## Reaction of Diphenyl Ditelluride with 2,3-Dichloroprop-1-ene in the System Hydrazine Hydrate–KOH

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Received September 20, 2013

Abstract—Diphenyl ditelluride reacts with 2,3-dichloroprop-1-ene in the system hydrazine hydrate–KOH along several parallel routes. Beside the nucleophilic chlorine substitution at the  $sp^3$ -hybridized carbon atom resulting in 2-chloro-3-phenyltellanylprop-1-ene the elimination of both chlorine atoms occurs affording a mixture of allene and methylacetylene. The reasons of the dual elimination reaction paths are considered.

DOI: 10.1134/S1070428014020055

At the treatment with "soft" nucleophiles, in particular, with chalcogen-containing anions, of geminal dihalides besides the reactions of classic nucleophilic substitution an abnormal redox process can occur involving the elimination of both halogen atoms as anions with the formation of an alkene and the oxidation of the nucleophilic reagent [1]. The interest in these reactions is not only caused by their application to the synthesis of unsaturated compounds and protection of double bonds [2], but also by the solution of important theoretic issues of organic chemistry, first of all regarding the problem of the competition between the substitution and the elimination. At the use of chalcogen-containing nucleophiles the theoretic interest consists also in the effect of the nature of the chalcogen atom (in going from sulfur to selenium and tellurium) on the direction of the process. At the treatment with the sulfur-containing nucleophilic reagents the elimination proceeds at the use of aprotic polar solvents [3] or phase-transfer catalysts [4, 5]. In the system hydrazine hydrate-alkali 1,2-dichloroethane reacted with potassium disulfide to give only substitution products (sulfur-containing oligomers), and with potassium diselenide and ditelluride only the elimination was observed [6]. The elimination occurs the most often in reactions with dihalides where the halogen atoms are bound to  $sp^3$ -hybridized carbon atoms, yet some examples exist of debromination of bromine linked to *sp*<sup>2</sup>-hybridized carbon atoms [3]. However from cis-1,2-dichloroethene and sodium selenide in the presence of a phase-transfer catalyst a series of unsaturated selenacrown ethers was obtained (the substitution process proceeded exclusively) [7].

As the most conventional mechanism of vicinal dehalogenation the synchronous mechanism is accepted involving a halophilic attack of the nucleophile on one of the halogen atoms [8]. When both halogen atoms are bound to carbon atoms in the same hybridization state the direction of the halophilic attack either is equally probable, or is governed mainly by steric factors. The reaction output therewith is the same: the formation of an unsaturated compound. In event the halogen atoms are linked to carbon atoms of different hybridization, the direction of the halophilic attack is ambiguous. The simplest compound with one chlorine atom attached to sp<sup>3</sup>-hybridized carbon atom and another, to sp<sup>2</sup>-hybridized carbon atom, is 2,3-dichloroprop-1-ene (I). The well known "inertness" of halogens at the double bond in the reactions of nucleophilic substitution [9] essentially affects the direction of 2,3-dichloroprop-1-ene (I) reactions with chalcogen-containing nucleophiles.

We formerly demonstrated that the elemental sulfur activated in the system hydrazine hydrate–KOH into  $S_2^{2-}$  anions reacted with dichloropropene I to give bis(2-chloroprop-1-en-3-yl) sulfide (a single chlorine atom bound to the *sp*<sup>3</sup>-hybridized carbon was involved in the reaction) [10]. At the use of the system hydrazine hydrate–aminoethanol we obtained from sulfur and dichlo-

ropropene I bis(2-chloroprop-2-ene-1-yl) disulfide [11]. Selenium in both basic reduction systems afforded only bis(2-chloroprop-2-ene-1-yl) selenide [12]. Elemental tellurium in the system hydrazine hydrate–KOH (activation to Te<sub>2</sub><sup>2–</sup>) reacted with compound I with the elimination of both chlorine atoms and the formation of allene [10, 13].

The reaction of  $Ph_2S_2$  [14] and  $Ph_2Se_2$  [15] with dichloropropene I proceeds as a series of successive transformations including the nucleophilic substitution of the chlorine atom at the *sp*<sup>3</sup>-hybridized carbon, the dehydrochlorination of the compound obtained into an allene derivative, the allene-acetylene rearrangement, and the addition of anions PhS<sup>-</sup> and PhSe<sup>-</sup> to the triple bond (domino-reaction).

