

Synthesis and structure of β -tellurovinylcarbonyl compounds

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Abstract

By coupling β -chlorovinylcarbonyl compounds or β -acylvinyltrium chlorides with arene (alkene) tellurolates and lithium telluride β -organytellurovinyl aldehydes, ketones **I** and bis(β -acylvinyl) tellurides **II** correspondingly have been prepared. β -Methyltellurovinyl aldehyde **VI** is readily oxidized by halogens, giving rise to previously undescribed β -methylhalogenotellurovinyl aldehydes **IX**, which convert to the respective β -halogenotellurenylvinyl aldehydes **X** via elimination of a molecule of methyl halogenide. Regardless of the initial configuration at the C_β center of the β -chlorovinylcarbonyl compounds, the nucleophilic vinylic substitution reaction results in the formation exclusively of *Z*-isomers of β -organytellurovinyl aldehydes and ketones. The stereochemical outcome of this reaction is explained in terms of the addition–elimination mechanism of the nucleophilic vinylic substitution reaction, as a consequence of strong stabilization of the intermediate carbanions **XVIII** by intramolecular coordination of $O \rightarrow Te$ bonds. For the same reason, nucleophilic addition of arenetellurolate anions to a triple bond of α -acetylenic aldehydes and ketones occurs stereospecifically, affording exclusively *Z*-(β -aryltellurovinylcarbonyl) diastereomers. The crystal and molecular structures of β -(4-ethoxyphenyltelluro)- β -phenylpropenal **Ip** and its *N*-(4-methylphenyl) imine **V** have been studied by X-ray. Both compounds exist in the crystal as *Z*-diastereomers, the tellurium centers possessing a T-shaped configuration due to the formation of intramolecular coordination corresponding to $O \rightarrow Te$ (2.725 Å) and $N \rightarrow Te$ (2.771 Å) bonds. © 1997 Elsevier Science S.A.

Keywords: Tellurium; Vinyl; Carbonyl; Crystal structure

1. Introduction

In contrast to β -thiovinylcarbonyl compounds and their aza analogues [1], the synthesis and reactions of their tellurium analogues have hitherto been studied little. First representatives of β -aryltellurovinyl aldehydes and ketones **I** have been obtained in rather high yields (67–88%) by the reaction of nucleophilic addition of arenetellurolate anions to a triple bond of α -acetylenic aldehydes and ketones [2,3]. When the telluride anion was used as the nucleophile in this reaction, bis(β -acylvinyl) tellurides **II** were obtained in low yield (3–11%) [4]. Of all the β -tellurovinylcarbonyl compounds known thus far, the most studied are β -chlorotellurenylvinyl ketones, a four-step synthesis of which has been developed by Detty and coworkers [5,6]. The method includes the steps (a) nucleophilic addition of arenetellurolate anions to esters of α -

acetylenecarboxylic acids, (b) hydrolysis of the formed β -aryltelluropropenoate esters, (c) conversion of β -aryltelluropropenoic acids to their acide chlorides, and (d) thermal or catalysed ($AlCl_3$) rearrangement of the latter. A common limitation of all the approaches considered above is that only those derivatives of β -tellurovinylcarbonyl compounds can be prepared which do not contain any substituents at the α -carbon center. Moreover, only β -chlorotellurenylvinyl ketones are obtainable by use of the latter method.

Clearly, the most general approach to the synthesis of structurally diverse β -tellurovinylcarbonyl compounds **I**, **II** and **VI** is associated with the reaction of nucleophilic vinylic substitution of chlorine at the sp^2 carbon atom of easily accessible β -chlorovinylaldehydes or ketones [7,8] by tellurium-centered nucleophiles. Some preliminary reports on the application of this reaction have been published previously [9,10].

This paper brings together some new data on the development of this reaction, gains insight into its stere-

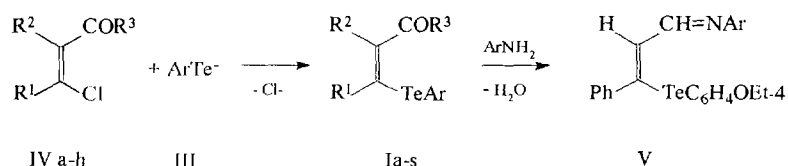
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ochemical course and explores the structure of the β -tellurovinylcarbonyl compounds obtained by use of ^1H NMR spectral and X-ray analyses.

2. Results and discussion

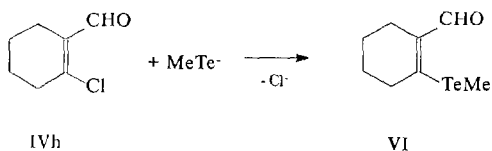
2.1. Synthesis of β -tellurovinylcarbonyl compounds

A broad series of β -aryltellurovinyl aldehydes and ketones **I** has been obtained in 37–65% yield by coupling arenetelluroolate anions **III** with corresponding β -chlorovinylcarbonyl compounds **IV** at -10 to -15°C



IV $\text{R}^1 = \text{R}^2 = \text{H}$: $\text{R}^3 = \text{Ph}$ (a), 4-MeC₆H₄ (b), 4-MeOC₆H₄ (c), 4-BrC₆H₄ (d); $\text{R}^1 = \text{Ph}$: $\text{R}^2 = \text{R}^3 = \text{H}$ (e), $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$ (f), $\text{R}^2 = \text{Et}$, $\text{R}^3 = \text{H}$ (g); $\text{R}^1 + \text{R}^2 = (\text{CH}_2)_4$, $\text{R}^3 = \text{H}$ (h)
 I Ar = Ph (a-e), 4-MeC₆H₄ (f-j), 4-MeOC₆H₄ (k), 4-EtOC₆H₄ (l-r), 4-ClC₆H₄ (s), $\text{R}^1 = \text{R}^2 = \text{H}$: $\text{R}^3 = \text{Ph}$ (a, f, l), 4-MeC₆H₄ (g, m), 4-MeOC₆H₄ (h, n), 4-BrC₆H₄ (i, o), $\text{R}^1 = \text{Ph}$: $\text{R}^2 = \text{R}^3 = \text{H}$ (b, p), $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$ (c, q), $\text{R}^2 = \text{Et}$, $\text{R}^3 = \text{H}$ (d, k), $\text{R}^1 + \text{R}^2 = (\text{CH}_2)_4$, $\text{R}^3 = \text{H}$ (e, j, r, s)
 V Ar = 4-MeC₆H₄

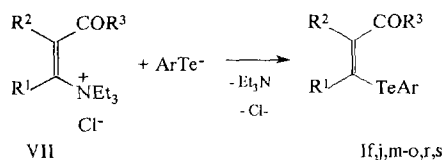
The reaction of 2-chlorocyclohexanal **IVh** with lithium methane telluroolate, generated by coupling methyl lithium with tellurium in tetrahydrofuran, proceeds smoothly only at temperatures as low as -70°C . The yield of β -alkyltellurovinylaldehyde **VI** achieved is 54%.



A stereochemical *Z*-configuration at the double bond of compounds **I** has been proven unequivocally for β -(4-ethoxyphenyltelluro)- β -phenylpropenal **Ip** by an X-ray structural investigation (Section 2.2). For a number of other β -organyltellurovinyl ketones **1a,f-i,l-o**, the conclusion about *Z*-configuration at their double bonds has been drawn on the ground of magnitudes of the $^3J_{\text{HH}}$ spin-spin couplings. These were found to fall into the range 8.8–9.9 Hz, characteristic of values of spin-spin couplings (6.0–11.8 Hz) in *cis*-(HC=CH) moieties not overlapped by those related to spin-spin couplings in *trans*-(HC=CH) fragments (13.2–19.1 Hz) [14].

(method A). The highly nucleophilic anions **III** were generated through either reaction of arenolithium ArLi (Ar = Ph, 4-MeC₆H₄) with powdered tellurium in tetrahydrofuran or reduction of diarylditellurides Ar₂Te₂ (Ar = 4-MeOC₆H₄, 4-EtOC₆H₄, 4-ClC₆H₄) by lithium in tetrahydrofuran in the presence of catalytic amounts of naphthalene. It is worth noting that employment of the most usable method of generation of sodium arenetelluroolates by reduction of diarylditellurides with either water-ethanol alkaline solution of NaBH₄ or dry powdered NaBH₄ [11–13] leads to rather low yields of compounds **I** in this reaction:

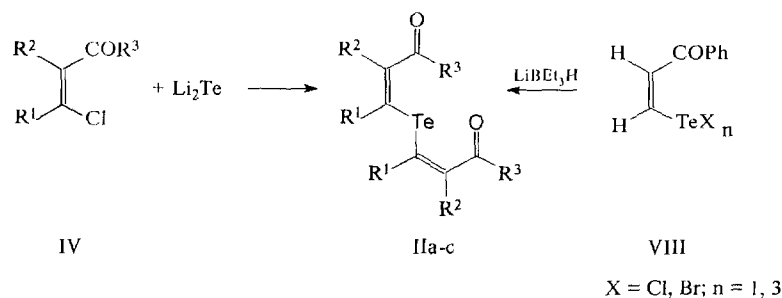
In another approach to the synthesis of β -aryltellurovinylcarbonyl compounds **I**, β -acylvinyltriethylammonium chlorides **VII** have been used as starting material (method B). The compounds **VII** were obtained in high yields by treatment of the respective β -chlorovinyl ketones with triethylamine according to an earlier described procedure [15]. Generation of arenetelluroolate anions **III** in method B has been carried out by reduction of diarylditellurides with NaBH₄ in anhydrous methanol.



The advantages of method B compared with method A lie in the stability of the ammonium salts **VII**, that can be stored for a long time, in a more convenient procedure for the preparation of arenetelluroolate anions and in, more importantly, higher yields (70–86%) of the final products **I**.

