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#### SYNTHESIS OF SUBSTITUTED CYCLOPENTANONES FROM 6-METHYLHEPT-5-EN-2-ONE

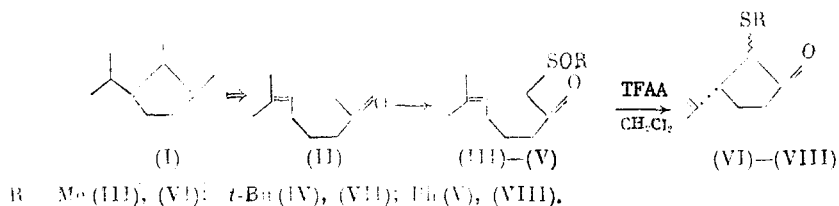
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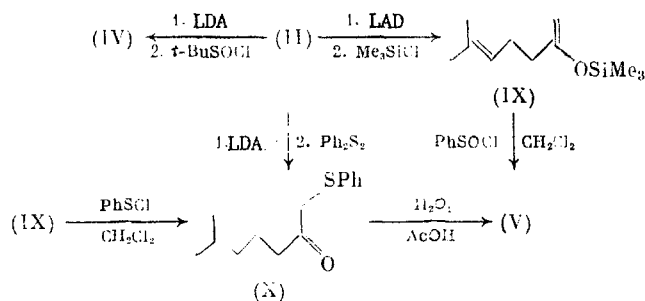
Readily available tert-butyl- and phenyl sulfoxide derivatives of methylheptenone were converted by the Pummerer method to the corresponding five-membered keto sulfides which are probable precursors of iridanes and related terpenic cyclopentanoids.

One of the approaches to a complete synthesis of terpene cyclopentanoids, for example, the iridanes widely found in nature (I) [1], could use easily accessible methylheptenone (II) as a starting synthone. This assumption is based on an observation made recently of the relative ease with which a simple derivative of (II) – the methyl sulfoxide (III) undergoes cyclization under the action of trifluoroacetic anhydride (TFAA) to a mixture of isomeric ketosulfides (VI) [2]. With the above goal in mind we examined as the initial step the synthesis of keto sulfoxides (IV) and (V) related to (III) and their conversion according to Pummerer to the corresponding cyclopentanones (VII) and (VIII), and then some of their selective chemical conversions.



Tert-butyl-(IV) and phenyl substituted (V) sulfoxides were prepared by two different methods from methylheptenone (II) (scheme 1). Thus, compound (IV) was obtained

Scheme 1

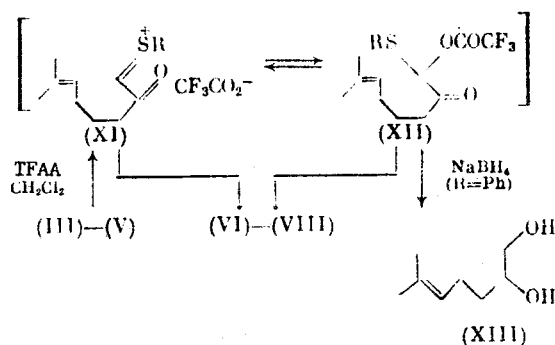


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in a yield of ~50% by direct sulfonylation with *t*-BuSOCl of the Li-enolate formed by kinetically controlled deprotonation of ketone (II) with lithium diisopropylamide (LDA) [3]. The competing formation of the secondary regioisomer does not exceed 2% (PMR data; 250 MHz). On the other hand, low-temperature sulfonylation of the Li enolate [3] or the vinylsilyl ether (IX) easily formed therefrom, upon treatment with Ph<sub>2</sub>S<sub>2</sub> or PhSOCl leads smoothly to  $\alpha$ -keto sulfide (X) which is then selectively oxidized to phenyl sulfoxide (V). However, it was more effective to synthesize of the latter by sulfonylation of ether (IX) with PhSOCl. The yield of (V) was ~70% after the two steps examined here.

