are equivalent on the NMR time scale. For tetramethylthiourea itself, the chemical shift was δ 3.08 in chloroform and δ 3.03 in dichloromethane. For $C_6H_5Te(tmtu)Br$ upfield shift to δ 3.05 in chloroform and δ 3.02 in dichloromethane were observed, while $C_6H_5Te(tmtu)Cl$ displayed shifts of δ 3.04 in chloroform and δ 3.01 in dichloromethane.

Addition of tetramethylthiourea to freshly prepared solutions of the two complexes resulted in one sharp peak of intermediate chemical shift. An exchange, rapid on the NMR time scale, between coordinated and free tetramethylthiourea evidently takes place.

1. Hauge, S. and Vikane, O. *Acta Chem. Scand. 27* (1973) 3596.
2. Foss, O. and Hauge, S. *Acta Chem. Scand. 13* (1959) 2155.
3. Haller, W. S. and Irgolic, K. J. *J. Organometal. Chem. 38* (1972) 97.

Received October 10, 1974.

Reactions of Diphenylditelluride with Halogens in Presence of Substituted Selenoureas as Ligands

OLAV VIKANE

Department of Chemistry, University of Bergen, N-5014 Bergen-Univ., Norway

Three-coordinated complexes of divalent tellurium containing thioureas as ligands are well known.[1-3] Far less known are the analogous complexes of divalent tellurium containing selenoureas as ligands.

The present paper discusses the preparation of some complexes of divalent tellurium with the formula $C_6H_5Te(L)X$ where L is ethyleneselenourea (esu), tetramethylselenourea (tmsu), or trimethyleneselenourea (trsu), and X is chlorine or bromine; also a complex $C_6H_5Te(esu)_2Cl$ has been prepared.

The selenourea complexes were prepared in the same way as the thiourea analogoues,[1,2] from diphenylditelluride, chlorine or bromine and the suitable selenourea. Diphenylditelluride was prepared by the method of Haller and Irgolic.[4] Tetramethylselenourea, ethyleneselenourea, and trimethyleneselenourea were prepared as described by Klayman and Griffin,[5] using the corresponding thiourea, iodomethane, selenium, and sodium borohydride in methanol. The crude products were recrystallized as described in the literature.[5,6]

Space groups and unit cell dimensions were determined from single-crystal oscillation and Weissenberg photographs, using Cu$K\alpha$ radiation. The unit cell dimensions are believed to be accurate to within 0.5 %. Densities were determined by flotation. Melting points are corrected.

Bromo(phenyl)tetramethylselenoureatellurium-(II), $C_6H_5Te(tmsu)Br$. 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.45 g) of tetramethylselenourea were dissolved in 30 ml of warm methanol. 1.25 mmol of bromine dissolved in 2.58 ml methanol was added. After filtering, the resulting clear orange red solution was placed at room temperature over night. Yield, 0.92 g (80 %). M.p. 162 – 163 °C. (Found: C 28.44; H 3.72; N 6.11; Br 17.31. Calc. for $C_{11}H_{12}N_2SeTeBr$: C 28.51; H 3.67; N 6.04; Br 17.24).

The compound forms orange-red monoclinic prisms extended along the a axis, with $a = 7.71$ Å, $b = 13.06$ Å, $c = 16.17$ Å, $\beta = 108.2°$. There are four formula units per unit cell; density, calc. 1.99, found 1.99 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14). The crystals are isomorphous with the corresponding tetramethylthiourea complex, and shows the same colour and morphology.[3]

Chloro(phenyl)tetramethylselenoureatellurium-(II), $C_6H_5Te(tmsu)Cl$, was prepared in the same way as the bromide, using 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.45 g) of tetramethylselenourea dissolved in 15 ml warm methanol and adding 1.25 mmol of chlorine dissolved in 2.35 ml tetrachloromethane. The mixture was filtered while hot and the resulting clear orange-red solution was placed at room temperature for 12 h. Yield, 0.77 g (73 %). M.p. 151 – 152 °C. (Found: C 31.52; H 3.98; N 6.59; Cl 8.52. Calc. for $C_{11}H_{17}N_2SeTeCl$: C 31.48; H 4.05; N 6.68; Cl 8.46).

The crystals are isomorphous with those of the bromide, and shows the same colour and morphology. The unit cell dimensions are, $a = 7.69$ Å, $b = 12.80$ Å, $c = 15.93$, $\beta = 109.2°$. Density, calc. 1.88, found 1.87 g/cm³.

Bromo(ethyleneselenourea)phenyltellurium-(II), $C_6H_5Te(esu)Br$, was prepared in a similar way as the compounds mentioned above, using 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.37 g) of ethyleneselenourea dissolved in 10 ml warm methanol, adding 1.25 mmol of bromide dissolved in 2.58 ml methanol. The resulting clear orange-red solution was placed at room temperature for 3 h. Yield, 0.87 g (80 %). M.p. 163 – 164 °C. (Found: C 24.87; H 2.61; N 6.39; Br 18.51. Calc for $C_9H_{11}N_2SeTeBr$: C 24.92; H 2.54; N 6.46; Br 18.43).

