

Stereoselective Addition of Diorganyl Chalcogenides to Cyclohexene Catalyzed with Tin(IV) Chloride

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Received November 30, 2004

Abstract—The addition of diorganyl disulfides and dimethyl diselenide to cyclohexene in the presence of tin(IV) chloride proceeded stereoselectively affording *trans*-adducts of 1:1 composition. No reaction occurs in the absence of tin(IV) chloride.

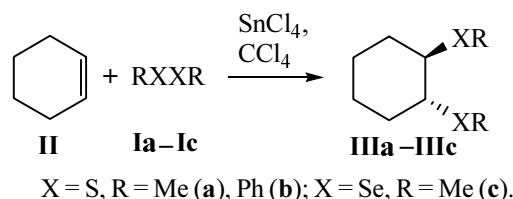
DOI: 10.1134/S1070428002120059

The electrophilic addition of diorganyl disulfides to alkenes and cycloalkenes catalyzed by BF_3 [1], GaCl_3 [2], and $[\text{PhIO-TfOH}]$ [3] is known to afford *trans*-adducts. The attempt to use other Lewis acids, like SnCl_4 , CaCl_2 , MgCl_2 , FeCl_3 , I_2 , and ZnCl_2 , by an example of disulfides addition to 3-carene revealed the inactivity of these acids (except for ZnCl_2) in these reactions. The reaction in the presence of ZnCl_2 gave rise to *anti*-addition [4]. The only example of *syn*-addition of diorganyl disulfides to a cyclic alkene, 2-norbornene, occurred under catalysis with a ruthenium complex and was described in [5].

It was shown [6] that tin(IV) chloride efficiently catalyzed the addition of diorganyl diselenides to alkenes, cycloalkenes, and terminal acetylenes. Hermans *et al.* assumed that with both alkenes and alkynes occurred the *anti*-addition, but the adducts with alkenes were not characterized either by physicochemical constants or by spectra. Moreover, further studies revealed that the catalysis with tin(IV) chloride resulted predominantly in the *syn*-addition of dialkyl diselenides to the terminal acetylenes [7]. Therefore the character of the tin(IV) chloride effect on the electrophilic addition of diorganyl dichalcogenides to alkenes remains unexplained.

In order to make clear this problem we studied the catalysis by this Lewis acid of addition reactions between diorganyl disulfides, diselenides, and ditellurides **Ia–Ie** and cyclohexene (**II**).

The reaction occurred at room temperature within several hours. The adducts formed as a single isomer, and their yields attained 88%; the disulfides proved to be the most active. No reaction occurred without catalyst.



We failed to obtain under these conditions adducts with dimethyl ditelluride (**Id**) and diphenyl diselenide (**Ie**). In the reaction mixture with diphenyl diselenide after 70 h the ^1H NMR spectroscopy showed only the presence of the initial diselenide. In the case of dimethyl ditelluride alongside the initial ditelluride was found chlorocyclohexane formed apparently by hydrochlorination of cyclohexene with HCl arising by hydrolysis of SnCl_4 during the treating of the reaction mixture with water.

The *anti*-addition at the catalysis with tin(IV) chloride was proved by the identity of the ^1H NMR spectra of 1,2-bis(methylsulfonyl)cyclohexane (**IIIa**) both obtained with the help of tin(IV) chloride and by cleavage of a cyclohexene sulfide with methylthiolate anion followed by the methylation of the intermediate product with dimethyl sulfate [8]. As additional confirmation of the *anti*-addition serves the identical physicochemical and spectral characteristics of oxidation product obtained from adduct **IIIa** which was synthesized in the presence of tin(IV) chloride, and those of the known *trans*-1,2-bis(methylsulfonyl)cyclohexane (**IVa**) [8]. Although *cis*-1,2-bis(methylsulfonyl)cyclohexane (**IVa**) and its selenium-containing analogs are not described, the *cis*- and *trans*-isomers of bis(organylsulfonyl)ethenes are known to possess quite different melting points [9, 10], and therefore

we may regard as identical the samples of compound **IVa** obtained by two the above mentioned methods.

The attempt to prepare a *cis*-isomer of adduct **IIIa** by *syn*-addition of dimethyl disulfide to cyclohexene under the catalysis of tetrakis(triphenylphosphine)palladium known as a catalyst of *syn*-addition to terminal acetylenes [11] was not successful.