The previously unknown sulfoxides (IV) and (V) and phenyl-keto sulfide (X) were characterized by elemental and spectral analyses. Moreover, it was shown (scheme 2)

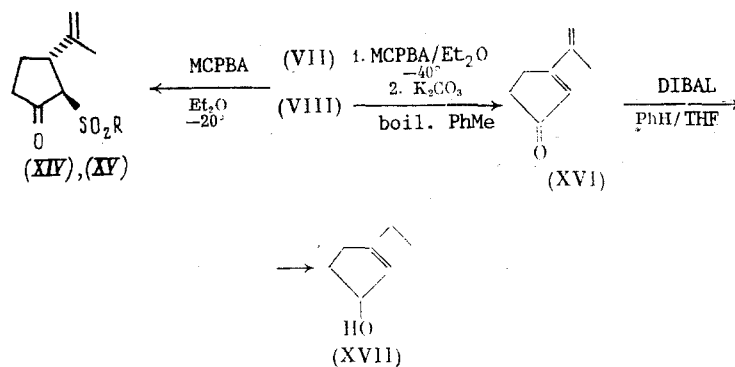
Scheme 2



that, similarly to methyl sulfoxide (III), compounds (IV) and (V) under the action of TFAA can be easily converted into the corresponding trans-disubstituted cyclopentanones (VII) and (VIII) with contamination in both cases by cis isomer in the amount of ~15%. This conversion is interpreted easily as an intramolecular reaction of the enone type for the Pummerer intermediate (XI) or the corresponding stabilized hemi-trifluoroacetoxy sulfide (XII), the existence of which can be recorded (see [2, 4]) by PMR spectroscopy. In case of tert-butyl derivative (IV) the spectrum of the reaction mixture at -40°C shows a signal due to the HCS proton of acyloxy intermediate (XII) at  $\delta \approx 6.0$  ppm. The integrated density becomes maximum at ~-20°C and then with temperature increase (to ~25°C), it gradually (in 2 h) subsides with the simultaneous intensification of the signal integrals of the final cyclization product (VII). For phenyl sulfoxide (V), the corresponding hemi-acyloxy sulfide (XII; R = Ph) turned out to be a fully stable compound and was isolated by flash chromatography of a reaction mixture on SiO<sub>2</sub>. Upon boiling in toluene (~1 h) ketone sulfides (VIII) were obtained in >60% yield, which were apparently formed by heterolysis in intermediate (XII; R = Ph) of the C-O bond, and by hydride reduction the known [5] glycol (XIII) was obtained.

Cyclopentanones (VII) and (VIII), obtained for the first time, were characterized by elemental and spectral analyses of mixtures of their stereoisomers which could not be separated by chromatography. The composition of these mixtures, shown above, follows from comparison in their PMR spectra of the HCS proton signal integrals for the cis- and trans isomers at  $\delta = 3.04$  and 3.36 ppm for (VII) and 3.66 and 3.38 ppm for (VIII), respectively.

By low-temperature oxidation with *m*-chloroperbenzoic acid (MCPBA) keto sulfides (VII) and (VIII) were converted selectively and with high yield into corresponding and previously unknown trans-keto sulfones (XIV) and (XV) without contamination by cis isomers, which follows from a comparative analysis of the PMR spectra of the starting and final substances. Moreover, by using a temperature low enough to prevent the oxidation of phenyl sulfide (VIII) to (XV) but which allows the intermediate isomeric sulfoxides to mildly thermolyze without isolation the known [2] isopropenylcyclopentenone (XVI) was easily obtained, which was reduced with diisobutylaluminum hydride (DIBAL) to allyl alcohol (XVII). Its structure was confirmed by elemental and spectral analysis.



Thus, from the industrially accessible methylheptenone (II) a simple synthesis was carried out of a series of functionalized cyclopentanones which are suitable for elaboration to iridanones (I) and related terpenoids.

