

## 디시클로헥실 텔루르염에 기반한 유기텔루로늄염의 합성과 분광학적 분석

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## Synthesis and Spectroscopic Investigations of Some New Organotelluronium Salts Based on Dicyclohexyl Telluride

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**요약.** 디시클로헥실 텔루르염은 에탄올 수용액에서 NaTeH와 디시클로헥실 브롬화물의 반응에 의해 높은 수율로 얻어진다. 일반식  $(cyclo-C_6H_{11})_2Te(R)X$  (where R = CH<sub>3</sub>, X = I (1); R = C<sub>2</sub>H<sub>5</sub>, X = Br(2); R = C<sub>2</sub>H<sub>5</sub>, X = I (3); R = C<sub>3</sub>H<sub>5</sub>, X = Br (4)) 인 유기텔루로늄의 새로운 시리즈는 그에 상응하는 알킬 할로젠화물과  $(cyclo-C_6H_{11})_2Te$ 의 반응에 의해 만들어진다. NaBPh<sub>4</sub>와 1의 반응은 78% 수율로 화합물 5를 제공하였다. 벤질 브롬화물과  $(cyclo-C_6H_{11})_2Te$ , 4-bromophenacyl bromide의 반응에서는 뜻밖에도 각각 dibenzylcyclohexyl-telluronium 브롬화물과 and bis(4-bromophenacyl)cyclohexyltelluronium bromide을 얻었다. 높은 수율의 tetraphenylborate 유도체는 NaBPh<sub>4</sub>과 6의 반응으로 얻었다. CDCl<sub>3</sub> 용매에서 <sup>1</sup>H NMR 분석을 통해 화합물 1이 알킬 할로젠화물의 제거 반응을 일으킴을 확인할 수 있었다. 새로운 화합물은 전도성, IR, <sup>1</sup>H와 <sup>13</sup>C NMR, 열분석를 통해 규명되었다.

**주제어:** 디시클로헥실 텔루르염, 텔루로늄염, 환원성 제거, 산화성 첨가, Tetraphenylborate

**ABSTRACT.** Dicyclohexyl telluride was obtained in a high yield by the reaction of cyclohexyl bromide with NaTeH(prepared *in situ*) in an aqueous ethanolic solution. A series of new organotelluronium salts of the general formula  $(cyclo-C_6H_{11})_2Te(R)X$  (where R = CH<sub>3</sub>, X = I (1); R = C<sub>2</sub>H<sub>5</sub>, X = Br(2); R = C<sub>2</sub>H<sub>5</sub>, X = I (3); R = C<sub>3</sub>H<sub>5</sub>, X = Br (4)) were prepared by the reaction of  $(cyclo-C_6H_{11})_2Te$  with the corresponding alkyl halide. Reaction of 1 with NaBPh<sub>4</sub> gave compound 5 (i.e. R = CH<sub>3</sub>, X = BPh<sub>4</sub><sup>-</sup>) in 78% yield. Reaction of  $(cyclo-C_6H_{11})_2Te$  with benzyl bromide and 4-bromophenacyl bromide gave unexpectedly dibenzylcyclohexyltelluronium bromide (6) and bis(4-bromophenacyl)cyclohexyltelluronium bromide (7), respectively. Reaction of 6 with NaBPh<sub>4</sub> gave the corresponding tetraphenylborate derivative (8) in high yield. <sup>1</sup>H NMR studies revealed that in CDCl<sub>3</sub> solution compound 1 eliminated alkyl halide. Conductivity, IR, <sup>1</sup>H and <sup>13</sup>C NMR and thermal data for the new compounds are presented and discussed.

**Keywords:** Dicyclohexyl telluride, Telluronium salts, Reductive elimination, Oxidative addition, Tetraphenylborate

### INTRODUCTION

Recently, the synthesis, structures and properties of triorganotelluronium salts have received considerable

attention.<sup>1,2</sup> Thus, new and general approaches to a variety of unsymmetrical telluronium salts have been developed.<sup>3,4</sup> A special attention is also given to the applications of these compounds in preparative

organic synthesis.<sup>5,6</sup> Our previous work described the synthesis and solution properties of a series of cyclic and non cyclic telluronium salts.<sup>7,8</sup> It was observed that some of these telluronium salts are unstable toward reductive elimination of alkyl halide in organic solvents,<sup>7,8</sup> such as  $\text{CDCl}_3$ , DMSO and DMF. Recently, we reported the synthesis and solution properties of some new telluronium salts based on bis(cyclohexylmethyl) telluride.<sup>7a</sup>

The synthesis of dicyclohexyl telluride<sup>9,10</sup> and its dihalo,<sup>11,12</sup> pseudohalido<sup>11</sup> and diazido<sup>13</sup> derivatives have been reported previously. No work has been done on the reactions of dicyclohexyl telluride with alkyl halides, as far as we aware. Thus, the present work describes the synthesis, solution properties and some solid state data of a new series of telluronium salts based on dicyclohexyl telluride. Some unexpected reactions are also reported.

