

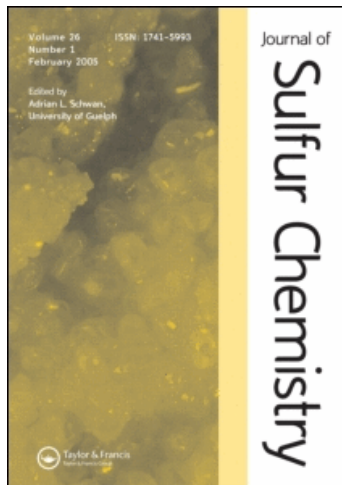
This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926081>

Vinyl Tellurides: Synthesis and Properties

N. K. Gusarova^a; A. A. Tatarinova^a; L. M. Sinegovskaya^a

^a USSR Academy of Sciences, Institute of Organic Chemistry, Siberian Branch, Irkutsk, USSR

To cite this Article Gusarova, N. K. , Tatarinova, A. A. and Sinegovskaya, L. M.(1991) 'Vinyl Tellurides: Synthesis and Properties', Journal of Sulfur Chemistry, 11: 1, 1 – 50

To link to this Article: DOI: 10.1080/01961779108048762

URL: <http://dx.doi.org/10.1080/01961779108048762>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

VINYL TELLURIDES: SYNTHESIS AND PROPERTIES

N. K. GUSAROVA, A. A. TATARINOVA and L. M. SINEGOVSKAYA
*Institute of Organic Chemistry, Siberian Branch, USSR Academy of Sciences,
1 Favorsky Street, SU-664033 Irkutsk, USSR*

(Received March 2, 1990)

Data on the synthesis, reactivity, structure, and physicochemical properties of vinyl tellurides, which are potential monomers, synthons, and intermediates, are given in the present review.

Key words: Alkyl vinyl tellurides, alkynes, aryl vinyl tellurides, divinyl tellurides, nucleophilic addition, superbasic reductive systems.

CONTENTS

I. INTRODUCTION	2
II. SYNTHESIS OF VINYL TELLURIDES	2
II.1. Addition of Telluride Anions to the $C\equiv C$ Triple Bond	2
II.1.1. Reaction of Tellurium with Acetylene	2
II.1.2. Vinyl Tellurides from Tellurium, Acetylene, and Organyl Halides	7
II.1.3. Reaction of Tellurium with Phenylacetylene and with Vinylacetylene	9
II.1.4. Interaction of Organotelluroolate Anions with Alkynes	9
II.2. Reaction of Organotelluroolate Anions with β -Bromostyrene	12
II.3. Synthesis of Vinyl Tellurides via Organometallic Compounds	13
II.4. Reaction of Ethenetelluroolate Anions with Alkyl Halides	15
II.5. Reduction of Bis(2,2-diarylviny)tellurium Dichlorides	16
III. REACTIVITY OF VINYL TELLURIDES	17
III.1. Reduction	17
III.2. Oxidation	18
III.3. Halogenation	18
III.4. Metallation	19
III.5. Reaction of Divinyl Telluride with Organyl Halides	20
III.6. Thiylation	20
III.7. Dehydrocyclization	21
III.8. Interaction with Grignard Reagents	21
III.9. Carbonylation of Vinyl Tellurides with Carbon Monoxide	22
III.10. Reaction of Divinyl Telluride with Thiourea	23
IV. PHYSICOCHEMICAL AND SPECTRAL CHARACTERISTICS OF VINYL ORGANYL TELLURIDES	24
IV.1. Vibrational Spectra of Methyl Vinyl Telluride	25
IV.2. Rotational Isomerism of Methyl Vinyl Telluride	26
IV.3. Divinyl Telluride	30
IV.4. Photoelectron Spectra of Vinyl Tellurides	31
IV.5. NMR Spectra	33

REFERENCES	42
SUBJECT INDEX	47
AUTHOR INDEX	49

I. INTRODUCTION

Telluriumorganic compounds have been known for one and a half century and occupy an important place in the chemistry of elemento-organic compounds.¹ On the basis of these compounds rubber vulcanization accelerators,^{2,3} metal corrosion inhibitors,^{4,5} sealant hardeners,⁶ detergents,⁷ complexing agents,⁸ and lubricant antioxidants,⁹ as well as additives to rubbers^{10,11} and to polymers¹² have been prepared in order to improve the respective products' thermal and mechanical properties; the above compounds are also used to obtain biologically active preparations for application in medicine¹³⁻²¹ and agriculture.^{22,23} Organotellurium compounds are of special concern in the development of materials possessing quite unique light-sensitive and semiconducting²⁴⁻³⁴ properties.

The last two decades have seen the development of the chemistry of unsaturated organyl tellurides, convenient model compounds for the investigation of fundamental problems of theoretical organic chemistry, and promising synthons, reactants, and intermediates.³⁵⁻⁴³

A great contribution to this research has been made in extensive work by Trofimov *et al.* concerned with a direct acetylene-assisted redox vinylation of metallic tellurium in the presence of strong bases and which allowed divinyl telluride and its derivatives to be prepared for the first time.^{35-39,44-56}

The present review is the first attempt to correlate and discuss the synthesis and properties of vinyl tellurides.

II. SYNTHESIS OF VINYL TELLURIDES

II.1. Addition of Telluride Anions to the C≡C Triple Bond

At present the reaction of telluride anions with acetylene and substituted acetylenes has become one of the most useful and convenient synthetic routes to vinyl tellurides. Telluride or organotelluride ions are generated by treatment of elemental tellurium with a base or by reduction of diorganyl ditellurides, respectively.

II.1.1 Reaction of tellurium with acetylene The reaction of tellurium with acetylene to give the previously unknown divinyl telluride **1** was carried out for the first time by Trofimov *et al.* in 1976.^{44,45} The reaction proceeds upon heating (110–120 °C) of the reactants in a superbasic multiphase system KOH-polar aprotic solvent-water under acetylenic pressure.

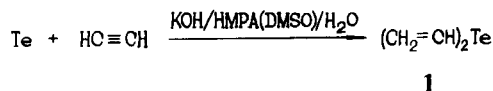
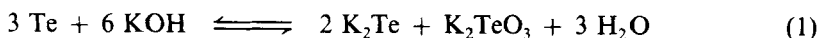


Table 1. Dependence of the yield of divinyl telluride and its by-products in reaction (2) upon the KOH concentration (105–115 °C, 10 h, initial pressure 14–15 atm)⁵¹

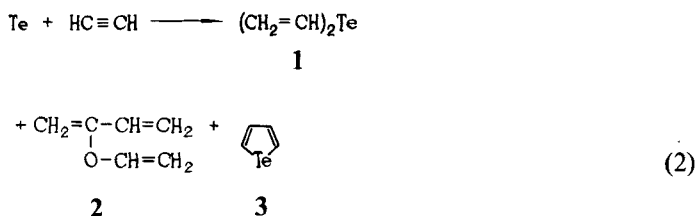
KOH, moles	Yield ^a , %		
	Divinyl telluride 1	Diene 2	Tellurophene 3
0.6	45	4	3
none	The reaction does not occur		
0.7	43	2	4
0.3	23	3	2

^a Here and in Table 2 the yields of compounds 1 and 3 have been calculated from the amount of tellurium employed with consideration of redox process (1), the yield of diene 2 is based on absorbed acetylene according to the scheme: $3 \text{ HC}\equiv\text{CH} + \text{H}_2\text{O} \rightarrow 2$

The yield of divinyl telluride 1 is 48% when HMPA is used and 26% with DMSO (the yield is calculated from the amount of tellurium employed with due regard for the redox process):

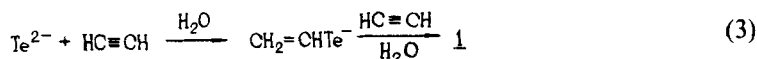


Later⁵¹ it was shown that upon heating (105–115 °C) of tellurium with acetylene in the KOH-HMPA-H₂O system, besides divinyl telluride 1 (main product), 2-vinyloxy-1,3-butadiene 2 and tellurophene 3 are formed in 4 and 3% yield, respectively (Table 1).



The most probable schemes for the formation of compounds 1–3 have been considered in.⁵¹

Divinyl telluride is formed as a result of consecutive nucleophilic addition to two acetylene molecules of the telluride ions generated from tellurium and potassium hydroxide without which process (2) does not occur (Table 1).⁵¹



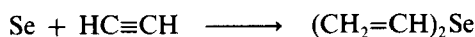
According to equation (1) the complete conversion of tellurium to telluride ions requires a twofold molar excess of KOH. Indeed, use of the above reactant ratio in reaction (2), other conditions being equal, leads to the highest yield (45%) of divinyl telluride (Table 1). With higher KOH contents the yield of divinyl telluride does not increase, and decreases when equimolar amounts of Te and KOH are used (Table 1). At the same time, the KOH concentration does not affect much the yield of by-products the formation of which can be inhibited by addition of water, i.e., by a slight decrease of the basicity of the system (Table 2).⁵¹ However, some decrease in the yield of divinyl telluride

Table 2. Effect of the concentration of water and SnCl₂ as an additive on the yield of divinyl telluride and the by-products of reaction (2) (105–115 °C, 10 h, initial acetylenic pressure 13–15 atm)⁵¹

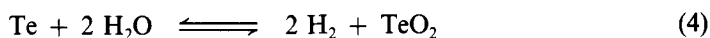
H ₂ O, ml	Yield, %		
	Divinyl telluride 1	Diene 2	Tellurophene 3
4	45	4	3
8	40	3	3
16	38	2	2
50	23	No	Traces
300 ^a	1	No	No
4 ^b	75	No	No

^aHMPA is excluded from the reaction mixture. ^b0.33 mole of SnCl₂ · 2H₂O added.

as well as nearly complete inhibition of reaction (2) in an aqueous alkaline medium, observed in this case (Table 2) cannot be attributed only to a lessened nucleophilic activity of the telluride ions under the above conditions, since the less nucleophilic selenide ions⁵⁷ do react with acetylene in the KOH-H₂O system to give divinyl selenide in 33% yield.⁵⁸



An attempt⁵¹ to improve the reaction by increasing the temperature to 120–130 °C (Table 3) and the KOH concentration (KOH:Te to 10:1) was unsuccessful: the yield of divinyl telluride was 2 and 8%, respectively. Under these conditions the telluride ions do not seem to be generated at all due to a competing reaction between tellurium and water which occurs at 100–160 °C and as low as room temperature when freshly prepared tellurium is used.⁵⁹



No similar reaction for selenium has been described.

Table 3. Effect of the SnCl₂ concentration on the yield of vinyl tellurides 1, 4 and 5 (100–120 °C, 10 h, initial acetylenic pressure 12–15 atm)⁵¹

SnCl ₂ , mole	Yield, %			Conversion of Te, %
	Divinyl telluride 1	Alcohol 4	Alcohol 5	
none	2 ^a	Traces	Traces	Not determined
none	8	1	1	Not determined
0.19	82 ^b	6	2	78
0.26	91 ^b	5	2	100
0.26	94 ^b	5	2	90
0.26	42 ^c	3	1	Not determined
0.32	70 ^b	5	1	87

^aReaction temperature 120–130 °C. ^bThe yield of products 1, 4, 5 is based on the tellurium consumed, in other cases the yield is based on Te taken. ^cZinc powder as a reducer.

In strong concentrated alkalis tellurium dioxide dissolves to form tellurites.

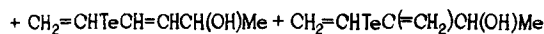


On the other hand,⁵⁹ compounds of tetravalent tellurium are known to be reduced to elemental tellurium under the action of different reducers (tin chloride, copper, silver, zinc, glucose, for example). Therefore, to displace the reactions (1, 3, 4) towards the formation of telluride ions process (2) was carried out in the presence of a reducer (SnCl_2) which allowed divinyl telluride to be prepared in a yield of 75% when the $\text{KOH-HMPA-H}_2\text{O}$ system was used (Table 2) and of 91–94% with the $\text{KOH-H}_2\text{O}$ system (Table 3). In the latter case (*Z*)-1-vinyltelluro-1-buten-3-ol **4** and 2-vinyltelluro-1-buten-3-ol **5** were also isolated from the reaction mixture.^{48,60–62} The introduction of SnCl_2 inhibits nearly completely the formation of tellurophene and diene **2**.⁵¹



1

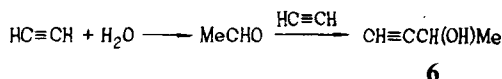
(5)



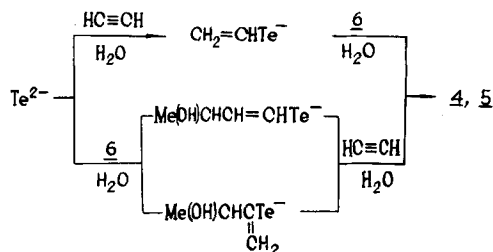
(*Z*)-**4**

5

Use of almost equimolar amounts of Te and SnCl_2 as well as an increase in the SnCl_2 concentration (Table 3) in reaction (5) decrease the yield of divinyl telluride to 82 and 70%, respectively.⁵¹ When SnCl_2 is replaced by zinc powder the yield of divinyl telluride decreases even more (by a factor of ~ 2.2, Table 3). The yields of alcohols **4** and **5** never exceeded 2–6%. These compounds are formed in the course of process (5), seemingly by addition of the corresponding ethenelluroolate anions and/or telluride ions to 1-butyne-3-ol **6** (Scheme 6), the product of a competing Favorsky reaction.⁵¹



6



SCHEME 6

The introduction of 1-butyne-3-ol **6** into the reaction mixture under otherwise identical conditions (Te 0.1 mole, KOH 0.87 mole, SnCl_2 0.13 mole, H_2O 145 ml, 105–115 °C, 10 h,

initial acetylenic pressure 12–13 atm) leads to a slight increase in the yields of the alcohols **4** and **5**.⁵¹

Vinyl tellurides formed	Yield of vinyl tellurides 1 , 4 , 5 , %	
	Without 6	With 0.1 mole 6
Divinyl telluride 1	89	31
(<i>Z</i>)-1-Vinyltelluro-1-buten-3-ol 4	5	28
2-Vinyltelluro-1-buten-3-ol 5	2	8

Thus, Trofimov and coworkers⁵¹ have shown for the first time that tellurium metal can react with acetylenic alcohols to give in one pot the previously unknown hydroxy substituted divinyl tellurides **4** and **5**, promising starting materials for the synthesis of new functional telluriumorganic compounds.

A special test has demonstrated the formation of tellurophene in reaction (2) to be the result of dehydrocyclization of divinyl telluride. Thus, heating (105–115 °C) of the latter in the KOH-HMPA-H₂O system furnishes tellurophene in about 3% yield.⁵¹

Elevation of the temperature to 130–140 °C or 160–170 °C caused the yield of tellurophene to increase to 8 and 11%, respectively, the yield of divinyl telluride decreasing concomitantly.⁵¹

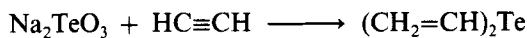
Temperature, °C	Yield, %		
	Divinyl telluride 1	Diene 2	Tellurophene 3
105–115	45	4	3
130–140	38	5	8
160–170	25	4	11

Above 130 °C and, especially, at 160–170 °C decomposition of HMPA⁶³ and, partially, of divinyl telluride takes place.⁵¹

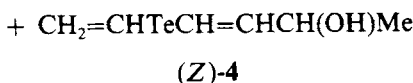
An efficient synthetic route to the diene **2** from acetylene and water in the presence of the superbasic catalytic KOH-DMSO system and a reaction scheme for the formation of **2** have been reported.^{64–66}

The synthesis of divinyl telluride from tellurium metal and acetylene has been performed by Trofimov and coworkers at atmospheric pressure as well.⁵¹ Bubbling acetylene through a Te-HMPA (or DMSO)-KOH-SnCl₂ mixture, heated at 120–130 °C, for 5 h leads to the formation of divinyl telluride in 30% yield.

The reaction of sodium tellurite with acetylene, discovered by Trofimov and coworkers,^{51,67} which proceeds in aqueous alkaline medium in the presence of SnCl₂ to give divinyl telluride in satisfactory yield (45%) and (*Z*)-1-vinyltelluro-1-buten-3-ol (3% yield), has provided principally new possibilities in the synthesis of unsaturated and functionalized telluriumorganic compounds.

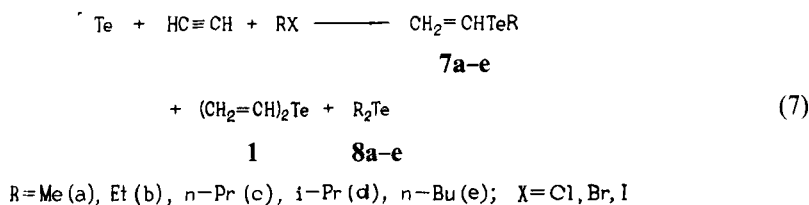


1



The reaction is carried out in an autoclave under acetylenic pressure at 105 °C with a ratio of reagents $\text{Na}_2\text{TeO}_3:\text{KOH}:\text{SnCl}_2 = 1:20:4$.

II.1.2 Vinyl tellurides from tellurium, acetylene, and organyl halides Alkyl vinyl tellurides were first prepared by Trofimov and coworkers^{68,69} in a one-pot synthesis from tellurium metal, acetylene, and alkyl halides. The reaction proceeds at 105–115 °C in a highly basic reducing multiphase $\text{KOH}:\text{SnCl}_2:\text{H}_2\text{O}$ system at an hydroxide ion concentration of about 7 mole/L. In the reaction course, along with the alkyl vinyl tellurides **7**, the divinyl telluride **1** and the corresponding dialkyl tellurides **8** are also formed.^{50,68,71}



Under otherwise identical conditions the product yield and ratio depend much on the nature of the alkyl halide. The reactivity of the latter decreases in the following order of the halogens (X): Br > I > Cl (Table 4, lines 6–8). Primary and secondary alkyl bromides are comparatively readily involved in reaction (7). It was not possible to obtain *t*-butyl vinyl and di-*t*-butyl telluride from *t*-butyl bromide (Table 4, line 9), evidently due to the fact that tertiary alkyl halides are very prone to base-induced elimination of hydrogen halide.^{50,71}

Table 4. Effect of the Alkyl Halide Structure on the Yield of Tellurides **1**, **7**, **8** (Te:RX:KOH:SnCl₂ = 0.1:0.1:0.87:0.13 moles, 150 ml H₂O, 105–115 °C, 5 h, initial acetylenic pressure 14–15 atm)^{50,71}

Run, No.	RX	Yield ^a , %		
		CH ₂ =CHTeR 7	(CH ₂ =CH) ₂ Te 1	R ₂ Te 8
1	MeI	Traces	Traces	Traces
2	MeI ^b	20	55	8
3	EtBr	35	26	10
4	<i>n</i> -PrBr	36	28	11
5	<i>i</i> -PrBr	33	32	12
6	<i>n</i> -BuBr	38	32	12
7	<i>n</i> -BuI	15	24	7
8	<i>n</i> -BuCl	5	12	Traces
9	<i>t</i> -BuBr	Not detected	50	Not detected

^aThe yield of **1** is calculated from the amount of tellurium, the yield of **7** and **8** is calculated from the amount of alkyl halide.

^bIn the presence of HMPA (80 ml) with MeI (0.01 mole).

The considerable decrease in the yields of the products of reaction (7) when butyl iodide is used instead of butyl bromide (Table 4, lines 6 and 7) is explained by the fact that the former reacts during the process with the tellurides **7e**, **1**, **8e** to give the corresponding triorganyltelluronium salts **9**.^{50,71}



$\text{R}^1 = \text{R}^2 = n\text{-Bu}$; $\text{R}^1 = n\text{-Bu}$, $\text{R}^2 = \text{CH}_2=\text{CH}$; $\text{R}^1 = \text{R}^2 = \text{CH}_2=\text{CH}$; $\text{R}^3\text{X} = n\text{-BuI}$

It is known⁴⁰ that reaction (8) takes place especially readily with aliphatic tellurides and alkyl iodides, dimethyl telluride and methyl iodide being most active. It has been established (see Section III.5.) that divinyl telluride readily reacts with alkyl iodides to form alkyldivinyltelluronium iodides.^{50,71}

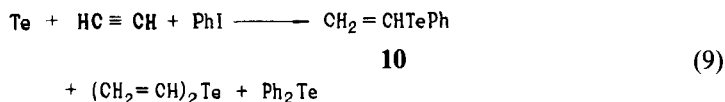
This sheds some light on the question why vinyl methyl telluride is not formed upon heating of methyl iodide, tellurium, and acetylene in the KOH-SnCl₂-H₂O system (Table 4, line 1). Tellurides **1** and **8a** have not been found, either, in the reaction mixture.