The compound forms orange-red monoclinic prisms extended along the a axis, with $a = 7.20$

Å, $b = 12.88$ Å, $c = 14.34$ Å, $\beta = 101.5°$. There are four formula units per unit cell; density, calc. 2.23, found 2.23 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14). The crystals are isomorphous with those of the corresponding ethylenethiourea compound.[2]

Bromo(phenyl)trimethyleneselenoureatellurium(II), $C_6H_5Te(trsu)Br$, was prepared using 1.25 mmol (0.5 g) of diphenylditelluride and 2.5 mmol (0.41 g) of trimethyleneselenourea dissolved in 10 ml of warm methanol. 1.25 mmol of bromine dissolved in 2.58 ml of methanol was added. The resulting clear orange red solution was placed at room temperature for 2 h. Yield, 0.83 g (74 %). M.p. 152–153 °C. (Found: C 26.86; H 2.84; N 6.19; Br 17.91. Calc. for $C_{10}H_{13}N_2SeTeBr$: C 26.80; H 2.90; N 6.25; Br 17.85).

The compound forms yellow monoclinic prisms and plates, the prisms are extended along the *a* axis. The unit cell dimensions are $a = 9.04$ Å, $b = 15.99$ Å, $c = 10.53$ Å, $\beta = 120.8°$, and there are four formula units per unit cell; density, calc. 2.27, found 2.25 g/cm³. The space group, from systematic absences, is $P2_1/c$ (No. 14).

Chlorobis(ethyleneselenourea)phenyltellurium(II), $C_6H_5Te(esu)_2Cl$, was prepared from 1.25 mmol (0.5 g) of diphenylditelluride and 5.4 mmol (0.8 g) of ethyleneselenourea dissolved in 15 ml warm methanol, adding 1.25 mmol of chlorine dissolved in 2.25 ml of tetrachloromethane. The resulting clear orange-red solution was placed at room temperature for 4 h. Yield, 0.93 g (68 %). M.p. 190–191 °C (dec.). (Found: C 26.71; N 10.32; Cl 6.67. Calc. for $C_{12}H_{17}N_4Se_2TeCl$: C 26.75; H 3.16; N 10.40; Cl 6.59).

The crystals are orange-red orthorhombic prisms extended along the *c* axis, with $a = 13.56$ Å, $b = 15.43$ Å, $c = 8.52$ Å. There are four formula units per unit cell; density, calc. 2.01, found 2.02 g/cm³. The space group, from systematic absences, is $P2_12_12_1$ (No. 19).

1. Hauge, S. and Vikane, O. *Acta Chem. Scand. 27* (1973) 3596.
2. Vikane, O. *Acta Chem. Scand. A 29* (1975) 150.
3. Foss, O. and Hauge, S. *Acta Chem. Scand. 13* (1959) 2155.
4. Haller, W. S. and Irgolic, K. J. *J. Organometal. Chem. 38* (1972) 97.
5. Klayman, D. L. and Griffin, T. S. *J. Amer. Chem. Soc. 95* (1973) 197.
6. Klayman, D. L. and Shine, R. J. *J. Org. Chem. 34* (1969) 3549.

Received December 6, 1974.

Distribution of Tritium Labeling between Alternative Sites in Carbon Compounds

ALPO KANKAANPERÄ, LEENA OINONEN and PENTTI SALOMAA

Department of Chemistry, University of Turku, SF-20500 Turku 50, Finland

The tritium labeling of carbon compounds leads usually to more than one product. Specific labeling is possible only if the replaceable protons differ greatly by their acidities. In other cases, however, an analysis of the products would be highly desirable but suitable methods for this kind of analysis have not been available. This paper reports a method which is based on the formal kinetics of the detritiation reactions. Labeled phenyl-2-propanone (I) was

$$\overset{a}{C_6H_5}-\overset{}{CH_2}-\overset{O}{\overset{\|}{C}}-\overset{b}{CH_3} \quad (I)$$

chosen as an example. Preliminary experiments indicated that the nonaromatic hydrogens of this compound were acidic enough to display isotope exchange reactions even in slightly alkaline solutions. In addition, the difference between the rates of the exchange reactions occurring at the two nonequivalent reaction sites was sufficient to make the kinetic analysis possible.

Tritiation of phenyl-2-propanone (Fluka) took place as follows. A mixture of 10^{-5} m³ of the ketone, 3×10^{-5} m³ of 100 mol m^{-3} sodium hydroxide, and 10^{-9} m³ of tritiated water (this amount of water had an activity of about 10^7 s^{-1}) were vigorously agitated at room temperature for 20 h, and the ketone was then extracted into diethyl ether. The ether was subsequently distilled off, and the remaining ketone was distilled under reduced pressure, b.p. 344 K at 0.40 kPa. The purity of the product (denoted by A) was ascertained by NMR spectroscopy. Its activity was 7.5×10^{11} s^{-1} m^{-3}. As will be shown later, about 57 % of the labeling was at the methylene group. The higher labeling of the methylene hydrogens must be the result of kinetic control, these hydrogens being obviously more acidic than those of the methyl group. In the case of thermodynamic control, at the final equilibrium, only 40 % of the labeling would be at the methylene hydrogens. This suggested that even higher labeling at the methylene group might be achieved by shortening the reaction time. Accordingly, the product (denoted by B) obtained after only 2 h reaction time gave an activity of 5×10^{11} s^{-1} m^{-3} with about 90 % of the label at the methylene group. When 3×10^{-6} m³ of product A was stirred at room