At the use of ethyl ether for extraction of compound **IIIa** a complex formed between adduct **IIIa** and SnCl_4 of 1:1 composition for the tin(IV) chloride was also extracted from the water layer into ether. The same complex was obtained by treating individual adduct **IIIa** with tin(IV) chloride. In other solvents, like chloroform and dichloromethane, the complex did not form.

Beside the already mentioned 1,2-bis(methylsulfonyl)-cyclohexane (**IVa**) the corresponding sulfone **IVb** was also obtained by oxidation of 1,2-bis(phenylsulfonyl)cyclohexane (**IIIb**) with hydrogen peroxide in acetic acid. In the IR spectra of sulfones **IVa** and **IVb** the characteristic absorption bands of the SO_2 group were observed at 1300, 1100 cm^{-1} . ^1H NMR spectra are characterized by the presence of multiplet signals of CH groups, but their multiplicity was less pronounced than in the spectra of initial bis-sulfides **IIIa** and **IIIb**.

Hence we established that tin(IV) chloride catalyzed a stereoselective *anti*-addition of diorganyl disulfides and diselenides to cyclohexene.

EXPERIMENTAL

Dimethyl diselenide (**Ic**), diphenyl diselenide (**Ie**), and dimethyl ditelluride (**Id**) were obtained as in [12, 13]. IR spectra were recorded on a spectrometer Bruker IPS 25 from KBr pellets (compounds **IVa** and **IVb**). ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were registered on a spectrometer Bruker DPX-400 from 5–10% solutions in CDCl_3 , internal reference HMDS. GC-MS measurements were carried out on HP 5971A instrument (70 eV).

1,2-Bis(methylsulfonyl)cyclohexane (IIIa). In 50 ml of CCl_4 were stirred for 100 h at room temperature 4.71 g (50 mmol) of dimethyl disulfide (**Ia**), 50 mmol of tin(IV) chloride, and 4.11 g (50 mmol) of cyclohexene (**II**). The reaction mixture was treated with water, extracted with chloroform, and on removing the solvent we obtained 7.78 g (88%) of adduct **IIIa**. ^1H NMR spectrum, δ , ppm: 2.12 s (6H, $2\text{CH}_3\text{S}$), 2.63 t (2H, 2CHS , $^3J_{\text{HH}}$ 3.7 Hz), 2.14–2.20 m (2H), 1.68–1.76 m (2H), 1.45–1.55 m (2H), 1.31–1.39 m (2H). ^{13}C NMR spectrum, δ ,

ppm: 14.05 ($\underline{\text{C}}\text{H}_3\text{S}$), 24.70 ($\text{C}^{4,5}$), 31.76 ($\text{C}^{3,6}$), 49.32 ($\text{C}^{1,2}$). Chromato-mass spectrum: $[M]^+$ 176 (100%), $[M - \text{CH}_3\text{S}]^+$ 129 (67.5%), $[\text{C}_6\text{H}_9]^+$ 81 (42%).

1,2-Bis(phenylsulfonyl)cyclohexane (IIIb). Similarly from 6.54 g (30 mmol) of diphenyl disulfide (**Ib**), 7.81 g (30 mmol) of tin(IV) chloride, and 2.46 g (30 mmol) of cyclohexene (**II**) dissolved in 50 ml of CCl_4 in 70 h at room temperature was obtained 6.40 g of mixture containing according to ^1H NMR data 72% of adduct **IIIb** and 28% of initial disulfide **Ib**. Yield 70.5% (at conversion 73%). ^1H NMR spectrum, δ , ppm: 7.47 d, 7.30–7.18 m (10H, $2\text{C}_6\text{H}_5$), 3.26 br.s (2H, 2CHS), 2.27–2.20 m (2H), 1.73–1.59 m (4H), 1.40–1.37 m (2H). ^{13}C NMR spectrum, δ , ppm: 22.36 ($\text{C}^{4,5}$), 28.70 ($\text{C}^{3,6}$), 48.60 ($\text{C}^{1,2}$), 126.14, 126.54, 128.03, 128.28, 131.30, 133.93, 135.84, 204.81.