By treatment of β -chlorovinylcarbonyl compounds **IV** with Li_2Te (suspension prepared by reaction of lithium with elemental tellurium in tetrahydrofuran in

the presence of catalytic amounts of naphthalene) in tetrahydrofuran, bis(β -acylviny) tellurides **II** have been prepared in 39–60% yields.

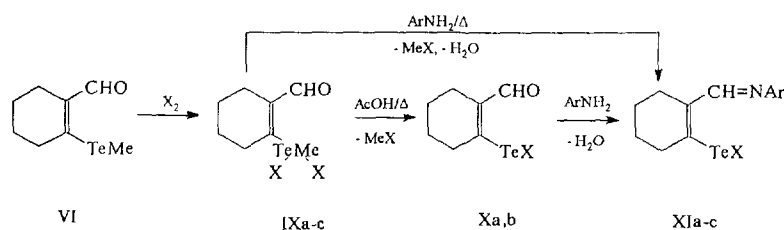


II $\text{R}^1 = \text{R}^2 = \text{H}$; $\text{R}^3 = \text{Ph}$ (a), $4\text{-MeC}_6\text{H}_4$ (b); $\text{R}^1 + \text{R}^2 = (\text{CH}_2)_4$, $\text{R}^3 = \text{H}$ (c)

As stems from the ^1H NMR spectrum, both the $\text{HC}=\text{CH}$ moieties in **IIa** are structurally equivalent, and take a *Z*-configuration at the double bond (one common AB pattern, $\delta = 8.36$ and 9.14 ppm, $^3J_{\text{HH}} = 9.67$ Hz). The spectrum is identical with that of the compound obtained by reduction of β -trihalogenotellurovinylbenzoyl ketone **VIII** ($n = 3$) or β -halogenotellurenylvinybenzoyl ketone **VIII** ($n = 1$) [16]. A *Z*-configuration at the double bond of the latter compound is justified by the X-ray structural study [15,16].

β -Methyltellurovinyl aldehyde **VI** served as a precursor for the synthesis of previously unknown β -methyl-

dihalogenotellurovinyl aldehydes **IX** and β -halogenotellurenylviny aldehydes **X**. Unlike their aryl analogues **I**, whose reaction with halogens leads to unidentified oily products, alkylvinyl telluride **VI** is readily oxidized by halogens in benzene solution at 0 to 5°C , affording β -methyl-dihalogenotellurovinyl aldehydes **IX** in almost quantitative yields. The aldehydes **IX**, much like (2-formylphenyl)alkyltellurium dibromides [17], eliminate a molecule of methyl halogenide under refluxing of their acetic acid solutions containing small amounts of corresponding hydrogen halogenides to give tellurenyl halogenides **X** in 50–60% yields.



IX $\text{X} = \text{Br}$ (a), I (b), Cl (c)

X $\text{X} = \text{Br}$ (a), I (b):

XI $\text{Ar} = 4\text{-CH}_3\text{C}_6\text{H}_4$; $\text{X} = \text{Br}$ (a), I (b), Cl (c)

The advantages of the approach described above for the synthesis of β -halogenotellurenylviny carbonyl compounds **X** compared with the methods of Refs. [5,6] lie not only in the lesser number of steps required, but mostly in the fact that it makes accessible β -halogenotellurenylviny carbonyl compounds with various sets of substituents in the carbon triad of the acylvinyl moieties of **X**. A characterization of the new compounds **I**, **VI**, **IX**, **X** is given in Table 1.

2.2. Molecular and crystal structure of β -tellurovinyl-carbonyl compounds

The structure of the *Z*- β -tellurovinylcarbonyl compounds **I**, **VI**, **X** and their imines **V**, **XI** makes possible the formation of a peculiar intramolecular coordination of $\text{O} \rightarrow \text{Te}$ and $\text{N} \rightarrow \text{Te}$ bonds, which have been studied mostly in the case of their derivatives benzoannulated at the carbon-carbon double bonds [18–21]. These bonds

Table 1
 β -Tellurovinyl aldehydes and β -tellurovinyl ketones I, VI, IX, X

N	Yield (%) (method of synthesis)	M.p. (°C)	Found (%)		Formula	Calc. (%)		NMR spectrum δ (ppm) ^a
			C	H		C	H	
1	2	3	4	5	6	7	8	9
Ia	47(A)	84–85 ^b	53.5	3.5	C ₁₅ H ₁₂ O ₂ Te	53.6	3.6	7.28–8.08 (m, 10H, 2C ₆ H ₅), 8.38 (d, 1H, CH, <i>J</i> 8.79 Hz), 9.20 (d, 1H, CH, <i>J</i> 8.79 Hz)
Ib	37(A)	96–97 ^b	53.5	3.7	C ₁₅ H ₁₂ O ₂ Te	53.6	3.6	6.90–7.40 (m, 11H, 2C ₆ H ₅ + 1CH), 9.95 (s, 1H, CHO)
Ic	60(A)	86–88 ^c	54.7	4.1	C ₁₆ H ₁₄ O ₂ Te	54.9	4.0	9.10 s, 9.92 s (1H, CHO, intensity ratio approx. 65:35 ^d)
Id	65(A)	80–82 ^c	55.9	4.3	C ₁₇ H ₁₆ O ₂ Te	56.1	4.4	9.08 s, 9.98 s (1H, CHO, intensity ratio approx. 95:5 ^d)
Ie	57(A)	73–74 ^b	49.9	4.4	C ₁₃ H ₁₄ O ₂ Te	49.8	4.5	1.65–3.05 (m, 8H, (CH ₂) ₄), 7.22–7.70 (m, 5H, C ₆ H ₅), 9.55 (s, 1H, CHO)
If	45(A) 86(B)	142–144 ^e	54.7	4.1	C ₁₆ H ₁₄ O ₂ Te	54.9	4.0	2.32 (s, 3H, CH ₃), 7.16 (d, 2H, H ^{3',5'} , <i>J</i> 8.91 Hz), 7.52–8.16 (m, 7H, C ₆ H ₅ + H ^{2,6}), 8.61 (d, 1H, CH, <i>J</i> 8.79 Hz), 9.26 (d, 1H, CH, <i>J</i> 8.79 Hz)
Ig	39(A)	127–128 ^e	56.0	4.3	C ₁₇ H ₁₆ O ₂ Te	56.1	4.4	2.36 (s, 3H, CH ₃), 2.40 (s, 3H, CH ₃), 7.12 (d, 2H, H ^{3',5'} , <i>J</i> 7.61 Hz, 7.26 (d, 2H, H ^{3,5} , <i>J</i> 8.21 Hz), 7.72 (d, 2H, H ^{2',6'} , <i>J</i> 7.92 Hz), 7.94 (d, 2H, H ^{2,6} , <i>J</i> 8.20 Hz), 8.33 (d, 1H, CH, <i>J</i> 8.79 Hz), 9.12 (d, 1H, CH, <i>J</i> 9.08 Hz)
Ih	45(A)	125–126 ^d	53.6	4.1	C ₁₇ H ₁₆ O ₂ Te	53.7	4.3	2.37 (s, 3H, CH ₃), 3.89 (s, 3H, OCH ₃), 6.97 (d, 2H, H ^{3',5'} , <i>J</i> 8.79 Hz), 7.13 (d, 2H, H ^{3,5} , <i>J</i> 7.62 Hz), 7.73 (d, 2H, H ^{2',6'} , <i>J</i> 7.91 Hz), 8.06 (d, 2H, H ^{2,6} , <i>J</i> 8.79 Hz), 8.32 (d, 1H, CH, <i>J</i> 9.09 Hz), 9.07 (d, 1H, CH, <i>J</i> 8.79 Hz)
Ii	55(A)	154–154.5 ^d	44.6	3.0	C ₁₆ H ₁₃ BrO ₂ Te	44.8	3.1	2.37 (s, 3H, CH ₃), 7.13 (d, 2H, H ^{3',5'} , <i>J</i> 7.62 Hz), 7.64 (d, 2H, H ^{3,5} , <i>J</i> 8.79 Hz), 7.72 (d, 2H, H ^{2',6'} , <i>J</i> 7.91 Hz), 7.92 (d, 2H, H ^{2,6} , <i>J</i> 8.79 Hz), 8.33 (d, 1H, CH, <i>J</i> 8.79 Hz), 9.26 (d, 1H, CH, <i>J</i> 8.79 Hz)
Ij	52(A) 71(B)	100–102 ^e	51.1	5.0	C ₁₄ H ₁₆ O ₂ Te	51.3	4.9	1.45–2.65 (m, 8H, (CH ₂) ₄), 2.35 (s, 3H, CH ₃), 7.15 (d, 2H, H ^{3',5'} , <i>J</i> 9.03 Hz), 7.72 (d, 2H, H ^{2',6'} , <i>J</i> 9.02 Hz), 9.68 (s, 1H, CHO)
Ik	58(A)	76–77	54.7	4.5	C ₁₈ H ₁₈ O ₂ Te	54.9	4.6	9.07 s, 9.97 s (1H, CHO, intensity ratio approx. 95:5 ^d)
Il	52(A)	94–96 ^e	53.6	4.2	C ₁₇ H ₁₆ O ₂ Te	53.8	4.2	1.32 (t, 3H, OCH ₂ CH ₃), 4.04 (q, 2H, OC H ₂ CH ₃), 6.88 (d, 2H, H ^{3',5'} , <i>J</i> 8.72 Hz), 7.50–8.12 (m, 7H, C ₆ H ₅ + H ^{2,6'}), 8.36 (d, 1H, CH, <i>J</i> 8.79 Hz), 9.17 (d, 1H, CH, <i>J</i> 8.79 Hz)
Im	53(A) 79(B)	128–129.5 ^e	54.6	4.5	C ₁₈ H ₁₈ O ₂ Te	54.9	4.6	1.42 (t, 3H, OCH ₂ CH ₃), 2.40 (s, 3H, CH ₃), 4.02 (q, 2H, OC H ₂ CH ₃), 6.84 (d, 2H, H ^{3',5'} , <i>J</i> 8.49 Hz), 7.29 (d, 2H, H ^{3,5} , <i>J</i> 7.92 Hz), 7.74 (d, 2H, H ^{2',6'} , <i>J</i> 8.79 Hz), 7.96 (d, 2H, H ^{2,6} , <i>J</i> 8.50 Hz), 8.33 (d, 1H, CH, <i>J</i> 8.79 Hz), 9.12 (d, 1H, CH, <i>J</i> 8.79 Hz)

