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Unexpected reaction of 2-chloro-1propen-3-yl isothiuronium chloride with potassium ditelluride: the first example of vicinal elimination of chlorine and sulfur-bearing moieties

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Unexpected reaction of 2-chloro-1-propen-3-yl isothiuronium chloride with potassium ditelluride: the first example of vicinal elimination of chlorine and sulfur-bearing moieties

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2-Chloro-1-propen-3-yl isothiuronium chloride reacts with potassium ditelluride in hydrazine hydrate to afford elemental tellurium and allene. The latter is formed due to the vicinal elimination of chlorine and a sulfur-bearing moiety.

$$S \xrightarrow{\text{NH}_2} CI^- \xrightarrow{\text{K}_2\text{Te}_2} H_2C = C = CH_2$$

Keywords: isothiuronium salt; elimination; allene; hydrazine hydrate; tellurium

1. Introduction

The reaction of mild nucleophiles (*e.g.* chalcogene-containing anions) with 1,2-dihalogen derivatives of alkanes or alkenes may involve, apart from classical nucleophilic substitution, the reductive elimination of both halogen atoms in the form of halogenide anions with simultaneous oxidation of the attacking reagent. For tellurium-containing anions, the latter direction is preferable (*1*), while for selenium and sulfur derivatives, the direction of the reaction (substitution or elimination) depends on the structure of the dihalogenide, the nature of the attacking anion, the solvent employed (2), and the phase-transfer catalysts used, which in some cases can favor substitution (*3*) and in other cases facilitates elimination (*4*). Halogen atoms attached to sp^3 -hybridized carbons are known to undergo elimination most easily. However, we have shown that the reaction of potassium ditelluride with 2,3-dichloro-1-propene can lead to the elimination of the chlorine atoms from both the sp^3 -hybridized and sp^2 -hybridized carbons (*5*). Elimination can also be observed

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in the presence of other leaving groups, such as halogen or oxygen incorporated into the oxirane entity (6), tosylate moiety and oxirane fragment (7). It has even been reported (8) during the reaction of potassium selenocyanate with 2-bromoethanol derivatives that the elimination of bromine and the hydroxide anion occurs. To the best of our knowledge, examples of sulfur-containing functional group elimination in reactions of this type are absent in the literature.

As part of our research exploring the reactivity of chlorine at sp^2 -hybridized carbon atoms in derivatives of 2,3-dichloro-1-propene 1, we have synthesized isothiuronium salt 2 from compound 1. As expected, the salt is formed only by attack at the chlorine atom attached to the sp^3 -hybridized carbon. Isothiuronium salts and their derivatives are known to possess unique biological and chemical properties, and their biological activity is mainly determined by their ability to react with the SH function of protein molecules (9).

2. Results and discussion

We have studied the behavior of isothiuronium salt 2 in the reaction with potassium ditelluride, a milder nucleophile as compared to thiol derivatives. Potassium ditelluride was prepared from elemental tellurium and potassium hydroxide in hydrazine hydrate, the Te:KOH molar ratio being 1:1 (10) (Scheme 1).

$$4\text{Te} + 4\text{KOH} + \text{N}_{2}\text{H}_{4} + \text{H}_{2}\text{O} \longrightarrow 2\text{K}_{2}\text{Te}_{2} + \text{N}_{2} + 5\text{H}_{2}\text{O}$$

Scheme 1. A synthesis of potassium ditelluride.

The addition of isothiuronium salt **2** to the reaction mixture formed during generation of K_2Te_2 (Scheme 1) unexpectedly led to the quantitative regeneration of elemental tellurium and formation of allene (the yield was 67% calculated by isothiuronium salt consumed) (Scheme 2). The formation of allene and elemental tellurium under the mild conditions (see Section 4) used in this reaction is indicative of an easy elimination of the chlorine and sulfur group in the vicinally substituted propenyl fragment of compound **2**.



Scheme 2. A synthesis of isothiuronium salt 2 and allene.

Despite all attempts, we failed to detect thiourea among the reaction products. After separation of allene and tellurium, the reaction mixture was treated with 1-iodobutane, whereupon dibutylsulfide 3 (yield 14% calculated by isothiuronium salt consumed), dibutyldisulfide 4 (31%), butylhydrazine 5, and, presumably, dibutylhydrazines 6 (total yield 54% based on the amount of BuI consumed) were formed. Butylhydrazine 5 was isolated from the reaction mixture and characterized by NMR. The reaction of 1-iodobutane with thiourea, dissolved in hydrazine hydrate (blank run), furnished sulfide 3 and disulfide 4 in trace amounts, in contrast to the larger amounts of substituted butylhydrazines that were the major reaction products.