## EXPERIMENTAL

### Physical measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Jeol EX-90FT (90 MHz) spectrometers with TMS as an internal reference. Infrared spectra were recorded with KBr discs in the range of  $4000\text{--}200\text{ cm}^{-1}$  on a Pye-Unicam SP-300s infrared spectrophotometer. Microanalysis for carbon, hydrogen and nitrogen was obtained on a Carlo-Ebra EA1-108 Elemental Analyzer. All melting points were determined by a Gallenkamp melting point apparatus and are uncorrected. Molar conductances at  $10^{-3}\text{--}10^{-5}$  dilution in DMSO were measured with a WTW D812 conductivity meter LBR, using a standard cell with cell constant of  $0.81\text{ cm}^{-1}$ . The thermal analyses were carried out using Du Pont thermoanalyser, model 990, which measure TGA and DTG simultaneously. All measurements were carried out under nitrogen atmosphere. The analyses were performed by heating the sample at a steady rate of  $50\text{ }^\circ\text{C min}^{-1}$ , from ambient temperature to  $600\text{ }^\circ\text{C}$ .

### Synthesis

All reactions were carried out in a dry oxygen-free, nitrogen atmosphere. Solvents were dried and distilled before use, using standard procedures.

### Dicyclohexyl telluride

$\text{NaBH}_4$  (2.1 g; 59 mmol) was added under nitrogen atmosphere at room temperature to a suspension of tellurium powder (2.55 g; 20 mmol) in  $70\text{ cm}^3$  ethanol/water (6/1). The reaction mixture was then refluxed whereupon a vigorous evolution of  $\text{H}_2$  started. All the tellurium was consumed within 20 min, producing a faintly yellow solution. To cooled resulting solution was added a solution of cyclohexyl bromide (6.52 g; 40 mmol) in ethanol ( $40\text{ cm}^3$ ). The resulting solution was refluxed for 1 h and then water bath was removed and the stirring continued for 2 h at room temperature. The solution was filtered, pored into  $500\text{ cm}^3$  of distilled water and extracted with chloroform ( $4 \times 50\text{ cm}^3$ ). The combined extracts were dried with anhydrous  $\text{MgSO}_4$ . Evaporation of solvent by a rotary evaporator, gave heavy orange oil with a persistent odour in 86% yield (4.70 g).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.35 (m, Te-CH, 2H); 0.80-2.26 (m, Cy- $\text{CH}_2$ , 20H).

### Methyldicyclohexyltelluronium iodide (1).

A freshly distilled methyl iodide (2.13 g; 15 mmol) and a solution of (*cyclo*- $\text{C}_6\text{H}_{11}$ ) $_2\text{Te}$  (2.94 g; 10 mmol) in diethyl ether ( $10\text{ cm}^3$ ) were placed in a flask flushed with dry nitrogen. The reaction mixture was stoppered and left overnight. A white precipitate was formed, recrystallized from ethanol and dried *in vacuo* to give 3.62 g (60%) of compound **1**, mp  $118\text{--}120\text{ }^\circ\text{C}$ .

Anal. Calc. for  $\text{C}_{13}\text{H}_{25}\text{TeI}$ : C, 35.82; H, 5.78. Found: C, 35.78; H, 5.99.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.45 (s,  $\text{CH}_3$ , 3H); 3.81 (m, Te-CH, 2H); 1.00-2.40 (m, Cy- $\text{CH}_2$ , 20H).

### Ethyldicyclohexyltelluronium bromide (2).

This compound was obtained as white crystals in 68% yield and prepared by the same way as compound **1** using ethyl bromide, mp  $205\text{ }^\circ\text{C}$ .

Anal. Calc. for  $\text{C}_{14}\text{H}_{27}\text{TeBr}$ : C, 41.74; H, 6.76. Found: C, 41.71; H, 6.69.

### Ethyldicyclohexyltelluronium iodide (3).

This compound was prepared by the reaction of ethyl iodide with (*cyclo*- $\text{C}_6\text{H}_{11}$ ) $_2\text{Te}$  under conditions reported for compound **1**. White crystals, mp  $> 300\text{ }^\circ\text{C}$ .

Anal. Calc. for  $C_{14}H_{27}TeI$ : C, 37.38; H, 6.05. Found: C, 36.96; H, 5.53.

