SELENYL CHLORIDE AS AN ACTIVE CHLORINATING AGENT

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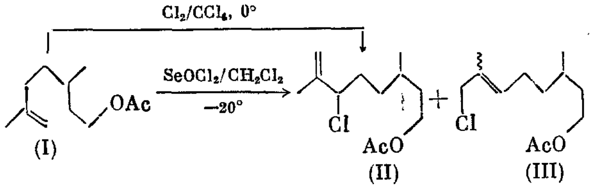
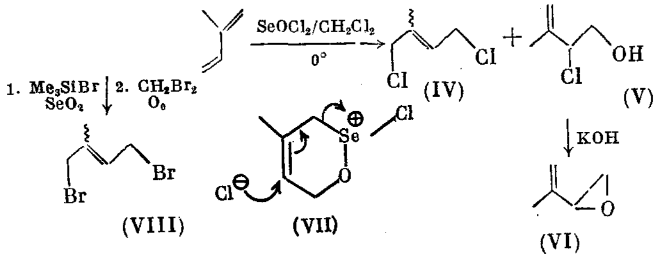
In contrast to thionyl halides, the related Se(IV) compounds have not found use in organic synthesis despite their pronounced oxidizing and halogenating properties. In the present communication, we examined a previously unreported method for the preparation of selenyl chloride and its use for the chlorination of isoprene and citronellyl acetate (I).

We have found that a suspension of freshly sublimed SeO_2 and Me_3SiCl in 1:2 ratio upon stirring at 25°C rapidly gives an emulsion. One component of this emulsion with lower density was identified by gas-liquid chromatography and PMR spectroscopy as HMDS. The second component was selenyl chloride, which is a mobile, readily volatile liquid: $SeO_2 + 2Me_3 \cdot SiCl \rightarrow Me_3SiOSiMe_3 + SeOCl_2$.

Selenyl chloride prepared by this method in the presence of HMDS (or after its separation) is highly soluble in chlorinated hydrocarbons and was then used in reactions with the abovementioned olefins. In this case, (I) and $SeOCl_2$ in CH_2Cl_2 at −20°C gave a moderate yield of chlorides (II) and (III) in $\sim$2:3 ratio as indicated by gas-liquid chromatographic analysis and PMR spectroscopy, of which regioisomer (II) [1] was independently synthesized as a mixture of diastereomers by the allylic chlorination of (I) according to Weill et al. [2]. The major product, (III), could not be isolated as a pure compound, but was characterized as a mixture of stereoisomers with $E/Z \approx 7:1$ with two triplets for the HC^6 vinyl protons at 5.42 and 5.28 ppm in this ratio.



Thus, in its reaction with trisubstituted monoolefin (I), $SeOCl_2$ in an active chlorinating agent in the allylic position similar to hypochlorites and SO_2Cl_2 [3, 4]. On the other hand, isoprene under analogous conditions, in addition to the standard product of its 1,4-chlorination, (IV) as a mixture with $E/Z \approx 2:1$ as indicated by gas-liquid chromatographic analysis and PMR spectroscopy, gives chlorohydrin (V) [5] in comparable amounts in overall yield of about 70%. The structure of (V) was confirmed by spectral analysis and conversion to the epoxide (VI) reported by Gevorkyan et al. [6]:



The formation of (V) may be attributed to an intermediate [2 + 4]-cycloadduct of $SeOCl_2$ with isoprene of the type established for the reaction of SeO_2 with 1,3-dienes [7] and subsequent S_N2' dissociation of the C—Se bond in (VII).

We should note that the reaction of SeO_2 with Me_3SiBr gives a selenium-containing reagent of undetermined structure which has exclusively brominating properties, as indicated by the isolation of only 1,4-dibromides (VIII) [8] as a mixture of isomers with $E/Z \approx 2:1$ as indicated by PMR spectroscopy in the case of reaction with isoprene.

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EXPERIMENTAL

The PMR spectra were taken on a Bruker WM-250 spectrometer in $CDCl_3$. The mass spectra were taken on a Varian MAT CH-6 spectrometer at 70 eV. The gas-liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph using a 2 m × 3 mm column packed with 15% Carbowax 20M on Chromaton N-AW-HMDS, flame ionization detector and nitrogen as the gas carrier.

Preparation of $SeOCl_2$. A suspension of 2.22 g (20 mmoles) SeO_2 and 4.43 g (41 mmoles) Me_3SiCl was stirred at about 25°C in an argon atmosphere until the formation of a stable emulsion (∿1 h). After standing, the upper layer of HMDS was carefully separated. The residue (3.2 g, 97%) was $SeOCl_2$ as a colorless liquid, bp 68°C (10 mm). Mass spectrum, m/z (ion): 166 M^+, 131 $[M- Cl]^+$, 96 $[M - 2Cl]^+$ (for ^{80}Se and ^{35}Cl isotopes).