#### EXPERIMENTAL

Melting points were determined on a Koffler block. IR spectra (in  $\text{CHCl}_3$ ) were taken on a UR-20 instrument. PMR spectra ( $\delta$ , ppm; J, Hz) of solutions in  $\text{CDCl}_3$  were measured on a Bruker WM-250 spectrometer. Mass spectra were obtained on Varian MAT CH-6 and Varian MAT 311a instruments at 70 eV.  $R_f$  values are given for Silufol  $\text{SiO}_2$  layers.

6-Methyl-1-tert-butylsulfinylhept-5-en-5-one (IV). To a solution of LDA, vigorously stirred at  $-50^\circ\text{C}$ , prepared from 35.8 ml of 1.8 M N-BuLi solution in hexane (64.5 mmoles) and 6.91 g (68.3 mmoles) of *i*-Pr<sub>2</sub>NH in 75 ml of THF, in 5 min 6 g (47.5 mmoles) of compound (II) was added. The reaction mixture after 5 min was treated for 10 min with 8.72 g (62 mmoles) of *t*-BuSOCl [6], heated for 1 h to  $\sim 25^\circ\text{C}$ , kept for 30 min at  $\sim 25^\circ\text{C}$ , decomposed with saturated  $\text{NH}_4\text{Cl}$  solution, and extracted with ether. The extract was washed with water, dried with  $\text{MgSO}_4$ , evaporated under vacuum, and the residue ( $\sim 10$  g) was chromatographed on 300 g  $\text{SiO}_2$ . Gradient elution from hexane to ether gave 1.08 g of the starting (II) and 4.23 g (47%) of (IV) as a light-yellow oil with  $R_f$  of 0.28 (ether). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1040, 1075, 1175, 1230, 1370, 1460, 1660, 1715, 2860-3030. PMR spectrum: 1.24 s (9H,  $\text{CH}_3$ ), 1.59 and 1.67 br. s (6H,  $\text{CH}_3$ ), 2.3 and 2.7 m (4H,  $\text{CH}_2$ ), 3.47 AB (2H, HCS,  $J_{AB} = 13.5$ ,  $\delta = 0.06$ ), 5.06 br. t (1H,  $\text{HC}=\text{C}$ ,  $J = 7$ ). High resolution mass spectrum for  $m/z$  174  $[\text{M} - \text{C}_4\text{H}_8]^+$ . Found: 174.07184. Calculated for  $\text{C}_8\text{H}_{14}\text{O}_2\text{S}$ : 174.07137.

6-Methyl-1-phenylthiohept-5-en-2-one (X). To a vigorously stirred at  $-70^\circ\text{C}$  (Ar) LDA solution, made from 20.1 ml of 1.7 M N-BuLi solution in hexane (34.2 mmoles) and 3.62 g (35.8 mmoles) of *i*-Pr<sub>2</sub>NH in 40 ml of THF, over 5 min a solution of 3.14 g (24.9 mmoles) of (II) in 4 ml of THF was added, then in 5 min 6.53 g (29.9 mmoles) of  $\text{Ph}_2\text{S}_2$  was added by portions over 10 min. The reaction mass was heated for 1 h to  $25^\circ\text{C}$ , maintained for 1.5 h at  $\sim 25^\circ\text{C}$ , and treated as described above. There was obtained  $\sim 3$  g of a product which was chromatographed on 100 g of  $\text{SiO}_2$ . Gradient elution from hexane to 50% ether gave 2.85 g (49%) of compound (X) in the form of yellow oil with bp of  $120\text{--}122^\circ\text{C}$  (2 mm),  $n_D^{20}$  1.5475. IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1030, 1075, 1190, 1245, 1380, 1440, 1485, 1590, 1710, 2860-3070. PMR spectrum: 1.60 and 1.66 br. s (6H,  $\text{CH}_3$ ), 2.25 dt (2H,  $\text{HC}^4$ ,  $J = 8$  and 6.5), 2.62 t (2H,  $\text{HC}^3$ ,  $J = 8$ ), 3.67 s (2H, HCS), 5.04 br. t (1H,  $\text{HC}=\text{C}$ ,  $J = 6.5$ ), 7.2-7.5 m (5H,  $\text{C}_6\text{H}_5$ ). Found: C 71.81; H 7.80; S 13.69%;  $M^+$  234.  $\text{C}_{14}\text{H}_{18}\text{OS}$ . Calculated: C 71.75; H 7.74; S 13.68%; Mol. wt. 234.4.