The side reaction of iodomethylation of tellurides **7** and **8** in the course of reaction (7) is suppressed to a considerable extent when the initial concentration of MeI is decreased by a factor of 10 and when the reaction mixture is homogenized and diluted by addition of HMPA. Under these conditions (Table 4, line 2) the yield of methyl vinyl telluride **7a** is 20% and that of tellurides **1** and **8a** 55 and 8%, respectively. The yield of alkyl vinyl tellurides is substantially increased by use of a 10:1 molar ratio of Te:RX in reaction (7), other reaction conditions being equal (0.1 mole Te, 0.87 mole KOH, 0.13 mole SnCl₂, 150 ml H₂O, 105–115 °C, 5 h, initial acetylenic pressure 13–15 atm).^{50,71}

Alkyl halide RX	Yield of CH ₂ =CHTeR, %	
	0.1 mole RX	0.01 mole RX
EtBr	35	69
<i>n</i> -PrBr	36	68
<i>i</i> -PrBr	33	65
<i>n</i> -BuBr	38	70

In this case the yield of divinyl telluride is 53–60% and the yield of the corresponding dialkyl tellurides 4–7%.

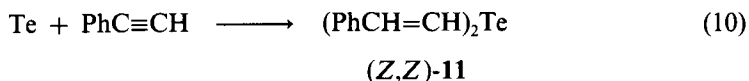
Later⁷² the list of organyl halides in reaction (7) was extended to include iodobenzene. Practically under the same conditions (autoclave, 100–120 °C, 10–12 atm) the latter also reacts with tellurium metal and acetylene in the KOH-HMPA-SnCl₂-H₂O system to give, as expected, vinyl phenyl telluride **10** in 20% yield based on the tellurium taken, as well as divinyl telluride (17% yield) and diphenyl telluride (2%).



The addition of radical inhibitors to the reaction mixture (hydroquinone) has been reported⁷² to completely suppress the formation of vinyl phenyl telluride. Unfortunately,

it is still uncertain whether hydroquinone influences the synthesis of alkyl vinyl tellurides in the same way and whether this can be regarded as an indication of one-electron transfer in reaction (7). When process (9) was carried out without SnCl_2 the telluride **10** was detected only in trace amounts. When iodobenzene is replaced by bromobenzene the yield of **10** is less than 1% and with chlorobenzene no **10** is formed at all.⁷²

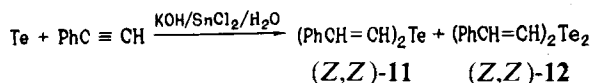
II.1.3. Reaction of tellurium with phenylacetylene and with vinylacetylene Tellurium reacts with phenylacetylene upon heating (110–115 °C) in the $\text{KOH-DMSO-SnCl}_2\text{-H}_2\text{O}$ system to form di(*Z*-styryl) telluride **11** in 41% yield based on tellurium consumed.⁷³⁻⁷⁵



In the HMPA medium under similar conditions, along with the telluride **11**, a compound $\text{C}_{16}\text{H}_{12}\text{Te}_2$ has been isolated and assigned the structure of 3-benzylidene-4-phenyl-1,2-ditellurole on the basis of IR, NMR, and mass spectra.⁷³⁻⁷⁵

However, recently⁷⁶ it was found by cyclic voltammetry and UV/VIS (dichloromethane) measurements that the products formed in the reaction of tellurium with phenylacetylene in the presence of strong bases (no details reported⁷⁶) are (*Z*)- and (*E*)-2,6-diphenyl-1,4-ditellurafulvene rather than 3-benzylidene-4-phenyl-1,2-ditellurole.

When carried out in the presence of a phase-transfer catalyst which provides superbasic conditions in the organic phase^{39,77} at 80–98 °C reaction (10) gives the telluride **11** and di(*Z*-styryl) ditelluride **12** in 15 and 6% yields, respectively, based on tellurium consumed.^{78,79}

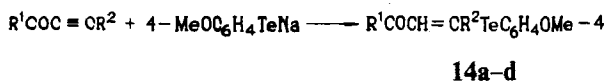


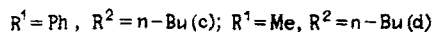
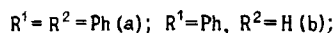
In the $\text{KOH-DMSO-H}_2\text{O}$ system tellurium reacts with vinylacetylene at 100 °C to form a multi-component mixture containing over 50% of di(*Z*-1,3-butadienyl) telluride **13** in about 3% yield.^{46,80,81}



The replacement of DMSO by HMPA, other conditions being equal, increases the yield of **13** to 20%.

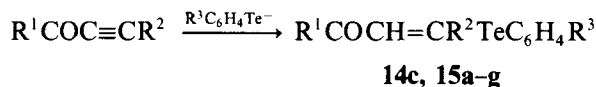
II.1.4 Interaction of organotelluroate anions with alkynes In 1976 arenetelluroate anions were shown⁸² to add readily to alkyl and aryl substituted ethynyl ketones to form the 2-arylketo vinyl tellurides **14a-d**. The reaction occurs smoothly at room temperature in ethanol under nitrogen and is completed in 30 min. The yields of the tellurides **14** are 68–74%.





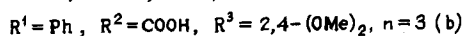
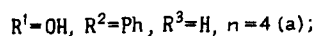
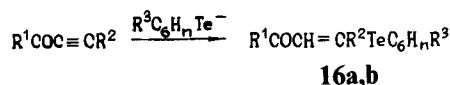
It should be noted that in this first brief report⁸² there are practically no data supporting the structure¹⁴ of the compounds obtained (only IR bands corresponding to C=C and C=O stretching vibrations presented); therefore, the question of the regio- or, especially, the stereodirection of this reaction remains open.

Later⁸³ it was found that not only α,β -acetylenic ketones, but also α,β -acetylenic aldehydes and esters can effectively be used for the synthesis of aryl vinyl tellurides **15** in yields of 67–88%.

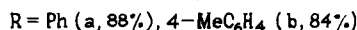
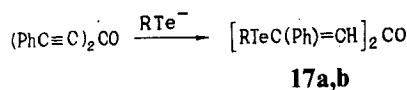


Compound	R ¹	R ²	R ³
14c	Ph	<i>n</i> -Bu	4-OMe
15a	Ph	Ph	H
15b	H	Ph	H
15c	H	Ph	4-OMe
15d	H	Ph	4-Me
15e	OEt	H	4-Me
15f	OEt	Ph	H
15g	OEt	Ph	2,4-(OMe) ₂

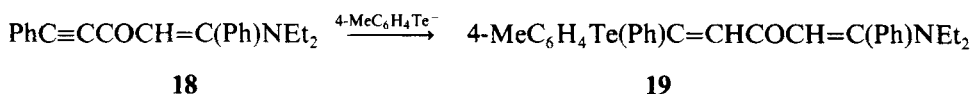
At the same time, the authors' statement⁸³ that the reaction with benzenetellurolate anions readily involves acetylenic acids is not quite correct since in this case the yields of the resulting vinyl tellurides **16a,b** are by no means high (14 and 21%, respectively).



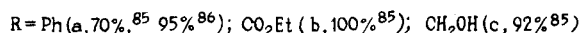
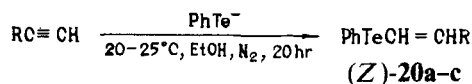
Symmetrical diacetylenic ketones add benzenetellurolate anions at room temperature to give the diadducts **17a,b** in high yields.⁸³



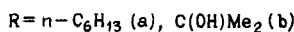
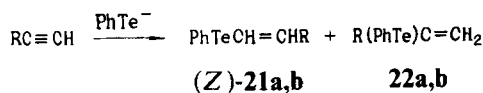
The aminovinyl ketone **18** whose C≡C triple bond does not add amines, alcohols, or phenols due to its low electrophilicity, reacts readily (20–25 °C, EtOH) with a stronger nucleophile, 4-methylbenzenetellurolate anion, to form the functionally substituted aryl telluride **19** (yield 68%).⁸³



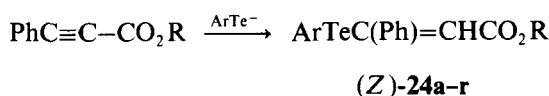
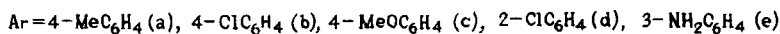
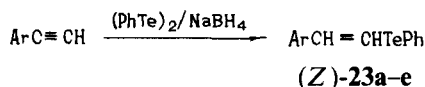
Later,⁸⁴⁻⁸⁶ with phenylacetylene, ethyl propiolate, and propargyl alcohol as examples it was shown that the addition of benzenetellurolate anion to the C≡C triple bond is both regio- and stereospecific to give the 2-substituted vinyl tellurides (*Z*)-**20**.



However, it was recently shown that refluxing of sodium benzenetellurolate with 1-octyne or 3-methyl-1-butyn-3-ol in ethanol gives, along with the expected (*Z*-2-organylvinyl) phenyl tellurides **21a,b** (in yields of 18 and 68%, respectively) a small amount of the regioisomers **22a,b** (yields 7-9%).⁸⁷

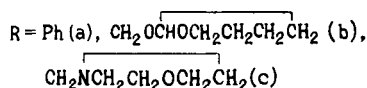
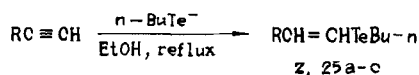


By use of a procedure reported in⁸²⁻⁸⁵ the (2-arylvinyl) phenyl tellurides **23a-e**⁸⁸ and **24**⁸⁹⁻⁹⁰ have been prepared.



R and Ar for the compounds **24a-r** are shown in Table 13.

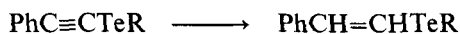
Recently, alkanetellurolate anions were shown to react with acetylenes by Dabdoub *et al.*⁴¹



The yield of alkyl (*Z*-organovinyl) tellurides **25** is 78–93%.

The alkylarene- and alkanetellurolate anions used in the synthesis of the vinyl tellurides **15–17** and **19–25** are generated *in situ* from the corresponding diaryl ditellurides^{82–90} and dialkyl ditellurides⁴¹ by treatment with sodium borohydride in dry ethanol.

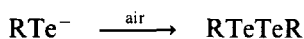
The alkyl (*Z*-styryl) tellurides **25a**, **25d**, **25e** have also been prepared by treatment of (alkyltelluro)phenylacetylenes either with an N_2H_4 –NaOH system in the presence of air oxygen or with sodium borohydride in ethanol under nitrogen in a yield of 8–14% in the first case and of 80–93% in the second case.⁹¹



(*Z*)-**25a,d,e**

R = *n*-Bu (**a**), Et (**d**), *n*-C₁₂H₂₅ (**e**)

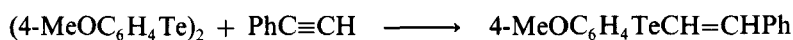
In the authors' opinion⁹¹ the reaction involves initial formation of phenylacetylene and alkanetellurolate anions which further add to the triple bond. In the presence of atmospheric oxygen the main trend of this process is the oxidation of the alkanetellurolate anions to form the corresponding dialkyl ditellurides in 86–91% yield.



R = Et, *n*-Bu, *n*-C₁₂H₂₅

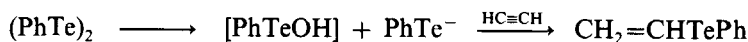
The arenetellurolate anions can also be prepared from diaryl ditellurides with strong bases generated from an alkali metal hydroxide under phase transfer catalysis (PTC) conditions⁴¹ or in the presence of a polar aprotic solvent (DMSO).⁸²

Thus, the reaction of bis(4-methoxyphenyl) ditelluride and phenylacetylene in THF in the presence of formamidinesulfinic acid, 50% sodium hydroxide, and a catalytic amount of a dialkyldimethylammonium chloride (85% *n*-C₁₈ and 15% *n*-C₁₆) forms 4-methoxyphenyl styryl telluride **26** of *Z*-configuration in 63% yield after 72 h stirring at room temperature.⁴¹



(*Z*)-**26**

Heating (105–115 °C) of diphenyl ditelluride under acetylenic pressure in the KOH–DMSO–SnCl₂–H₂O system leads to the formation of phenyl vinyl telluride **10** in 34% yield.⁹²

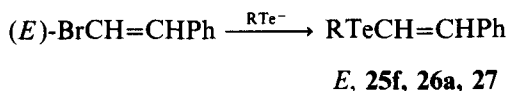


10

II.2. Reaction of Organotellurolate Anions with β -Bromostyrene

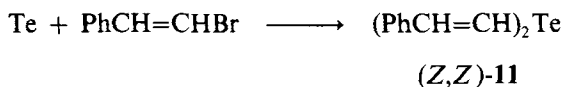
Butanetellurolate and 4-methoxybenzenetellurolate anions⁴¹ as well as benzenetel-

lurolate anions,⁸⁷ generated from the corresponding diorganyl ditellurides under the action of LiAlH_4 ⁴¹ or NaBH_4 ⁸⁷ interact with (*E*)- β -bromostyrene when heated in a THF-HMPA medium to form the vinyl tellurides **25f** and **26a** of *E*-configuration in 86% yield and (*E*-2-phenylvinyl) phenyl telluride **27** in 34% yield.



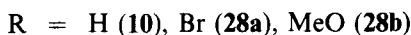
The reaction is believed to proceed either by direct nucleophilic substitution of the halogen in β -bromostyrene or according to an addition-elimination scheme.⁴¹

It has also been reported⁸⁶ that the interaction of tellurium metal, sodium hydride and β -bromostyrene in a DMSO-THF system gives di(*Z*-styryl) telluride **11** in 41% yield.



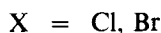
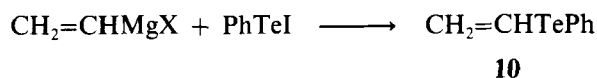
II.3. Synthesis of Vinyl Tellurides via Organometallic Compounds

Phenyl vinyl telluride **10** as well as its substituted derivatives, (4-bromophenyl) vinyl telluride **28a** and (4-methoxyphenyl) vinyl telluride **28b**, have been obtained by boiling divinylmercury and the corresponding diaryl ditelluride in dioxane.⁹³

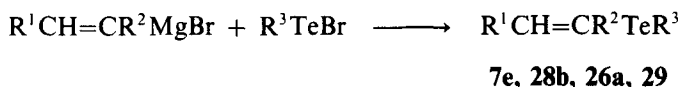


The yield of phenyl vinyl telluride is 70%, those of the tellurides **28a,b** have not been reported.⁹³

Later,^{94,95} the telluride **10** was synthesized in 78% yield by interaction of vinylmagnesium chloride (or bromide) with benzenetellurenyl iodide. The reaction is carried out at -10°C in dry THF.

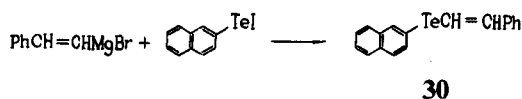


Also arene- and alkanetellurenyl bromides can be used:⁴¹

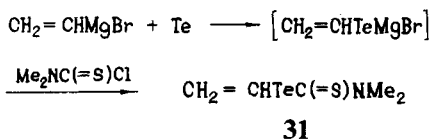


Compound	R ¹	R ²	R ³	Yield, %
7e	H	H	<i>n</i> -Bu	71
28b	H	H	4-MeOC ₆ H ₄	74
26a	Ph	H	4-MeOC ₆ H ₄	72
29	H	Me	4-MeOC ₆ H ₄	86

From styrylmagnesium bromide and 2-naphthalenetellurenyl iodide 2-naphthyl styryl telluride **30** of unidentified configuration has been prepared.⁹⁶

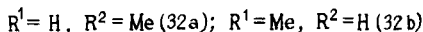
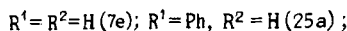
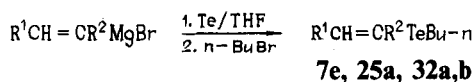


Vinyl telluride **31** containing a thiocarbamoyl moiety, has been synthesized in 72% yield by successive treatment of vinylmagnesium bromide with tellurium metal and *N,N*-dimethylthiocarbamoyl chloride.⁹⁷



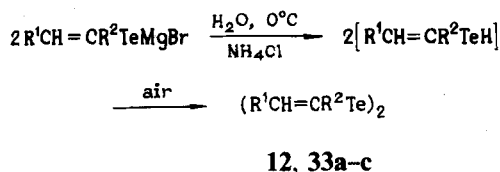
The synthesis is performed at -78°C in dry THF.

Later this method was used for the synthesis of the vinyl tellurides **7e**, **25a**, **32a,b** in 73–79% yield.⁴¹



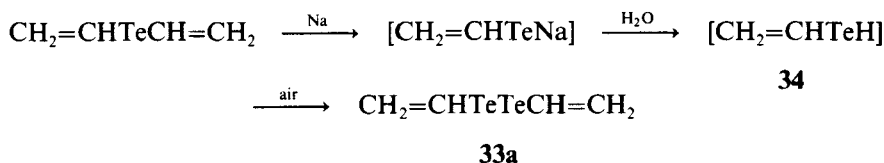
Insertion of tellurium into the C–Mg bond takes place when the reactants are boiled in THF under nitrogen, the subsequent alkylation being performed at room temperature.⁴¹

When the bromomagnesium ethenellurolates which are formed as the first intermediates are treated with water in the presence of air oxygen the divinyl ditellurides **12**, **33a–c** are obtained in 58–67% yield.^{41,42}

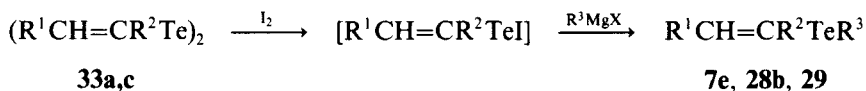


Compound	R ¹	R ²
12	Ph	H
33a	H	H
33b	Me	H
33c	H	Me

Recently,⁹⁸ the same procedure was applied to ethenetellurole **34** prepared by cleavage of divinyl telluride with sodium metal in liquid ammonia. Divinyl ditelluride **33a** was synthesized in the same way in 70% yield.⁹⁸



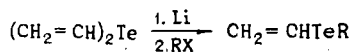
The alkenyl organyl tellurides **7e**, **28b**, and **29b** have been prepared in good yields (64–71%) by reaction of organylmagnesium halides and alkenetellurenyl iodides generated *in situ* from the divinyl ditellurides **33a–c** under the action of elemental iodine.⁴¹



Compound	R ¹	R ²	R ³
7e	H	H	<i>n</i> -Bu
28b	H	H	4-MeOC ₆ H ₄
29	H	Me	4-MeOC ₆ H ₄

II.4. Reaction of Ethenetellurolate Anions with Alkyl Halides

By use of the method mentioned in the title alkyl vinyl tellurides were prepared for the first time by Trofimov *et al.*,⁹⁹ *i.e.* by successive treatment of divinyl telluride with lithium and an alkyl halide in liquid ammonia.

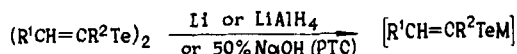


7a–c

RX = MeI, EtBr, *n*-PrBr

The yield of the vinyl tellurides **7** is 30% when methyl iodide is used and about 60% with alkyl bromides.^{30,71,99}

Later, Dubdoub *et al.*⁴¹ suggested a method for generating ethenetellurolate anions from divinyl ditellurides **12**, **33a–c** with lithium in liquid ammonia or with lithium aluminum hydride in THF as well as in the system: thiourea dioxide-NaOH-H₂O-THF-phase transfer catalyst (PTC). Subsequent treatment of the reaction mixture with butyl bromide gives the alkyl vinyl tellurides **7e**, **25f**, **32a,b** in 63–68% yield.⁴¹



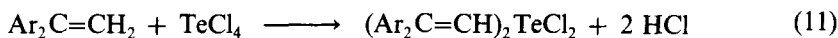
7e, 25f, 32a,b

M = Li, Na

Compound	R ¹	R ²
7e	H	H
25f	Ph	H
32a	H	Me
32b	Me	H

II.5. Reduction of Bis(2,2-diarylvinyl)tellurium Dichlorides

It has been suggested¹⁰⁰⁻¹⁰² to utilize the reduction of bis(2,2-diarylvinyl)tellurium dichlorides **35** for the synthesis of the bis(2,2-diarylvinyl) tellurides **36**. The starting dichlorides **35** are obtained by reaction of 1,1-diarylethenes with tellurium tetrachloride in dry ether at room temperature.



