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SHORT COMMUNICATIONS

Chlorovinylation of Diphenyl Dichalcogenides with Dichloroacetylene—A New Method of Synthesis of 1,2-Dichlorovinyl Phenyl Chalcogenides

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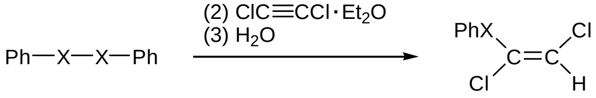
1,2-Dichlorovinyl chalcogenides **Ia**–**Ic** of the general formula RXCCl=CHCl [R = Ar, Alk; X = S (**a**), Se (**b**), Te (**c**)] can be prepared by nucleophilic replacement of chlorine in trichloroethylene [1–5] or tetrachloroethane [6] by thiolate ion, addition of selenols [7, 8] to dichloroacetylene, phase-transfer reaction of benzeneselenol with trichloroethylene [9, 10], and addition of sulfenyl chlorides to chloroacetylene [5]. 1,2-Dichlorovinyl selenides are also formed together with other compounds in phase-transfer reactions of organic diselenides with tri- and tetrachloroethylenes, catalyzed by ammonium salts [11]. However, none of the above procedures can be applied to obtain tellurenyl derivatives, for tellurols are extremely unstable due to their high sensitivity to oxidation [12]. Only in the reaction of diphenyl ditelluride (**IIc**) with dichloroacetylene–ether complex, 1,2-dichlorovinyl phenyl telluride (**Ic**) was detected by ^{1}H NMR spectroscopy and gas chromatography–mass spectrometry [13]. Individual dichlorovinyl tellurides have not been isolated so far.

We have found that *trans*-1,2-dichlorovinyl telluride (**Ic**) is formed by reaction of dichloroacetylene–ether complex with lithium benzenetellurolate generated from diphenyl ditelluride by the action of lithium tetrahydridoaluminate. This reaction is general for all diphenyl dichalcogenides (X = S, Se, Te). From the corresponding disulfide **IIa** and diselenide **IIb**, *trans*-1,2-dichlorovinyl sulfide (**Ib**) and *trans*-1,2-dichlorovinyl selenide (**Ib**) are formed, respectively.



IIa–**IIc** **Ia**–**Ic**

X = S (**a**), Se (**b**), Te (**c**).

The *trans* configuration of the double bond in chalcogenides **I** follows from the ^{1}H NMR spectra of sulfide **Ia** and selenide **Ib**, which are fully identical to those reported in [6, 7]. Telluride **Ic** is resistant to the action of such dehydrochlorinating agent as a 50% solution of NaOH in benzene [14]. It is known that sodium ethoxide abstracts hydrogen chloride only from *cis*-1,2-dichlorovinyl phenyl selenide [10].

***trans*-1,2-Dichlorovinyl phenyl telluride (Ic).** Excess $LiAlH_4$ was added with stirring under argon to a solution of 1 g (2.4 mmol) of ditelluride **IIc** in 20 ml of THF until the solution turned colorless, and 20 ml of a 30% solution of dichloroacetylene in ether (prepared as described in [15]) was then added dropwise under stirring. After 3 h, the mixture was carefully treated with water to neutralize excess lithium tetrahydridoaluminate, the ether layer was separated, the aqueous layer was extracted with ether, and the extract was combined with the organic layer and dried over $CaCl_2$. The solvent was distilled off, and the residue was distilled under reduced pressure to isolate 0.47 g (32%) of 1,2-dichlorovinyl phenyl telluride (**Ic**) as a light orange liquid with bp 117–118°C (1.5 mm), n_D^{23} = 1.6625. ^{1}H NMR spectrum, δ, ppm: 7.86 m and 7.26 m (5H, C_6H_5), 6.64 s (1H, =CH). Found, %: C 33.26, 33.18; H 2.10, 2.22; Cl 20.33, 20.10; Te 43.61, 42.89. $C_8H_6Cl_2Te$. Calculated, %: C 31.96; H 2.01; Cl 23.58; Te 42.44.

The still residue (obtained after separation of 1,2-dichlorovinyl phenyl telluride) was 0.47 g of

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a crystalline substance which, according to the TLC data, was a mixture of diphenyl ditelluride (**IIc**) and 1,2-bis(phenyltelluro)-1,2-dichloroethylene, the latter being formed by reaction of diphenyl ditelluride with dichloroacetylene [13].

Previously known 1,2-dichlorovinyl phenyl sulfide (**Ia**) and 1,2-dichlorovinyl phenyl selenide (**Ib**) were synthesized in a similar way (yield 17.5 and 43%, respectively) by treatment of diphenyl disulfide (**IIa**) and diphenyl diselenide (**IIb**) first with $LiAlH_4$ and then with dichloroacetylene in ether.

A solution of 0.2 g of telluride **Ic** in 5 ml of benzene and 5 ml of a 50% solution of sodium hydroxide containing 0.01 g of 18-crown-6 was stirred for 5 h. According to the GLC data, no dehydrochlorination occurred. Removal of the solvent from the organic phase gave 0.18 g of initial telluride **Ic**.

The ^1H NMR spectra were recorded on a Bruker DPX-400 spectrometer from 5–10% solutions in $CDCl_3$ using HMDS as internal reference.

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