**Allyldicyclohexyltelluronium bromide (4).**

Reaction of allyl bromide with dicyclohexyl telluride under conditions reported for compound **1**, gave white crystals of compound **4**, mp 158 °C (dec.). Yield: 65%.

Anal. Calc. for  $C_{15}H_{27}TeBr$ : C, 43.42; H, 6.56. Found: C, 43.22; H, 6.32.

$^1H$  NMR ( $CDCl_3$ )  $\delta$ : 1.02-2.38 (m, Cy- $CH_2$ , 20H); 2.72 (d,  $CH_2$ -Te, 2H,  $J = 7.3$  Hz); 3.81 (qui, Te- $CH$ , 2H,  $J = 6.9$  Hz); 5.11 (m,  $CH_2 = CH$ , 2H); 5.78 (m,  $CH_2 = CH-CH_2$ , 1H).

**Methyldicyclohexyltelluronium tetraphenylborate (5).**

Compound **1** (0.40 g; 0.92 mmol) dissolved in 30  $cm^3$  of hot ethanol/water (3/1) was added to a solution of sodium tetraphenylborate (0.34 g; 1 mmol) in hot ethanol (10  $cm^3$ ). A voluminous white precipitate was immediately formed. The reaction mixture was stirred at room temperature for 1 h. The white precipitate was collected and washed several times with hot ethanol. Recrystallization from DMF and water gave a white solid of compound **5** in 78% yield, mp 161-162 °C.

Anal. Calc. for  $C_{37}H_{45}BTe$ : C, 70.75; H, 7.22. Found: C, 70.53; H, 7.08.

$^1H$  NMR ( $CDCl_3$ )  $\delta$ : 2.90 (s,  $CH_3$ , 3H); 3.90 (m, Te- $CH$ , 2H); 0.80-2.20 (m, Cy- $CH_2$ , 20H); 6.80-7.90 (m, Ar- $H$ , 20H).

**Dibenzylcyclohexyltelluronium bromide (6).**

This compound was prepared by the oxidative addition of benzyl bromide (2.57 g; 15 mmol) to dicyclohexyl telluride (2.94 g; 10 mmol) under previous conditions reported for compound **1**. White crystals, mp 106-108 °C. Yield: 69%.

Anal. Calc. for  $C_{20}H_{25}TeBr$ : C, 50.79; H, 5.33. Found: C, 50.55; H, 5.11.

$^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.50 (m, Te- $CH$ , 1H); 0.80-2.40 (m, Cy- $CH_2$ , 10H), 4.45 (q, Ph- $CH_2$ , 4H,  $J = 7.2$  Hz); 6.70-7.80 (m, Ar- $H$ , 10H).

$^{13}C$  NMR ( $CDCl_3$ )  $\delta$ : 25.1, 27.5, 29.1, 30.5, 45.0, 121.5, 126.8, 129.0, 136.7.

**Bis(4-bromophenyl)cyclohexyltelluronium bromide (7).**

4-Bromophenacyl bromide (4.17 g; 15 mmol) in 20  $cm^3$  of diethyl ether was added to dicyclohexyl telluride (2.94 g; 10 mmol) in 30  $cm^3$  of diethyl ether. The flask was stoppered and left overnight. The deposited white precipitate was separated and washed with chloroform and ethanol, respectively. Recrystallization from ethanol gave a white solid, mp 99-101 °C. Yield: 52%.

Anal. Calc. for  $C_{22}H_{23}O_2TeBr_3$ : C, 38.82; H, 3.38. Found: C, 39.28; H, 3.27.

$^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.40 (m, Te- $CH$ , 1H); 1.00-2.70 (m, Cy- $CH_2$ , 10H), 4.45 (q, Ph-CO- $CH_2$ , 4H,  $J = 7.4$  Hz); 7.40-8.70 (m, Ar- $H$ , 8H).

**Dibenzylcyclohexyltelluronium tetraphenylborate (8).**

This compound was prepared by the same above method for compound **5** and gave white crystals in 75% yield, mp 138-140 °C.

Anal. Calc. for  $C_{44}H_{45}BTe$ : C, 74.20; H, 6.37. Found: C, 74.03; H, 6.14.

$^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.35 (m, Te- $CH$ , 1H); 1.00-2.10 (m, Cy- $CH_2$ , 10H), 3.50 (s, Ph- $CH_2$ , 4H); 6.90-7.78 (m, Ar- $H$ , 30H).