To a solution of 0.65 g (3.28 mmoles) of (IX) [3] in 6 ml  $\text{CH}_2\text{Cl}_2$ , stirred at  $-70^\circ\text{C}$  (Ar) in 5 min a solution of 0.49 g (3.39 mmole) of  $\text{PhSCl}$  [7] in 2 ml  $\text{CH}_2\text{Cl}_2$  was added. The reaction mixture was heated for 20 min to  $0^\circ\text{C}$ , diluted with ether, and neutralized with saturated  $\text{NaHCO}_3$  solution. The aqueous layer was separated and extracted with ether. By the usual treatment of the combined organic layer there was obtained  $\sim 0.7$  g of a substance which was chromatographed on 25 g  $\text{SiO}_2$ . Gradient elution from hexane to ether (to 50% of the latter) gave 0.3 g (39%) of compound (X), the characteristics of which are practically identical with the ones cited above for this compound.

6-Methyl-1-phenylsulfinylhept-5-en-2-one (V). To a stirred at  $5^\circ\text{C}$  solution of 0.6 g (2.56 mmoles) of (X) in 1 ml of AcOH for 5 min 1.45 g of aqueous 30%  $\text{H}_2\text{O}_2$  (12.8 mmoles) was added. The reaction mixture was heated for 20 min to  $25^\circ\text{C}$ , kept at this temperature

for 4 h, then treated with ether, and neutralized with a saturated  $\text{NaHCO}_3$  solution. The aqueous layer was separated and extracted with ether. By the usual treatment of the combined organic layer there was obtained ~0.6 g of a substance which was chromatographed on 30 g  $\text{SiO}_2$ . Gradient elution from hexane to ether gave 0.39 g (61%) of compound (V) in the form of colorless crystals, mp 30-31.5°C (hexane). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1050, 1090, 1245, 1380, 1450, 1670, 1715, 2870-3080. PMR spectrum: 1.52 and 1.61 br. s (6H,  $\text{CH}_3$ ), 2.15 and 2.45 m (4H,  $\text{CH}_2$ ), 3.80 AB (2H, HCS,  $J_{AB} = 14.5$ ,  $\delta = 0.1$ ), 4.95 br. t (1H,  $\text{HC}=\text{C}$ ,  $J = 8$ ), 7.4-7.7 m (5H,  $\text{C}_6\text{H}_5$ ). Found: S 12.78%; 125  $[\text{M} - \text{PhSO}]^+$ .  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}$ . Calculated: S 12.81%, Mol. wt. 250.4.

To a solution of 1.95 g (9.83 mmoles) of (IX) in 10 ml  $\text{CH}_2\text{Cl}_2$ , vigorously stirred, over 10 min a solution of 1.77 g (11 mmole) of  $\text{PhSOCl}$  [8] in 5 ml  $\text{CH}_2\text{Cl}_2$  was added. The reaction mixture was heated for 10 min to 0°C, then diluted with ether, and neutralized with saturated  $\text{NaHCO}_3$  solution. The aqueous layer was separated and extracted with ether. The usual treatment of the combined organic layer gave ~2.6 g of a substance which was chromatographed under the conditions of the preceding experiment. There was obtained 1.88 g (76%) of compound (V), identical to the sample of this compound described above.

