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β-Telluroacroleins and tellurovinyl ketones: synthesis, reactions and structures

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Contents

I.	Introduction	929
II.	Synthesis and reactions of β-tellurovinylcarbonyl compounds	929
III.	Structures and spectral characteristics of β-tellurovinylcarbonyl compounds	938
IV.	Conclusion	940

Abstract. The published data on the synthesis, reactions and structures of novel organotellurium synthones, *viz*., β-tellurovinylcarbonyl compounds, are systematised and generalised. Special attention is given to the use of these compounds in the synthesis of tellurium-containing heterocycles. The bibliography includes 57 references.

I. Introduction

β-Tellurovinylcarbonyl compounds (aldehydes and ketones) are of particular interest as starting compounds for the synthesis of various tellurium-containing heterocycles and metal chelates with the coordination sites MO_2Te_2 and MN_2Te_2 (M is metal). However, the chemistry of these compounds has not been adequately investigated. The first β-telluroacroleins and β-aryltellurovinyl ketones were prepared by nucleophilic addition of arenetellurolate anions $ArTe^-$ to α-acetylenic aldehydes and ketones (yields 65% – 75%).[1] Bis(β-acylvinyl) tellurides were synthesised in 3% – 11% yields[2] using a similar approach, *i.e*., by nucleophilic addition of the telluride anion Te^{2-} to α-acetylenic ketones (the reasons for the low yields of ketone will be discussed below). Two other types of β-tellurovinylcarbonyl compounds, *viz*., aryl β-chlorotellurovinyl ketones and aryl β-trihalogenotellurovinyl ketones were prepared in the 1980's.[3] The former were synthesised in four steps; the final step included the rearrangement of 3-(aryltelluro)propenoyl chlorides (yields 50% – 95%).[3] Aryl (β-trihalogenotellurovinyl) ketones were obtained in good yields by oxidation of tellurenyl halides with halogens.[4]

Earlier, β-tellurovinylcarbonyl compounds were used exclusively for the preparation of tellurophenes containing strong electron-withdrawing groups in position 2 (NO_2, CHO, COMe, CO_2Et)[5] and 1,6-dioxa-6*a*-tellurapentalenes.[6]

Significant progress in the chemistry of β-telluroacroleins and β-tellurovinyl ketones has been achieved over the last 8 – 10 years owing to the development of methods for their synthesis. (β-Formylvinyl)(methyl)tellurium dihalides, a novel class of β-tellurovinylcarbonyl compounds, have proved to be convenient starting compounds in the synthesis of (β-halogenotellurovinyl)carbonyl derivatives and the previously unknown β-halogenotellurovinyl aldimines. Preparative procedures for the synthesis of various tellurium-containing heterocycles based on β-tellurovinylcarbonyl compounds have been developed.

The distinguishing feature of organotellurium compounds is the formation of intramolecular hypervalent coordinative bonds between the oxygen (or nitrogen) atom and the tellurium atom [O(N) → Te]; their lengths vary over a wide range, sometimes being close to the lengths of ordinary covalent bonds. Similar bond types were studied mostly for aromatic derivatives in which tellurium-centred groups [TeHal, TeOR, TeOCOR, TeSCN, TeR, $Te(R)Hal_2$, $TeHal_3$, *etc*.] were in the *ortho*-position relative to the substituents containing sp^2- or sp^3-hybridised oxygen or nitrogen atoms (CHO, COR, CO_2R, NO_2, CH = N, N = N, CH_2NR_2).[7 – 9] The intramolecular coordination O(N) → Te ensures stabilisation of various organotellurium compounds, primarily of dicoordinated tellurium derivatives, which are thermodynamically and kinetically unstable in the absence of these bonds, and significantly affects their reactivities. The preparation of pure arenetellurenyl halides,[7 – 10] azides,[8, 10] acylates,[7, 8, 10] and alkoxides[8, 10] is possible provided they contain the coordinative bond O(N) → Te. Tellurium-centred cyclopentadienes are stable if they contain tellurium-containing substituents with *o*-formyltelluranylbenzene or their respective azomethine fragments.[11] However, data on X-ray diffraction analysis of β-tellurovinylcarbonyl compounds and (β-halogenotellurovinyl) aldimines containing intramolecular coordinative bonds O(N) → Te are very scarce.