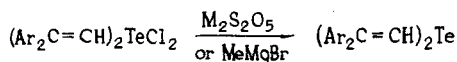
35a,b

Ar = Ph (a), 4-MeC₆H₄ (b)

The yields of the tellurium dichlorides **35a,b** are 10 and 19%, respectively.

It should be noted that the compounds formed in the course of reaction (11) have been reported¹⁰⁰ to be π -complexes with the formula $(Ar_2C=CH_2)_2TeCl_2$.

Later,^{101,102} however, fairly strong evidence for divinyltellurium dichlorides **35** as the end products of reaction (11) has been provided. When treated with K₂S₂O₅,¹⁰⁰ Na₂S₂O₅,¹⁰¹ or methylmagnesium bromide¹⁰⁰ the divinyltellurium dichlorides **35** are reduced to the bis(2,2-diarylvinyl) tellurides **36a,b** in 80 and 56% yield, respectively.



35a,b

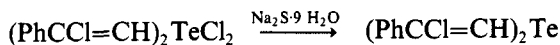
36a,b

Ar = Ph (a), 4-MeC₆H₄ (b);

M = K, Na

With M₂S₂O₅, the reaction is performed by boiling of the reactants in water.

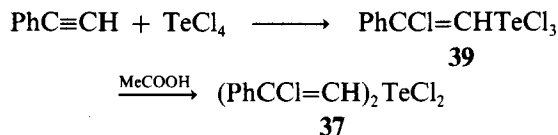
Sodium sulfide has been reported⁹⁶ to be reducer of divinyltellurium dichloride **37**. Bis(2-chloro-2-phenyl-vinyl) telluride **38** is formed in quantitative yield.



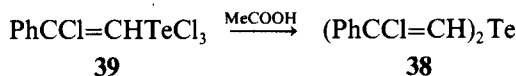
37

38

The divinyltellurium dichloride **37** was prepared in two steps from phenylacetylene and TeCl_4 with subsequent heating of the intermediate 2-chloro-2-phenylvinyltellurium trichloride **39** for several minutes in glacial acetic acid.⁹⁶



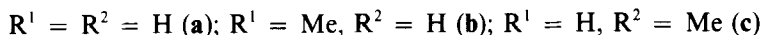
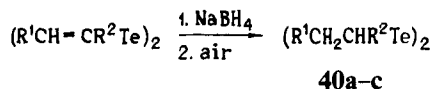
Later it was shown^{103,104} that prolonged refluxing of the trichloride **39** in acetic acid gives the divinyl telluride **38** in 74% yield.



III. REACTIVITY OF VINYL TELLURIDES

III.1. Reduction

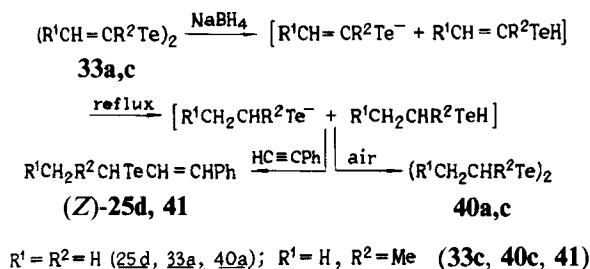
Recently it was reported that refluxing of the divinyl ditellurides **33a-c** with NaBH_4 in ethanol and in an inert atmosphere, followed by air oxygen treatment of the reaction mixture at room temperature, leads to the formation of the corresponding dialkyl ditellurides **40a-c**.⁴²



This reaction is not a general procedure for the vinyltelluro group since, under analogous conditions, the corresponding divinyl tellurides are not affected at all.⁴²

In the authors' opinion,⁴² the divinyl ditellurides **33a-c** first form ethenellurolates or -telluroles which then, under the action of NaBH_4 , are reduced to their saturated analogs. In the presence of air oxygen, the latter are transformed to the corresponding dialkyl ditellurides **40a-c**.⁴²

The authors substantiate this suggestion by the finding that the alkyl *Z*-styryl tellurides **25d**, **41** are formed when the divinyl ditellurides **33a,c** are refluxed with NaBH_4 in the presence of phenylacetylene (Scheme 12).⁴²



SCHEME 12

However, according to⁹² the alkyl styryl tellurides **25d**, **41** could also be formed by direct reaction of the ditellurides with phenylacetylene in the presence of a proton donor, in this case ethanol; therefore, the scheme suggested cannot be regarded as established beyond reasonable doubt.

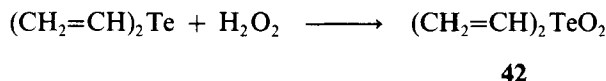
III.2. Oxidation

The literature only contains scarce and ambiguous data concerning the possible preparation of diorganyl tellurones.^{105,106} For the first time a synthesis of tellurones was reported in 1920.^{107,108} Dimethyl tellurone was prepared by the oxidation of dimethyl telluride with excess hydrogen peroxide upon prolonged reflux. The yield was not reported.

Its structure, supported only by element analysis, was doubted later in.¹⁰⁹

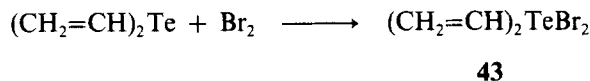
Not very long ago,¹¹⁰ it has been reported that *n*-dodecyl (4-methoxyphenyl) telluride is oxidized in benzene by one equivalent of *t*-butyl hydroperoxide to give *n*-dodecyl (4-methoxyphenyl) telluroxide and *n*-dodecyl (4-methoxyphenyl) tellurone (or its hydrate). The latter was also prepared by oxidation of the corresponding telluroxide with sodium periodate. No additional data (spectral characteristics, physicochemical constants, element analysis) confirming the structure of the tellurone obtained have been reported in this work.¹¹⁰

As shown by Trofimov *et al.*^{53,111} divinyl telluride reacts readily with aqueous hydrogen peroxide solution at room temperature or when slightly heated (20–30 °C), to form in 1–2 h divinyl tellurone **42** in 85% yield.



III.3. Halogenation

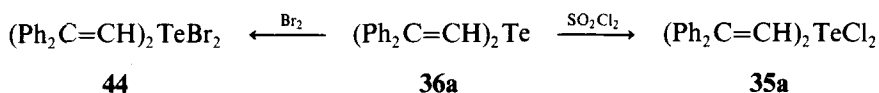
Trofimov *et al.*¹¹² found for the first time that, against all expectations, divinyl telluride does not add bromine at the double bonds and instead forms divinyltellurium dibromide **43**.



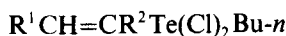
The reaction proceeds under mild conditions (from 0 to 10 °C, CCl₄), the yield of **43** is 65%. When heated with sodium sulfide under the conditions described for dialkyltellurium dibromides¹ divinyltellurium dibromide is reduced to form the initial divinyl telluride.¹¹²

Subsequent research by Engman¹⁰¹ confirmed that halogenating agents interact with vinyl tellurides *via* the tellurium atom without involvement of the double bond. Thus, the reaction of divinyl telluride **36a** with sulfonyl chloride or bromine occurs under mild conditions (temperature range from –15 to 20 °C, CCl₄ as solvent) to give divinyltel-

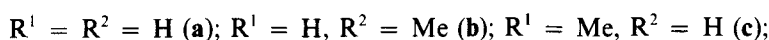
lurium dichloride **35a** or dibromide **44** in 83 and 75% yield, respectively.¹⁰¹



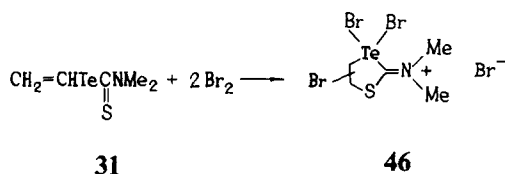
Under analogous conditions (room temperature, petroleum ether as solvent) reaction of the vinyl tellurides **7e**, **32a,b**, **25a** with SO_2Cl_2 to afford the corresponding vinyltellurium dichlorides **45a-d** in quantitative yield has been carried out.⁴¹



45a-d



Vinyltellurothiocarbamates such as **31** have been briefly reported⁹⁷ to react with bromine with the formation of a product of the hypothetical structure **46** assigned by the authors on the basis of the elemental analysis only (Scheme 13).

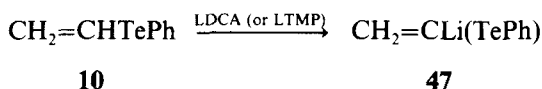


SCHEME 13

An attempt to carry out dehydrobromination or reductive elimination with **46** was unsuccessful, inasmuch as treatment of **46** with triphenylphosphine, zinc, and tin chloride immediately caused precipitation of tellurium metal.⁹⁷

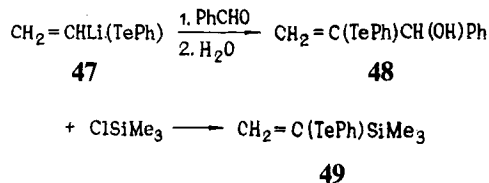
III.4. Metallation

Under the action of superbases such as lithium dicyclohexylamide (LDCA) or lithium (2,2,6,6-tetramethyl)piperidide (LTMP) phenyl vinyl telluride **10** undergoes deprotonation in the α -position to form α -lithiumvinyl phenyl telluride **47**.^{94,95}



It is convenient to carry out the reaction at -78°C in THF. The yield of the metallated derivative **47** is 49–51%. Lithium diisopropylamide and butyllithium are less efficient in this process: with these reactants the yield of **47** drops to 39 and 10%,

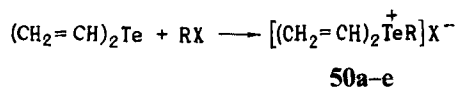
respectively. Treatment (-78°C , THF) of the latter with electrophiles such as benzaldehyde and trimethylchlorosilane, gave the α -substituted vinyl tellurides **48** and **49** in good yields.⁹⁴



An attempt to perform reactions of lithium derivative **47** with 1-iodopropane and allyl bromide was unsuccessful.⁹⁴

III.5. Reaction of Divinyl Telluride with Organyl Halides

With divinyl telluride as an example it has been shown by Trofimov *et al.*^{50,71} that vinyl tellurides react with organyl halides to form the divinylorganyltelluronium halides **50**. With alkyl iodides, among which methyl iodide is the most active, this reaction is readily realized at room temperature or upon slight heating (30 – 40°C); with allyl bromide, the reaction proceeds exothermally and requires cooling to 8 – 10°C . The yields are 77–98%.^{50,71}



$\text{R} = \text{Me}$, $\text{X} = \text{I}$ (a); $\text{R} = \text{Et}$, $\text{X} = \text{I}$ (b); $\text{R} = n\text{-Pr}$, $\text{X} = \text{I}$ (c);

$\text{R} = n\text{-Bu}$, $\text{X} = \text{I}$ (d); $\text{R} = \text{CH}_2=\text{CHCH}_2$, $\text{X} = \text{Br}$ (e)

III.6. Thiylation

The thiylation of vinyltelluro group was first performed by Trofimov *et al.* with divinyl telluride as an example.^{48,113} In the reaction of divinyl telluride with alkanethiols in the presence of radical initiators the (2-alkylthioethyl) vinyl tellurides **51a–c** in yields ranging from 25 to 35% have been prepared.



$\text{R} = \text{Et}$ (a), $n\text{-Pr}$ (b), $n\text{-Bu}$ (c)

Variation of the reaction conditions (temperature, initiator, heating time) does not affect the yield much (Table 5). The radical thiylation of divinyl telluride proceeds nearly with the same result both with UV irradiation at 25 – 30°C for 18–19 h (Table 5, lines 3, 7) and in the presence of azodiisobutyronitrile (AIBN) (80 – 97°C , 24–29 h) (Table 5, lines 2, 4–6). Simultaneous use of both initiators (UV, AIBN) does not lead to increased yields

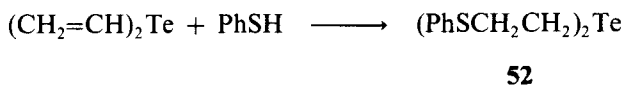
Table 5. Conditions of Thiylation of Divinyl Telluride 1

Run, No	RSH	Molar ratio 1:RSH	t, °C	Time, h	Initiator	Adduct yield, %
1	EtSH	1:2.08	70–80	18	No	No reaction
2	EtSH	1:2.08	95–97	24	AIBN	51a 35
3	EtSH	1:2.08	25–30	18	UV	51a 25
4	<i>n</i> -PrSH	1:3	80–85	29	AIBN	51b 31
5	<i>n</i> -PrSH	1:3.2	95–97	29	AIBN	51b 25
6	<i>n</i> -BuSH	1:2	95–97	24	AIBN	51c 25
7	<i>n</i> -BuSH	1:2.36	25–30	19	UV	51c 23
8	<i>n</i> -BuSH	1:2.36	25–30	15	UV, AIBN	51c 21
9	PhSH	1:3	75–80	18	AIBN	52 55

(Table 5, line 8). It should be emphasized that no reaction takes place when divinyl telluride is heated with ethanethiol without initiator (Table 5, line 1).^{48,113}

This example indicates that the readily available divinyl telluride can be successfully employed for the synthesis of functionally substituted vinyl tellurides via selective addition of certain addends to one of the double bonds.

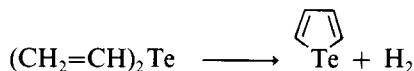
Thiophenol, as should be expected,¹¹⁴ proved to be more reactive than alkanethiols in divinyl telluride thiylation.^{48,113} Heating (75–80°C, 18 h) of the above reactants (divinyl telluride:thiophenol molar ratio 1:3) in the presence of AIBN leads to the formation of bis(2-phenylthioethyl) telluride **52** in 55% yield (Table 5, line 9). The corresponding monoadduct was detected in the reaction mixture by mass spectrometry.^{48,113}



III.7. Dehydrocyclization

It has been shown (see Section II.1.)⁵¹ that heating (105–115°C) of divinyl telluride in the KOH-HMPA-H₂O system gives tellurophene in about 3% yield.

The dehydrocyclization of divinyl telluride proceeds more effectively in the gas phase at atmospheric pressure and at temperatures of 380–430°C.

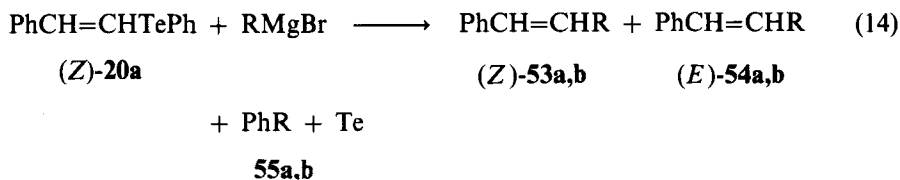


Under optimized conditions (380–390°C, exposure time 160–168 s) the yield of tellurophene is 76%.

III.8. Interaction with Grignard Reagents

When treated with phenyl- or butylmagnesium bromide in the presence of catalytic amounts of NiCl₂(PPh₃)₂ or CoCl₂(PPh₃)₂, phenyl *Z*-styryl telluride **20a** forms the *Z*-isomers **53a,b** and the *E*-isomers **54a,b** of alkenes and the alkylbenzenes **55a,b** with

precipitation of tellurium metal.^{84,85} The reaction occurs at room temperature in THF (or diethyl ether) and a nitrogen atmosphere.

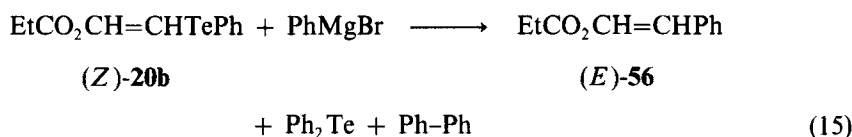


R = Ph (a), *n*-Bu (b)

With phenylmagnesium bromide the total yield of the alkenes **53a** and **54a** is 62% (in the ratio 9:1).^{84,85}

Use of butylmagnesium bromide in reaction (14) considerably decreases the yield of **53b** and **54b** which does not exceed 20% (*Z:E* ratio = 8:2) even when the reagents are refluxed in THF or diethyl ether.

Under the conditions of reaction (14) the vinyl telluride **20b** reacts with phenylmagnesium bromide by another mechanism than **20a**, *i.e.* it forms the *E*-isomer of the ethyl ester of cinnamic acid **56**, diphenyl telluride and biphenyl in 28, 38 and 38% yield, respectively. Neither the *Z*-isomer of compound **56** nor elemental tellurium have been found in this case.^{84,85}

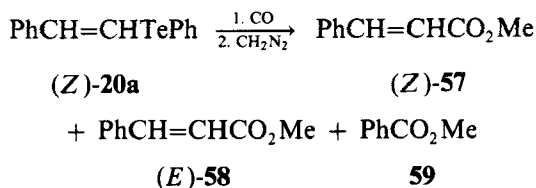


A mechanism for reactions (14, 15) which involves the initial formation of diorganonickel or diorganocobalt complexes from the Grignard reagents and NiCl₂(PPh₃)₂ or CoCl₂(PPh₃)₂ has been suggested.^{84,85}

III.9. Carbonylation of Vinyl Tellurides with Carbon Monoxide

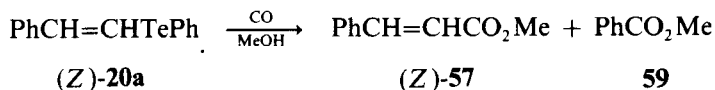
Some data on the facile Pd(II) salt-induced insertion of carbon monoxide into C-Te bonds of organyl tellurides including vinyl tellurides were reported recently.^{87,88,115}

Thus, phenyl *Z*-styryl telluride **20a** interacts with CO at room temperature in the presence of PdCl₂, PdCl₂/LiCl or Pd(OAc)₂ to form *Z*- and *E*-cinnamic acid as well as benzoic acid which, after treatment of the reaction mixture with diazomethane, were identified as their methyl esters **57-59**.^{87,115}

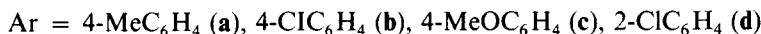
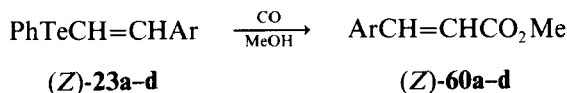


The yields and ratios of the reaction products depend to a considerable extent on the nature of the catalyst and the carbon monoxide pressure. In the presence of PdCl_2 or $\text{PdCl}_2/\text{LiCl}$ and at atmospheric pressure methyl *E*-cinnamate **58** is the major reaction product, whereas use of $\text{Pd}(\text{OAc})_2$ favored the presumable formation of the *Z*-isomer **57**. The latter can also be formed as the major product when the carbonylation is carried out under CO pressure (5–50 atm). In this case, both Pd(II) chloride and acetate can be used with the same result.⁸⁷ At the same time, an attempt to carry out the carbonylation of **20a** in the absence of Pd salts proved unsuccessful, even under a CO pressure of 100 atm and at 100 °C. Other transition metal salts such as those of nickel and platinum, palladium(0) or -(II) phosphine complexes were also shown to be ineffective for this reaction.⁸⁷

Phenyl *E*-styryl and (*Z*)-1-octenyl phenyl telluride are also involved in this reaction.⁸⁷ On treatment of phenyl *Z*-styryl telluride **20a** with CO and a stoichiometric amount of PdCl_2 under atmospheric pressure in methanol in the presence of triethylamine at 25 °C for 5 h, methyl *Z*-cinnamate **57** and methyl benzoate **59** were obtained in 96 and 30% yield, respectively.⁸⁸



When the binary catalyst $\text{PdCl}_2/\text{CuCl}_2$ is employed the vinyl tellurides **23a–d** react with carbon monoxide in a triethylamine-methanol system to form exclusively the *Z*-propenoates **60a–d** in 60–80% yield.⁸⁸

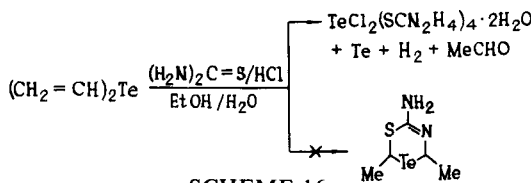


The authors^{87,88} believe that the carbonylation of vinyl tellurides involves the initial formation of the monomeric and dimeric complexes $[(\text{PhCH}=\text{CH})\text{PhTe}]_2\text{PdCl}_2$ and $[(\text{PhCH}=\text{CH})\text{PhTePdCl}_2]_2$, respectively.