In	39(A) 83(B)	136–137.5 ^e	52.5	4.3	C ₁₈ H ₁₈ O ₃ Te	52.7	4.4	1.43 (t, 3H, OCH ₂ CH ₃), 3.87 (s, 3H, OCH ₃), 4.04 (q, 2H, OCH ₂ CH ₃), 6.84 (d, 2H, H ^{3',5'} , J 8.5 Hz), 6.97 (d, 2H, H ^{3,5} , J 8.79 Hz), 7.73 (d, 2H, H ^{2',6'} , J 8.50 Hz), 8.04 (d, 2H, H ^{2,6} , J 8.79 Hz), 8.32 (d, 1H, CH, J 9.89 Hz), 9.04 (d, 1H, CH, J 8.78 Hz)
Io	47(A) 85(B)	143–144.5 ^e	44.3	3.3	C ₁₇ H ₁₅ BrO ₂ Te	44.5	3.3	2.42 (t, 3H, OCH ₂ CH ₃), 4.03 (q, 2H, OCH ₂ CH ₃), 6.85 (d, 2H, H ^{3,5} , J 8.79 Hz), 7.62 (d, 2H, H ^{3',5'} , J 8.79 Hz), 7.70 (d, 2H, H ^{2,6} , J 6.44 Hz), 7.91 (d, 2H, H ^{2',6'} , J 6.74 Hz), 8.30 (d, 1H, CH, J 8.79 Hz), 9.22 (d, 1H, CH, J 9.09 Hz)
Ip	45(A)	110 ^c	53.5	4.0	C ₁₇ H ₁₆ O ₂ Te	53.8	4.2	1.33 (t, 3H, OCH ₂ CH ₃), 3.89 (q, 2H, OCH ₂ CH ₃), 6.42–7.37 (m, 10H, C ₆ H ₅ + 4-EtOC ₆ H ₄ + 1CH), 9.90 (s, 1H, CHO)
Iq	52(A)	114–115 ^e	54.7	4.7	C ₁₈ H ₁₈ O ₂ Te	54.9	4.6	9.12 s, 9.88 s (1H, CHO, intensity ratio approx. 10:90 ^d)
Ir	37(A) 70(B)	89.5–90.5 ^b	50.1	5.0	C ₁₅ H ₁₈ O ₂ Te	50.3	5.1	1.40 (t, 3H, OCH ₂ CH ₃), 1.50–2.56 (m, 8H, (CH ₂) ₄), 4.02 (q, 2H, OCH ₂ CH ₃), 6.78 (d, 2H, H ^{3',5'} , J 9.00 Hz), 7.71 (d, 2H, H ^{2',6'} , J 9.00 Hz), 9.66 (s, 1H, CHO)
Is	79(B)	132.5–133.5 ^c	44.6	3.8	C ₁₃ H ₁₃ ClOTe	44.8	3.8	1.53–2.64 (m, 8H, (CH ₂) ₄), 7.24 (d, 2H, H ^{2',6'} , J 8.92 Hz), 7.76 (d, 2H, H ^{3',5'} , J 8.92 Hz), 9.71 (s, 1H, CHO)
VI	54(A)	54–55 ^c	38.3	4.6	C ₈ H ₁₂ OTe	38.2	4.8	1.70–2.58 (m, 8H, (CH ₂) ₄), 1.91 (s, 3H, CH ₃), 9.65 (s, 1H, CHO)
IXa	97 ^f	105–106 ^g	23.3	2.8	C ₈ H ₁₂ Br ₂ OTe	23.5	2.9	1.82–2.92 (m, 8H, (CH ₂) ₄), 2.96 (s, 3H, CH ₃), 9.62 (s, 1H, CHO)
IXb	95 ^f	92–93 ^g	19.1	2.2	C ₈ H ₁₂ I ₂ OTe	19.0	2.4	1.82–2.91 (m, 8H, (CH ₂) ₄), 2.16 s, 2.94 s (3H, CH ₃ , intensity ratio approx. 1:3), 9.62 s, 9.82 s (1H, CHO, intensity ratio approx. 1:2.8)
IXc	96 ^f	126–127 ^g	29.6	3.6	C ₈ H ₁₂ Cl ₂ OTe	29.8	3.8	1.81–2.92 (m, 8H, (CH ₂) ₄), 2.87 (s, 3H, CH ₃), 9.62 (s, 1H, CHO)
Xa	63 ^h	53–54 ⁱ	26.7	2.7	C ₇ H ₉ BrOTe	26.6	2.9	1.81–3.03 (m, 8H, (CH ₂) ₄), 9.99 (s, 1H, CHO)
Xb	67 ^h	67–68 ⁱ	23.1	2.4	C ₇ H ₉ IOTe	23.1	2.5	1.82–3.04 (m, 8H, (CH ₂) ₄), 9.82 s, 9.98 s (1H, CHO, intensity ratio approx. 1:2)

^a Hydrogen atoms at the aryl ring attached to the tellurium center are labeled.

^b Recrystallized from hexane.

^c Recrystallized from MeOH.

^d The signals of other protons of two isomeric forms are overlapped.

^e Recrystallized from benzene–hexane mixture.

^f Prepared by oxidation of telluride **VI** with corresponding halogene.

^g Recrystallized from toluene–hexane mixture.

^h Prepared by refluxing of corresponding compounds **IX** in AcOH solution.

ⁱ Recrystallized from AcOH.

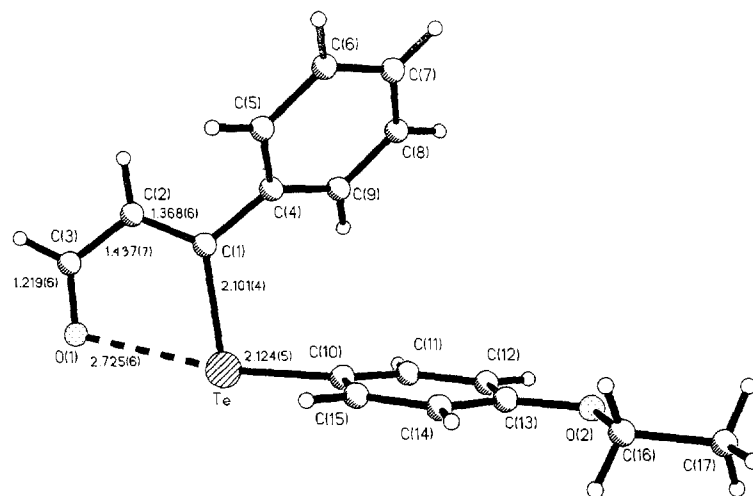
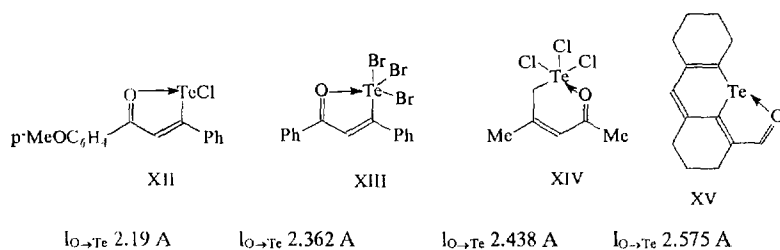


Fig. 1. The molecular geometry of (β-4-ethoxyphenyltelluro)-β-phenylpropenal **Ip**.

provide for enhanced thermodynamic and kinetic stability of those arenetellurenylhalogenides, thiocyanates, acetates, azides and tritellurides that contain carbonyl or azomethine groups in *o*-position to these functionalities. X-ray structural data available for about 40 compounds of this type [21] help to elucidate the principal factors that govern the strength of the $O \rightarrow Te$ and $N \rightarrow Te$ intramolecular coordination bonds in aromatic organ-

otellurium compounds. At the same time, the structure of only four compounds of type **XII–XV**, in which a tellurium-centered functionality and carbonyl group are placed in vicinal position at a carbon–carbon double bond not annelated to an aromatic ring, has been studied so far by X-ray. No such study has yet been carried out for the imino derivatives of the respective ethenes containing an intramolecular coordination $N \rightarrow Te$ bond.



The present paper reports the structures of (β-4-ethoxyphenyltelluro)-β-phenylpropenal **Ip** and *N*-(4'-methylphenyl)-β-(4-ethoxyphenyltelluro)-β-phenylpropenalidimine **V**. The molecular structures of these com-

pounds are shown in Figs. 1 and 2. Atomic coordinates, bond lengths and angles are given in Tables 2–7. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

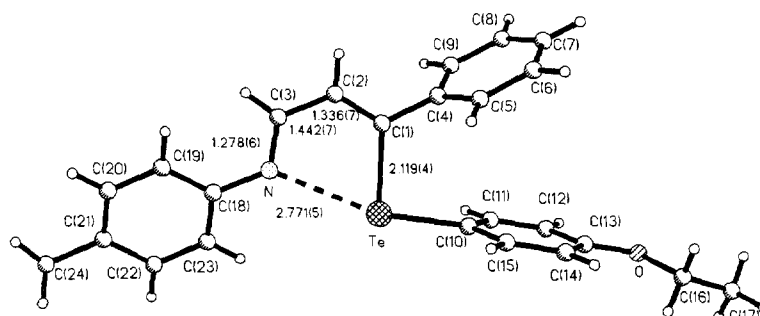


Fig. 2. The molecular geometry of (β-4-ethoxyphenyltelluro)-β-phenylpropenalidene-(4'-methylphenyl) **V**.