Several alternative ways for allene formation are shown in Schemes 3–9. They differ in the direction of the nucleophilic attack by Te_2^{2-} -nucleophile. The possible electrophilic centers in the structure of isothiuronium salt **2** are the carbon atoms bonded to the sulfur atom (ways **a** and **b**, Scheme 3) and the chlorine atom conjugated with the unsaturated bond (way **c**, Scheme 3).



Scheme 3. The possible directions of the nucleophilic attack by Te_2^{2-} -nucleophile.

If $\text{Te}_2^{2^-}$ -nucleophile attacks the carbon atom of CH_2-S – fragment (direction **a**), a molecule of thiourea is expected to be eliminated followed by an intramolecular cyclization of intermediate anion **7** into unstable methylenetellurirane **8** or methyleneditelluretane **9**, which in turn eliminate tellurium to produce allene (Scheme 4).

$$2 \xrightarrow{\operatorname{Te}_2^{2^-}} \xrightarrow{\operatorname{Cl}} \operatorname{Te}_2^{2^-} \xrightarrow{\operatorname{Te}_2^{2^-}} \xrightarrow{Te}_2^{2^-}} \xrightarrow{Te}_2^{2^-}} \xrightarrow{Te}_2^{2^-}} \xrightarrow{Te}_2^{2^-}} \xrightarrow{Te$$

Scheme 4. The formation of allene according to the direction **a**.

A similar mechanism of elimination is discussed in the papers (7, 8). However, the formation of heterocycles **8** and **9** from intermediate **7** requires a stage of a nucleophilic substitution of the chlorine atom bonded to sp²-hybridized carbon atom. A substitution of such type is known to proceed with difficulty. So, one can suggest another path of allene formation from intermediate **7**: intramolecular halophilic attack of the chlorine atom with the tellurane moiety, as shown in Scheme 5.

$$\mathbf{7} \longrightarrow \begin{bmatrix} \mathbf{T} \mathbf{e}^{-} \\ \mathbf{C} \mathbf{I} \\ \mathbf{T} \mathbf{e} \end{bmatrix} \longrightarrow \begin{bmatrix} \mathbf{T} \mathbf{e}_{2} \mathbf{C} \mathbf{I} \end{bmatrix}^{-} + \mathbf{H}_{2} \mathbf{C} = \mathbf{C} = \mathbf{C} \mathbf{H}_{2}$$

Scheme 5. Intramolecular halophilic attack of the chlorine atom with the tellurane moiety.

As opposed to the direction **a**, we determined by an independent experiment that the formation of thiourea could not lead to the essential quantity of dibutylsulfide **3** and dibutyldisulfide **4** under the action of 1-iodobutane on the reaction mixture after separation of allene and tellurium.

The attack of Te_2^{2-} at the carbon atom of isothiuronium moiety (direction **b**) is expected to result in the formation of tellurourea, tellurium, and intermediate thiolate anion **10** (Scheme 6).

The same thiolate **10** can be produced also under the action of a base on isothiuronium salt **2** (a classical cleavage) (Scheme 7).

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$$2 \xrightarrow{\text{Te}_2^{2^-}}_{-\text{Te}} \begin{bmatrix} \text{Te}_2^{\text{NH}_2} \\ \text{NH}_2 \end{bmatrix} + \underbrace{\text{CI}}_{\text{NH}_2}^{\text{CI}}$$

Scheme 6. The attack of Te_2^{2-} on the carbon atom of isothiuronium moiety according to the direction **b**.

$$2 \xrightarrow{H_2O,base} 10$$

Scheme 7. A cleavage of isothiuronium salt 2 under the action of a base.

A further intramolecular cyclization of thiolate **10** via nucleophilic substitution of the chlorine atom at double bond could lead to intermediate methylenethiirane **11** followed by an elimination of sulfur to produce allene (Scheme 8).

$$10 \xrightarrow{-C\Gamma} \left[\begin{array}{c} \\ S \\ 11 \end{array} \right] \xrightarrow{-S} H_2C = C = CH_2$$

Scheme 8. A formation of allene via methylenethiirane intermediate 11.

A halophilic attack of Te_2^{2-} (direction **c**) is expected to proceed via elimination of thiourea and formation of allene in one stage (Scheme 9). Such a mechanism is most commonly used for an explanation of 1,2-elimination (5, 6, 11, 12).

$$Te_{2}^{2-} CI$$

$$S \xrightarrow{H}_{2}^{2-} CI^{-} \xrightarrow{H}_{2}^{2-} CI^{-} \xrightarrow{SC(NH_{2})_{2}, -CI^{-}} [Te_{2}CI]^{-} + H_{2}C=C=CH_{2}$$

$$Te_{2}CI^{-} + Te_{2}^{2-} \xrightarrow{CI^{-} + Te_{4}^{2-}} Te_{4}^{2-} \xrightarrow{Te_{2}^{2-} + Te}$$

Scheme 9. A halophilic attack with Te_2^{2-} .