III.10. Reaction of Divinyl Telluride with Thiourea

It is known¹¹⁶ that divinyl sulfide with thiourea in the presence of equimolar amounts of acids, form *2H*,*6H*-2,6-dimethyl-4-amino-1,3,5-dithiazine as the corresponding salts in 70–90% yield.

With divinyl telluride, however, cycloaddition with isothiuronium salts is not observed in the given example with hydrochloric acid; instead, cleavage of the Te–C bond to afford acetaldehyde and tellurium-thiourea complexes takes place (Scheme 16).¹¹⁷



SCHEME 16

Table 6. Observed Bands* and Proposed Assignment of the Vibrational Spectrum of Methyl Vinyl Telluride¹²³

IR (liquid, cm ⁻¹)	Raman (liquid, cm ⁻¹)	$\nu_{\text{calc.}}$, cm ⁻¹	Assignment
3061 m		3065	$\nu_{\text{as}}(=\text{CH}_2)$
3015 m sh		3013	$\nu(=\text{CH})$
3004 m		3000	$\nu_{\text{s}}(=\text{CH}_2)$
2982 m		2987	$\nu'(\text{CH}_3)$
		2986	$\nu''(\text{CH}_3)$
2921 s		2920	$\nu_{\text{s}}(\text{CH}_3)$
1574 v s	1576 v s	1573	$\nu(\text{C}=\text{C})$
1420 m sh		1415	$\delta'_{\text{as}}(\text{CH}_3)$
1414 m		1414	$\delta''_{\text{as}}(\text{CH}_3)$
1375 s	1374 m	1372	$\delta_{\text{s}}(=\text{CH}_2)$
1240 s	1240 m	1248	$\delta(=\text{CH}), \delta_{\text{as}}(=\text{CH}_2)$
1214 s		1217	$\delta_{\text{s}}(\text{CH}_3)$
987 m		994	$\delta_{\text{as}}(=\text{CH}_2), \delta(=\text{CH})$
964 s		962	$\tau(=\text{CH}_2), \omega(\text{C}=\text{C}, \text{TeCH})$
892 s		895	$\omega(\text{C}=\text{C}, \text{CH}_2)$
834 m		833	$\rho(\text{CH}_3)$
		830	$\rho(\text{CH}_3)$
	527**	525	$\nu_{\text{as}}(\text{CTeC})$
519 s	521**	515	$\omega(\text{C}=\text{C}, \text{TeCH}), \tau(=\text{CH}_2)$
	512**	513	$\nu_{\text{s}}(\text{CTeC})$
330 w	330 w	323	$\delta(\text{TeCC}, \text{CTeC})$
305 w	310 w		$\delta(\text{TeCC}, \text{CTeC})$
			other conformer
		216	$\tau(\text{CH}_3)$
	180 w	181	$\delta(\text{CTeC}, \text{TeCC})$
		128	τ_{skel}

*Abbreviations used: s - strong, m - medium, w - weak, v s - very strong, sh - shoulder, s sh - strong shoulder, m sh - medium shoulder.

** CS₂ solution.

When a mixture of these complexes is dissolved in a saturated aqueous solution of thiourea, yellow crystals, m.p. 175 °C, precipitate. The elemental analysis and IR spectroscopy provide evidence that the crystals isolated are a complex, TeCl₂(SCN₂H₄)₄·2 H₂O. Its structure and properties have been reported in.¹¹⁸⁻¹²⁰

The characteristic data of vinyl tellurides are listed in Tables 6-13.

IV. PHYSICOCHEMICAL AND SPECTRAL CHARACTERISTICS OF VINYL ORGANYL TELLURIDES

Data concerning the physicochemical characteristics of vinyl organyl tellurides have been mostly reported in publications by Trofimov *et al.*¹²¹⁻¹²⁵

The reactivity of vinyl organyl tellurides is determined, to a considerable extent, by interaction of the olefinic π -electrons with the lone electron pair of the heteroatom. This interaction is responsible for the electronic and conformational structure of the com-

pounds under consideration. The close relationship between electron distribution and conformation in vinyl tellurides leads to unusual manifestations in their physical properties which are very interesting, not only in a purely analytical aspect, but also of great importance for the chemistry of organic tellurides.

IV.1. Vibrational Spectra of Methyl Vinyl Telluride

Analysis of the vibrational spectra of methyl vinyl chalcogenides suggests the presence of rotational isomers and makes it possible to estimate the torsional angles between the CXC and XCC planes as well as to bring out more clearly the character of the interactions within the molecules. In the case of methyl vinyl sulfide an assignment of the characteristic absorption bands has been made and the conformational isomerism has been studied.¹²⁶⁻¹²⁸ The planar *cis*-conformation has been shown to be the most stable in this molecule.¹²⁶⁻¹³⁰ Quantum-chemical *ab-initio* examination of the structure of methyl vinyl sulfide with full optimization of the geometrical parameters indicates a conformation with a torsional angle of 120–130° to be possible for the second, less stable form.¹³¹ An analogous conclusion has been drawn in the investigation of the temperature dependence of the shape of the double-bond stretching band in the IR spectra of vinyl sulfides.¹²⁹ An assignment of the absorption bands in the Raman and IR spectra of methyl vinyl selenide and methyl vinyl telluride (on the basis of normal vibration calculations) has been suggested.^{123,132} The double-bond stretching band of methyl vinyl selenide in heptane displays a doublet structure with absorption maxima at 1582 and 1585 cm⁻¹.^{132,133} This change in the stretching band shape is analogous to the behavior of the corresponding band in the IR spectrum of methyl vinyl sulfide.¹²⁹ The high-frequency component of the νC=C doublet at 1585 cm⁻¹, which weakens considerably with decreasing temperature, has been assigned to the second, less stable conformation, and that at 1582 cm⁻¹ to the vibration of the planar *s-cis* form of methyl vinyl selenide.

The calculated and observed methyl vinyl telluride frequencies are presented in Table 6.¹²³ The calculated model of the stable methyl vinyl telluride conformer contains a plane of symmetry with *cis*-orientation of the methyl and the vinyl group.

In the analysis of the bands in the 500–600 cm⁻¹ region, there should be, according to the calculations, bands of non-planar deformational to τ(CH₂) vibrations of the vinyl group and of symmetric and antisymmetric CTeC vibrations. In the Raman and IR spectra of neat liquid methyl vinyl telluride at 25 °C only one band with maxima at 530 and 519 cm⁻¹, respectively, is observed. However, in the IR spectrum of methyl vinyl telluride solution in CS₂ at –80 °C this band consists of three components at 512, 521, and 527 cm⁻¹.¹²³

The experimental and calculated methyl vinyl telluride frequencies for various torsional angles between the CTeC and TeCC planes with a 30° tracing (Θ = 0° corresponds to a *cis*-orientation) have been compared. The calculated deformational vibration at 323 cm⁻¹ (Θ = 0°, δ(TeCC) and δ(CTeC)) turned out to be susceptible to variations in Θ with retention of the force constant matrix. The frequency shows its minimum at Θ = 120° (by 16 cm⁻¹ lower than that for the *cis*-conformation). Together with the band at 330 cm⁻¹ a weak band at 305 cm⁻¹ is observed in the IR spectrum and at 310 cm⁻¹ in the Raman spectrum, which seems to correspond to the less stable conformer. Thus, on the basis of normal vibration calculations an assignment of the bands in

the Raman and IR spectra of methyl vinyl telluride has been made. According to this analysis of the vibrational spectra, methyl vinyl telluride exists as a mixture of two conformers. The $\delta(\text{TeCC})$ and $\delta(\text{CTeC})$ vibrations are sensitive to changes in the torsional angle.¹²³

IV.2. Rotational Isomerism of Methyl Vinyl Telluride

Examination of the rotational isomerism of methyl vinyl telluride is of interest for both the determination of the molecular structure of stable conformers and for the evaluation of the interaction between the lone electron pairs of the Te atom and the π -electrons of the double bond. In the general problem of the investigation of molecular movements of large amplitude^{134,135} the rotational isomerism of the vinyl chalcogenides ($\text{CH}_2=\text{CHXR}$ with $\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$; $\text{R} =$ organic substituent) is of great importance.^{55,124,126} The structure of the energetically favored methyl vinyl telluride rotamer has been proven by IR spectroscopy on the basis of the determination of the isomerization enthalpy and entropy.¹²⁴

For a methyl vinyl telluride analog, methyl vinyl sulfide, the molecular structure has been determined by means of gas electronography and microwave spectroscopy.¹²⁶ The most complete information concerning the rotational isomerism of methyl vinyl sulfide was obtained by analysis of the temperature variations of the contour of the double-bond stretching band in the IR spectrum of methyl vinyl sulfide solutions in heptane.¹²⁹ The methyl vinyl sulfide molecule can exist in several rotameric forms, the planar *s-cis* conformer having the lowest energy.

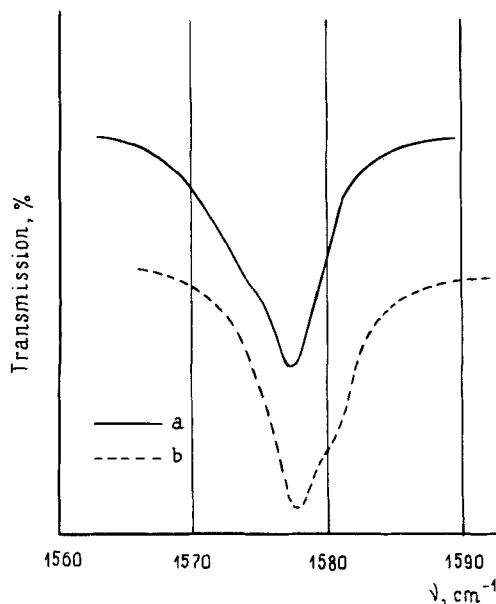


Figure 1. C=C Stretching mode in the IR spectra of methyl vinyl telluride at -58°C (a) and methyl vinyl sulfide at 19°C (b) (in heptane).¹²⁴

Table 7. Temperature Dependence of the Integral Intensities of the Doublet Components of the Double-Bond Stretching Vibration Band in the IR spectrum of Methyl Vinyl Telluride¹²⁴

Temperature, °C	Integral intensity, 1/mole cm ²	
	I ₁	I ₂
-78	4.39	3.23
-58	2.91	3.64
-30	1.74	4.18
-10	1.22	4.24
0	1.08	4.13
10	0.94	4.32
19	0.74	4.23

In the IR spectra of methyl vinyl telluride solutions in heptane there is also a doublet in the region of double-bond stretching vibrations, 1570–1580 cm⁻¹.¹²⁴ A detailed analysis of the dependence of the shape of this doublet within the temperature range +19 to -78 °C has been carried out. The experimentally obtained band contours in the region studied were approximated by a generalized Lorentz-Gaussian equation.¹²⁴

The contours of the band of methyl vinyl telluride solutions in heptane at -58 °C and of methyl vinyl sulfide solutions at 19 °C are presented in Figure 1. The methyl vinyl telluride doublet components lie at 1572 ± 0.3 and 1577 ± 0.3 cm⁻¹. The difference in the position of the bands of the double-bond stretching vibrations of this compound as well as that for methyl vinyl sulfide, is negligible (5 cm⁻¹). With increasing temperature the integral intensity of the low-frequency band for the two compounds decreases, whereas that of the high-frequency band increases (Table 7). The difference in the frequencies of the doublet components for the temperature range studied is on the average about 5.1 cm⁻¹ (methyl vinyl telluride) and 5.0 cm⁻¹ (methyl vinyl sulfide).

The above data taken in total provide evidence for the assumption that in the methyl vinyl telluride spectrum, like that of methyl vinyl sulfide, the doublet shape of the double-bond stretching vibration band is caused by the presence of several rotamers in the solution. This is confirmed by a mutual linear relationship of the integral intensities of the doublet components.¹²⁴

Figure 2 shows the dependence of the logarithm of the integral intensity ratio (ln I₁/I₂) for the doublet components for methyl vinyl telluride on the 1/RT value (R = universal gas constant, T = absolute temperature). A clearly defined linearity of this dependence is observed. With methyl vinyl sulfide there is no linearity of this kind due to the lack of constancy of the extinction ratio of two methyl vinyl sulfide rotamers, which varies from 1.10–1.35 in the temperature range studied (from -83 to 59 °C). Consideration of the temperature dependence of the extinction ratio of the rotamers, based on a spectral investigation of *t*-butyl vinyl sulfide, shows a linear dependence of the logarithm of the concentration ratio of the methyl vinyl sulfide rotamers on the inverse absolute temperature (Figure 2). The linear dependence of the logarithm of the integral intensity ratio in the case of methyl vinyl telluride is likely related to the fact that in the methyl vinyl telluride molecule the double-bond stretching vibration is localized at the vinyl group to an even greater extent than in methyl vinyl sulfide. This allows the differences in the extinctions of the methyl vinyl telluride rotamers to be neglected and the integral intensity ratio to be considered identical to the ratio of rotamer mole fractions. Under

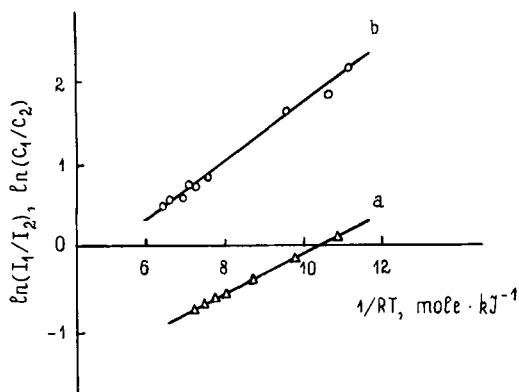


Figure 2. Temperature dependence of the integral intensity ratio for methyl vinyl telluride (a) and the concentration ratio of rotamers for methyl vinyl sulfide (b).¹²⁴

these conditions the differences in the enthalpies, ΔH , and entropies, ΔS , of the methyl vinyl telluride rotamers have been calculated: $\Delta H = 4.60 \pm 0.2 \text{ kJ/mole}$, $\Delta S = -11.1 \pm 0.3 \text{ kJ/K} \cdot \text{mole}$ ¹²⁴ (for methyl vinyl sulfide $\Delta H = 6.1 \pm 0.2 \text{ kJ/mole}$, $\Delta S = -7.3 \pm 0.3 \text{ kJ/K} \cdot \text{mole}$ ¹²⁹). The ΔH values reflect the regular lowering of the rotation barrier about the $C_{sp^2}\text{-X}$ bond in going from S to Te. As with methyl vinyl sulfide, the high-frequency component of the doublet in the spectrum of methyl vinyl telluride seems to correspond to several rotamers having a large amplitude motion of torsional vibration or a free rotation state. The fairly high ΔS value indicates the presence of a large number of steady-state energy levels corresponding to a high-frequency absorption band.¹²⁴

The above data indicate an analogy in the conformational structures of methyl vinyl telluride and methyl vinyl sulfide. It is quite logical to suggest the low-frequency component of the doublet in the spectrum of methyl vinyl telluride (as with methyl vinyl sulfide) to belong to the planar *s-cis* form. This is also supported by comparison of the component half-widths of the doublet. The half-width of the low-frequency component in the spectrum of methyl vinyl telluride is on the average 8.3 cm^{-1} , *i.e.* nearly the same as that in the spectrum of methyl vinyl sulfide (7.5 cm^{-1}). The half-widths of the high-frequency component of the doublet differ to a considerably larger extent (5.5 and 10.2 cm^{-1} for methyl vinyl telluride and sulfide, respectively). The lower value for methyl vinyl telluride means that in this case again the high-frequency component of the doublet is related to the steady states of the same type. Evidently, the contribution from the p,π -interaction which stabilizes the planar conformations, is smaller in methyl vinyl telluride and the barrier separating the two *gauche* forms is higher in methyl vinyl telluride than in methyl vinyl sulfide.

The smaller half-width of the high-frequency component of the doublet in the spectrum of methyl vinyl telluride compared with that of methyl vinyl sulfide, is in good agreement with the difference between their isomerization entropies. For methyl vinyl sulfide, the rotamer concentration ratio 1:5.7 at $T \rightarrow \infty$ ($\Delta S = -7.3 \pm 0.3 \text{ kJ/K} \cdot \text{mole}$) is caused by a great number of steady states of the rotamer corresponding to the high-frequency component of the doublet.^{121,124} The twofold increase of the steady

states due to the existence of two *gauche* conformers does not manifest itself to any considerable extent. For methyl vinyl telluride the isomerization entropy value ($-11.1 \pm 0.3 \text{ K} \cdot \text{mole}$) means that at $T \rightarrow \infty$ the rotamer concentration ratio approaches 1:14, i.e., the number of energy levels of the rotamer responsible for the high-frequency component of the doublet is even greater than in methyl vinyl sulfide. Thus, the suggestion of a decreased contribution of p, π -interaction to the barrier of internal rotation of the vinyl group readily explains the increased number of steady states in terms of doubling of the energy levels corresponding to two *gauche* conformations. This may contribute to the entropy of isomerization the additional amount $R \ln 1/2 = -2.9 \text{ kJ/K} \cdot \text{mole}$ which is in good agreement with the difference between the entropies of isomerization of methyl vinyl telluride and sulfide, $-3.8 \text{ kJ/K} \cdot \text{mole}$.¹²⁴

An alternative hypothesis suggesting a lower stability of the *s-cis* form of methyl vinyl telluride compared with the rotamer which corresponds to the low-frequency doublet component whose intensity decreases with increasing temperature, encounters much difficulty in the interpretation of the spectral behavior of methyl vinyl telluride. In this case, the number of steady states for the energetically disadvantageous non-planar conformer should be doubled, which would inevitably lead to a smaller ΔS for methyl vinyl telluride than for methyl vinyl sulfide.

It should be noted that the high isotropic polarizability of methyl vinyl telluride makes it highly improbable that the problem of conformational isomerism can be solved by measurement of the degree of line depolarization in the Raman spectrum. Considerable difficulties are also encountered in solving this problem by other traditional methods since the differences between the enthalpies of the methyl vinyl telluride rotamers are very small and due to this fact all possible rotamer forms occur in the accessible temperature range, an equal rotamer content being observed at -68°C . Some additional difficulties are due to the expected lowering of the barrier which separates the stable methyl vinyl telluride rotamers, as compared to methyl vinyl sulfide, and with the increase of the torsional vibration amplitudes.

In order to solve another question of p, π -interaction in methyl vinyl telluride a calculation of the conformational energy of methyl vinyl telluride and methyl vinyl

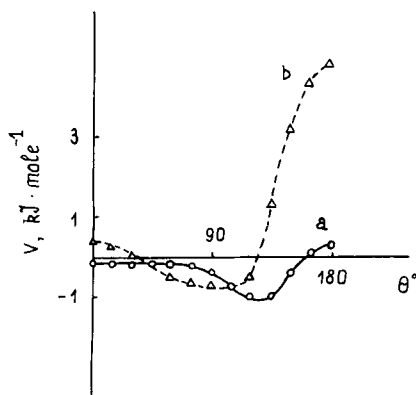


Figure 3. Dependence of the steric strain energy (V) in methyl vinyl telluride (a) and methyl vinyl sulfide (b) upon the angle of vinyl internal rotation. In the planar *s-trans* form $\Theta = 0^\circ$.¹²⁴

sulfide as the sum of the energy of the interaction of atoms separated by more than two bonds and the energy of valence angle strain has been carried out.¹³⁷ The dependence of the conformational energy on the angle of rotation around the C_{sp^2} -Te and the C_{sp^2} -S bond is presented in Figure 3.¹²⁴ It follows from Figure 3 that in the *s-cis* form of methyl vinyl telluride the steric strain is negligible. The difference between the strain energies of the planar *s-cis* and *s-trans* rotamers is 0.7 kJ/mole (4.4 kJ/mole for methyl vinyl sulfide). The planar *s-cis* form of methyl vinyl telluride is stabilized by electronic interactions of the same type as those in methyl vinyl sulfide, *i.e.* due to p,π -conjugation. The energy of the latter is 5.3 kJ/mole, which is by a factor of two lower than in the case of methyl vinyl sulfide (10.4 kJ/mole from analogous calculations).