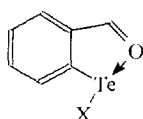
Table 2

Atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for compound **Ip**

Atom	x	y	z	U
Te	6016(1)	370(1)	6801(1)	28(1) ^a
O(1)	3965(3)	1470(4)	7522(2)	40(1) ^a
O(2)	9835(3)	-2637(3)	4780(2)	32(1) ^a
C(1)	4275(4)	-1159(5)	6715(2)	22(1) ^a
C(2)	3076(4)	-809(5)	7009(2)	27(1) ^a
C(3)	2982(5)	549(5)	7402(2)	35(2) ^a
C(4)	4334(4)	-2627(4)	6361(2)	23(1) ^a
C(5)	3187(4)	-3081(5)	5823(2)	30(1) ^a
C(6)	3156(6)	-4529(5)	5546(3)	40(2) ^a
C(7)	4278(6)	-5509(5)	5807(3)	46(2) ^a
C(8)	5402(5)	-5071(5)	6338(3)	41(2) ^a
C(9)	5450(4)	-3635(5)	6614(2)	29(1) ^a
C(10)	7244(4)	-713(5)	6109(2)	27(1) ^a
C(11)	8382(4)	-1694(5)	6365(2)	27(1) ^a
C(12)	9221(4)	-2324(5)	5911(2)	29(1) ^a
C(13)	8951(4)	-1954(5)	5185(2)	27(1) ^a
C(14)	7843(4)	-942(5)	4920(2)	29(1) ^a
C(15)	7002(4)	-335(5)	5387(2)	29(1) ^a
C(16)	9644(5)	-2245(6)	4034(2)	35(2) ^a
C(17)	10790(5)	-3095(6)	3722(3)	45(2) ^a

^a Equivalent isotropic U defined as one third of the trace of the orthogonalised $U(i, j)$ tensor

As seen from Figs. 1 and 2, the molecules of **Ip** and **V** possess *Z*-configuration at the carbon–carbon double bonds that provides for the formation of intramolecular coordination $O \rightarrow \text{Te}$ and $N \rightarrow \text{Te}$ bonds. Taking these bonds into account, the configuration at the tellurium centers can be described as a slightly distorted T-shaped



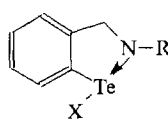
XVI

X = Br, $d(\text{O} \rightarrow \text{Te}) = 2.31 \text{ \AA}$,

$\chi = 0.81$

X = Cl, $d(\text{O} \rightarrow \text{Te}) = 2.848 \text{ \AA}$,

$\chi = 0.50$



XVII

X = Cl, R = $\text{C}_6\text{H}_4\text{Me-4}$, $d(\text{N} \rightarrow \text{Te}) = 2.22 \text{ \AA}$, $\chi = 0.93$

X = OCOMe, R = $\text{C}_6\text{H}_4\text{Me-4}$, $d(\text{N} \rightarrow \text{Te}) = 2.287 \text{ \AA}$,

$\chi = 0.89$

X = $2\text{-C}_6\text{H}_4\text{CH=NR}$, R = $\text{C}_6\text{H}_4\text{OMe-4}$, $d(\text{N} \rightarrow \text{Te}) = 2.702 \text{ \AA}$, $\chi = 0.63$

The relatively low covalent character of the intramolecular coordination $O \rightarrow \text{Te}$ and $N \rightarrow \text{Te}$ bonds in the compounds **Ip** and **V** is in accord with the observations [18–21] that it is strongly affected by the electronegativity of the substituent X attached to the tellurium center, and the coordination number of the latter.

polyhedron (the angles O1-Te-C10 and N-Te-C10 are equal to 168.3° and 164.4° correspondingly), and the compounds **Ip** and **V** should thus be attributed to the structural type of 10-Te-3 telluranes [22]. The lengths of the C–Te bonds in **Ip** (2.101 and 2.124 \AA) and **V** (2.119 and 2.138 \AA) lie within the limits typical of the Te–C(aromatic) bonds (the mean value for bonds of this type is 2.166 \AA [23]). The magnitudes of the angle C1-Te-C10 in **Ip** (98.5°) and **V** (95.6°) also fall into the range characteristic of aromatic tellurides.

The intramolecular O–Te (2.725 \AA) and N–Te (2.771 \AA) contacts are substantially shorter than the sum of the van der Waals radii (3.60 \AA for O and Te and 3.70 \AA for N and Te) [24]. However, they belong to the longest, and therefore weakest, known intramolecular coordination $O \rightarrow \text{Te}$ and $N \rightarrow \text{Te}$ bonds [21]. The so-called ‘covalency ratio’ values χ for the $O \rightarrow \text{Te}$ bond in **Ip** and the $N \rightarrow \text{Te}$ bond in **V** are calculated according to Ref. [25] as

$$\chi = \frac{(R_A + R_B) - d_{AB}}{(R_A + R_B) - (r_A + r_B)}$$

where R and r are respectively the van der Waals and covalent radii of an atom and d_{AB} is the distance between atoms A and B in a molecule or an associate, equal correspondingly to 0.59 and 0.58. These values are to be compared with those for the compounds **XII–XV** ($\chi = 0.95, 0.83, 0.78$ and 0.69 respectively) and some other *o*-tellurated benzaldehydes **XVI** and their imines **XVII** [21].

More electronegative substituents X and lower coordination numbers of the tellurium center are the factors providing for the formation of the shortest intramolecular coordination (secondary) bonds [26]. Their higher covalent character is due to enhanced $n_{\text{Te}} - \sigma_{\text{Te-X}}^*$ interaction, caused by the lower energy gap and better

Table 3

Atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for compound **V**

Atom	x	y	z	U
Te	3643(1)	3241(1)	789(1)	53(1) ^a
O	7614(6)	5537(3)	4074(3)	60(1) ^a
N	1817(7)	1791(4)	-209(3)	54(1) ^a
C(1)	4719(7)	1642(4)	1416(4)	46(2) ^a
C(2)	4023(8)	802(4)	1066(4)	53(2) ^a
C(3)	2528(8)	874(4)	264(4)	56(2) ^a
C(4)	6201(7)	1480(4)	2274(4)	46(2) ^a
C(5)	8166(8)	1863(4)	2163(4)	53(2) ^a
C(6)	9529(8)	1676(4)	2972(5)	62(2) ^a
C(7)	8975(9)	1119(4)	3884(5)	67(2) ^a
C(8)	7058(9)	734(5)	4008(4)	70(2) ^a
C(9)	5680(8)	908(5)	3208(4)	61(2) ^a
C(10)	5094(8)	3999(4)	1891(4)	52(2) ^a
C(11)	4237(8)	4012(4)	2857(4)	56(2) ^a
C(12)	5120(8)	4513(4)	3567(4)	58(2) ^a
C(13)	6899(8)	5041(4)	3318(4)	50(2) ^a
C(14)	7778(8)	5052(4)	2359(4)	55(2) ^a
C(15)	6883(8)	4524(4)	1647(4)	55(2) ^a
C(16)	9336(8)	6187(5)	3828(4)	64(2) ^a
C(17)	9529(11)	6792(6)	4731(5)	79(3) ^a
C(18)	348(8)	1848(4)	-992(4)	48(2) ^a
C(19)	455(8)	1151(4)	-1718(4)	56(2) ^a
C(20)	-1054(8)	1237(4)	-2444(4)	57(2) ^a
C(21)	-2722(8)	2014(4)	-2486(4)	54(2) ^a
C(22)	-2817(9)	2725(5)	-1770(4)	64(2) ^a
C(23)	-1307(8)	2651(4)	-1042(4)	59(2) ^a
C(24)	-4375(10)	2098(6)	-3290(6)	77(3) ^a

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalised $U(i,j)$ tensor

overlap between these orbitals achieved in the case of Te(II) centers neighboring such electronegative groups as chlorine [25,27,28].

The five-membered tellurium-containing rings are planar, whereas phenyl rings at the C1 atom of **Ip** and **V** are turned out from the planes of the heterocyclic rings by 57.3° and 60° respectively. The N–Ar ring in the latter compound lies at an angle of 38.5° relative to the five-membered heterocycle. The heterocycles of **Ip** and **V** and the phenyl rings attached to the tellurium centers in these are virtually orthogonal (angles between the planes of the rings 90.8° in **Ip** and 102.9° in **V**).

Table 1 contains some data on the ^1H NMR spectra of compounds **I**, **VI**, **IX** and **X**. The *Z*-configuration of the β -aryltellurovinyl ketones **Ia,f–i,l–o** in solution is justified by the magnitudes of the $^3J_{\text{HH}}$ spin–spin cou-

Table 4

Bond lengths in β -(4-ethoxyphenyltelluro)- β -phenylpropenal **Ip**

Te–C(10)	2.101(4)	C(2)–C(3)	1.437(7)	C(10)–C(11)	1.391(6)
Te–C(10)	2.114(5)	C(4)–C(5)	1.393(5)	C(10)–C(15)	1.388(6)
O(1)–C(3)	1.219(6)	C(4)–C(9)	1.391(6)	C(11)–C(12)	1.383(6)
O(2)–C(13)	1.367(5)	C(5)–C(6)	1.397(7)	C(12)–C(13)	1.394(6)
O(2)–C(16)	1.439(5)	C(6)–C(7)	1.381(7)	C(13)–C(14)	1.393(6)
C(1)–C(2)	1.368(6)	C(7)–C(8)	1.368(7)	C(14)–C(15)	1.393(7)
C(1)–C(4)	1.481(6)	C(8)–C(9)	1.386(7)	C(16)–C(17)	1.513(7)

Te...O 2.725 Å.