1,2-Bis(methylselenyl)cyclohexane (IIIc). Similarly from 1.88 g (10 mmol) of dimethyl diselenide (**Ic**), 2.60 g (10 mmol) of tin(IV) chloride, and 0.82 g (10 mmol) of cyclohexene (**II**) dissolved in 30 ml of CCl_4 after 200 h of stirring at room temperature we obtained 0.86 g (33%) of adduct **IIIc**. ^1H NMR spectrum, δ , ppm: 2.00 s (6H, $2\text{CH}_3\text{Se}$), 3.07 t (2H, 2CHSe , $^3J_{\text{HH}}$ 2.9 Hz), 2.22 m (2H), 1.67–1.64 m (4H), 1.42–1.39 m (2H). ^{13}C NMR spectrum, δ , ppm: 3.72 ($\underline{\text{C}}\text{H}_3\text{Se}$), 24.85 ($\text{C}^{4,5}$), 31.97 ($\text{C}^{3,6}$), 44.53 ($\text{C}^{1,2}$).

Complex of 1,2-bis(methylsulfonyl)cyclohexane (IIIa) with tin(IV) chloride. To a solution of 1.96 g (11 mmol) of compound **IIIa** in 15 ml of CCl_4 was added 2.90 g (11 mmol) of tin(IV) chloride in 15 ml of CCl_4 , and the mixture was stirred for 3 h. The separated precipitate was filtered off and dried in a vacuum. We obtained 3.47 g (72%) of 1:1 complex as colorless crystals that did not melt in a capillary up to 300°C. Found, %: C 23.25; H 3.90; Cl 30.55; S 17.08; Sn 27.14. $\text{C}_8\text{H}_{16}\text{Cl}_4\text{S}_2\text{Sn}$. Calculated, %: C 22.00; H 3.69; Cl 32.46; S 14.68; Sn 27.17.

1,2-Bis(methylsulfonyl)cyclohexane (IVa). In 9 ml of acetic anhydride was dissolved 0.90 g of compound **IIIa**, and 9 ml of 30% hydrogen peroxide was added dropwise at 5–10°C. After stirring for 5 h at room temperature the reaction mixture was cooled to 0°C. The separated crystals were filtered off, washed with water, and dried in a vacuum desiccator over P_2O_5 to obtain 0.88 g (72%) of compound **IVa** as fine colorless crystals, mp 174–176°C (publ.: mp 170–172°C [8]). IR spectrum, ν , cm^{-1} : 3026, 2938, 2864 (CH), 1293, 1122 (SO_2). ^1H NMR spectrum, δ , ppm: 3.02 s (6H, $2\text{CH}_3\text{SO}_2$), 3.78 t (2H, CHSO_2 , $^3J_{\text{HH}}$ 3.7 Hz), 2.19–2.26 m (4H), 1.82–

1.94 m (2H), 1.61–1.68 m (2H). ^{13}C NMR spectrum, δ , ppm: 19.53 ($\text{C}^{3,6}$), 22.22 ($\text{C}^{4,5}$), 39.84 (CH_3SO_2), 55.67 ($\text{C}^{1,2}$). Found, %: C 42.07; H 7.35; S 26.67. $\text{C}_8\text{H}_{16}\text{O}_4\text{S}_2$. Calculated, %: C 39.98; H 6.71; S 26.68.

1,2-Bis(phenylsulfonyl)cyclohexane (IVb).

Similarly from 1.51 g (5 mmol) of compound **IIIb** in 20 ml of AcOH and 10 ml of 30% hydrogen peroxide in 5 h we obtained 1.26 g (70%) of compound **IVb**, mp 169–171°C (EtOH). IR spectrum, ν , cm^{-1} : 3172, 3088, 3066 (=CH), 2956, 2940, 2907, 2865 (CH), 1305, 1152, 1132 (SO_2). ^1H NMR spectrum, δ , ppm: 7.70 d (J 7.34 Hz), 7.64 t (J 7.46 Hz), 7.48 t (J 7.70 Hz) (10H, $2\text{C}_6\text{H}_5$), 3.66 br.s (2H, 2CHSO_2), 2.21 br.s (4H), 1.87–2.00 m (2H), 1.60–1.72 m (2H). Found, %: C 60.18; H 5.82; S 18.01. $\text{C}_{18}\text{H}_{20}\text{O}_4\text{S}_2$. Calculated, %: C 59.31; H 5.5; S 17.59.

The study was carried out under a financial support of the Presidium of the Russian Academy of Sciences (project 9.3).

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