It is well known [16] that the chemical behavior of

$$2Ph_2Te_2 + 4KOH + N_2H_4 H_2O$$

$$\longrightarrow 4PhTeK + N_2 + 5H_2O \qquad (1)$$

organotellurium compounds often is unlike that of the corresponding sulfur and selenium compounds. Here we report on the study on the direction of the reaction of diphenyl ditelluride with 2,3-dichloroprop-1-ene (I). Diphenyl ditelluride was brought into the reaction with dichloropropene I after its preliminary dissolution in the system hydrazine hydrate-alkali. The system is an efficient reducer for the activation of elemental chalcogens and organic dichalcogenides [17]. Potassium phenyltellurolate obtained in reaction (1) was used without isolation directly as a solution in hydrazine hydrate. At 50°C gas liberation was observed; the latter proved to be a mixture of allene and methylacetylene in 2:1 ratio (1H NMR data). In order to collect a considerable amount of gas we were obliged to add to the reaction mixture a 4-fold excess of dichloropropene I. After that the reaction was stopped, and we isolated from the extract a mixture of three compounds: [(2-chloroprop-2-ene-1-yl)tellanyl]benzene (II), (2-chloroprop-2-en-1-yl)hydrazine (III), and diphenyl ditelluride in the molar ratio 1:0.5:0.1.

Hence the reaction of 2,3-dichloro-prop-1-ene (I) with PhTe<sup>-</sup> anions takes two main directions: the nucleophilic substitution (2) of the chlorine at the  $sp^3$ -hybridized carbon, and the elimination (3) of both chlorine atoms with



the formation of allene or methylacetylene and regeneration of the initial diphenyl ditelluride.

Regardless the relative high temperature (50°C) only

$$I + 2PhT\bar{e} \xrightarrow{-2Cl_{,}^{-}} \underbrace{\longrightarrow}_{-Ph_{2}Te_{2}} (3)$$

the first stage occurs of the previously observed [14, 15] domino-reaction (2). The yield of compound **II** reaches 80% with respect to the reacted  $Ph_2Te_2$ .  $Ph_2Te_2$  formed in reaction (3) suffers again the reductive cleavage (1) in the presence in the reaction mixture of alkali and hydrazine, and thus obtained anions PhTe<sup>-</sup> enter reactions (2) and (3). Therefore the completion of the process requires excess of reagent **I**. It should be taken into account that a part of 2,3-dichloroprop-1-ene (**I**) is consumed by reaction (2) and by the formation of propenylhydrazine **III** (reaction 4).

Therefore the overall yield of allene and methylacety-

lene calculated with respect to dichloride I consumed only in reaction (3) reaches 72%.

Thus the reaction of 2,3-dichloroprop-1-ene (I) with diphenyl ditelluride can be summarized in expression (5). In the reaction of arises To  $\frac{2}{2}$  with dishlaride I

In the reaction of anions  $Te_2^{2-}$  with dichloride I



[13] even in more severe conditions (85°C) allene was obtained practically free of methylacetylene impurity. Consequently, the formation of a mixture of allene and methylacetylene in reaction (3) is evidently not caused by the isomerization of allene in methylacetylene, but by elimination chlorine atoms in two ways distinguished by the direction of the primary halophilic attack. We showed formerly [18] that the reaction of (2-chloroprop-2-en-1yl)isothiuronium chloride containing a single chlorine atom covalently bound to an *sp*<sup>2</sup>-hybridized carbon atom

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with  $\text{Te}_2^{2-}$  anions was also accompanied with allene formation. It was therefore concluded that the ditelluride anion attacked prevailingly the chlorine atom at the *sp*<sup>2</sup>hybridized carbon atom. Allene obtained in [18] also was practically free of methylacetylene.

However sufficiently bulky and easily polarizable PhTe- anions can apparently attack both chlorine atoms in the molecule of 2,3-dichloroprop-1-ene (I) thus leading to the formation of allene and methylacetylene (6).

The elimination E2 (a) proceeds synchronously (A), as is common in such processes (see, e.g., [6, 8]), and the halophilic attack in this case is aimed at the chlorine atom possessing a partial positive charge due to the mesomeric interaction with the multiple bond. The path b proceeding apparently through the transition state **B** may occur not synchronously but with a partial delay of the cleavage of the second chlorine atom with the intermediate formation of a kinetically independent carbocation C. This direction may be interpreted in the framework of the concept of the nucleophilic substitution at the chlorine atom [19]. In this case the process may be accompanied with a rearrangement involving a proton transfer from the carbon atom at the double bond to the anion site resulting finally in the formation of methylacetylene. Apparently the route *a* is preferable, therefore allene is formed in a higher yield.