A further participation of Te_4^{2-} anions in a halophilic attack could finally lead to elemental tellurium. But, as mentioned above, the elimination of thiourea cannot explain the formation of dibutylsulfide **3** and dibutyldisulfide **4** under the action of 1-iodobutane.

If cleavage of isothiuronium salt **2** runs sufficiently fast, intermediate thiolate **10** can undergo a halophilic attack (Scheme 10).

$$Te_2^{2^-} + \underbrace{CI}_{10} S^- \xrightarrow{-Te_2CI^-; -S^{2^-}} H_2C=C=CH_2$$

Scheme 10. The halophilic attack of thiolate 10 under the action of Te_2^{2-} .

Dehalogenation reactions for vicinal dihaloalkanes under the action of mild nucleophiles proceed via halophilic attack (12). In the process studied, the attack of Te_2^{2-} at the negatively charged sulfur atom in thiolate **10** seems to be improbable. Consequently, the reaction is realized as a result of the halophilic attack at the chlorine atom attached to the sp²-hybridized carbon. The process takes place under the mild conditions, as noted previously, and is remarkably facile.

The reaction of 2,3-dichloropropene **1** with ditelluride anions was previously shown to result in allene formation (5). This brings up the question: at which chlorine atom does the halophilic attack occur? It is tempting to suggest, given the results of the present work, that the halophilic attack is directed at the chlorine atom attached to sp^2 -hybridized carbon both for 2,3-dichloropropene and thiolate **10**.

Sulfide anions, formed according to Scheme 10, are partially alkylated by 1-iodobutane to deliver sulfide **3** (Scheme 11). In the absence of free alkali (13), the sulfide anions are also oxidized by hydrazine to generate disulfide anions (Scheme 11).

$$2Bul + S^{2-} \xrightarrow{-2l^{-}} Bu_2S$$

$$3$$

$$2S^{2-} + N_2H_4 + 2H_2O \xrightarrow{S_2^{2-}} S_2^{2-} + 2NH_3 + 2OH_2$$

$$2Bul + S_2^{2-} \xrightarrow{Bu_2S_2}$$

$$4$$

Scheme 11. A formation of dibutylsulfide 3 and dibutyldisulfide 4.

High reactivity of 1-iodobutane as an electrophile and the low concentrations of S^{2-} and S_2^{2-} anions in the reaction mixture containing excess hydrazine also allow formation of butyl derivatives of hydrazine. Consistent with this suggestion, butylhydrazines **5** and *N*,*N*-dibutylhydrazine **6** have been prepared independently by the reaction of BuI with hydrazine hydrate.

So, in our opinion, Scheme 10 is more preferable, since it provides an explanation for the formation of allene, dibutylsulfide **3**, and dibutyldisulfide **4**.

3. Conclusion

In conclusion, the reaction of 2-chloro-1-propen-3-yl isothiuronium salt with potassium ditelluride in the presence of hydrazine hydrate leads to reductive elimination of a chlorine atom and a sulfurbearing functional group. This fact complements and expands fundamental knowledge on the elimination reactions in the synthesis of chalcogene-containing compounds, especially polymers which possess valuable electro-physical and other properties (14).

4. Experimental

4.1. General

IR spectra were recorded on a Bruker IFS instrument. ¹H and ¹³C NMR spectra were run on a Bruker DPX-400 spectrometer (400.13 and 100.61 MHz, respectively) in CDCl₃, DMSO- d_6 . Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane as an internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer (SPB-5 column, $60,000 \times 0.25$ mm) operating at an ionization potential of 70 eV, quadruple mass analyzer, temperature of ion source 190°C, range of detected masses 34-650 D.

4.1.1. 2-Chloro-1-propen-3-yl isothiuronium chloride 2

2,3-Dichloropropene **1** (200 mmol, 22.20 g), thiourea (200 mmol, 15.20 g) in ethanol (120 ml) were boiled for 17.5 h. The reaction mixture was diluted with diethyl ether (50 ml), the precipitate of salt **2** was filtered off, washed with ether and dried in vacuum. Colorless solid; yield: 33.60 g (90%); m.p. 135–137°C. IR (KBr, ν , cm⁻¹): 3274, 3187, 3046, 2969, 2929, 2707, 1655, 1544, 1423, 1385, 1252, 1212, 1125, 1079, 900, 720, 629, 593, 456. ¹H NMR (DMSO-*d*₆): δ = 4.45 (s, 2H, SCH₂), 5.46 (d, ²*J*_{*H*-*H*} = 1.3 Hz, 1H, =C−H), 5.81 (d, ²*J*_{*H*-*H*} = 1.3 Hz, =C−H), 9.41 (br. s, 2H, NH₂), 9.54 (br. s, 2H, NH₂). ¹³C NMR (DMSO-*d*₆): δ = 37.9 (CH₂S), 118.05 (=CH₂), 135.61 (=CCl), 168.64 (C=N). Anal. calcd. for C₄H₈Cl₂N₂S: C, 25.68; H, 4.31; N, 14.97; Cl, 37.90; S, 17.14. Found: C, 25.61; H, 4.27; N, 15.07; Cl, 37.86; S, 17.24.