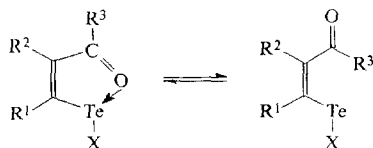
Table 5

Bond angles (°) in β -(4-ethoxyphenyltelluro)- β -phenylpropenal **Ip**

C(1)–Te–C(10)	98.5(2)	C(7)–C(8)–C(9)	120.8(4)
C(13)–O(2)–C(16)	117.8(3)	C(4)–C(9)–C(8)	120.1(4)
Te–C(1)–C(2)	119.4(3)	Te–C(10)–C(11)	122.1(3)
Te–C(1)–C(4)	121.4(3)	Te–C(10)–C(15)	119.4(3)
C(2)–C(1)–C(4)	119.3(4)	C(11)–C(10)–C(15)	118.3(4)
C(1)–C(2)–C(3)	122.4(4)	C(10)–C(11)–C(12)	121.3(4)
O(1)–C(3)–C(2)	123.7(4)	C(11)–C(12)–C(13)	119.9(4)
C(1)–C(4)–C(5)	120.3(3)	O(2)–C(13)–C(12)	115.6(4)
C(1)–C(4)–C(9)	120.4(3)	O(2)–C(13)–C(14)	124.6(4)
C(5)–C(4)–C(9)	118.9(4)	C(12)–C(13)–C(14)	119.9(4)
C(4)–C(5)–C(6)	120.4(4)	C(13)–C(14)–C(15)	119.1(4)
C(5)–C(6)–C(7)	119.5(4)	C(10)–C(15)–C(14)	121.6(4)
C(6)–C(7)–C(8)	120.3(5)	O(2)–C(16)–C(17)	107.1(4)

O1...Te–C1 71.1°; O1...Te–C10 168.3°; Te...O1–C3 103.2°.

plings. For all the compounds these magnitudes fall into the range characteristic of *cis*-vinylic protons (Section 2.1). An existence in solution of only *Z*-diastereomers in their energy preferable conformation determined by the intramolecular coordination O \rightarrow Te bond is corroborated by the appearance of a single signal of the formyl proton in the ^1H NMR spectra of **Ip**. The position of these signals correlates well with those of formyl protons in **Ie,j,r,s**, **VI** with sterically enforced *Z*-configuration. The one exception to the conformational homogeneity of tellurovinylcarbonyl compounds is represented by the iodine derivatives **IXb** and **Xb**, whose ^1H NMR spectra contain two distinct signals of the formyl protons. Such a spectral pattern can be assigned to the conformational *s-cis*–*s-trans* equilibrium that becomes possible because of the relative weakness of the O \rightarrow Te bonds in these compounds.



A similar equilibrium has previously been observed between conformers with and without an intramolecular

Table 6
Bond lengths (°) in β -(4-ethoxyphenyltelluro)- β -phenylpropenilidene-(4'-methylaniline) V

Te–C(1)	2.119(4)	C(4)–C(9)	1.385(7)	C(14)–C(15)	1.397(8)
Te–C(10)	2.138(5)	C(5)–C(6)	1.383(8)	C(16)–C(17)	1.52(1)
O–C(13)	1.367(7)	C(6)–C(7)	1.360(8)	C(18)–C(19)	1.392(8)
O–C(16)	1.444(7)	C(7)–C(8)	1.368(9)	C(18)–C(23)	1.396(7)
N–C(3)	1.278(6)	C(8)–C(9)	1.381(8)	C(19)–C(20)	1.373(8)
N–C(18)	1.414(7)	C(10)–C(11)	1.382(7)	C(20)–C(21)	1.382(7)
C(1)–C(2)	1.336(7)	C(19)–C(15)	1.392(7)	C(21)–C(22)	1.394(8)
C(1)–C(4)	1.483(7)	C(11)–C(12)	1.371(8)	C(21)–C(24)	1.514(9)
C(2)–C(3)	1.442(7)	C(12)–C(13)	1.389(7)	C(22)–C(23)	1.377(8)
C(4)–C(5)	1.396(7)	C(13)–C(14)	1.376(7)		

Te...N 2.771 Å.

coordination N \rightarrow Te bond in a solution of chloro-*p*-ethoxyphenyl-(2'-pyridyl)phenyl telluronium trichloromercurate [29].

2.3. Stereochemical outcome of the reaction of nucleophilic vinylic substitution in β -chlorovinylcarbonyl compounds by tellurolate anions

Whereas the stereochemistry of nucleophilic vinylic substitution of chlorine by various nucleophiles has been amply studied [30], data about the stereochemical outcome of this reaction with tellurium-centered nucleophiles are lacking. Depending on the nature of the nucleophiles (Nu), substitution of chlorine at the sp^2 -hybridized carbon atom in β -chlorovinylcarbonyl compounds occurs with retention of the stereochemical configuration at the double bond (Nu = I^- , CN^- , Me_2NH [31], N_3 [32,33], R_3N [31,34], $FeCp(CO)_2^-$ [35]); or formation of an equilibrium mixture of *E*- and *Z*-isomers, whose composition remains the same regardless of the stereochemical configuration at the double bond

Table 7
Bond angles (°) in β -(4-ethoxyphenyltelluro)- β -phenylpropenalidene-(4'-methylaniline)

C(1)–Te–C(10)	95.6(2)	C(10)–C(11)–C(12)	121.6(5)
C(13)–O–C(16)	117.7(4)	C(11)–C(12)–C(13)	120.1(5)
C(3)–N–C(18)	120.0(5)	O–C(13)–C(12)	115.2(5)
Te–C(1)–C(2)	120.5(3)	O–C(13)–C(14)	125.2(5)
Te–C(1)–C(4)	118.5(3)	C(12)–C(13)–C(14)	119.6(5)
C(2)–C(1)–C(4)	120.9(4)	C(13)–C(14)–C(15)	119.8(5)
C(1)–C(2)–C(3)	125.1(4)	C(10)–C(15)–C(14)	120.8(5)
N–C(3)–C(2)	120.7(5)	O–C(16)–C(17)	105.9(5)
C(1)–C(4)–C(5)	121.8(4)	N–C(18)–C(19)	123.8(4)
C(1)–C(4)–C(9)	120.2(4)	N–C(18)–C(23)	118.2(5)
C(5)–C(4)–C(9)	118.0(5)	C(19)–C(18)–C(23)	118.0(5)
C(4)–C(5)–C(6)	120.3(5)	C(18)–C(19)–C(20)	120.7(5)
C(5)–C(6)–C(7)	120.6(5)	C(19)–C(20)–C(21)	121.7(5)
C(6)–C(7)–C(8)	120.1(5)	C(20)–C(21)–C(22)	117.7(5)
C(7)–C(8)–C(9)	120.2(5)	C(20)–C(21)–C(24)	121.1(5)
C(4)–C(9)–C(8)	120.8(5)	C(22)–C(21)–C(24)	121.2(5)
Te–C(10)–C(11)	120.8(4)	C(21)–C(22)–C(23)	121.1(5)
Te–C(10)–C(15)	121.2(4)	C(18)–C(23)–C(22)	120.7(5)
C(11)–C(10)–C(15)	118.0(5)		

N–Te...C1 70.3°; N–Te...C10 164.4°.

of the initial β -chlorovinylcarbonyl compound (Nu = SCN^- [36]). The reaction of β -chlorovinyl ketones **IV** in aqueous [37] or acetone–water [38,39] solutions with arenethiolate anions results in the formation of β -arythiovinyl ketones retaining their initial configuration at the carbon–carbon double bond. However, if hydrogens at the double bond are substituted by bulky phenyl groups, as was the case for 2,3-diphenyl-3-chloropropenal, then both *E*- and *Z*-diastereomers are afforded when treated with 4-methyl thiophenolate anion in DMF solution, exclusively *E*-2,3-diphenyl-2-phenylthiopropenal [40].

In order to judge the stereochemistry of nucleophilic substitution at the sp^2 carbon center of β -chlorovinyl aldehydes and ketones **IV**, the configuration of the substrates at the double carbon–carbon bonds must be assigned. It is known that, depending on the method employed for preparation of β -chlorovinyl ketones [7,31], these can be obtained as either pure *Z*-diastereomers (via addition of acylchlorides to alkynes catalyzed by $AlCl_3$ [7,31]) or a mixture of *Z*- and *E*-diastereomers (via addition–elimination reaction of acylchlorides with vinyl chloride in the presence of $AlCl_3$ [7,31]). In the present work, β -chlorovinyl ketones **IV** have been prepared by the reaction of the corresponding hydroxymethylene ketones with thionyl chloride [41]. Both *Z*- and *E*-diastereomers of **IV** were formed in this reaction, their ratio being substantially affected by the properties of substituents in the aryl ring of the ketones. The stronger the electron releasing ability of the substituent R^3 , the greater the relative content of *Z*-isomers of **IV** in the mixture obtained in the reaction. This finding is illustrated by the sequence below, where *Z*:*E* ratios are given as determined from intensities of signals of vinylic protons in 1H NMR spectra:

$R^3 = C_6H_4Br-4$ (0:1); C_6H_5 (1:12);

C_6H_4Me-4 (1:5); C_6H_4OMe-4 (1:1.5)

The stereochemical outcomes of the nucleophilic vinylic substitution of chlorine in **IVa–d** by tellurolate anions were elucidated through determination of the configuration at the double bonds of the β -aryltel-

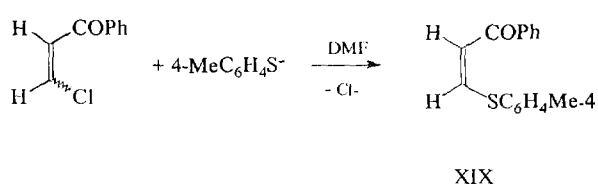
lurovinylcarbonyl compounds **I** and **VI** formed. Since all these compounds have *Z*-configuration, a conclusion has to be drawn on the highly stereospecific course of the reaction. Whereas retention of the configuration at the carbon–carbon double bond takes place in the case of *Z*- β -chlorovinyl ketones **IVa–d**, the reaction with their *E*-diastereomers occurs with inversion of configuration. It is worth noting that the nature of the solvent does not affect the stereochemical outcome of the reaction.