Thus, in the IR spectrum of methyl vinyl telluride solutions in heptane the doublet shape of the stretching band is defined by rotational isomerism. By analysis of the temperature dependence of the doublet shape the low-frequency component of the doublet has been assigned to the *s-cis* rotamer.^{121,123,124}

IV.3. Divinyl Telluride

The analysis of the vibrational spectra of divinyl chalcogenides is of considerable interest for the examination of the rotational isomerism of these molecules, which, in some cases, is needed for the understanding of their chemical behavior.

The analysis of the rotational structure and shape of the band at 837 cm^{-1} in the IR spectrum of divinyl ether provides evidence for the existence of the planar *cis,trans* conformation of C_s symmetry, the non-planar form of C_1 symmetry being the other stable conformation.¹³⁸ Thus, in the IR spectrum, one should expect the appearance of bands common to both planar and non-planar conformations of divinyl ether. In the planar *cis,trans* form the double bonds are non-equivalent due to lack of an axis of symmetry,¹³⁸ which should lead to splitting of the corresponding bands. In fact, the low-frequency band in the region of double-bond stretching vibration is split into two maxima (1619 and 1623 cm^{-1}).¹³⁹ To the non-planar conformer may be assigned a band at 1641 cm^{-1} , whereas a weak absorption at 1672 cm^{-1} is most likely to be due to Fermi resonance with participation of the $\omega(\text{CH}_2=)$ and one of the $\nu(\text{C}=\text{C})$ vibrations.¹³⁹ Divinyl ether in solution exists as a mixture of two conformers with an energy difference of 2.5 kJ/mole.¹⁴⁰ Analysis of the relative intensities and the polarizability of the lines in the IR and Raman spectra allows the conclusion to be drawn that the planar *trans-trans* conformer is the most stable form, the other conformer containing no elements of symmetry.

Spectral studies of divinyl sulfide are limited and apparently unavailable for divinyl selenide and divinyl telluride. The IR spectra of divinyl sulfide in the liquid state and in solution show two conformers whereas in the crystalline state a *trans-trans* conformation is adopted.¹⁴¹ The Raman and IR spectra of divinyl sulfide in the liquid and solid state have also been examined.¹⁴² For a rotamer existing in the solid state a conformation of C_2 symmetry is assumed, the second rotamer possessing no elements of symmetry. There are two conformers in the liquid state as well, with a negligible energy difference between them.

Trofimov *et al.*¹²⁵ have obtained vibrational spectra of divinyl telluride and, on the basis of calculations of the normal vibrations in the valent force approximation, suggested

Table 8. Observed Frequencies and Vibrational Assignments for Divinyl Telluride

liquid	Infrared (cm ⁻¹)		Raman (cm ⁻¹) liquid	Assignment
	solution (CCl ₄)	solution (CS ₂)		
3062 m	3066	3062	3062	$\nu_{as}(=CH_2)$
3013 m	3016	3013	3014	$\nu_{as}(=CH)$
2983 s	2986	2983	2984	$\nu_s(=CH)$
2925 w	2928	2924	2928	
1578 s sh	1578 sh		1578	
1574 v s	1574			$\nu(C=C)$
1376 s	1376	1376	1376	$\delta_{as}(=CH_2)$
1238 s sh	1240	1239	1239	$\rho(=CH)$
1228 s	1228	1226	1222	$\rho(=CH)$
	1224 sh	1229		
984 m sh	985 sh	964 sh		
962 s	961	957		$\tau(=CH_2), \omega(C=C, TeCH)$
902 s	902	895		$\omega(C=C, CH_2)$
547 m	540		544	$\nu_{as}(CTeC)$
530 m sh	530 sh		534	$\omega(C=C, TeCH),$ $\tau(=CH_2)$
510 m	510		513	$\nu_s(CTeC)$
			320	$\delta(TeCC)$
			288	δ_{skel}

an assignment of the absorption bands in the IR and Raman spectra of this molecule. A planar *s-trans-trans* conformation has been adopted as a basic model of divinyl telluride. Measured frequencies and their assignments are presented in Table 8.

Along with fairly well-identified vibrations in the IR spectrum of the telluride there are broadened bands for which the above assignment is less probable. A considerable broadening of the band corresponding to non-planar vibrations of the vinyl group CH₂ fragment is observed in the 900–980 cm⁻¹ region. This broadening like that for methyl vinyl chalcogenides, is related to rotational isomerism.^{123,126,132} Rotational isomerism may also be responsible for the splitting of the band due to deformational vibration of the CH bond in the 1220–1245 cm⁻¹ region.

One of the features of the IR spectrum of divinyl telluride, as well as that of methyl vinyl telluride,^{121,123,124} is absorption multiplicity in the double-bond absorption region, which appears due to conformational inhomogeneity of these molecules. Comparison of the vibrational spectra of the methyl vinyl chalcogenides and those of their divinyl derivatives allows the conclusion to be drawn that the principal spectral features of these molecules are those stipulated by the changes in the geometrical parameters of the CXC fragments (X = S, Se, Te) and the differences in the atomic masses of S, Se, and Te.

IV.4. Photoelectron Spectra of Vinyl Tellurides

The photoelectron (PE) spectra of vinyl tellurides have been studied in comparison with those of dialkyl tellurides by Trofimov *et al.*¹²²

In the PE spectra of dialkyl tellurides three absorption bands are observed in the 7.5–11.6 eV region (Table 9, Figure 4). According to,¹⁴³ the low-energy band of dimethyl telluride corresponds to electron loss from the molecular orbital (MO) the main contribution to which is made by the lone electron pairs of the tellurium atom. The remaining

Table 9. Vertical Ionization Energies (eV) of Organyl Tellurides, R-Te-R'

R	R'	Ionization energy values (eV)			
		$\pi_{(p_{Te})}$	σ	$\pi_{(C=C)}$	σ
Me	Me ^a	7.89	10.35		11.32
CH=CH ₂	Me	7.86	10.32	10.60	11.40
Et	Et	7.86	9.90		10.10
CH=CH ₂	Et	7.96	10.05	10.68	11.57
<i>n</i> -Bu	<i>n</i> -Bu	7.57	9.60		10.21
CH=CH ₂	<i>n</i> -Bu	7.70	9.77	10.52	10.52
CH=CH ₂	<i>i</i> -Pr	7.78	9.70	10.54	10.97
CH=CH ₂	CH=CH ₂	7.90	10.05	10.43	11.43
				11.03	

^aThe values for MeTeMe are taken from¹⁴³

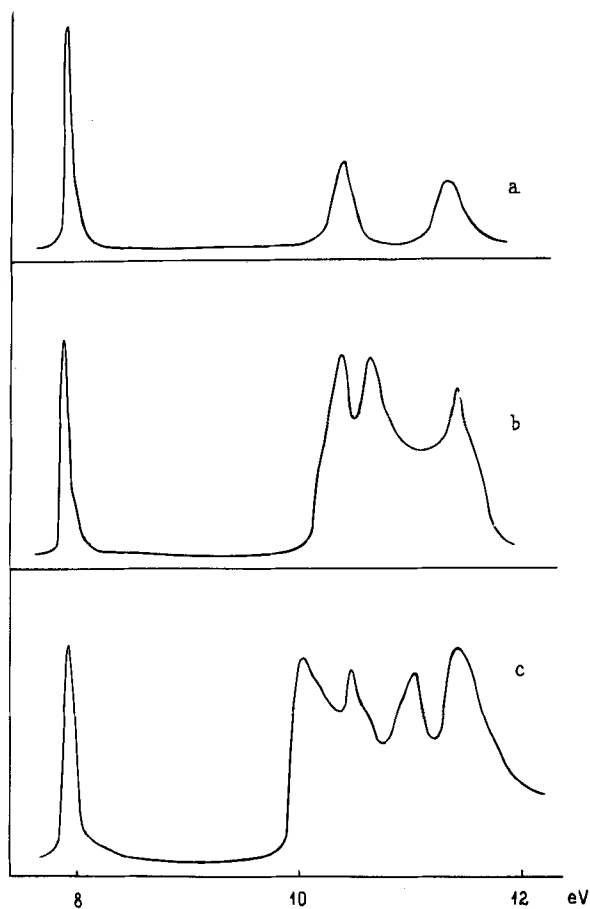


Figure 4. He(I) Photoelectron spectra of dimethyl telluride¹⁴⁴ (a), methyl vinyl telluride (b), and divinyl telluride (c).

two bands arise because of ionization from the σ -bond MO. With increasing size of the alkyl group, Me \rightarrow Et \rightarrow *n*-Bu, the expected shift of the PE bands towards the low-energy region takes place. The PE spectra of alkyl vinyl tellurides contain four fairly well-resolved bands (Table 9, Figure 4).

The spectrum of divinyl telluride shows five bands in this range (Figure 4). The low-energy band in the PE spectra of vinyl tellurides remains narrow and is slightly shifted towards the high-energy region with respect to the band in Et₂Te and (*n*-Bu)₂Te (~ 0.1 eV). In the spectrum of methyl vinyl telluride the band retains practically the same position. This suggests nearly the same nature of the first bands: they characterize an MO with the main contribution from the Te atom lone electron pair. From Figure 5 it is evident that the second and the fourth bands of alkyl vinyl tellurides are identical with those of dialkyl tellurides and correspond to the σ -MO. The third MO, with its energy in the 10.4–11.0 eV range, is a bonding combination of the ethylene group π -MO and the Te atom lone electron pair, the contribution from the latter being small. This is evidenced by a slight deviation of this π -MO from its position in the free ethylene molecule and by a small perturbation of the first ionization potential. Besides, a small gap between the π -MOs of divinyl telluride (Figure 5) may present another argument for the above statement. It should also be taken into account that the small effect of the second double bond in divinyl telluride is, evidently, due to unequal orientation of the planes of the vinyl group π -systems with respect to the Te atom lone electron pair. Thus, a comparative analysis of the absorption PE spectra of dialkyl and alkyl vinyl tellurides and of divinyl telluride allows not only a good understanding of the band nature, but also empiric band assignments, according to which the low-energy band is caused by the ionization of the MO with a predominant contribution from the Te atom lone electron pair, the second and the fourth bands correspond to σ -MOs and the third band arises from π -MOs (Figure 5).

IV.5. NMR Spectra

Due to the high sensitivity of the ¹³C screening to the charge distribution and conformational features of molecules, ¹³C chemical shifts, δ_C , provide a convenient parameter for the examination of the internal structure of compounds.

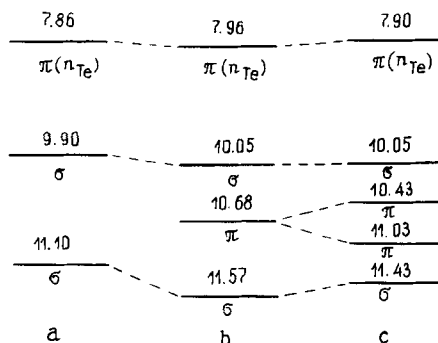
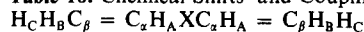


Figure 5. Correlation of the energy levels of Et₂Te (a), EtTeCH=CH₂ (b), and CH₂=CHTeCH=CH₂ (c).

Table 10. Chemical Shifts^a and Coupling Constants^b in Divinyl Chalcogenides¹⁴⁴

X	δ_{H_A}	δ_{H_B}	δ_{H_C}	δ_{C_α}	δ_{C_β}	δ_X
O	6.37	4.21	4.51	148.56	92.72	129
S	6.39	5.26	5.26	129.88	114.34	—
SO	6.77	5.81	5.92	140.98	119.38	—
SO ₂	6.73	6.13	6.29	136.94	129.63	—
Se	6.68	5.70	5.70	125.52	118.90	367.4
Te	7.05	6.30	5.84	109.00	127.90	529.9

X	$J_{\text{HH}}^{\text{cis}}$	$J_{\text{HH}}^{\text{trans}}$	$J_{\text{C}_\alpha\text{H}_\alpha}$	$J_{\text{C}_\beta\text{H}_\beta}$	$J_{\text{C}_\beta\text{H}_C}$
O	6.4	14.0	183.0	161.4	157.4
S	9.6	16.8	172.0	162.0	159.6
SO	9.7	16.5	175.0	164.3	162.4
SO ₂	9.4	16.2	183.2	166.4	165.8
Se	9.7	16.9	171.5	160.4	159.6
Te	10.2	17.6	170.0	158.8	160.1

^aChemical shifts (ppm) of ¹H (δ_{H}) and ¹³C (δ_{C}) were measured relative to TMS; ¹⁷O (δ_{O}) relative to H₂O, ⁷⁷Se (δ_{Se}) relative to Me₂Se, ¹²⁵Te (δ_{Te}) with respect to Me₂Te.

^bSSCC of C-X (J_{CX}) and H-X (J_{HX}) are as follows, Hz: $J_{\text{C}_\alpha\text{Se}} = 106.3$, $J_{\text{C}_\beta\text{Se}} = 7.8$, $J_{\text{C}_\alpha\text{Te}} = 285.2$, $J_{\text{C}_\beta\text{Te}} = 9.9$, $J_{\text{H}_A\text{Se}} = 22.0$, $J_{\text{H}_B\text{Se}} = 21.8$, $J_{\text{H}_C\text{Se}} = 9.7$, $J_{\text{H}_A\text{Te}} = 48.8$, $J_{\text{H}_B\text{Te}} = 41.8$, $J_{\text{H}_C\text{Te}} = 20.3$

In this section some general tendencies in the change of δ_{C} of divinyl chalcogenides (including divinyl telluride) (Table 10) are considered and compared with those of ethyl phenyl chalcogenides whose ¹³C NMR spectral parameters are given in Table 11.¹⁴⁴

In Figure 6 the dependences of the δ_{C_α} values in divinyl chalcogenides upon δ_{C_1} of the phenyl fragment and C_{CH_2} of the ethyl group in ethyl phenyl chalcogenides show the spectral parameters to change in a symbatic way.

$$\delta_{\text{C}_1} = -9.3(14.4) + 1.1(0.1)\delta_{\text{C}_\alpha}, r = 0.98, s_0 = 3.4, n = 6$$

$$\delta_{\text{C}_{\text{CH}_2}} = -184.7(19.7) + 1.7(0.2)\delta_{\text{C}_\alpha}, r = 0.98, s_0 = 4.6, n = 6$$

Table 11. Chemical Shifts^a of Ethyl Phenyl Chalcogenides¹⁴⁷

X	δ_{C_1}	δ_{C_o}	δ_{C_m}	δ_{C_p}	$\delta_{\text{C}_{\text{CH}_2}}$	$\delta_{\text{C}_{\text{CH}_3}}$	δ_X
O	159.27	114.54	129.37	120.44	63.02	14.85	78
S	136.88	128.59	128.46	125.27	27.19	14.85	—
SO	144.12	123.77	128.57	130.01	49.52	5.30	—
SO ₂	138.42	127.83	129.07	133.42	50.10	7.12	—
Se	130.37	132.29	128.62	126.24	20.91	15.42	327.0
Te	111.99	138.05	128.74	127.02	-0.42	16.23	548.6

^aThe δ_{C} values (ppm) are given with respect to TMS, δ_{O} with respect to H₂O, δ_{Se} with respect to Me₂Se, δ_{Te} with respect to Me₂Te. SSCC J_{CX} are as follows, Hz: $J_{\text{C}_1\text{Se}} = -104.9$, $J_{\text{C}_o\text{Se}} = 10.1$, $J_{\text{C}_{\text{CH}_2}\text{Se}} = -60.4$, $J_{\text{C}_{\text{CH}_3}\text{Se}} = 12.9$, $J_{\text{C}_1\text{Te}} = 204.6$, $J_{\text{C}_o\text{Te}} = 19.2$, $J_{\text{C}_{\text{CH}_2}\text{Te}} = 150.4$, $J_{\text{C}_{\text{CH}_3}\text{Te}} = 10.6$.

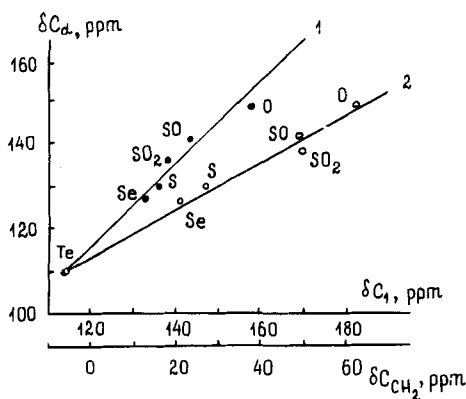


Figure 6. Correlation of the δ_{C_α} in divinyl chalcogenides and δ_{C_1} of the phenyl fragment (1) and $\delta_{C_{CH_2}}$ of the Et group (2) in ethyl phenyl chalcogenides.¹⁴⁴

r is the correlation coefficient, s_0 is the regression standard as a whole, in brackets the standard deviations of the coefficients are given; n is the number of observations.

The sensitivity of δ_C to variations of X is higher in $\delta_{C_{CH_2}}$ (Table 10, range of changes of $\delta_{C_{CH_2}}$, δ_{C_1} and δ_{C_2}).

Upon variation of X (O, S, Se and Te) the δ_{C_β} values in divinyl chalcogenides change in a symbatic manner with the δ_{C_o} values in ethyl phenyl chalcogenides (Figure 7).¹⁴⁴

$$\delta_{C_\beta} = -78.0(3.6) + 1.5(0.03) \delta_{C_o}, r = 0.9996, s_0 = .0.5, n = 4$$

The points corresponding to sulfoxides and sulfones deviate noticeably from a linear

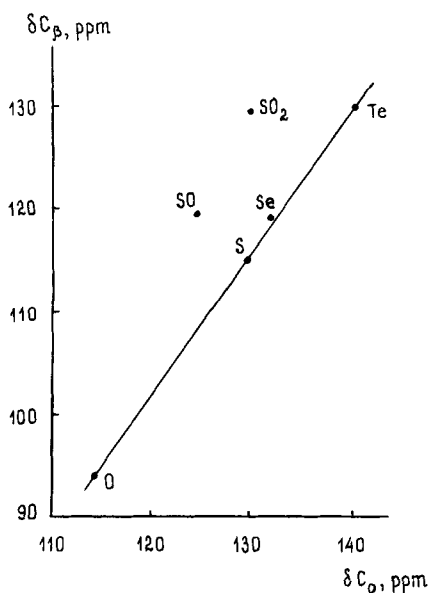


Figure 7. Correlation of the δ_{C_β} in divinyl chalcogenides and δ_{C_o} in ethyl phenyl chalcogenides.¹⁴⁴

Table 12. Resonance Constants σ_R^0 , Effective Group Electronegativity (EN) and Steric Factors (s) of the $XCH=CH_2$ and XCH_2CH_3 Fragments with $X = O, S, SO, SO_2, Se,$ or Te ¹⁴⁴

Fragment	σ_R^0	EN	s	Fragment	σ_R^0
OCH=CH ₂	-0.33	3.37	0.20	OCH ₂ CH ₃	-0.45
SCH=CH ₂	-0.11	2.61	0.13	SCH ₂ CH ₃	-0.16
SOCH=CH ₂	0.07	2.68	0.04	SOCH ₂ CH ₃	0.07
SO ₂ CH=CH ₂	0.21	2.75	0.05	SO ₂ CH ₂ CH ₃	0.22
SeCH=CH ₂	-0.09	2.59	0.13	SeCH ₂ CH ₃	-0.12
TeCH=CH ₂	-0.08	2.45	0.14	TeCH ₂ CH ₃	-0.09

dependence. The δ_{C_β} and δ_{C_0} values show no linear relationship with the chemical shifts of the alkyl carbons located in the β -position with respect to X ($\delta_{C_{CH_2}}$).