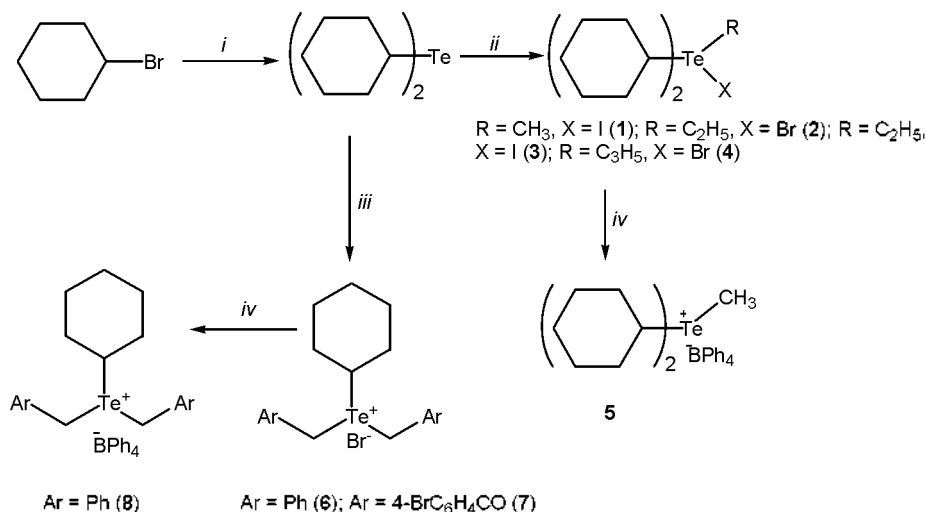
$^{13}C$  NMR ( $CDCl_3$ )  $\delta$ : 25.0, 27.5, 29.1, 30.5, 45.1, 121.3, 125.3, 126.4, 128.6, 129.2, 132.3, 136.7, 164.5, 167.

## RESULTS AND DISCUSSION

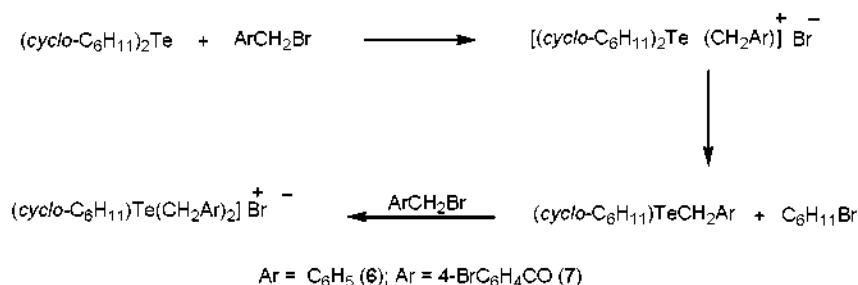
Reaction of NaTeH, prepared in situ from reaction of tellurium powder with  $NaBH_4$  in an aqueous ethanol, with cyclohexyl bromide gave dicyclohexyl telluride in 86% yield. This method gave dicyclohexyl telluride in a high yield compare with other reported methods.<sup>9,10</sup> This compound starts to decompose if left under ambient conditions for more than a day and should be used immediately to prepare its derivatives.

Oxidative addition of methyl iodide, ethyl bromide, ethyl iodide and allyl bromide to dicyclohexyl telluride produce the corresponding telluronium salts (*i.e.* compounds **1**, **2**, **3** and **4**) in good yields. Reaction of **1** with sodium tetraphenylborate gave compound **5** in 78% yield (*Scheme 1*).

Unexpectedly, addition of benzyl bromide and



Scheme 1. Methods of preparation of compounds 1-8. (i) Te/NaBH<sub>4</sub>/ EtOH-H<sub>2</sub>O. (ii) alkyl halides. (iii) benzyl bromide or 4-phenacyl bromide. (iv) NaBPh<sub>4</sub>.



Scheme 2

4-bromophenacyl bromide to dicyclohexyl telluride gave dibenzylcyclohexyltelluronium bromide (6) and bis(4-bromophenacyl)cyclohexyltelluronium bromide (7), respectively as unexpected products. Thus it seems likely that in both reactions, telluronium salt species were initially formed and reductively eliminated cyclohexyl bromide to form the unsymmetrical telluride ((cyclo-C<sub>6</sub>H<sub>11</sub>)Te-CH<sub>2</sub>Ar). These unsymmetrical tellurides react again with benzyl bromide or 4-bromophenacyl bromide to afford compounds 6 and 7, respectively as shown in Scheme 2.