To explain the stereospecific character of the reaction with tellurium-centered nucleophiles, the two-step mechanism of nucleophilic vinylic ‘addition–elimination’ substitution [30] may be invoked (Scheme 1). At the first step, highly nucleophilic tellurolate anions [42] add on the carbon–carbon double bond of **IV**, which reaction is facilitated by electron-withdrawing carbonyl-containing groups enhancing the electrophilicity of this bond. Of all possible conformers of the intermediate anions thus formed, the most stable are clearly those stabilized by the intramolecular O \rightarrow Te bonds of **XVIII**. The subsequent fast elimination of chloride anions from **XVIII** leads to *Z*- β -organyltellurovinylcarbonyl compounds **I**, whose configuration and conformation are stabilized by the intramolecular O \rightarrow Te coordination.

In a similar way, β -chloro- β -phenylpropenal **IVe** obtained as a 9:1 mixture of *Z*- and *E*-isomers [43] affords, in reaction with tellurolate anions, exclusively *Z*-diastereomers of **Ib,p**. The same stereochemical course of the reaction between 2-chlorocyclohexenal **IVh** and tellurolate anions is, obviously, predetermined by the cyclic structure of the former compound.

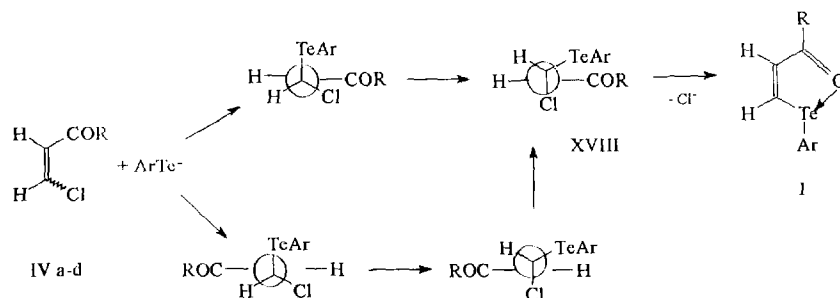
The difference in stereochemical outcome of the reactions of β -chlorovinylcarbonyl compounds **IVa–d** with arenethiolate (full retention of the configuration [38,39]) and arenetellurolate anions may be ascribed to the following two factors: (i) lower strength of the O \rightarrow S intramolecular coordination bonds compared with those for O \rightarrow Te coordination in **XVIII** (see Ref. [44]); and (ii) use of solvents (aqueous acetone) capable of forming strong hydrogen bonds with the carbonyl group of the intermediate anion that can shield it from the

interaction with the chalcogen center in the reaction of arenethiolate anions with β -chlorovinylcarbonyl compounds. The importance of the latter factor stems from the study undertaken in the present work of the reaction between β -chlorovinylbenzoyl ketone **IVa** (obtained as a mixture in approximate 12:1 ratio of *E*- and *Z*-isomers) and 4-methylthiophenolate anion in DMF. The only product of this reaction was *Z*-1-phenyl-3-(4-methylphenylthio)-2-propen-1-one **XIX**.



In contrast to β -chlorovinyl ketones **IVa–d** and aldehydes **IVe**, **IVh**, α -alkyl- β -phenyl- β -chlorovinyl aldehydes **IVf**, **IVg** react with arenetellurolate anions to give mixtures of *Z*- and *E*-isomers **Ic,d,k,q** in variable ratios. Table 8 contains data on ^1H NMR spectra of the initial β -chlorovinyl aldehydes and products of the nucleophilic substitution of chlorine by arenetellurolate anions. Relative amounts of *Z*- and *E*-diastereomers of **Ic,d,k,q** were estimated by intensities of signals of formyl protons, assignments of which to a certain isomeric form have been made through comparison with positions [40] of signals of formyl protons of their closest structural analogues **XX–XXII** [40] (see Table 8).

The difference in stereochemical courses of α -unsubstituted β -chlorovinylcarbonyl compounds and those, **IVf,g**, containing methyl or ethyl groups in the α position may be explained in terms of the ‘addition–elimination’ mechanism of nucleophilic vinylic substitution reaction. As stems from the analysis [30], stereochemical outcomes of this reaction (under the condition of fast step elimination of a nucleofuge) are mostly determined by two competitive factors: (i) the relative stability of the conformers formed at the step of nucleophile addition to a double bond; and (ii) the energy



Scheme 1.

Table 8
Chemical shifts and *Z/E* ratios for β -chlorovinyl aldehydes **IVf,g**, β -aryltellurovinyl aldehydes **I**, their oxygen **XX**, **XXI** and sulfur **XXII** analogues

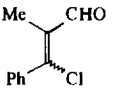
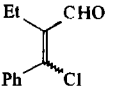
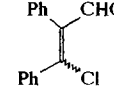
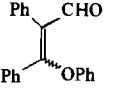
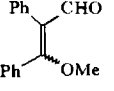
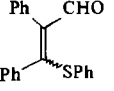
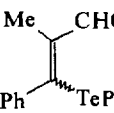
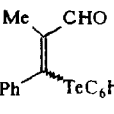
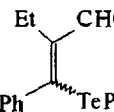
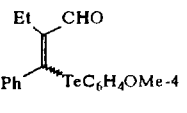
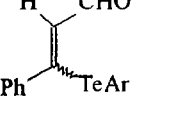
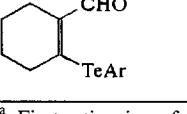
Aldehyde	$\delta_{\text{CHO}}(\text{Z})$ (ppm)	$\delta_{\text{CHO}}(\text{E})$ (ppm)	<i>Z/E</i> -ratio	Reference
1	2	3	4	5
IVf 	10.34	9.42	~ 1/13	[45]
IVg 	10.36	9.42	~ 1/4.2	This work
	10.60	9.68	~ 2/3	[40]
XX 	10.43	9.73	0/1 (3/7) ^a	[40]
XXI 	10.48	9.36	1/9 (1/24) ^a	[40]
XXII 	—	9.39	^b	[40]
Ic 	9.92	9.10	~ 1/2	This work
Iq 	9.89	9.12	~ 1/9	This work
Id 	9.98	9.08	~ 1/19	This work

Table 8 (continued)

Aldehyde	$\delta_{\text{CHO}}(\text{Z})$ (ppm)	$\delta_{\text{CHO}}(\text{E})$ (ppm)	<i>Z/E</i> -ratio	Reference
1	2	3	4	5
Iq 	9.97	9.07	~ 1/10	This work
Ib,p 	9.90–9.95	—	—	This work
Ie,j,r,s 	9.55–9.71	—	—	This work

^a First ratio given for the mixture of isomers obtained by the reaction of a nucleophile with *E*-2,3-diphenyl-3-chloropropenal; the second one relates to the same reaction with the *Z*-isomer.

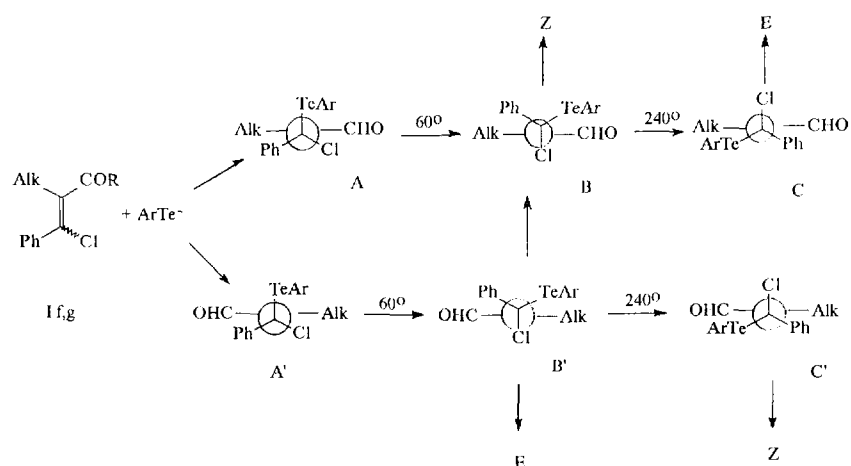
^b No *Z*-isomer of aldehyde obtained.

barriers to their interconversion. As distinct from the addition of arenetelluroate anions to **IVa–d,e,h**, which result was fully determined by formation of the O \rightarrow Te bond stabilizing the conformer **XVIII**, in the carbanions formed upon addition of arenetelluroate anions to **IVf,g** (Scheme 2), this stabilizing interaction in conformers B, C' is counteracted by steric repulsion of bulky aryl and alkyl substituents taking on eclipsed positions (Scheme 2).

The result of this counteraction is increased energy barriers to the conformational interconversions A \rightarrow B and B' \rightarrow C', that lead to the conformations of the intermediate carbanions that precede formation of *Z*- β -aryltellurovinylcarbonyl compounds. The competition of the two interactions described leads to relative destabilization of the conformers B, C', and thus to loss of stereospecificity of the reaction shown in Scheme 2.