The authors believe¹⁴⁴ that in spite of the difference in both the structures of the fragments and the hybridization of the carbon atoms, the changes in the screening of the carbon atoms closest to X are mainly determined by equal or linearly related (non-orthogonal) factors. Such factors may also involve the electronegativity (EN) of X

$$\delta_{C_x} = 61.2(15.1) + 25.5(5.6)EN_x, r = 0.95, s_0 = 5.9, n = 4$$

$$\delta_{C_1} = 53.7(17.2) + 30.8(6.4)EN_x, r = 0.96, s_0 = 6.8, n = 4$$

$$\delta_{C_{CH_2}} = -84.3(14.8) + 42.7(5.5)EN_x, r = 0.98, s_0 = 5.8, n = 4$$

and the heteroatom size which can be estimated from the covalent radius values (r_{cov} , Å): O (0.66), S (1.04), Se (1.17), Te (1.37).¹⁴⁵

$$\delta_{C_x} = 185.2(6.4) - 53.7(5.9)r_{cov}, r = 0.99, s_0 = 3.0, n = 4$$

$$\delta_{C_1} = 203.2(6.2) - 64.7(5.8)r_{cov}, r = 0.99, s_0 = 2.9, n = 4$$

$$\delta_{C_{CH_2}} = 120.7(5.6) - 87.8(5.1)r_{cov}, r = 0.99, s_0 = 2.7, n = 4$$

The δ_{C_β} values in monosubstituted ethylenes are related to the π -charge on this atom.¹⁴⁶ The resonance effect of the $XCH=CH_2$ groups: is expressed by the σ_R^0 constant whose values can be determined from the ¹³C NMR spectra of monosubstituted benzenes.¹⁴⁴ By use of the ¹³C spectral parameters of the previously examined VIA Group element phenyl vinyl ($PhXCH=CH_2$) and ethyl phenyl derivatives (see Table 11)¹⁴⁷ it was possible to evaluate the resonance constants σ_R^0 of the $XCH=CH_2$ and XCH_2CH_3 fragments with $X = O, S, SO, SO_2, Se,$ or Te (Table 12, values σ_R^0).¹⁴⁴ It is seen that the σ_R^0 values for the $XCH=CH_2$ and XCH_2CH_3 groups differ much for the ethers ($\Delta = 0.12$) and to a smaller extent for the sulfides, selenides and tellurides ($\Delta = 0.05, 0.03,$ and $0.01,$ respectively). The decrease in the resonance effect of $XCH=CH_2$ groups compared with XCH_2CH_3 groups is connected with competing p,π -conjugation of the heteroatoms X with the double bond and levels out as this interaction becomes weaker. The positive values for $X = SO$ and SO_2 indicate a predominantly π -acceptor character of the interaction of these groups with an unsaturated moiety, the strength of this interaction being largely independent of the character of the other substituent.¹⁴⁴

The screening of the H_A atoms (Table 10, δ_{H_A}) in the compounds studied above is higher than in ethylene (5.25 ppm). The δ_{H_A} values do not correlate with the corresponding δ_{C_x} values. However, it can be seen that when X varies in the series O, S, Se, Te the H values increase whereas the δ_{C_x} values decrease.

The proton chemical shifts at the C_β atom (Table 10, δ_{H_B} and δ_{H_C}) correlate well in all the compounds studied.

$$\delta_{H_B} = -0.9(1.1) + 1.2(0.2) \delta_{H_C}, r = 0.95, s_0 = 0.3, n = 6$$

There are correlations with the δ_{C_β} values as well

$$\delta_{C_\beta} = 20.6(7.9) + 17.3(1.4) \delta_{H_B}, r = 0.99, s_0 = 2.4, n = 6$$

$$\delta_{C_\beta} = 3.4(17.9) + 20.4(3.1) \delta_{H_C}, r = 0.96, s_0 = 4.4, n = 6$$

In substituted ethylenes the dependence of the vicinal coupling constants (Table 10, J_{HH}^{cis} and J_{HH}^{trans}) upon the configuration and the effect of the substituents permits these parameters to be used for the interpretation of various aspects of the electronic structure of vinyl compounds. Thus, the J_{HH}^{cis} and J_{HH}^{trans} values are linearly related with the EN of the substituents, and empirical relations correlating these values have been found.^{148,149} Making use of the equation suggested in,¹⁴⁹

$$J_{HH}^{trans} = \frac{39.3}{2.5 + \sum_{i=1}^2 \Delta EN} + 3.3$$

$$J_{HH}^{cis} = 11.7 \left[1 - 0.33 \left(\sum_{i=1}^2 \Delta EN + s \right) \right]$$

[ΔEN is the difference between the EN values for hydrogen (2.20) and the substituent] the authors calculated the EN values of the $XCH=CH_2$ moieties and the s factors which allow evaluation of the relative orientation and steric interaction of the substituents (see Table 12).¹⁴⁴

As seen from Table 12, the effective EN of the fragments $XCH=CH_2$ decreases in the series $O > SO_2 > SO > Se > Te$ and the EN values are close to the corresponding EN_s of the elements according to Pauling: O (3.5), S (2.5), Se (2.4), and Te (2.1).¹⁵⁰ According to,¹⁴⁹ when $s = 0$, there are no steric interactions between the substituents, when $s > 0$ there appear some effects caused by the fact that the substituent is positioned far from the $C=C$ bond, and when $s < 0$ the substituent is approaching the $C=C$ bond. Evidently, the two vinyl fragments in the divinyl chalcogenides are most remote from each other in the *trans-trans* conformation. Therefore, the high factor s (0.20) in divinyl ether may be regarded as an argument for the predominance of the *trans-trans* conformer which is in agreement with the conclusions reported in,⁵⁵ but contradicts data^{151,152} according to which the non-planar *cis-trans* conformer is the most favored. The decrease in the s values upon going from ethers to sulfides, selenides, and tellurides seems to correspond to an increase in the conformational inhomogeneity in this series whereas the s values for divinyl sulfoxide and sulfone being close to zero indicate the *trans-trans* conformer not to be the dominating form in these compounds.¹⁴⁴

There are some data implying that use can be made of J_{HH}^{cis} and J_{HH}^{trans} for evaluating the length of the C_{sp^2} -substituent bond.¹⁵³ Calculations by means of correlations suggested in,¹⁵⁴ gave the following lengths for the C_{sp^2} -X bonds in divinyl chalcogenides, (Å): 1.34 (X = O), 1.79 (X = S), 1.92 (X = Se) and 2.10 (X = Te); although tentative, these values properly outline a tendency towards lengthening (and, consequently, decreasing order) of this bond in the series with X varying from oxygen to tellurium.¹⁴⁴

Table 13. Vinyl tellurides

Compound	Formula	Structure	Yield, %	B.p., °C (mm), m.p., °C	Spectra	References
7a	C ₃ H ₆ Te	CH ₂ =CHTeMe	30 ⁵⁰	115–116 (720) ⁵⁰	¹ H, ¹³ C NMR, ⁵⁰ IR, ⁵⁰ UV ⁵⁰	50, 68, 69, 71, 99
1	C ₄ H ₆ Te	(CH ₂ =CH) ₂ Te	94 ⁵¹	131–132 (720) ⁵¹	¹ H, ¹³ C NMR, ⁵¹ IR, ⁵¹ UV ¹⁵⁴	44–56, 60–62, 67, 70, 111, 112, 154, 155
33a	C ₄ H ₆ Te ₂	(CH ₂ =CHTe) ₂	67 ⁴¹ 70 ⁹⁸	Oil	¹ H NMR, ^{41,42} IR ⁴²	41, 42, 98
7b	C ₄ H ₈ Te	CH ₂ =CHTeEt	69 ⁵⁰	138 (720) ⁵⁰	¹ H, ¹³ C NMR, ⁵⁰ IR, ⁵⁰ UV ⁵⁰	50, 70, 71, 99
31	C ₅ H ₉ NSTe	CH ₂ =CHTeC(=S)NMe ₂	72	25	¹ H NMR, IR	97
7c	C ₅ H ₁₀ Te	CH ₂ =CHTePr- <i>n</i>	68 ⁷¹	60–62 (10) ⁵⁰	¹ H NMR, ⁵⁰ IR, ⁵⁰ UV ⁵⁰	50, 70, 71
7d	C ₅ H ₁₀ Te	CH ₂ =CHTePr- <i>i</i>	65 ⁵⁰	71–73 (17) ⁵⁰	¹ H NMR, ⁵⁰ IR, ⁵⁰ UV ⁵⁰	50, 70, 71
4	C ₆ H ₁₀ OTe	Z-CH ₂ =CHTeCH=CHCH(OH)Me	28 ⁵¹	96–97	¹ H NMR, ⁵¹ IR ⁵¹	48, 49, 51, 60–62, 67
5	C ₆ H ₁₀ OTe	CH ₂ =CHTeC(=CH ₂)CH(OH)Me	8 ⁵¹	(1) ⁵¹ 94–96 (1) ⁵¹	¹ H NMR ⁵¹	48, 51
33b	C ₆ H ₁₀ Te ₂	(MeCH=CHTe) ₂	61 ⁴¹	Oil	¹ H NMR, ^{41,42} IR ^{41,42}	41, 42
33c	C ₆ H ₁₀ Te ₂	[CH ₂ =C(Me)Te] ₂	64 ⁴¹ 68 ⁴²	Oil	¹ H NMR, ^{41,42} IR ^{41,42}	41, 42
7e	C ₆ H ₁₂ Te	CH ₃ =CHTeBu- <i>n</i>	82 ⁴¹	60 (4), ⁴¹	¹ H NMR, ^{41,50} IR, ^{41,50} UV ⁵⁰	41, 42, 50, 70, 71
51a	C ₈ H ₁₂ STe	CH ₂ =CHTeCH ₂ CH ₂ SEt	70 ⁵⁰	52–54 (3) ⁵⁰	UV ⁵⁰	48, 113
32a	C ₈ H ₁₄ Te	CH ₂ =C(Me)TeBu- <i>n</i>	35	83 (1)	¹ H NMR, IR	41
32b	C ₇ H ₁₄ Te	MeCH=CHTeBu- <i>n</i>	81	52 (2,75)	¹ H NMR, IR	41
51b	C ₈ H ₁₄ STe	CH ₂ =CHTeCH ₂ CH ₂ SPr- <i>n</i>	84	70 (3,75)	¹ H NMR, IR	48, 113
28a	C ₈ H ₇ BrTe	CH ₂ =CHTeC ₆ H ₄ Br-4	31	108 (4)	¹ H, ¹³ C, ¹²⁵ Te NMR	93
47	C ₈ H ₇ LiTe	CH ₂ =CLiTePh	High 50 ⁹⁵	130–132 (2)		94, 95

Table 13. Vinyl tellurides (continued)

1	2	3	4	5	6	7
10	C ₈ H ₈ Te	CH ₂ =CHTePh	20, ⁷² 34, ⁹² 70, ⁹³ 78 ⁹⁵ 20 ⁹⁶	97-98 (1), ⁹³ 43 (0.2) ⁹⁵ 80-86 (4) ⁹⁶	¹ H, ¹³ C NMR, ^{93,95,125} Te NMR, ⁹³ IR, ⁹⁵ MS ⁹⁵	72, 92-95
13	C ₈ H ₁₀ Te	(Z,Z)-CH ₂ =CHCH=CH) ₂ Te	25	117 (1)	¹ H, ¹³ C NMR, ⁸⁰ IR ⁴⁶	46, 80, 81 156
51c	C ₉ H ₁₆ STe	CH ₂ =CHTeCH ₂ CH ₂ SBu- <i>n</i>	92 ⁸⁵	Oil ⁸⁴	¹ H NMR, ⁸⁵ IR ⁸⁵	48, 113
20c	C ₉ H ₁₀ OTe	Z-HOCH ₂ CH=CHTePh	74 ⁴¹	83-84	¹ H, ¹³ C, ¹²⁵ Te NMR ⁹³	84, 85
28b	C ₉ H ₁₀ OTe	CH ₂ =CHTeC ₆ H ₄ OMe-4		(0.5), ⁴¹ 110-113 (1) ⁹⁵		41, 93
25d	C ₁₀ H ₁₂ Te	Z-PhCH=CHTeEt	8		¹ H NMR	91
29	C ₁₀ H ₁₂ O ₂ Te	CH ₂ =C(Me)TeC ₆ H ₄ OMe-4	86	68 (0.05)	¹ H NMR, IR	41
20b	C ₁₁ H ₁₂ O ₂ Te	Z-EtCO ₂ CH=CHTePh	100 ⁸⁵	Oil	¹ H, ¹³ C NMR, ⁸⁵ IR, ⁸⁵ MS ⁸⁵	84-86
41	C ₁₁ H ₁₄ Te	Z-PhCH=CHTeCHMe ₂	86		¹ H NMR	42
21b	C ₁₁ H ₁₄ OTe	Z-Me ₂ C(OH)CH=CHTePh	68	51-53	¹ H NMR	87
22b	C ₁₁ H ₁₄ OTe	CH ₂ =C(TePh)C(OH)Me ₂	9	51-53	¹ H NMR	87
49	C ₁₁ H ₁₆ SiTe	CH ₂ =C(TePh)SiMe ₃	80		¹ H NMR	94
25c	C ₁₁ H ₂₁ NOTe	Z-CH ₂ CH ₂ OCH ₂ CH ₂ NCH ₂ CH=CHTeBu- <i>n</i>	81	82 (1)	¹ H NMR, IR	41
15c	C ₁₂ H ₁₄ O ₂ Te	EtCO ₂ CH=CHTeC ₆ H ₄ Me-4	70	53-54	¹ H NMR, IR	83
25a	C ₁₂ H ₁₆ Te	Z-PhCH=CHTeBu- <i>n</i>	93	105 (5.10 ⁻³)	¹ H NMR, IR	41, 91
25f	C ₁₂ H ₁₆ Te	E-PhCH=CHTeBu- <i>n</i>	86	95 (5.10 ⁻¹)	¹ H NMR, IR	41
25b	C ₁₂ H ₂₂ O ₂ Te	Z-CH ₂ CH ₂ CH ₂ CH ₂ OCHOCH ₂ CH=CHTeBu- <i>n</i>	78	96 (0.2)	¹ H NMR, IR	41
23b	C ₁₄ H ₁₁ ClTe	(Z)-4-ClC ₆ H ₄ CH=CHTePh	86	72-74	¹ H, ¹³ C NMR	88
23d	C ₁₄ H ₁₁ ClTe	(Z)-2-ClC ₆ H ₄ CH=CHTePh	95	Oil	¹ H NMR	88
20a	C ₁₄ H ₁₂ Te	Z-PhCH=CHTePh	70, ⁸⁵ 95 ⁸⁶	43-44 ⁸⁴ (ethanol)	¹ H NMR, ^{84,85} IR, ⁸⁵ MS ⁸⁵	84-88, 115
27	C ₁₄ H ₁₂ Te	E-PhCH=CHTePh	34	Oil	¹ H NMR, IR, MS	87
23c	C ₁₄ H ₁₃ NTe	(Z)-3-NH ₂ C ₆ H ₄ CH=CHTePh	60	Oil	¹ H NMR, IR	88

Table 13. Vinyl tellurides (continued)

1	2	3	4	5	6	7
21a	C ₁₄ H ₂₀ Te	Z- <i>n</i> -C ₆ H ₁₃ CH=CHTePh	18		¹ H NMR	87
22a	C ₁₄ H ₂₀ Te	CH ₂ =C(TePh)C ₆ H ₁₃₋₇	7			87
24a	C ₁₅ H ₁₁ FO ₂ Te	3-FC ₆ H ₄ Te(Ph)C=CHCO ₂ H	90	158 (dec.)	¹ H NMR, IR	90
15b	C ₁₅ H ₁₂ FO ₂ Te	PhTe(Ph)C=CHCHO	88	94-95	IR	83
16a	C ₁₅ H ₁₂ O ₂ Te	PhTe(Ph)C=CHCO ₂ H	14	132-133	IR	83
23a	C ₁₅ H ₁₄ Te	(Z)-4-MeC ₆ H ₄ CH=CHTePh	74	54.5-55.5	¹ H NMR	88
23c	C ₁₅ H ₁₄ OTe	(Z)-4-MeOC ₆ H ₄ CH=CHTePh	72	60.5-62	¹ H NMR	88
26	C ₁₅ H ₁₄ OTe	(Z)-PhCH=CHTeC ₆ H ₄ OMe-4	63	68-69	¹ H NMR, IR	41
26a	C ₁₅ H ₁₄ OTe	<i>E</i> -PhCH=CHTeC ₆ H ₄ OMe-4	86	68-69	¹ H NMR, IR	41
48	C ₁₅ H ₁₄ OTe	CH ₂ =C(TePh)CH(OH)Ph	88			94
14d	C ₁₅ H ₂₀ O ₂ Te	MeCOCH=C(<i>n</i> -Bu)TeC ₆ H ₄ OMe-4	71	195-200 (1)	IR	82
38	C ₁₆ H ₁₂ Cl ₂ Te	(PhCCl=CH) ₂ Te	100	59-61		96
11	C ₁₆ H ₁₄ Te ₂	(Z, <i>Z</i> -PhCH=CH) ₂ Te	45, ⁷⁴ 41 ⁸⁶	46-47 ⁷⁵	¹ H NMR, ^{73,86} ¹³ C NMR, ⁸⁶ IR, ^{75,86} MS ⁷⁵	73-75, 78, 79, 86
12	C ₁₆ H ₁₄ Te ₂	(Z, <i>Z</i> -PhCH=CH) ₂ Te ₂	58, ⁴² 6 ^{78,79}	82 ⁷⁸	¹ H NMR, ⁷⁸ IR, ⁷⁸ MS ⁷⁸	41,42, 78, 79
15d	C ₁₆ H ₁₄ OTe	4-MeC ₆ H ₄ Te(Ph)C=CHCHO	76	93-94	IR	83
15c	C ₁₆ H ₁₄ O ₂ Te	4-MeOC ₆ H ₄ Te(Ph)C=CHCHO	68	86-87	IR	83
14b	C ₁₆ H ₁₄ O ₂ Te	4-MeOC ₆ H ₄ TeCH=CHCOPh	71	83-84	IR	82
24b	C ₁₆ H ₁₄ O ₂ Te	(Z)-3-MeC ₆ H ₄ Te(Ph)C=CHCO ₂ H	93	148-149.5	¹ H NMR, IR	90
24c	C ₁₆ H ₁₄ O ₂ Te	2-MeC ₆ H ₄ Te(Ph)C=CHCO ₂ H	68	193-196	¹ H NMR, IR	89
24d	C ₁₆ H ₁₄ O ₂ Te	4-MeC ₆ H ₄ Te(Ph)C=CHCO ₂ H	95	187-189	¹ H NMR, IR	89
24e	C ₁₆ H ₁₄ O ₂ Te	PhTe(Ph)C=CHCO ₂ Me	95	92-95	¹ H NMR, IR	89
24f	C ₁₆ H ₁₄ O ₃ Te	3-MeOC ₆ H ₄ Te(Ph)C=CHCO ₂ H	94	145-147	¹ H NMR, IR	90
24q	C ₁₆ H ₁₄ O ₃ Te	4-MeOC ₆ H ₄ Te(Ph)C=CHCO ₂ H	89	182-185	¹ H NMR, IR	89
24h	C ₁₇ H ₁₄ O ₃ Te	4-MeCOC ₆ H ₄ Te(Ph)C=CHCO ₂ H	93	188-192	¹ H NMR, IR	89
24i	C ₁₇ H ₁₅ FO ₂ Te	3-FC ₆ H ₄ Te(Ph)C=CHCO ₂ Et	60	81-84	¹ H NMR, IR	90
15f	C ₁₇ H ₁₆ O ₂ Te	PhTe(Ph)C=CHCO ₂ Et	81	92-93	IR	83
24j	C ₁₇ H ₁₆ O ₄ Te	3,5-(MeO) ₂ C ₆ H ₃ Te(Ph)C=CHCO ₂ H	96	174.5- 177.5	IR	90
30	C ₁₈ H ₁₄ Te	2-C ₁₀ H ₇ TeCH=CHPh				96
16b	C ₁₈ H ₁₆ O ₅ Te	2,4-(MeO) ₂ C ₆ H ₃ Te(CO ₂ H)C=CHCOPh	21	215-218	IR	83
24k	C ₁₈ H ₁₈ O ₂ Te	3-MeC ₆ H ₄ Te(Ph)C=CHCO ₂ Et	68	79-81	¹ H NMR, IR	90
24l	C ₁₈ H ₁₈ O ₂ Te	4-MeC ₆ H ₄ Te(Ph)C=CHCO ₂ Et	87	95-96.5	¹ H NMR, IR	89
24m	C ₁₈ H ₁₈ O ₃ Te	4-MeOC ₆ H ₄ Te(Ph)C=CHCO ₂ Et	71	100-102	¹ H NMR	89
24n	C ₁₈ H ₁₈ O ₃ Te	3-MeOC ₆ H ₄ Te(Ph)C=CHCO ₂ Et	98	57-58	¹ H NMR, IR	90