cis/trans-3-Isopropenyl-2-tert-butylthiocyclopenta-1-ones (VII). To a stirred solution at 0°C (Ar) of 3.6 g (15.6 mmoles) of (IV) in 50 ml  $\text{CH}_2\text{Cl}_2$  over 5 min 4.27 g (20.3 mmoles) of TFAA was added. The reaction mixture was heated in 30 min to 25°C, kept at this temperature for 2 h, then diluted with ether and neutralized with saturated  $\text{NaHCO}_3$  solution. The aqueous layer was separated and extracted with ether. By the usual treatment of the combined organic layer there was obtained ~4 g of a substance which was chromatographed on 120 g  $\text{SiO}_2$ . Gradient elution from hexane to ether (up to 30% of the latter) gave 2.34 g (71%) of an epimeric mixture (VII) (trans/cis  $\approx$ 5:1; PMR data) in the form of colorless oil,  $R_f$  0.41 (ether-hexane, 1:4). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 900, 1160, 1240, 1370, 1460, 1490, 1660, 1740, 2870-3030, 3100.

PMR spectrum of cis (VII): 1.34 s (9H,  $\text{CH}_3$ ), 1.59 br. s (3H,  $\text{CH}_3$ ), 2.0-2.7 m (5H,  $\text{CH}_2$ ,  $\text{HC}^3$ ), 3.04 d (1H, HCS,  $J = 8$ ), 4.80 and 4.87 br. s (2H,  $\text{H}_2\text{C}=\text{C}$ ).

PMR spectrum of trans (VII): 1.34 s (9H,  $\text{CH}_3$ ), 1.78 br. s (3H,  $\text{CH}_3$ ), 2.0-2.7 m (4H,  $\text{CH}_2$ ), 2.85 m (1H,  $\text{HC}^3$ ), 3.36 d (1H, HCS,  $J = 6$ ), 4.71 and 4.95 br. s (2H,  $\text{H}_2\text{C}=\text{C}$ ). Found: C 67.68; H 9.57; S 15.06%;  $\text{M}^+$  212,  $\text{C}_{12}\text{H}_{20}\text{OS}$ . Calculated: C 67.87; H 9.49; S 15.10%; Mol. wt. 212.4.

6-Methyl-1-trifluoroacetoxy-1-phenylthiohept-5-en-2-one (XII). To a solution stirred at 0°C (Ar) of 0.11 g (0.44 mmole) of (V) in 2 ml  $\text{CH}_2\text{Cl}_2$  0.11 g (0.52 mmole) of TFAA was added in one portion. The reaction mixture over 20 min was heated to ~25°C, then diluted with ether, and neutralized with saturated  $\text{NaHCO}_3$  solution. The aqueous layer was separated and extracted with ether. By the usual treatment of the combined organic layer there was obtained 0.14 g of a substance which was chromatographed on 5 g  $\text{SiO}_2$ . Gradient elution from hexane to ether (up to 20% of the latter) gave 0.1 g (66%) of (XII) in the form of colorless oil,  $R_f$  0.43 (ether-hexane; 3:7). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 825, 995, 1020, 1060, 1170, 1230, 1265, 1380, 1440, 1580, 1710, 1740, 1770, 2860-3040. PMR spectrum: 1.58 and 1.67 br. s (6H,  $\text{CH}_3$ ), 2.2-2.8 m (4H,  $\text{CH}_2$ ), 4.99 br. t (1H,  $\text{HC}=\text{C}$ ,  $J = 7.5$ ), 6.31 s (1H, HCS), 7.3-7.6 m (5H,  $\text{C}_6\text{H}_5$ ). Found: C 55.45; H 5.09%; 232  $[\text{M} - \text{CF}_3\text{CO}_2\text{H}]^+$ .  $\text{C}_{16}\text{H}_{17}\text{F}_3\text{O}_3\text{S}$ . Calculated: C 55.48; H 4.95%; Mol. wt. 246.4.