2.4. Stereochemistry of the addition reaction of arenetelluroate anions to the carbon–carbon triple bonds

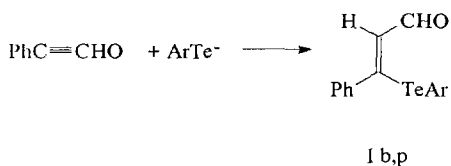
A comparison may be of interest between the stereochemical configuration of aryltellurovinylcarbonyl compounds **I** prepared by the reaction of nucleophilic vinylic substitution with that of the same compounds obtained by nucleophilic addition of arenetelluroate anions to the triple bonds of α -acetylenic aldehydes and ketones. No



Scheme 2.

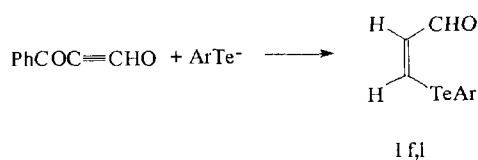
study of the stereochemistry of this reaction has previously been undertaken. According to the literature data, addition of arenetelluroate anions to the triple bond of acetylenecarboxylic acids occurs stereospecifically, giving rise exclusively to *Z*-aryltelluropropenoic acids [5,6,46–48]. *Trans*-addition is also the prevailing stereochemical course in the reaction of telluroate anions with other terminal acetylenes $\text{RC}\equiv\text{CH}$ [46–55], although in some cases the formation of appreciable relative amounts of *E*-diastereomers of the alkenes $\text{RCH}=\text{CHTeR}'$ [56] or even regioisomers $\text{RC}(\text{TeR}')=\text{CH}_2$ [50,54] was observed.

In the present work we have studied the nucleophilic addition reaction of arenetelluroate anions **III** (generated by reduction of the corresponding diarylditellurides with NaBH_4 in mixed benzene–methanol (1:1) solvent) with phenylpropynal. The ^1H NMR spectra and all other characteristics of the products of this reaction, isolated in 60–90% yields, were fully consistent with those for the aldehydes **Ib,p** prepared from β -chlorovinyl aldehyde **IVe**.



Such a coincidence unambiguously plays witness to the *Z*-configuration of the aldehydes **I**, and therefore the *trans*-addition reaction pathway. Likewise, addition of arenetelluroate anions to the triple bond of 1-phenylpropyn-2-one-1 results in the exclusive formation of *Z*-diastereomers of β -aryltellurovinyl ketones **If,l**. Only one set of vinylic protons has been seen in their ^1H

NMR spectra, the $^3J_{\text{HH}}$ spin–spin coupling constant being equal to 8.79 Hz.



3. Experimental

^1H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) using CDCl_3 as solvent and tetramethylsilane as internal reference. The solvent used was dried and distilled in accordance with the standard procedure. The data on chemical shifts and spin–spin coupling constants of the compounds **I**, **VI**, **IX** and **X** are given in Table 1, and of the compounds **II**, **V** and **XI** in the text.

3.1. X-ray crystallographic studies of the compounds **Ib** and **V**

The $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Te}$ **Ib** crystals are monoclinic, at -120°C : $a = 9.279(9)$, $b = 8.950(8)$, $c = 18.978(14)$ Å, $\beta = 100.58(2)^\circ$, $V = 1549(4)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.629$ g cm⁻³, space group $P2_1/n$. The crystal size was $0.1 \times 0.3 \times 0.3$ mm³. The linear absorption coefficient $\mu = 19.2$ cm⁻¹.

The $\text{C}_{24}\text{H}_{23}\text{NOTe}$ **V** crystals are triclinic, at -120°C : $a = 6.460(2)$, $b = 12.587(3)$, $c = 13.243(4)$ Å, $\alpha = 81.41(2)$, $\beta = 88.47(2)$, $\gamma = 84.62(2)^\circ$, $V = 1060.0(8)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.629$ g cm⁻³, space

group $P\bar{1}$. The crystal size was $0.2 \times 0.4 \times 0.4$ mm. The linear absorption coefficient $\mu = 14.6 \text{ cm}^{-1}$. No absorption correction was applied for either of the crystals.

The intensity of 2918 reflections with $I > 2\sigma(I)$ for **Ip** and 3008 reflections with $I > 2\sigma(I)$ for **V** were measured at -120°C on a Siemens R3m diffractometer ($\lambda(\text{Mo K}\alpha)$, $\theta/2\theta$ scan type, $2\theta < 46^\circ$ for **Ip** and $2\theta < 44^\circ$ for **V**).

The structures were solved by direct methods and refined by the F^2 full-matrix least-squares method in anisotropic approximation, using 2283 reflections with $I > 6\sigma(I)$ for **Ip** and 2586 reflections with $I > 6\sigma(I)$ for **V**. Hydrogen atom positions were founded geometrically and included in the refinement in riding mode with isotropic U . For **Ip**: $R = 0.032$, $R_w = 0.037$, $S = 2.07$; $w = 1/(\sigma(F) + 0.0001 \cdot F^2)$; $\Delta\rho_{\text{max}} = 0.88 \text{ e } \text{\AA}^{-3}$, $\Delta\rho_{\text{min}} = -0.91 \text{ e } \text{\AA}^{-3}$. For **V**: $R = 0.041$, $R_w = 0.053$, $S = 3.33$; $w = 1/(\sigma(F) + 0.0002 \cdot F^2)$; $\Delta\rho_{\text{max}} = 1.22 \text{ e } \text{\AA}^{-3}$, $\Delta\rho_{\text{min}} = -1.69 \text{ e } \text{\AA}^{-3}$. Tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Starting materials β -chlorovinyl aldehydes **IVe–h** were obtained according to the procedures described in Refs. [45,57]. β -Chlorovinyl ketones **IVa–d** and β -acylvinyl triethylammonium chlorides **VII** were prepared as described in Refs. [15,41]. The synthesis of phenylpropynal and 1-phenylpropyn-2-one-1 were performed as in Refs. [58,59]. Diarylditellurides used in this work were synthesized according to Ref. [60].

3.2. Synthesis of β -aryltellurovinylcarbonyl compounds **I**

3.2.1. Method A

3.2.1.1. 1-(4-Methoxyphenyl)-3-(4-methylphenyltelluro)-2-propen-1-one **Ih**. To a suspension of finely powdered elemental tellurium (3.1 g, 0.0243 mol) in THF (30 ml) cooled to -10°C , a solution of 4-methylphenyllithium, obtained in accordance with the procedure of Ref. [61] from 4-bromotoluene (4.15 g, 0.0243 mol) and lithium (0.34 g, 0.0486 mol) in ether (50 ml), was added dropwise under stirring in argon atmosphere. The mixture was kept at 10°C and stirred during 1 h, cooled to -15°C , after which a solution of 1-(4-methoxyphenyl)-3-chloro-2-propen-1-one (4.40 g, 0.0243 mol) **IVc** in THF (15 ml) was added dropwise. The temperature of the reaction mixture (-15°C) was supported, and stirring continued for 30 min. The mixture was allowed to come to room temperature, refluxed for 30 min, cooled and poured into water (250 ml) under stirring. The product was extracted with ether (3×50 ml), the ether layer was dried and the solvent removed under vacuum. The residue was crystallized from benzene/hexane (1:1)

to give **Ih** as yellow crystals (4.15 g, 45%), m.p. $125\text{--}126^\circ\text{C}$.

The compounds **Ia–j** (Table 1) were prepared in a similar way.

3.2.1.2. 1-(4-Methoxyphenyl)-3-(4-ethoxyphenyltelluro)-2-propen-1-one **In**. A mixture of di(4-ethoxyphenyl)diteLLuride (4.97 g, 0.01 mol), lithium (0.14 g, 0.02 mol) and naphthalene (0.40 g, 0.001 mol) in THF (50 ml) was refluxed for 3 h in argon atmosphere; the colour of the solution gradually changed from dark-red to yellowish. The solution of lithium 4-ethoxyphenyltelluroate thus formed was added dropwise under stirring in argon atmosphere at -10°C to a solution of 1-(4-methoxyphenyl)-3-chloro-2-propen-1-one **IVc** in ether (50 ml). The reaction mixture was stirred for 30 min at -10°C , poured into water (200 ml) and then extracted with ether (3×50 ml). The organic layer was separated, the solvent removed under vacuum, and the residue crystallized from benzene/hexane (1:1) to give 3.20 g (39% yield) of yellow needles of **In**, m.p. $136\text{--}137.5^\circ\text{C}$.

The series of β -aryltellurovinylcarbonyl compounds **Ik–r** (Table 1) was similarly prepared.

3.2.2. Method B

3.2.2.1. 1-(4-Bromophenyl)-3-(4-ethoxyphenyltelluro)-2-propen-1-one **Io**. To a suspension of di(4-ethoxyphenyl)diteLLuride (4.47 g, 0.009 mol) in methanol (30 ml) stirred under argon atmosphere, dry powdered NaBH_4 was added in small portions until full decoloration of the solution occurred. A solution of 1-(4-bromophenyl)-3-triethylammonio-2-propen-1-one chloride (6.25 g, 0.018 mol) in methanol (10 ml) was then added under stirring. Deposition of the telluride **Io** occurred, starting when approximately 2/3 of the ammonium salt solution was added. The reaction mixture was refluxed under stirring for 30 min, cooled to room temperature, and filtered off. Water (100 ml) was added to the filtrate, and the telluride **Io** remaining in solution was extracted with benzene (3×25 ml). The solvent was removed in vacuum to give an addition amount of **Io**. The total yield of **Io** was 7 g (85%). Yellow crystals, m.p. $143\text{--}144.5^\circ\text{C}$ (from benzene/hexane (1:1)).