Table 13. Vinyl tellurides (continued)

1	2	3	4	5	6	7
24o	C ₁₉ H ₁₄ O ₇ Te	1-C ₁₀ H ₇ Te(Ph)C=CHCO ₂ H	90	205-208	¹ H NMR, IR	89
24p	C ₁₉ H ₁₈ O ₃ Te	4-MeCOC ₆ H ₄ Te(Ph)C=CHCO ₂ Et	77	66-66.5	¹ H NMR, IR	89
15g	C ₁₉ H ₂₀ O ₄ Te	2,4-(MeO) ₂ C ₆ H ₃ Te(Ph)C=CHCO ₂ Et	70	73-74	IR	83
24q	C ₁₉ H ₂₀ O ₄ Te	3,5-(MeO) ₂ C ₆ H ₃ Te(Ph)C=CHCO ₂ Et	86	81-82	¹ H NMR, IR	90
24r	C ₂₀ H ₁₆ O ₇ Te	1-C ₁₀ H ₇ Te(Ph)C=CHCO ₂ Me	84	129-133	¹ H NMR, IR	89
14c	C ₂₀ H ₂₂ O ₂ Te	4-MeOC ₆ H ₄ Te(n-Bu)C=CHCOPh	68	79-80	IR	82, 83
25c	C ₂₀ H ₃₂ Te	Z-PhCH=CHTeC ₁₂ H ₂₅ - <i>n</i>	80		¹ H NMR, IR	91
15a	C ₂₁ H ₁₆ O ₇ Te	PhTe(Ph)C=CHCOPh	86	118-119	IR	83
14a	C ₂₂ H ₁₈ O ₂ Te	4-MeOC ₆ H ₄ Te(Ph)C=CHCOPh	74	151-151.5	IR	82
36a	C ₂₈ H ₂₂ Te	(Ph ₂ C=CH) ₂ Te	80 ¹⁰⁰	119-120 ¹⁰⁰	¹ H NMR, ¹⁰⁰ IR, ¹⁰⁰ UV ¹⁰⁰	100-102
19	C ₂₈ H ₂₉ NOTe	4-MeC ₆ H ₄ Te(Ph)C=CHCOCH=C(Ph)NEt ₂	68	143-144	IR	83
17a	C ₂₉ H ₂₂ O ₇ Te	[PhTe(Ph)C=CH] ₂ CO	88	235	IR	83
17b	C ₃₁ H ₂₆ O ₇ Te ₂	[4-MeC ₆ H ₄ Te(Ph)C=CH] ₂ CO	84	222-223	IR	83
36b	C ₃₂ H ₃₀ Te	[(4-MeC ₆ H ₄) ₂ C=CH] ₂ Te			¹ H NMR, IR, UV	100

REFERENCES

1. K. J. Irgolic, *The Organic Chemistry of Tellurium* (Gordon and Breach, New York-London, 1974), p.452.
2. G. Figini and J. A. Cousans, *Brit.* **1,157,588** (1969); *Chem. Abstr.*, **71**, 62176 (1969).
3. T. Colclough, *Brit.* **1,160,486** (1969); *Chem. Abstr.*, **71**, 82420 (1969).
4. Standard Oil Development Co., *Brit.* **498,315** (1939); *Chem. Abstr.*, **33**, 3816 (1939).
5. L. A. Mikeska and C. A. Cohen, *U.S.* **2,195,539** (1940); *Chem. Abstr.*, **34**, 5093 (1940).
6. R. C. Doss, *U.S.* **4,224,436** (1980); *Chem. Abstr.*, **95**, 44929 (1981).
7. C. F. Reed, *U.S.* **2,174,110** (1940); *Chem. Abstr.*, **34**, 554 (1940).
8. D. I. Ryabchikov and I. I. Nazarenko, *Usp. Khim.*, **33**, 108 (1964).
9. N. V. de Bataafsche Petroleum Maatschappij, *Fr.* **805,666** (1936); *Chem. Abstr.*, **31**, 4345 (1937).
10. B. Dobias and K. Heckmann, *Ger. Offen.* **2,832,235** (1980); *Chem. Abstr.*, **92**, 148281 (1980).
11. D. E. Jablonski, *U.S.* **4,399,262** (1983); *Chem. Abstr.*, **99**, 196459 (1983).
12. D. C. Lamb, *U.S.* **3,554,992** (1971); *Chem. Abstr.*, **77**, 89137 (1972).
13. G. P. Basmdjian, R. A. Magarian, G. R. Parker, S. L. Mills, A. S. Kirschner, and R. D. Ice, *J. Labelled Compd. Radiopharm.*, **16**, 160 (1979).
14. T. N. Srivastava, R. C. Srivastava, and M. Srivastava, *J. Indian Chem. Soc.*, **59**, 1028 (1982).
15. T. N. Srivastava, R. C. Srivastava, and M. Srivastava, *Indian J. Chem.*, **21A**, 539 (1982).
16. I. D. Sadekov, I. A. Barchan, A. A. Ladatko, G. M. Abakarov, E. I. Sadekova, Yu. N. Simkina, and V. I. Minkin, *Khim. Farm. Zh.*, **9**, 1070 (1982).
17. I. D. Sadekov, I. A. Barchan, A. A. Maksimenko, B. B. Rivkin, M. L. Cherkinskaya, E. I. Sadekova, Yu. N. Simkina, and V. I. Minkin, *Khim. Farm. Zh.*, **9**, 1073 (1982).
18. M. M. Goodman, F. F. Knapp, A. P. Callahan, and L. A. Ferren, *J. Med. Chem.*, **25**, 613 (1982).
19. M. M. Goodman and F. F. Knapp, *J. Org. Chem.*, **47**, 3004 (1982).
20. M. M. Goodman and F. F. Knapp, *Organometallics*, **2**, 1106 (1983).
21. F. F. Knapp, R. C. Srivastava, A. P. Callahan, E. B. Cunningham, G. W. Kabalka, and K. A. R. Sastry, *J. Med. Chem.*, **27**, 57 (1984).
22. V. S. Petrenko, L. I. Reidalova, E. A. Stukalo, V. P. Borisenko, L. N. Markovskii, N. I. Zhuravaskaya, V. G. Telyuk, and E. M. Yur'eva, *U.S.S.R.* **1,051,074** (1983); *Chem. Abstr.*, **100**, 81243 (1984).
23. J. N. Borglin, *U.S.* **2,275,606** (1942); *Chem. Abstr.*, **36**, 4240 (1942).
24. M. Tsuboi, *Ger. Offen.* **2,556,886** (1976); *Chem. Abstr.*, **86**, 363 (1977).
25. S. A. Gardner and H. J. Gysling, *Brit.* **2,007,859** (1979); *Chem. Abstr.*, **91**, 220322 (1979).
26. H. J. Gysling, M. Lental, M. G. Mason, and L. S. Gerenser, *J. Photogr. Sci.*, **30**, 55 (1982).
27. J. L. Vuyts, F. C. Heugebaert, and W. Janssens, *Ger. Offen.* **2,808,010** (1978); *Chem. Abstr.*, **90**, 64523 (1979).
28. H. J. Gysling, *Eur.* **11,754** (1980); *Chem. Abstr.*, **93**, 177337 (1980).
29. W. Janssens, F. C. Heugebaert, and H. E. Kokelenberg, *Ger. Offen.* **2,802,666** (1978); *Chem. Abstr.*, **90**, 31931 (1979).
30. T. Ohta, N. Akahira, T. Nakamura, and T. Yamashita, *Ger. Offen.* **2,933,253** (1980); *Chem. Abstr.*, **93**, 177320 (1980).
31. S. Ovshinsky, L. Hines, R. Citkowski, and T. Yu, *Ger. Offen.* **3,033,554** (1981); *Chem. Abstr.*, **95**, 52695 (1981).
32. Eastman Kodak Co., *Jpn. Kokai Tokkyo Koho* **79,135,707** (1979); *Chem. Abstr.*, **92**, 138664 (1980).
33. M. R. Detty, B. J. Murray, and J. H. Perlstein, *U.S.* **4,431,586** (1984); *Chem. Abstr.*, **100**, 174686 (1984).
34. T. Yu., *Eur.* **98,019** (1984); *Chem. Abstr.*, **100**, 148632 (1984).
35. B. A. Trofimov, *Geteroatomnye Proizvodnye Atsetilena* (Nauka, Moskva, 1981), p. 320.
36. B. A. Trofimov, *Usp. Khim.*, **50**, 248 (1981).
37. B. A. Trofimov, *Sulfur Rep.*, **3**, 83 (1983).
38. B. A. Trofimov, *Z. Chem.*, **26**, 41 (1986).
39. B. A. Trofimov, *Zh. Org. Khim.*, **22**, 1991 (1986).
40. I. D. Sadekov, A. A. Maksimenko, and V. I. Minkin, *Khimiya Tellurorganicheskikh Soedinenii*, Ed. V. I. Naddaka (Rostov Universitet, Rostov-na-Donu, 1983), p. 328.
41. M. J. Dabdoub, V. B. Dabdoub, J. V. Comasseto, and N. Petragnani, *J. Organomet. Chem.*, **308**, 2111 (1986).
42. M. J. Dabdoub, and J. V. Comasseto, *J. Organomet. Chem.*, **344**, 167 (1988).
43. S. Uemura, *J. Synth. Org. Chem.*, **41**, 804 (1983).
44. B. A. Trofimov, N. K. Gusarova, S. V. Amosova, *Zh. Org. Khim.*, **13**, 456 (1977).

45. B. A. Trofimov, S. V. Amosova, A. I. Mikhaleva, N. K. Gusarova, and E. P. Vyalykh, in *Fundamentalnye Issledovaniya. Khimicheskie Nauki*, Ed. G. K. Borekov (Nauka, Novosibirsk, 1977), p. 174–178.
46. B. A. Trofimov, S. V. Amosova, N. K. Gusarova, and G. K. Musorin, *Tetrahedron*, **38**, 713 (1982).
47. B. A. Trofimov, N. K. Gusarova, A. A. Tatarinova, S. V. Amosova, V. A. Potapov, and V. I. Skorobogatova, *U.S.S.R.* **996,411** (1981); *Chem. Abstr.*, **99**, 5208 (1983).
48. B. A. Trofimov, S. V. Amosova, N. K. Gusarova, V. A. Potapov, and A. A. Tatarinova, *Sulfur Lett.*, **5**, 151 (1983).
49. S. V. Amosova, B. A. Trofimov, N. K. Gusarova, V. A. Potapov, and A. A. Tatarinova, *Xth Symp. Org. Sulfur Chem. Bangor, Abstracts*, p. 5 (1982).
50. B. A. Trofimov, N. K. Gusarova, A. A. Tatarinova, V. A. Potapov, L. M. Sinegovskaya, S. V. Amosova, and M. G. Voronkov, *Tetrahedron*, **44**, 6739 (1988).
51. N. K. Gusarova, B. A. Trofimov, A. A. Tatarinova, V. A. Potapov, A. V. Gusarov, S. V. Amosova, and M. G. Voronkov, *Zh. Org. Khim.*, **25**, 39 (1989).
52. B. A. Trofimov, N. K. Gusarova, S. V. Amosova, and E. A. Polukhina, *U.S.S.R.*, **660,974** (1977); *Chem. Abstr.*, **91**, 91171 (1979).
53. B. A. Trofimov, N. K. Gusarova, and A. A. Tatarinova, *Tezisy Dokl. IV Vses. Nauch. Konf. po Khim. Atsetilena i ego Proizvodnykh* (AzINEFTEKHIM, Baku, 1979), p. 189.
54. B. A. Trofimov, S. V. Amosova, N. K. Gusarova, and G. K. Musorin, *IXth Symp. Org. Sulfur Chem. Riga, Abstracts*, p. 88 (1980).
55. B. A. Trofimov and S. V. Amosova, *Divinilsulfid i ego Proizvodnye* (Nauka, Novosibirsk, 1983), p. 264.
56. B. A. Trofimov and S. V. Amosova, *Sulfur Rep.*, **3**, 323 (1984).
57. E. T. Denisov, *Kinetika gomogenykh reaktivov* (Vysshaya Shkola, Moskva, 1978), p. 368.
58. N. K. Gusarova, B. A. Trofimov, V. A. Potapov, S. V. Amosova, and L. M. Sinegovskaya, *Zh. Org. Khim.*, **20**, 484 (1984).
59. A. A. Kudryavtsev, *Khimiya i Tekhnologiya Selena i Tellura* (Vysshaya Shkola, Moskva, 1961), p. 286.
60. B. A. Trofimov, A. A. Tatarinova, N. K. Gusarova, S. V. Amosova, L. M. Sinegovskaya, and V. M. Bzhezovskii, *Zh. Org. Khim.*, **18**, 2459 (1982).
61. S. V. Amosova, B. A. Trofimov, N. K. Gusarova, V. A. Potapov, and A. A. Tatarinova, *XIth Symp. Org. Sulfur Chem. Lindau, Abstracts*, p. 5 (1984).
62. B. A. Trofimov, V. A. Potapov, N. K. Gusarova, A. A. Tatarinova, and S. V. Amosova, *Tezisy Dokl. IV Vses. Simp. po Org. Sintezu* (Moskva, 1984), p. 49.
63. H. G. Richey and J. Farkas, *J. Org. Chem.*, **52**, 479 (1987).
64. B. A. Trofimov, S. V. Amosova, and O. A. Tarasova, *U.S.S.R.* **789,486** (1980); *Chem. Abstr.*, **94**, 120833 (1981).
65. O. A. Tarasova, S. V. Amosova, and B. A. Trofimov, *Zh. Org. Khim.*, **18**, 2042 (1982).
66. O. A. Tarasova, S. V. Amosova, S. N. Istomina, and B. A. Trofimov, *Zh. Org. Khim.*, **20**, 1353 (1984).
67. B. A. Trofimov, N. K. Gusarova, A. A. Tatarinova, and S. V. Amosova, *Zh. Obshch. Khim.*, **53**, 1680 (1983).
68. B. A. Trofimov, N. K. Gusarova, A. A. Tatarinova, S. V. Amosova, L. M. Sinegovskaya, V. V. Keiko, and V. A. Potapov, *Zh. Org. Khim.*, **20**, 1802 (1984).
69. B. A. Trofimov, V. A. Potapov, N. K. Gusarova, S. V. Amosova, A. S. Kashik, and A. A. Tatarinova, *Tezisy Dokl. VII Vses. Konf. po Khimii Atsetilena* (Erevan, 1984), p. 112.
70. B. A. Trofimov, N. K. Gusarova, A. A. Tatarinova, S. V. Amosova, V. A. Potapov, L. M. Sinegovskaya, V. I. Skorobogatova, V. M. Bzhezovskii, and L. B. Krivdin, *U.S.S.R.* **1,203,088** (1984); *Chem. Abstr.*, **105**, 225777 (1986).
71. N. K. Gusarova, B. A. Trofimov, A. A. Tatarinova, V. A. Potapov, L. M. Sinegovskaya, S. V. Amosova, and M. G. Voronkov, *Zh. Org. Khim.*, **24**, 1869 (1988).
72. V. A. Potapov, S. V. Amosova, A. S. Kashik, and D. G. Sokolova, *Izv. Akad. Nauk S.S.S.R.*, **1988**, 200.
73. N. K. Gusarova, B. A. Trofimov, V. A. Potapov, S. V. Amosova, A. A. Tatarinova, and A. S. Kashik, *Tezisy Dokl. IV Vses. Simp. po Org. Sintezu* (Moskva, 1984), p. 47.
74. V. A. Potapov, N. K. Gusarova, S. V. Amosova, A. S. Kashik, and B. A. Trofimov, *Sulfur Lett.*, **4**, 13 (1985).
75. V. A. Potapov, N. K. Gusarova, S. V. Amosova, A. A. Tatarinova, L. M. Sinegovskaya, and B. A. Trofimov, *Zh. Org. Khim.*, **22**, 220 (1986).
76. H. B. Singh and F. Wudl, *Tetrahedron Lett.*, **30**, 441 (1989).
77. B. A. Trofimov and A. I. Mikhaleva, *N-Vinylpirroly* (Nauka, Novosibirsk, 1984), p. 262.