cis/trans-3-Isopropenyl-2-phenylthiocyclopentan-1-ones (VIII). Compound (XII), obtained as above from 0.8 g (3.19 mmoles) of (V) and 0.81 g (3.86 mmoles) of TFAA in 5 ml  $\text{CH}_2\text{Cl}_2$ , without additional purification was heated (Ar) in 5 ml of PhMe for 1 h at 95°C. The reaction mixture was diluted with ether and water. By the usual treatment of the organic layer there was obtained ~1 g of a substance which was chromatographed on 30 g  $\text{SiO}_2$ . Gradient elution from hexane to ether (up to 30% of the latter) gave 0.45 g (61%) of a mixture of epimers (VIII) (trans/cis  $\approx$ 7:1; PMR data) in the form of colorless oil,  $R_f$  0.31 (ether-hexane; 1:4). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 895, 1030, 1135, 1230, 1370, 1405, 1440, 1480, 1580, 1650, 1750, 2880-3060.

PMR spectrum of cis(VIII): 1.7-2.4 m (4H,  $\text{CH}_2$ ), 1.90 br. s (3H,  $\text{CH}_3$ ), 3.0 m (1H,  $\text{HC}^3$ ), 3.66 d (1H, HCS,  $J = 7$ ), 4.86 and 5.04 br. s (2H,  $\text{H}_2\text{C}=\text{C}$ ), 7.2-7.5 m (5H,  $\text{C}_6\text{H}_5$ ).

PMR spectrum of trans(VIII): 1.7-2.4 m (4H,  $\text{CH}_2$ ), 1.75 br. s (3H,  $\text{CH}_3$ ), 2.65 m (1H,  $\text{HC}^3$ ), 3.38 d (1H, HCS,  $J = 10$ ), 4.82 and 4.92 br. s (2H,  $\text{H}_2\text{C}=\text{C}$ ), 7.2-7.5 m (5H,  $\text{C}_6\text{H}_5$ ). Found: S 13.44%;  $\text{M}^+$  232.  $\text{C}_{14}\text{H}_{16}\text{OS}$ . Calculated: S 13.80%; Mol. wt. 232.4.

6-Methyl-5-en-1,2-diol (XIII). To a vigorously stirred solution at 25°C (Ar) of 1.77 g (5.1 mmoles) of (XII) in 15 ml of methanol and 5 ml of water, by portions over 5 min 2 g (52.9 mmoles) of NaBH<sub>4</sub> was added. The reaction mixture was kept for 5 h at ~25°C, then diluted with ether and water. The aqueous layer was separated, neutralized with 50% H<sub>2</sub>SO<sub>4</sub>, and extracted with ether. By the usual treatment of the combined organic layer there was obtained 0.8 g of a substance which was chromatographed on 30 g SiO<sub>2</sub>. Gradient elution from hexane to ether gave 0.52 g (71%) of (XIII) in the form of a colorless liquid; bp 82-84°C (0.06 mm), n<sub>D</sub><sup>20</sup> 1.4651, {see [5]}.