Hence in the reaction of diphenyl ditelluride with 2,3-dichloroprop-1-ene along with the nucleophilic substitution of the allyl chlorine the chlorine elimination can proceed in two direction with the formation of a mixture of allene and methylacetylene. The elimination in this case is an undesirable process just because of the formation of the mixture of isomers  $C_3H_4$  and is of interest only from the theoretical viewpoint. Unsaturated organotelluric compounds **II** may be applied as important reagents in the organic synthesis.

## EXPERIMENTAL

The purity of initial 2,3-dichloroprop-1-ene was checked and the products obtained were analyzed by GLC on a chromatograph LKhM 80-MD-2 (column 2000  $\times$  3 mm, stationary phase silicone XE-60, 5% on the carrier Chromaton N-AW-HMDS, ramp from 30 to 230°C at a rate 12 deg/min, carrier gas helium). IR spectra were recorded on a spectrophotometer Bruker IFS from thin films. <sup>1</sup>H, <sup>13</sup>C, and <sup>125</sup>Te NMR spectra were registered on a spectrometer Bruker DPX-400 (operating frequencies 400.13, 100.61, and 126.2 MHz respectively) in CDCl<sub>3</sub>, internal reference TMS [(CH<sub>3</sub>)<sub>2</sub>Te for <sup>125</sup>Te].

Mass spectra were obtained on a GC-MS instrument Shimadzu GCMS-QP5050A (column SPB-5, 60000  $\times$  0.25 mm), film of the stationary phase 0.25  $\mu$ m thick; injector temperature 250°C, carrier gas helium, flow rate 0.7 mL/min, ramp from 60 to 260°C at a rate 15 deg/min. Detector temperature 250°C, quadrupole mass analyzer, electron impact, ionizing electrons energy 70 eV, temperature of ion source 200°C, range of mass detected 34–650 Da.

**Reaction of dichloropropene I with diphenyl ditelluride.** In 8 ml of hydrazine hydrate containing 1.71 g (0.0305 mol) of KOH was dissolved 2.5 g (0.0061 mol) of diphenyl ditelluride at  $80-85^{\circ}$ C. The solution obtained was cooled to  $30^{\circ}$ C, the reaction vessel was connected to two cooled traps (-30 and  $-85^{\circ}$ C). The reaction mixture was heated to  $45-50^{\circ}$ C and simultaneously 2.8 g (0.025 mol) of dichloropropene I was added dropwise. In the second trap 0.37 g of colorless liquid was collected containing according to <sup>1</sup>H NMR data 0.25 g [49% with respect to dichloropropene consumed in reaction (3)] of allene and 0.12 g (yield 23%) of methylacetylene. The reaction mixture after the end of gas condensation was extracted with dichloromethane (2×10 ml). The combined extracts were dried with MgSO<sub>4</sub>. On removing the solvent the residue (3.14 g) contained according to <sup>1</sup>H NMR data 2.36 g of compound II (yield 80% with respect to reacted Ph<sub>2</sub>Te<sub>2</sub>), 0.44 g of (2-chloroprop-2-ene-1-yl)hydrazine (III) (yield 16% with respect to used propenedichloride I) and 0.34 g of diphenyl ditelluride (conversion 86%). Spectral characteristics of allene are identical to data of [13]. Spectral characteristics of (2-chloroprop-2-ene-1yl)hydrazine (III) are in agreement with our previous data [10].

**Methylacetylene.** <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.805 s (1H, CH=), 1.811 s (3H, CH<sub>3</sub>). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 3.16 (CH<sub>3</sub>), 67.42 (CH=), 80.01 (–C=).

[(2-Chloroprop-2-ene-1-yl)tellanyl]benzene (II). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.76 s (2H, CH<sub>2</sub>Te, <sup>2</sup>J<sub>Te,H</sub> 14.4 Hz), 4.95 s, 4.97 s (2H, CH<sub>2</sub>=), 7.11–7.77 m (5H, Ph). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 16.56 (CH<sub>2</sub>Te, <sup>1</sup>J<sub>C,Te</sub> 88.2 Hz), 112.34 (CH<sub>2</sub>=), 139.57 (CCl=), we failed to reliably assign the signals of the carbon atoms of the benzene ring. <sup>125</sup>Te NMR spectrum,  $\delta$ , ppm: 616.5 {for Ph<sub>2</sub>Te<sub>2</sub> <sup>125</sup>Te 421.5 ppm (420.8 ppm [20])}. Mass spectrum was not possible to register apparently due to the thermal instability of compound **II** in the chromatographic column of the GC-MS instrument.