The proposed mechanism is not unique, since it is well established that oxidative addition of alkyl halides to diorganyl tellurides proceeded *via* radical pathways and the products depended on the stability of alkyl radicals.<sup>14,15</sup> The reaction of compounds 6

with sodium tetraphenylborate gave compound 8 in good yield, which supports the formation of compound 6. Scheme 1. An authentic sample of 6 was prepared by reaction of dibenzyl telluride with cyclohexyl bromide and gave the same melting point and the same IR spectrum in comparison with compound 6. Compounds 2 and 3 are insoluble in most common organic solvents and have high melting points in compare with other derivatives.

The IR spectra of 1-8 display characteristic band at certain region. All compounds showed medium to strong bands due to C-H asymmetric and symmetric stretching ( $\nu_{as}$  and  $\nu_s$ ) in the range 2960-2900 and 1260-1240  $\text{cm}^{-1}$ , respectively. Two weak to medium bands due to  $\nu_{as}(\text{C-Te})$  and  $\nu_s(\text{C-Te})$  generally appeared at 510-495 and 663-635  $\text{cm}^{-1}$ , respectively.

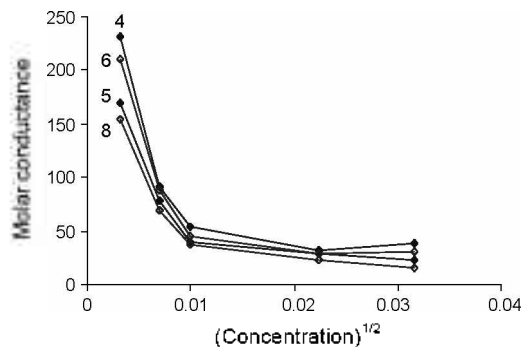


Fig. 1. Plots of molar conductance ( $(\Lambda_M) \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) against  $(\text{concentration})^{1/2}$  for compounds **4**, **5**, **6** and **8** in DMSO solution.

Thus, it seems that energy differences between  $\nu_{\text{as}}(\text{C-Te})$  and  $\nu_s(\text{C-Te})$  for  $(\text{cyclo-C}_6\text{H}_{11})_2\text{Te}$  and its derivatives is increased significantly in compare with other alkyl and heterocyclic tellurium compounds.<sup>7-9</sup>

<sup>1</sup>H NMR spectra of compounds **1** and **5-8** show all the expected peaks in proper intensity ratio.

The <sup>1</sup>H NMR spectrum of compound **1** in  $\text{CDCl}_3$  shows signals due to  $\text{CH}_2\text{-cyclo}$ ,  $\text{CH-Te}$  and  $\text{CH}_3\text{-Te}$  at  $\delta$  1.00-2.40(m), 3.81(m) and 2.45(s), respectively, but as time passes (24 h) the spectrum shows two extra new signals at  $\delta$  2.16(m) and at  $\delta$  3.36(s), due to  $\text{CH-Te}$  and  $\text{CH}_3\text{I}$ , respectively. This may due to methylation and demethylation equilibrium of compound **1** in  $\text{CDCl}_3$  solution and as shown in the following equation:



Such behavior was also observed with other tellurium salt.<sup>7,8,16,17</sup>

The molar conductivities compounds **4**, **5**, **6** and **8** in  $10^{-3}$  M of DMSO were determined and their values approach those expected for 1:1 electrolytes ( $\Lambda_M \approx 30 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ). Plots of molar conductance ( $\Lambda_M$ ) against  $(\text{concentration})^{1/2}$  are typical of weak electrolytes (Fig. 1) which agree well with previous works.<sup>7,8,16,17</sup>

The thermogravimetric curve for compound **1** shows one decomposition peak at  $190^\circ\text{C}$ . This loss reaches value of 48.8% (calculated 48.2%), which

points to loss  $\text{C}_6\text{H}_{11}\text{I}$  and formation of  $\text{C}_6\text{H}_{11}\text{TeCH}_3$  as a residual product. A loss at  $210^\circ\text{C}$  is observed for compound **6**. This effect corresponds to removal of  $\text{C}_6\text{H}_{11}\text{Br}$  (mass loss observed 43.8% compared with the calculated 43.4%). Thus, same decomposition pattern can be applied for both compounds. On the other hand, compound **6** was completely evaporated at  $190^\circ\text{C}$ . On heating compound **8**, a massive loss occurs at  $210^\circ\text{C}$ , amounting to 82.5% (calculated 82.0%), which can be attributed to the thermal extrusion of tellurium and as residual product. Extrusion of tellurium may be promoted thermally<sup>18</sup> or photochemically.<sup>19</sup> Thus we believe that tellurium is thermally extruded from compound **8**.

In conclusion, a series of new organotellurium compounds derived from dicyclohexyl telluride have been prepared in good yield and their solid decomposition and solution properties have been studied.

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