trans-3-Isopropenyl-2-tert-butylsulfonycyclopentan-1-one (XIV). To a stirred solution at -30°C (Ar) of 2.18 g (10.3 mmoles) of (VII) in 25 ml of ether 3.58 g (20.8 mmoles) of MCPBA was added in portions over 10 min. The reaction mixture was kept for 1 h at -20°C, over 20 min warmed to ~25°C, then diluted with ether and neutralized with saturated NaHCO<sub>3</sub> solution. The aqueous layer was separated and extracted with ether. By the usual treatment of the ether extract there was obtained ~3 g of a substance which was chromatographed on 150 g SiO<sub>2</sub>. Gradient elution from hexane to ether gave 2.25 g (89%) of (XIV) in the form of colorless crystals; mp 53-55°C (hexane). IR spectrum (ν, cm<sup>-1</sup>): 900, 970, 1110, 1135, 1220, 1300, 1400, 1460, 1650, 1750, 2940-3020, 3090. PMR spectrum: 1.42 s (9H, CH<sub>3</sub>), 1.7-2.5 m (4H, CH<sub>2</sub>), 1.79 br. s (3H, CH<sub>3</sub>), 3.55 m (1H, HC<sup>3</sup>), 3.81 d (1H, HCS, J = 4), 4.70 and 4.87 br. s (2H, H<sub>2</sub>C=C). Found: C 58.90; H 8.22; S 12.95%; M<sup>+</sup> 244. C<sub>12</sub>H<sub>20</sub>O<sub>3</sub>S. Calculated: C 58.99; H 8.25; S 13.12%; Mol. wt. 244.4.

trans-3-Isopropenyl-2-phenylsulfonycyclopentan-1-one (XV). Analogously, from 0.42 g (1.81 mmoles) of (VIII) and 0.72 g (4.17 mmoles) of MCPBA in 5 ml ether there was obtained 0.5 g of a substance which was chromatographed on 20 g SiO<sub>2</sub>. Gradient elution from hexane to ether (up to 50% of the latter) gave 0.38 g (79%) of (XV) in the form of colorless crystals; mp 131-132°C (ether-hexane). IR spectrum (ν, cm<sup>-1</sup>): 900, 1025, 1140, 1280, 1355, 1380, 1410, 1440, 1585, 1640, 1730, 2860-3000, 3080. PMR spectrum: 1.7-2.6 m (4H, CH<sub>2</sub>), 1.80 br. s (3H, CH<sub>3</sub>), 3.4-3.8 m (2H, HCS, HC<sup>3</sup>), 4.73 and 4.84 br. s (2H, H<sub>2</sub>C=C), 7.5-8.0 m (5H, C<sub>6</sub>H<sub>5</sub>). Found: S 11.83%; M<sup>+</sup> 264. C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>S. Calculated: S 12.13%; Mol. wt. 264.3.

Isopropenylcyclopentenone (XVI). To a stirred solution at 40°C (Ar) of 1.15 g (4.95 mmoles) of (VIII) in 20 ml of ether 0.85 g (4.95 mmoles) of MCPBA was added in portions over 5 min. The reaction mixture after 5 min was diluted with ether and neutralized with saturated NaHCO<sub>3</sub> solution. The aqueous layer was separated, extracted with ether, the combined organic layer was dried with MgSO<sub>4</sub>, and evaporated under vacuum. The obtained residue (~1.5 g) was dissolved in 20 ml of toluene and boiled (Ar) for 45 min in the presence of 1.3 g (9.41 mmoles) of K<sub>2</sub>CO<sub>3</sub>. Then the residue was filtered and washed on the filter with ether. The combined filtrate was evaporated under vacuum and the residue (~1 g) was chromatographed on 50 g SiO<sub>2</sub>. Gradient elution from hexane to ether (up to 70% of the latter) gave 0.44 g (73%) of (XVI) in the form of colorless crystals; mp 45-46°C (pentane), the PMR spectrum of which is practically identical with the one cited in [2].