4.1.2. The reaction of isothiuronium salt 2 with potassium ditelluride

Potassium hydroxide (37.4 mmol, 2.09 g) was dissolved in hydrazine hydrate (40 ml) and tellurium (37.4 mmol, 4.78 g) was added portion-wise to the solution obtained (5). The reaction mixture was heated for 2 h. The flask was connected to two traps (temperatures of the traps were -30° C and -80° C, respectively). Isothiuronium salt 2 (28 mmol, 5.25 g) was added to the flask at 25°C and the mixture was stirred for 4.5 h at 35–45°C. Allene was collected in the second trap. Yield: 0.75 g (67% calculated by the isothiuronium salt 2 consumed). ¹H NMR (CDCl₃): $\delta = 4.72$ (s, 4H, =CH₂) (cf. (5)). ¹³C NMR (CDCl₃): $\delta = 73.91$ (=CH₂), 212.61 (=C=). Tellurium was filtered off from the remaining reaction mixture. Yield of tellurium: 4.45 g (100%). The filtrate after separation of tellurium was treated with 1-iodobutane (37.8 mmol, 6.95 g). The mixture was stirred for 3 h at $40-50^{\circ}$ C. The organic layer was separated and dried over MgSO₄ to give 1.92 g of the light-yellow oil, containing sulfide **3** (0.61 g), MS: 146 (M^+), calcd. for C₈H₁₈S (146.29), disulfide **4** (0.81 g), MS: 178 (M⁺), calcd. for $C_8H_{18}S_2$ (178.35), and N,N-dibutylhydrazine **6** (0.50 g), which were identified, using gas-liquid chromatography (GLC) and chromato-mass spectrometry techniques in comparison with standards. Yield was calculated in according with GLC data. The residue obtained after separation of the organic layer was extracted with dichloromethane $(2 \times 50 \text{ ml})$, the extracts were combined and dried over $MgSO_4$ to give practically pure (after removal of the solvent) butylhydrazine 5. Yield 1.20 g (36%); b.p. 79°C (80 Torr), reference data (15): b.p. 141–142°C (750 Torr). ¹H NMR (CDCl₃): $\delta = 0.91$ (t, ³ $J_{H-H} = 7.3$ Hz, 3H, CH₃), 1.35 (m, 2H, CH₂), 1.46 (m, 2H, CH₂), 2.75 (t, ${}^{3}J_{H-H} = 7.0$ Hz, 2H, CH₂N), 3.14 (br. s, 3H, HN–NH₂). 13 C NMR (CDCl₃): $\delta = 13.80$ (CH₃), 20.16 (CH₂), 29.65 (CH₂), 55.99 (NCH₂).

4.1.3. Reaction of 1-iodobutane with thiourea in hydrazine hydrate

Thiourea (28 mmol, 2.14 g) was added to hydrazine hydrate (40 ml) at 50°C. Then 1-iodobutane (38 mmol, 6.95 g) was added to the reaction mixture dropwise at 40–45°C for 1.5 h. The mixture was stirred for 3 h at 40°C. The light-yellow organic layer (0.55 g), containing *N*,*N*-dibutylhydrazine **6** and traces of sulfide **3** and disulfide **4**, was separated. Compounds **3** and **4** were identified, using GLC and chromato-mass spectrometry techniques in comparison with standards without isolation in a pure form. The residue was extracted with dichloromethane $(2 \times 50 \text{ ml})$, the extract was dried over MgSO₄, and the solvent was removed to give 1.70 g (51%) of butylhydrazine **5**.

4.1.4. Reaction of 1-iodobutane with hydrazine

1-Iodobutane (37.8 mmol, 6.95 g) was added to hydrazine hydrate (40 ml) and the reaction mixture was stirred for 3 h at 40–45°C. The reaction products were extracted with diethyl ether (2×50 ml), the extract was dried over MgSO₄, and the solvent was removed to afford 3.46 g of light-yellow oil containing butylhydrazine **5**. Products of a reaction of 1-iodobutane with water were not found.

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