m (2H, CH_2O), 5.20 br. t (1H, $C{=}CH$, J = 7), 7.1-7.4 m (5H, C_6H_5). Found: C 73.30; H 9.44; S 11.02%; M^+ 278. $C_{17}H_{26}OS$. Calculated: C 73.33; H 9.41; S 11.51%, molec. wt. 278.5.

Chloride (XIa). A solution of 1.56 g (4.35 mmoles) of perchlorate (IIb; B) and 1.49 g (6.53 mmoles) of $BnEt_3N/Cl$ in 20 ml of chloroform was boiled for 7 h under argon, then diluted with hexane, the solid filtered off, the filtrate evaporated in vacuo, and the residue (0.9 g) chromatographed on 80 g of silica. Gradient elution from hexane to ether (up to 10% of the latter) gave 0.7 g (70%) of (XIa), bp 94-96°C (1 mm), identical with an authentic sample [5].

Chloride (XIb). Similarly, from 0.92 g (2.58 mmoles) of the perchlorate (IIc; B) and 1.16 g (5.1 mmoles) of $BnEt_3N/Cl$ in 15 ml of chloroform there was obtained 0.42 g (70%) of (XIb), bp 72-74°C (0.06 mm), identical with an authentic sample [5].

Bromide (XIc). A solution of 0.82 g (2.3 mmoles) of the perchlorate (IIc; B) and 1.48 g (4.6 mmoles) of $n\text{-}Bu_4N/Br$ in 15 ml of chloroform was boiled for 2 h under argon, then evaporated in vacuo, the residue suspended in ~5 ml of CCl_4 and transferred to a chromatographic column with 30 g of silica. Gradient elution from hexane to ether (up to 10% of the latter) gave 0.2 g (32%) of (XIc), the PMR spectrum of which was identical with that of a previously prepared sample [5].

Diacetate (XId) and 3,7-Dimethyl-6-methylthiooct-7-en-1-ol Acetate (XIe). A suspension of 1.3 g (3.62 mmoles) of the perchlorate (IIb; B) and 0.71 g (7.24 mmoles) of AcOK in 15 ml of acetonitrile was boiled with stirring under argon for 7 h, then diluted with hexane, the solid filtered off, the filtrate evaporated, and the residue (0.9 g) acetylated in the usual way (Ac_2O/Py) and chromatographed on 50 g of silica. Gradient elution from hexane to ether (up to 30% of the latter) gave 310 mg (35%) of (XIe) and 325 mg (35%) of (XId) [12] as colorless liquids, R_f 0.62 and 0.28, respectively (ether—hexane, 1:2).

IR spectrum of diastereomeric acetates (XId) (ν, cm^{-1}): 910, 1030, 1060, 1245, 1370, 1460, 1740, 2885, 2970. PMR spectrum: 0.91 and 0.92 d (3H, CH_3, J = 7), 1.1-1.8 m (7H, CH, CH_2), 1.72 br. s (3H, CH_3), 2.04 and 2.06 s (6H, CH_3CO), 4.08 m (2H, CH_2O), 4.88 and 4.93 br. s (2H, $C{=}CH_2$), 5.13 br. t (1H, CHO, J = 6). Found: C 65.88; H 9.43%; M^+ 256. $C_{14}H_{24}O_4$. Calculated: C 65.59; H 9.43%; molec. wt. 256.3.

IR spectrum of the mixture of diastereomeric sulfides (XIe) (ν, cm^{-1}): 960, 1035, 1060, 1240, 1365, 1460, 1740, 2870, 2960. PMR spectrum: 0.92 and 0.97 d (3H, CH_3, J = 6.5), 1.1-1.8 m (7H, CH, CH_2), 1.71 and 1.76 br. s (3H, CH_3), 1.91, 1.93, 2.03, and 2.14 s (6H, CH_3CO, CH_3S), 3.08 m (1H, CHS), 4.10 m (2H, CH_2O), 4.74 and 4.85 br. s (2H, $C{=}CH_2$). Found: S 12.83%; M^+ 244. $C_{13}H_{24}O_2S$. Calculated: S 13.11%; molec. wt. 244.4.

2,6-Dimethyl-1-phenylsulfonyloct-2E/Z-en-8-ol Acetate (XII) and Acetoxysulfide (XId). A solution of 1.3 g (3.62 mmoles) of the perchlorate (IIb; B) and 1.19 g (7.24 mmoles) of $PhSO_2Na$ in 10 ml of DMF was heated for 3 h at 80°C under argon, then diluted with ether, washed with water, and dried over $MgSO_4$. The residue (0.9 g) after removal of the solvents in vacuo was chromatographed on 50 g of silica. Gradient elution from hexane to ether (up to 40% of the latter) gave 0.2 g (23%) of (XIe), identical with the sample prepared above, and 0.65 g (53%) of (XII).

E/Z-Acetoxysulfone (XII). Colorless oil, R_f 0.60 (ether—hexane, 4:1). IR spectrum (ν, cm^{-1}): 910, 1030, 1090, 1160, 1240, 1320, 1450, 1740, 2875, 2960. PMR spectrum: 0.82 and 0.87 d (3H, CH_3, J = 6.5), 0.9-1.6 m (5H, CH, CH_2), 1.63 and 1.70 br. s (3H, CH_3), 1.90 m (2H, $CH_2C{=}C$), 2.00 s (3H, CH_3CO), 3.68 br. s (2H, CH_2S), 4.00 m (2H, CH_2O), 4.99 br. t (1H, $C{=}CH$, J = 7), 7.4-7.9 m (5H, C_6H_5). Found: C 64.10; H 7.70; S 8.99%; M^+ 338. $C_{18}H_{26}O_4S$. Calculated: C 63.88; H 7.74; S 9.47%; molec. wt. 338.5.

CONCLUSIONS

1. Using DMSO and MeSOPh it has been shown for the first time that O-trifluoroacetylated sulfoxides react with unactivated trisubstituted olefins to give allylsulfonium salts.

2. $LiClO_4$ has been found to accelerate this ene-type reaction.

3. It has been found for the first time in the aliphatic series that the competition between [3, 2]-rearrangement and the Stevens rearrangement of the S-ylid generated from the allylsulfonium salt is governed by the type of counterion present, and this observation has been rationalized.

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