Chloride (II) and E/Z-1-acetoxy-8-chloro-3,7-dimethyl-6-octene (III). A solution of 1.98 g (10 mmoles) (I) in 3 ml CH_2Cl_2 was added to a solution of $SeOCl_2$ obtained from 1.11 g (10 mmoles) SeO_2 and 2.16 g (20 mmoles) Me_3SiCl without the separation of HMDS in 15 ml Ch_2Ch^2 stirred at −20°C in an argon atmosphere over 15 min. After 30 min, the mixture was diluted with ether, washed with saturated aq. $NaHCO_3$ and then water, and dried over $MgSO_4$. The solvents were removed and the residue (2.3 g) was subjected to chromatography on 150 g silica gel. Elution with 9:1 hexane—ether gave 0.7 g (30%) of a mixture of (II) and (III) as a colorless liquid with bp 75-85°C ($1.3 \cdot 10^{-2}$ mm).

PMR spectrum of (II) (δ, ppm): 0.86 d (3H, CH_3, J = 7 Hz), 1.71 br. s (3H, CH_3) 1.2-1.8 m (7H, HC^3, CH_2), 1.93 s (3H, Ch_3CO), 4.0 m (2H, CH_2O), 4.25 t (1H, HC^6, J = 7 Hz), 4.79 and 4.990 br. s (2H, $H_2C{=}C$).

PMR spectrum of (III) (δ, ppm): 0.86 d (3H, CH_3, J = 7 Hz), 1.53 and 1.64 br. s (3H, CH_3), 1.2-1.8 m (7H, HC^3, CH_2), 1.93 s (3H, CH_3CO), 3.91 and 3.98 br. s (2H, HC^8), 4.0 m (2H, CH_2O), 5.28 and 5.42 br. t (1H, HC^6, J = 7 Hz).

A solution of 0.71 g (10 mmoles) Cl_2 in 15 ml CCl_4 was added over 15 min to a solution of 1.98 g (10 mmoles) (I) in 15 ml CCl_4 stirred at 0°C. After 20 min, the mixture was evaporated and the residue (2 g) was subjected to chromatography on 100 g silica gel. Elution with 9:1 hexane—ether gave 1.56 (67%) chloride (II), bp 67-72°C ($1.0 \cdot 10^{-2}$ mm), n_D^{20} 1.4605. The PMR spectrum of this product was identical to that presented above. Found: C, 62.29; H, 8.93; Cl, 15.31%. Calculated for $C_{12}H_{21}ClO_2$: C, 61.92; H, 9.09; Cl, 15.23%.

Chlorides (IV) and Chlorohydrin (V). A solution of 2.0 g (30 mmoles) isoprene in 5 ml CH_2Cl_2 was added over 15 min to a stirred solution of $SeOCl_2$ obtained from 1.66 g (15 mmoles) SeO_2 and 3.24 g (30 mmoles) Me_3SiCl without the separation of HMDS at 0°C in an argon atmosphere. After 1 h, the mixture was diluted with either, washed with saturated aq. $NaHCO_3$ and water and dried over $MgSO_4$. The solvents were removed and the residue (1.8 g) was subjected to chromatography on 100 g silica gel. Gradient elution from pentane to ether (up to 40% ether) gave 0.81 g (39%) (IV), bp 57-59°C (15 mm) and 0.5 g (28%) (V), bp 62-64° C (14 mm) [5].

PMR spectrum of (V) (δ, ppm): 1.81 br. s (3H, CH_3), 3.78 d (2H, CH_2O, J = 7 Hz), 4.46 t (1H, HC^2, J = 7 Hz), 5.01 and 5.12 br. s (2H, $H_2C{=}C$).

Epoxide (VI). An emulsion of 0.24 g (V) in 0.5 ml pentane and 0.2 g KOH in 0.4 ml water was stirred vigorously for 4 h at 30°C and then diluted with pentane. The organic layer was removed and subjected to ordinary work-up to give 0.14 g (70%) (VI). PMR spectrum (δ, ppm): 1.61 br. s (3H, CH_3), 2.71 and 2.85 d. d (2H, CH_2O, J_{AB} = 5.5, J_{AX} = 2.5, J_{BX} = 1.5 Hz), 3.36 br. d. d (1H, CH, J_{AX} = 2.5, J_{BX} = 1.5 Hz), 5.0 and 51.6 m (2H, $H_2C{=}C$).

Bromides (VIII). A suspension of 1.11 g (10 mmoles) SeO_2 and 3.06 g (20 mmoles) $Me_3Si \cdot Br$ in 25 ml CH_2Cl_2 was stirred at about 25°C in an argon atmosphere for 1 h. The red-orange emulsion was cooled to 0°C and treated with 1.3 g (20 mmoles) isoprene over about 5 min. After 1 h, the mixture was diluted with ether, washed with saturated aq. $NaHCO_3$ (1.3 g) was subjected to chromatography on 50 g silica gel. Elution with pentane gave 0.87 g (38%) (VIII) as a light yellow liquid, bp 104-105°C (15 mm). PMR spectrum (δ, ppm): 1.83 and 1.90 br. s (3H, CH_3), 3.9 m (4H, CH_2), 5.69 and 5.88 br. t (1H, $HC{=}C$, J = 8 Hz).

CONCLUSIONS

A new method was discovered for the preparation of selenyl chloride and its chlorinating properties in reactions with isoprene and citronellyl acetate were studied.

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