## ACKNOWLEDGMENTS

The principal results were obtained on the equipment of the Baikal analytical center in general use of the Siberian Department of the Russian Academy of Sciences.

## REFERENCES

- Reutov, O.A., Kurts, A.L., and Butin, K.P., *Organicheskaya khimiya*. *Ch. 1* (Organic Chemistry, Part 1), Moscow: BINOM. Laboratoriya znanii, 2004, p. 567.
- Protective Groups in Organic Chemistry, McOmie, J., Ed., Springer, 1995.
- 3. Fukunaga, K. and Yamaguchi, H., *Synthesis*, 1981, vol. 11, p. 4292.
- 4. Nakayma, J., Machida, H., and Hoshino, M., *Tetrahedron Lett.*, 1983, vol. 24, p. 3001.
- Landini, D., Milesi, L., Quadri, M.L., and Rolla, F., J. Org. Chem., 1984, vol. 49, p. 152.
- 6. Russavskaya, N.V., Grabel'nykh, V.A., Levanova, E.P.,

Sukhomazova, E.N., Klyba, L.V., Zhanchipova, E.R., Albanov, A.I., Tatarinova, A.A., Elaev, A.V., Deryagina, E.N., Korchevin, N.A., and Trofimov, B.A., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 672.

- Shimizu, T., Kawaguchi, M., Tsuchiya, T., Hirabayashi, K., and Kamigata, N., J. Org. Chem., 2005, vol. 70, p. 5036.
- Zefirov, N.S. and Makhon'kov, D.I., *Chem. Rev.*, 1982, vol. 82, p. 615.
- 9. Traven', V.F., *Organicheskaya khimiya* (Organic Chemistry), Moscow: IKTs "Akadem-kniga," 2006, vol. 1, p. 727.
- Levanova, E.P., Grabel'nykh, V.A., Russavskaya, N.V., Klyba, L.V., Zhanchipova, E.R., Albanov, A.I., Tarasova, O.A., and Korchevin, N.A., *Russ. J. Gen., Chem.*, 2009, vol. 79, p. 1097.
- Levanova, E, P., Grabel'nykh, V.A., Russavskaya, N.V., Rozen-tsveig, I.B., Tarasova, O.A., and Korchevin, N.A., *Russ. J. Gen., Chem.*, 2011, vol. 81, p. 611.
- Levanova, E.P., Grabel'nykh, V.A., Russavskaya, N.V., Albanov, A.I., Elaev, A.V., Tarasova, O.A., and Korchevin, N.A., *Russ. J. Gen., Chem.*, 2011, vol. 81, p. 1560.
- Levanova, E.P., Vshivtsev, V.Yu., Grabel'nykh, V.A., E.N. Sukhomazova, N.V. Russavskaya, N.V., Albanov, A.I., Tarasova, O.A., and Korchevin, N.A., *Russ. J. Gen., Chem.*, 2008, vol. 78, p. 1900.
- Levanova, E.P., Grabel'nykh, V.A., Elaev, A.E., Russavskaya, N.V., Klyba, L.V., Albanov, A.I., Tarasova, O.A., and Korchevin, N.A., *Russ. J. Gen., Chem.*, 2013, vol. 83, p. 1088.
- Levanova, E.P., Grabel'nykh, V.A., Vakhrina, V.S., Russavskaya, N.V., Albanov, A.I., Klyba, L.V., Tarasova, O.A., Rozentsveig, I.B., and Korchevin, N.A., *Russ. J. Gen., Chem.*, 2013, vol. 83, p. 1434.
- Sadekov, I.D. and Minkin, V.I., Usp. Khim., 1995, vol. 64, p. 525.
- Deryagina, E.N., Russavskaya, N.V., Papernaya, L.K., Levanova, E.P., Sukhomazova, E.N., and Korchevin, N.A., *Izv. Akad. Nauk, Ser. Khim.*, 2005, p. 2395.
- Levanova, E.P., Grabelnykh, V.A., Elaev, A.V., Albanov, A.I., Klyba, L.V., Russavskaya, N.V., Tarasova, O.A., Rozentsveig, I.B., and Korchevin, N.A., *J. Sulfur Chem.*, 2012, vol. 33, p. 505.
- 19. Sazonov, P.K., Artamkina, G.A., and Beletskaya, I.P., *Usp. Khim.*, 2012, vol. 81, p. 317.
- Granger, P., Chapelle, S., McWhinnie, W.R., and Al-Rubaie, A., J. Organometal. Chem., 1981, vol. 220, p. 149.