78. V. A. Potapov, A. S. Kashik, and S. V. Amosova, *Zh. Org. Khim.*, **24**, 200 (1988).
79. V. A. Potapov, S. V. Amosova, and A. S. Kashik, *Tetrahedron Lett.*, **30**, 613 (1989).
80. G. A. Kalabin, B. A. Trofimov, G. K. Musorin, D. F. Kushnarev, and S. V. Amosova, *Izv. Akad. Nauk S.S.S.R.*, **1980**, 1305.
81. B. A. Trofimov, G. K. Musorin, G. A. Kalabin, and S. V. Amosova, *Zh. Org. Khim.*, **16**, 518 (1980).
82. S. P. Buzilova, L. I. Vereshchagin, I. D. Sadekov, and V. I. Minkin, *Zh. Obshch. Khim.*, **46**, 932 (1976).
83. S. P. Buzilova, I. D. Sadekov, T. V. Lipovich, T. M. Filippova, and L. I. Vereshchagin, *Zh. Obshch. Khim.*, **47**, 1999 (1977).
84. S. Uemura and S. Fukuzawa, *Tetrahedron Lett.*, **1982**, 1181.
85. S. Uemura, S. Fukuzawa, and S. R. Patil, *J. Organomet. Chem.*, **243**, 9 (1983).
86. K. Ohe, H. Takahashi, S. Uemura, and N. Sugita, *J. Chem. Soc. Jap., Chem. Ind. Chem.*, **7**, 1469 (1987).
87. K. Ohe, H. Takahashi, S. Uemura, and N. Sugita, *J. Organomet. Chem.*, **326**, 35 (1987).
88. K. Ohe, H. Takahashi, S. Uemura, and N. Sugita, *J. Org. Chem.*, **52**, 4859 (1987).
89. M. R. Detty, B. J. Murray, D. L. Smith, and N. Zumbulyadis, *J. Am. Chem. Soc.*, **105**, 875 (1983).
90. M. R. Detty and B. J. Murray, *J. Am. Chem. Soc.*, **105**, 883 (1983).
91. M. J. Dabdoub and J. V. Comasseto, *Organometallics*, **7**, 84 (1988).
92. V. A. Potapov, A. S. Kashik, N. K. Gusarova, V. I. Minkin, I. D. Sadekov, B. A. Trofimov, and S. V. Amosova, *Zh. Org. Khim.*, **23**, 658 (1987).
93. T. I. Bychkova, G. A. Kalabin, and D. F. Kushnarev, *Zh. Org. Khim.*, **17**, 1329 (1981).
94. T. Kauffmann, *Angew. Chem.*, **94**, 401 (1982).
95. T. Kauffmann and H. Ahlers, *Chem. Ber.*, **116**, 1001 (1983).
96. M. M. Campos and N. Petragnani, *Tetrahedron*, **18**, 527 (1962).
97. F. Wudl and D. Nalewajek, *J. Organomet. Chem.*, **217**, 329 (1981).
98. S. V. Amosova, V. I. Gostevskaya, G. M. Gavrilova, V. A. Potapov, and A. S. Kashik, *Zh. Org. Khim.*, **24**, 454 (1988).
99. B. A. Trofimov, V. A. Potapov, N. K. Gusarova, A. A. Tatarinova, and S. V. Amosova, *Zh. Org. Khim.*, **21**, 1130 (1985).
100. D. Elmaleh, S. Patai, and Z. Rappoport, *J. Chem. Soc. Chem. Comm.*, **1971**, 3110.
101. L. Engman, *Organometallics*, **3**, 1308 (1984).
102. M. Albeck and S. Shaik, *J. Chem. Soc., Perkin Trans 1*, **13**, 1223 (1975).
103. J. Bergman and L. Engman, *J. Organomet. Chem.*, **199**, 377 (1980).
104. J. Bergman and L. Engman, *Tetrahedron Lett.*, **1979**, 1509.
105. K. Begnal, *Khimiya Seleny, Tellury, and Poloniya* (Khimiya, Moskva, 1971), p. 205.
106. *Obshchaya Organicheskaya Khimiya. Soedineniya Seleny, Tellury, Kremniya, and Bora*, Eds. N. K. Kochetkov and Yu. N. Bubnov (Khimiya, Moskva, 1984), Vol. 6, p. 544.
107. R. H. Vernon, *J. Chem. Soc.*, **1920**, 86.
108. R. H. Vernon, *J. Chem. Soc.*, **1920**, 889.
109. H. D. K. Drew, *J. Chem. Soc.*, **1929**, 560.
110. H. Lee, and M. P. Cava, *J. Chem. Soc. Chem. Comm.*, **1981**, 277.
111. B. A. Trofimov, N. K. Gusarova, A. A. Tatarinova, S. V. Amosova, V. K. Voronov, L. M. Sinegovskaya, and V. I. Skorobogatova, *U.S.S.R.* **875,317** (1980); *Chem. Abstr.*, **95**, 191695 (1981).
112. B. A. Trofimov, N. K. Gusarova, A. A. Tatarinova, S. V. Amosova, V. M. Bzhezovskii, and V. V. Shcherbakov, *Zh. Org. Khim.*, **19**, 457 (1983).
113. V. A. Potapov and A. A. Tatarinova, *Tezisy Dokl. XVI Konf. po Khim. i Teknol. Org. Soedin. Sery i Sern. Neftei* (Riga, 1984), p. 95.
114. D. Nonkhibel, J. Tedder, and J. Walton, *Radicals* (Cambridge University Press: New York, N.Y., 1979), p. 300.
115. S. Uemura, K. Ohe, J.-R. Kim, K. Kudo, and N. Sugita, *J. Chem. Soc. Chem. Comm.*, **1985**, 271.
116. B. A. Trofimov and G. M. Gavrilova, *U.S.S.R.* **554,100** (1977); *Chem. Abstr.*, **87**, 135342 (1977).
117. S. V. Amosova, G. M. Gavrilova, A. A. Tatarinova, V. I. Gostevskaya, L. M. Sinegovskaya, N. K. Gusarova, and B. A. Trofimov, *Zh. Org. Khim.*, **22**, 453 (1986).
118. J. Vrestal, *Coll. Czech. Chem. Comm.*, **25**, 443 (1960).
119. O. Foss and S. Hauge, *Acta Chem. Scand.*, **15**, 1616 (1962).
120. O. Foss, *Acta Chem. Scand.*, **16**, 779 (1962).
121. L. M. Sinegovskaya, V. V. Keiko, N. K. Gusarova, and B. A. Trofimov, *11th Soviet-Indian Symp. on Organomet. Chem.*, Abstracts (Irkutsk, 1989), p. 34.
122. L. M. Sinegovskaya, Yu. L. Frolov, A. A. Tatarinova, N. K. Gusarova, and B. A. Trofimov, *11th Soviet-Indian Symp. on Organomet. Chem.*, Abstracts (Irkutsk, 1989), p. 35.

123. A. N. Surushkin, L. M. Sinegovskaya, Yu. L. Frolov, and N. K. Gusarova, *Izv. Akad. Nauk S.S.S.R.*, **1986**, 2783.
124. V. V. Keiko, L. M. Sinegovskaya, N. K. Gusarova, A. A. Tatarinova, N. A. Kalinina, and B. A. Trofimov, *Izv. Akad. Nauk S.S.S.R.*, **1987**, 331.
125. *Atlas Spektrov Aromaticheskikh i Geterotsiklicheskikh Soedinenii*, Ed. V. A. Koptyug (Nauka, Novosibirsk, 1982), Vol. 23, p. 124.
126. S. Samdal, H. M. Seip, and T. Torgimsen, *J. Mol. Struct.*, **57**, 105 (1979).
127. J. Fabian, H. Krober, and R. Mayer, *Spectrochim. Acta*, **24A**, 727 (1968).
128. B. A. Trofimov, Yu. L. Frolov, L. M. Sinegovskaya, V. B. Modonov, E. I. Kositsyna, S. V. Amosova, N. K. Gusarova, and G. G. Efremova, *Izv. Akad. Nauk S.S.S.R.*, **1977**, 340.
129. V. V. Keiko, L. M. Sinegovskaya, N. A. Kalinina, N. K. Gusarova, M. L. Alpert, and B. A. Trofimov, *Zh. Obshch. Khim.*, **52**, 875 (1982).
130. S. Samdal and H. M. Seip, *J. Mol. Struct.*, **28**, 193 (1975).
131. J. Kao, *J. Amer. Chem. Soc.*, **100**, 355 (1978).
132. A. N. Surushkin, L. M. Sinegovskaya, Yu. L. Frolov, N. K. Gusarova, V. A. Potapov, and B. A. Trofimov, *Izv. Akad. Nauk S.S.S.R.*, **1987**, 1283.
133. L. M. Sinegovskaya, V. V. Keiko, V. A. Potapov, N. K. Gusarova, and B. A. Trofimov, *XVIIth Eur. Cong. on Mol. Spectroscopy*, Abstracts (Sofia, 1983), p. 165.
134. D. G. Lister, J. N. McDonald, and N. L. Owen, *Internal Rotation and Inversion. An Introduction to Large Amplitude Motions in Molecules* (Academic Press, London-New York, 1978), p. 245.
135. *Internal Rotation in Molecules*, Ed. W. J. Orville-Thomas (John Wiley and Sons, London-New York, 1974), p. 606.
136. L. M. Sinegovskaya, V. V. Keiko, and B. A. Trofimov, *Sulfur Rep.*, **7**, 337 (1987).
137. V. G. Dashevskii, *Konformatsii Organicheskikh Molekul* (Khimiya, Moskva, 1974), p. 432.
138. A. D. H. Claque and A. Danti, *J. Mol. Spectrosc.*, **22**, 371 (1967).
139. B. A. Trofimov, N. I. Shergina, E. I. Kositsyna, A. V. Gusarov, G. M. Gavrilova, and A. S. Atavin, *Zh. Prikl. Spektroskop.*, **14**, 282 (1971).
140. B. Cadioli, B. Fortunato, E. Gallinella, P. Mirone, and U. Pincelli, *Gazz. Chim. Ital.*, **104**, 369 (1974).
141. A. B. Remizov, T. G. Mannafov, and F. R. Tantasheva, *Zh. Obshch. Khim.*, **45**, 1405 (1975).
142. B. Fortunato and M. G. Georgini, *Gazz. Chim. Ital.*, **106**, 1005 (1976).
143. S. Cradock and R. A. Whiteford, *J. Chem. Soc. Faraday Transact.*, **2**, 281 (1972).
144. V. M. Bzhezovskii, D. F. Kushnarev, B. A. Trofimov, G. A. Kalabin, N. K. Gusarova, and G. G. Efremova, *Izv. Akad. Nauk*, **1981**, 2507.
145. F. Cotton and D. Wilkinson, *Basic Inorganic Chemistry* (Editorial Limusa; Mexico City, Mex., 1978), p. 656.
146. G. Miyajima, K. Takahashi, and K. Nishimoto, *Org. Magn. Reson.*, **6**, 413 (1974).
147. G. A. Kalabin, V. M. Bzhezovskii, D. F. Kushnarev, and A. G. Proidakov, *Zh. Org. Khim.*, **17**, 1143 (1981).
148. S. V. Yalymova and Yu. Yu. Samitov, *Zh. Org. Khim.*, **6**, 1945 (1970).
149. Yu. Yu. Samitov and S. V. Yalymova, *Zh. Org. Khim.*, **8**, 441 (1972).
150. L. Pauling, *General Chemistry* (W. H. Freeman and Company, San Francisco, 1970), p. 767.
151. I. G. John and L. Radom, *J. Mol. Spectrosc.*, **72**, 62 (1978).
152. C. Hirose and S. Maeda, *J. Mol. Spectrosc.*, **72**, 62 (1978).
153. S. V. Yalymova, Yu. Yu. Samitov, and A. Sh. Agishev, *Zh. Struktur. Khim.*, **16**, 991 (1975).
154. L. M. Sinegovskaya, Yu. L. Frolov, N. K. Gusarova, V. A. Potapov, and B. A. Trofimov, *Izv. Akad. Nauk S.S.S.R.*, **1985**, 115.
155. R. J. Tedeschi, *Encyclopedia of Physical Science and Technology* (Academic Press Inc., New York, 1987), Vol. 1, p. 45.
156. G. K. Musorin, *Nukleofilnoe Prisoedinenie Anionov Elementov VI A Gruppy k Vinilatsetilenu*, Kand. Diss. (Irkutsk, 1980), p. 117.

SUBJECT INDEX

- Alkali metals 15–16
Alkali metal hydroxyides 2–7, 12, 15, 16
Alkyldivinyltelluronium iodides 8, 20
2-(Alkylthio)ethyl vinyl tellurides 20, 21, 38, 39
Alkyl vinyl tellurides 1, 2, 7–9, 14–16, 19, 32, 38
Alkynes 1–12, 17
Aryl vinyl tellurides 1, 2, 8–10, 12–15, 19, 38, 39
- Benzoic acid 22, 23
 β -Bromostyrene 1, 12, 13
1-Butyn-3-ol 5, 6
- Carbon monoxide 1, 22, 23
Cinnamic acid 22, 23
- Dialkyl ditellurides 12, 17
Dialkyl tellurides 7, 8, 32
Diaryl ditellurides 12, 13
Diorganyl telluronones 18
Diorganyltellurium dihalides 1, 16–19
2,6-Diphenyl-1,4-ditellurafulvene 9
Di(Z-styryl) ditelluride 9, 14, 15, 40
Di(Z-styryl) telluride 9, 13, 40
Divinyl ditelluride 14–17, 38
Divinylmercury 13
Divinylorganyltelluronium halides 20
Divinyl selenide 30, 34
Divinyl sulfide 30, 34
Divinyl sulfone 34
Divinyl sulfoxide 34
Divinyl telluride 1–8, 15, 18, 20, 21, 23, 31, 32, 34, 38
- Energy conjugation 29, 30
- Grignard reagents 1, 13, 14, 21, 22
- Halogens 7, 18, 19
Hydrogen halides 7
Hydrogen peroxide 18
- IR spectra 1, 25, 31, 38–41
- Lithium aluminum hydride 13, 16
- Methyl vinyl sulfide 25–28
Methyl vinyl telluride 1, 24–28, 30, 32, 38
- NMR spectra 1, 33, 38–41
- Organometallic compounds 1, 13, 19, 22
Organotellurenyl halides 13, 14
Organyl halides 1, 7–9, 15, 16, 20
Organylmagnesium halides 13, 14, 22
1-Organylvinyl tellurides 11, 12, 14–16, 19, 20, 38–41
2-Organylvinyl tellurides 9–14, 16, 17, 19, 21–23, 38–40, 42
- Photoelectron spectra 1, 31, 32
- Sodium borohydride 12, 13, 17
Sodium hydride 13
Sodium periodate 18
Sodium tellurite 6, 7
Sulfuryl chloride 19
Superbase reductive systems 1–9, 12, 13, 15–17, 20
- Tellurium 1–9, 13, 14, 23
Tellurium dioxide 4
Tellurophene 3, 5, 6, 20
Thiols 20, 21
Thiourea 1, 23
Tin(II) chloride 4–7, 9, 12
- Vinylmagnesium halides 13, 14
2-(Vinyloxy)-1,3-butadiene 3, 5, 6
2-(Vinyltelluro)-1-buten-3-ol 5, 6, 38
(Z)-1-(Vinyltelluro)-1-buten-3-ol 5–7, 38
- Zinc 4, 5

AUTHOR INDEX

- Abakarov, G. M. 2
Agishev, A. Sh. 37
Ahlers, H. 13, 19, 38, 39
Akahira, N. 2
Albeck, M. 16, 41
Alpert, M. L. 25, 26, 28
Amosova, S. V. 2-9, 12, 15, 18, 20, 21, 23, 25,
26, 37-40
Atavin, A. S. 30
- Barchan, I. A. 2
Basmadjian, G. P. 2
Begna, K. 18
Bergman, J. 17
Borglin, J. N. 2
Borisenko, V. P. 2
Boreskov, G. K. 2, 38
Bubnov, Yu. N. 18
Buzilova, S. P. 9-12, 39-41
Bychkova, T. I. 13, 38, 39
Bzhezovskii, V. M. 5, 7, 18, 32, 34-38
- Cadioli, B. 30
Callahan, A. P. 2
Campos, M. M. 14, 16, 17, 40
Cava, M. P. 18
Cherkinskaya, M. L. 2
Citkowski, R. 2
Claque, A. D. H. 30
Cohen, C. A. 2
Colclough, T. 2
Comasseto, J. V. 2, 10, 12-15, 17, 19, 38-41
Cotton, F. 36
Cousans, J. A. 2
Cradock, S. 31, 32
Cunningham, E. B. 2
- Dabdoub, M. J. 2, 11-15, 17, 19, 38-41
Dabdoub, V. B. 2, 11-15, 19, 38-40
Danti, A. 30
Dashevskii, V. G. 30
Denisov, E. T. 4
Detty, M. R. 2, 11, 12, 40, 41
Dobias, B. 2
Doss, R. C. 2
Drew, H. D. K. 18
- Efremova, G. G. 25, 32, 34-37
Elmaleh, D. 16, 41
Engman, L. 16-19, 41
- Fabian, J. 25
Farkas, J. 6
Ferren, L. A. 2
- Figini, G. 2
Filippova, T. M. 10-12, 39-41
Fortunato, B. 30
Foss, O. 24
Frolov, Yu. L. 24-26, 30, 31, 37, 38
Fukuzawa, S. 11, 12, 22, 39
- Gallinella, E. 30
Gardner, S. A. 2
Gavrilova, G. M. 15, 23, 30, 38
Georgini, M. G. 30
Gerenser, L. S. 2
Goodman, M. M. 2
Gostevskaya, V. I. 15, 23, 38
Gusarov, A. V. 2-6, 30
Gusarova, N. K. 1-9, 12, 15, 18, 20, 21, 23-32,
34-40
Gysling, H. J. 2
- Hauge, S. 24
Heckmann, K. 2
Heugebaert, F. C. 2
Hines, L. 2
Hirose, C. 37
- Ice, R. D. 2
Irgolic, K. J. 2
Istomina, S. N. 6
- Jablonski, D. E. 2
Janssens, W. 2
John, I. G. 37
- Kabalka, G. W. 2
Kalabin, G. A. 9, 13, 32, 34, 36, 37, 39
Kalinina, N. A. 24-31, 35, 36, 38
Kao, J. 25
Kashik, A. S. 7-9, 12, 15, 18, 38-40
Kauffmann, T. 13, 19, 20, 38-40
Keiko, V. V. 7, 24-31, 38
Kim, J.-R. 22, 39
Kirschner, A. S. 2
Knapp, F. F. 2
Kochetkov, N. K. 18
Kokelenberg, H. E. 2
Koptuyug, V. A. 24, 30
Kositsyna, E. I. 25, 30
Krividin, L. B. 7, 38
Krober, H. 25
Kudo, K. 22, 39
Kudryavtsev, A. A. 4, 5
Kushnarev, D. F. 9, 13, 32, 34-37, 39

- Ladatko, A. A. 2
 Lamb, D. C. 2
 Lee, H. 18
 Lelental, M. 2
 Lipovich, T. V. 10-12, 39-41
 Lister, D. G. 26
- McDonald, J. N. 26
 Maeda, S. 37
 Magarian, R. A. 2
 Maksimenko, A. A. 2, 8
 Mannafov, T. G. 30
 Markovskii, L. N. 2
 Mason, M. G. 2
 Mayer, R. 25
 Mikeska, L. A. 2
 Mikhaleva, A. I. 2, 9, 38
 Mills, S. L. 2
 Minkin, V. I. 2, 8-12, 18, 39-41
 Mirone, P. 30
 Miyajima, G. 36
 Modonov, V. B. 25
 Murray, B. J. 2, 11, 12, 40, 41
 Musorin, G. K. 2, 9, 38, 39
- Naddaka, V. I. 2, 8
 Nakamura, T. 2
 Nalewajek, D. 14, 19, 38
 Nazarenko, I. I. 2
 Nishimoto, K. 36
 Nonkhibel, D. 21
- Ohe, K. 11, 12, 13, 22, 23, 39, 40
 Ohta, T. 2
 Orville-Thomas, W. J. 26
 Ovshinsky, S. 2
 Owen, N. L. 26
- Parker, G. R. 2
 Patai, S. 16, 41
 Patil, S. R. 11, 12, 22, 39
 Pauling, L. 37
 Perlstein, J. H. 2
 Petraghani, N. 11-17, 19, 38-40
 Petrenko, V. S. 2
 Pincelli, U. 30
 Polukhina, E. A. 2, 38
 Potapov, V. A. 2-9, 12, 15, 18, 20, 21, 25, 31, 37-40
 Proidakov, A. G. 34, 36
- Radom, L. 37
 Rappoport, Z. 16, 41
 Reed, C. F. 2
 Reidalova, L. I. 2
 Remizov, A. B. 30
 Richey, H. G. 6
 Rivkin, B. B. 2
 Ryabchikov, D. I. 2
- Sadekova, E. I. 2
 Sadekov, I. D. 2, 8-12, 18, 39-41
 Samdal, S. 25, 26, 31
 Samitov, Yu. Yu. 37
 Sastry, K. A. R. 2
 Seip, H. M. 25, 26, 31
 Shaik, S. 16, 41
 Shcherbakov, V. V. 18, 38
 Shergina, N. I. 30
 Simkina, Yu. N. 2
 Sinegovskaya, L. M. 1, 2, 4, 5, 7-9, 15, 18, 20, 23-31, 37, 38, 40
 Singh, H. B. 9
 Skorobogatova, V. I. 2, 7, 18, 38
 Smith, D. L. 11, 12, 40, 41
 Sokolova, D. G. 8, 9, 39
 Srivastava, M. 2, 10
 Srivastava, R. C. 2, 10
 Srivastava, T. N. 2, 10
 Stukalo, E. A. 2
 Sugita, N. 11-13, 22, 23, 39, 40
 Surushkin, A. N. 24-26, 30, 31
- Takahashi, H. 11-13, 22, 23, 39, 40
 Takahashi, K. 36
 Tantasheva, F. R. 30
 Tarasova, O. A. 6
 Tatarinova, A. A. 1-9, 15, 18, 20, 21, 23, 24, 26-31, 38-40
 Tedder, J. 21
 Tedeschi, R. J. 38
 Telyuk, V. G. 2
 Torgriksen, T. 25, 26, 31
 Trofimov, B. A. 2-9, 12, 15, 18, 20, 21, 23-32, 34-40
 Tsuboi, M. 2
- Uemura, S. 2, 11-13, 22, 23, 39, 40
- Vereshchagin, L. I. 9-12, 39-41
 Vernon, R. H. 18
 Voronkov, M. G. 2-8, 15, 20, 38
 Voronov, V. K. 18, 38
 Vrestal, J. 24
 Vuyts, J. L. 2
 Vyalkyh, E. P. 2, 38
- Walton, J. 21
 Whiteford, R. A. 31, 32
 Wilkinson, D. 36
 Wudl, F. 9, 14, 19, 38
- Yalymova, S. V. 37
 Yamashita, T. 2
 Yu, T. 2
 Yur'eva, E. M. 2
- Zhuravskaya, N. I. 2
 Zumbulyadis, N. 11, 12, 40, 41