3-Isopropenylcyclopent-2-en-1-ol (XVII). To a stirred solution at 0°C (Ar) of 0.44 g (3.6 mmoles) of (XVI) in 5 ml of THF over 10 min was added 4.54 ml of 1.27 M solution of DIBAL in benzene (5.77 mmoles). The reaction mixture was kept for 1 h at 0°C, then treated with ether and excess of aNa<sub>2</sub>SO<sub>4</sub> and zeolite mixture (1:1 by volume) (see [9]). The precipitate after filtration was washed on the filter with ether, the combined filtrate was evaporated under vacuum, and the residue (~0.5 g) was chromatographed on 15 g SiO<sub>2</sub>. Gradient elution from hexane to ether (to 70% of the latter) gave 0.39 g (87%) of (XVII) as a colorless liquid; bp 79-81°C (2.5 mm), n<sub>D</sub><sup>20</sup> 1.5179. IR spectrum (ν, cm<sup>-1</sup>): 860, 900, 970, 1030, 1055, 1240, 1380, 1440, 1455, 1600, 1670, 2860-3000, 3420, 3600. UV spectrum (EtOH, λ<sub>max</sub>, nm): 234 (ε 14 800). PMR spectrum: 1.7-2.7 m (4H, CH<sub>2</sub>), 1.94 br. s (3H, CH<sub>3</sub>), 4.9 m (1H, HCO), 5.01 br. s (2H, H<sub>2</sub>C=C), 5.80 br. s (1H, HC=C). Found: C 76.97; H 9.46%; M<sup>+</sup> 124. C<sub>8</sub>H<sub>12</sub>O. Calculated: C 77.37; H 9.74%; Mol. wt. 124.2.

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FUNCTIONALLY SUBSTITUTED SULFUR-CONTAINING COMPOUNDS.

9.\* REACTIONS OF 2-[(ORGANYLTHIO)METHYL]OXIRANES WITH ACETIC ANHYDRIDE AND ACETYL CHLORIDE

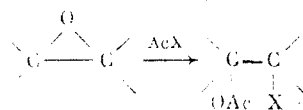
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Reaction of 2-[(organylthio)methyl]oxiranes with acetic anhydride gives a mixture of 3-(organylthio)-1,2-diacetoxypropane and 2-(organylthio)-1,3-diacetoxypropane, and with acetyl chloride a mixture of 2-chloro-3-(organylthio)-1-acetoxypropane and 3-chloro-2-(organylthio)-1-acetoxypropane. In both cases, the ratio of the isomers depends on the nature of the organylthio group and on the nature of the electrophile.

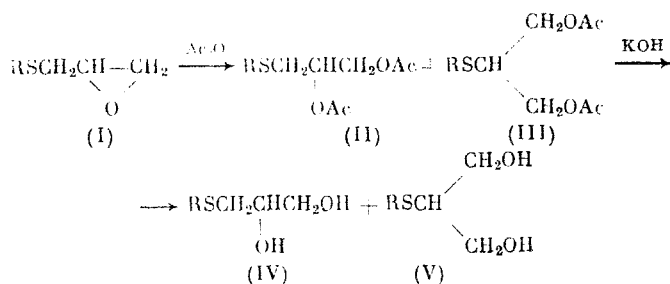
In the course of a study of the reactivity of 2-[(organylthio)methyl]oxiranes [2, 3], their reaction with electrophiles - acetic anhydride and acetyl chloride - was examined.

It is well known that acetic anhydride and acetyl chloride react with epoxycompounds to form the corresponding diacetoxy and chloroacetoxy derivatives [4]



X -- AcO, Cl.

A reaction of this type has not been reported for sulfur-containing epoxides. We have established that the reaction of 2-[(organylthio)methyl]oxiranes (I) with acetic anhydride for 4 h at 130°C and molar ratio 1:1.5 gives a mixture of 3-(organylthio)-1,2-diacetoxypropane (II) and 2-(organylthio)-1,3-diacetoxypropane (III) (Table 1).



R -- Et (a), Bu (b), *t*-Bu (c), C<sub>6</sub>H<sub>13</sub> (d), C<sub>10</sub>H<sub>21</sub> (e), PhCH<sub>2</sub> (f), CH<sub>2</sub>=CHCH<sub>2</sub> (g), Ph (h).

It follows that 1,2-migration of the organylthio group takes place in the course of the reaction in a similar way to the reaction of 2-[(alkylthio)methyl]oxiranes with carboxylic acids [5].

\*For previous communication, see [1].

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