A number of other β -aryltellurovinylcarbonyl compounds, **If,j,m–o,r,s** (Table 1), were synthesized in a similar way. [The triethylammonium salt from 2-chlorocyclohexenal was not isolated as a pure compound and was prepared by treatment of 2-chlorocyclohexenal with an equimolar amount of triethylamine in THF solution.]

3.3. Di(β -benzoylvinyl)telluride **IIa**

A mixture of powdered tellurium (2.54 g, 0.02 mol), finely cut lithium (0.28 g, 0.04 mol) and naphthalene (0.5 g, 0.004 mol) in dry THF (75 ml) was refluxed

under stirring in argon atmosphere for 3 h. The suspension of colorless Li_2Te formed was cooled to -15°C , and a solution of 1-phenyl-3-chloro-2-propen-1-one **IVa** in THF (15 ml) was added under intense stirring. The reaction mixture was allowed to stand at -15°C under stirring for 30 min, then the temperature was gradually raised and the solution refluxed under stirring for 30 min. The solvent was removed in vacuum and the residue crystallized from benzene/hexane (1:1) to give **IIa** (6.08 g) in 39% yield. Yellow needles, m.p. $225\text{--}227^\circ\text{C}$ ($215\text{--}216^\circ\text{C}$ [16]). $^1\text{H NMR}$ (CDCl_3): 7.24–8.10 (m, 10H, arom.), 8.36 (d, 2H, CH, J 9.67 Hz), 9.14 (d, 2H, CH, J 9.67 Hz). Anal. Found: C, 55.2; H, 3.4. $\text{C}_{18}\text{H}_{14}\text{O}_2\text{Te}$ Calc.: C, 55.4; H, 3.6%.

The tellurides **IIb,c** were obtained in a similar way in 55% and 60% yields correspondingly.

3.4. Di(β -4-methylbenzoylvinyll)telluride **IIb**

M.p. $250\text{--}252^\circ\text{C}$ (from toluene). $^1\text{H NMR}$ (CDCl_3): 3.42 (s, 6H, CH_3), 7.26 (d, 4H, $\text{H}^{3,5}$, J 7.91 Hz), 7.97 (d, 4H, $\text{H}^{2,6}$, J 8.20 Hz), 8.34 (d, 2H, CH, J 9.66 Hz), 9.08 (d, 2H, CH, J 9.67 Hz). Anal. Found: C, 57.3; H, 4.3. $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Te}$ Calc.: C, 57.5; H, 4.3%.

3.5. Di(2-formylcyclohexen-1-yl)telluride **IIc**

Orange crystals, m.p. $137\text{--}138^\circ\text{C}$ (from toluene/hexane (1:1)). $^1\text{H NMR}$ (CDCl_3): 1.64–2.66 (m, 16H, $(\text{CH}_2)_4$), 9.90 (s, 2H, CHO). Anal. Found: C, 48.3; H, 5.1. $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Te}$ Calc.: C, 48.6; H, 5.2%.

3.6. β -(4-Ethoxyphenyltelluro) β -phenylpropenalidene-(4'-methylaniline) **V**

Obtained by standard procedure from aldehyde **Ip** and *p*-toluidine in 81% yield. Yellow crystals, m.p. $122\text{--}124^\circ\text{C}$. $^1\text{H NMR}$ (CDCl_3): 1.36 (t, 3H, OCH_2CH_3), 2.38 (s, 3H, CH_3), 3.91 (q, 2H, OCH_2CH_3), 6.43–7.42 (m, 14H, arom. + H_α), 8.51 (d, 1H, $\text{CH}=\text{N}$, J 6.20 Hz). Anal. Found: C, 61.3; H, 4.7. $\text{C}_{24}\text{H}_{23}\text{NOTe}$ Calc.: C, 61.5; H, 4.9%.

3.7. β -Methyltellurocyclohexenal **VI**

To a suspension of powdered tellurium (14.1 g, 0.11 mol) in THF (250 ml) stirred at -5°C in argon atmosphere, a solution of methyl lithium, prepared by the standard procedure [61] from methyl iodide (15.6 g, 0.11 mol) and lithium (1.53 g, 0.22 mol) in ether (100 ml) was added. The mixture was kept under stirring for 30 min and cooled to -70°C , after which a solution of 2-chlorocyclohexenal **IVh** (14.5 g, 0.1 mol) in THF (50 ml) was added dropwise. The mixture was slowly (40 min) heated to a temperature of 0°C and poured into ice. The ether layer was separated and washed with a

saturated aqueous solution of NaHCO_3 (3×50 ml), water (3×50 ml) and dried (Na_2SO_4). The solvent was evaporated to give the precipitate as yellow crystals. After crystallization from methanol, 13.6 g (54%) of pure product was obtained. M.p. $54\text{--}55^\circ\text{C}$.

3.8. 2-Methyldichlorotellurocyclohexenal **IXc**

Dry chlorine was bubbled through a solution of 2-methyltellurocyclohexenal **VI** (2.52 g, 0.01 mol) in benzene (25 ml) under stirring at 0 to 5°C for 15–20 min. The mixture was kept at this temperature for 30 min, the precipitate formed was filtered off, washed with hexane and dried. Colorless crystals (3.11 g, 96%). M.p. $126\text{--}127^\circ\text{C}$ (from toluene/hexane (1:1)).

When equimolar amounts of bromine or iodine were used in this reaction instead of chlorine, the compounds **IXa** and **IXb** were obtained respectively in almost quantitative yields (see Table 1).

3.9. 2-Bromotellurenylcyclohexenal **Xa**

A solution of 2-methyldibromotellurocyclohexenal **IXa** (4.12 g, 0.01 mol) in acetic acid (40 ml) containing 2 ml of 48% hydrobromic acid was refluxed for 20 min. The precipitated solid residue was filtered off, washed with a small portion of ether and crystallized from acetic acid to yield **Xa** as red crystals (2.0 g, 63%). M.p. $53\text{--}53^\circ\text{C}$.

The compound **Xb** (Table 1) was synthesized in a similar way.

3.10. 2-Bromotellurenylcyclohexylidene-(4'-methylaniline) **XIa**

A solution of *p*-toluidine (1.07 g, 0.01 mol) and compound **IXa** (4.12 g, 0.01 mol) in methanol (20 ml) was refluxed for 30 min. The precipitate formed was filtered off, washed with ether and dried to give **XIa** (3.53 g, 87%) as yellow crystals. M.p. $136\text{--}137^\circ\text{C}$ (from methanol). $^1\text{H NMR}$ (CDCl_3): 1.88–3.17 (m, 8H, $(\text{CH}_2)_4$), 2.40 (s, 3H, CH_3), 7.16–7.27 (m, 4H, arom.), 8.76 (s, 1H, $\text{CH}=\text{N}$). Anal. Found: C, 41.3; H, 3.9. $\text{C}_{14}\text{H}_{16}\text{BrNTe}$ Calc.: C, 41.4; H, 4.0%.

The compound **XIa** was also prepared in 89% yield by condensation of equimolar amounts of tellurenyl bromide **Xa** and *p*-toluidine in methanol solution.

3.11. 2-Iodotellurenylcyclohexylidene-(4'-methylaniline) **XIb**

Obtained similarly to **XIa**, starting from **IXb** in 86% yield. Yellow crystals. M.p. $160\text{--}161^\circ\text{C}$ (from methanol). $^1\text{H NMR}$ (CDCl_3): 1.88–3.07 (m, 8H, $(\text{CH}_2)_4$), 7.18–7.27 (m, 4H, arom.), 8.62 (s, 1H, $\text{CH}=\text{N}$). Anal. Found: C, 36.9; H, 3.5. $\text{C}_{14}\text{H}_{16}\text{INTe}$ Calc.: C, 37.1; H, 3.6%.

3.12. 2-Chlorotellurenylcyclohexylidene-(4'-methyl-aniline) XIc

Prepared similarly to XIa starting from IXc in 91% yield. Yellow crystals. M.p. 129–130 °C (from methanol). ¹H NMR (CDCl₃): 1.82–3.20 (m, 8H, (CH₂)₄), 7.15–7.26 (m, 4H, arom.), 8.80 (s, 1H, CH=N). Anal. Found: C, 46.3; H, 4.3. C₁₄H₁₆CINTe Calc.: C, 46.5; H, 4.5%.

3.13. Synthesis of β-aryltellurovinyl aldehydes and ketones by addition of arenetelluroate anions to phenylpropynal and 1-phenylpropyn-2-one-1

3.13.1. 1-Phenyl-3-(4-methylphenyltelluro)-2-propen-1-one If

Dry powdered NaBH₄ was added in small portions to a rapidly stirred dark-red solution of di(4-methylphenyl)ditelluride (2.19 g, 0.005 mol) in benzene/methanol (1:1) solution (40 ml) under refluxing in argon atmosphere until the solution became colorless. The solution formed was cooled to 0 °C, and a solution of 1-phenylpropyn-2-one-1 (1.3 g, 0.01 mol) in benzene (10 ml) added dropwise under stirring. Stirring was continued for 20–30 min, and then the solution was refluxed for 30 min, cooled and diluted with an equal volume of water. The benzene layer was separated and the water layer extracted by additional portions of benzene (2 × 30 ml). The organic extracts were washed with water, dried (Na₂SO₄) and the solvent evaporated. The solid residue was crystallized from benzene/hexane (1:1) to give If (3.01 g, 86%) as yellow crystals. M.p. 142–144 °C.

Other β-aryltellurovinylcarbonyl compounds Ib (90%), II (89%) and Ip (61%) were prepared similarly to If.

Acknowledgements

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