II. Synthesis and reactions of β-tellurovinylcarbonyl compounds

In this review, the synthesis and reactions of β-telluroacroleins and β-tellurovinyl ketones will be considered separately for each individual group of β-tellurovinylcarbonyl compounds. Reactions typical of carbonyl groups and tellurium-containing substituents (reactions involving double bonds are still unknown) and conversions resulting in the formation of tellurium-containing heterocycles from β-tellurovinylcarbonyl compounds and their derivatives will be discussed.

1. Synthesis of β-alkyl(aryl)telluroacroleins and β-tellurovinyl ketones

Two main approaches to the synthesis of β-alkyl(aryl)telluroacroleins and β-substituted tellurovinyl ketones of the general formula $RTeC(R^1)=C(R^2)COR^3$ are known, *viz*., nucleophilic substitution of the tellurolate anions RTe^- for chlorine atoms in β-chlorovinylcarbonyl compounds and nucleophilic addition of RTe^- to the triple bonds of α-acetylenic aldehydes and ketones.

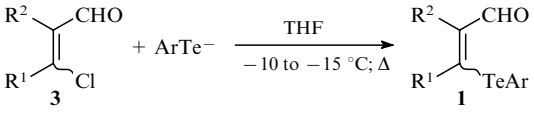
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The former approach is more general and allows the preparation of compounds containing a broad range of substituents in the carbon triad C=C–C(O). As far as the nucleophilic addition is concerned, this yields only β-tellurovinylcarbonyl derivatives devoid of α-substituents.

β-Aryltelluroacroleins (**1**) and β-aryltellurovinyl ketones (**2**) were prepared by reaction of β-chlorovinylcarbonyl compounds **3** and **4** with arenetellurolate anions [12–15] generated in the reaction of aryllithium with tellurium powder in THF or by reduction of diaryl ditellurides with lithium in THF in the presence of catalytic amounts of naphthalene (Tables 1 and 2).

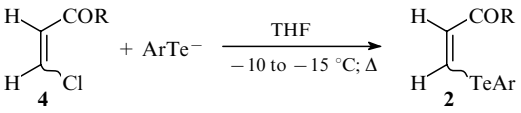
Table 1. Synthesis of β-aryltelluroacroleins **1** from β-chloroacroleins **3**.



Compound **1**	R^1	R^2	Ar	Yield (%)	*Z* : *E* ratio	Ref.
a	Ph	H	Ph	37	1 : 0	12–15
b	Ph	H	4-$EtOC_6H_4$	45	1 : 0	14, 15
c	Ph	Me	Ph	60	1 : 2	14, 15
d	Ph	Me	4-$EtOC_6H_4$	52	1 : 9	14, 15
e	Ph	Et	Ph	65	1 : 19	14, 15
f	Ph	Et	4-$MeOC_6H_4$	58	1 : 10	14, 15
g	$(CH_2)_4$		Ph	57	1 : 0	13–15
h	$(CH_2)_4$		4-MeC_6H_4	52	1 : 0	14–16
i	$(CH_2)_4$		4-$EtOC_6H_4$	37	1 : 0	12–16

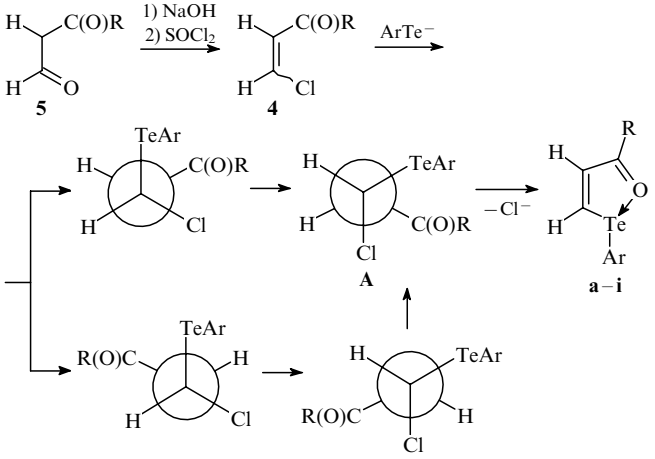
Note. The ratios of the *Z*- and *E*-isomers were determined from the ^1H NMR spectra.

Table 2. Synthesis of β-aryltellurovinyl ketones **2** from β-chlorovinyl ketones **4**.



Compound **2**	R	Ar	Yield (%)	Ref.
a	Ph	Ph	47	12–15
b	Ph	4-$MeOC_6H_4$	45	12, 14–16
c	Ph	4-$EtOC_6H_4$	52	13–15
d	4-MeC_6H_4	4-MeC_6H_4	39	14, 15
e	4-MeC_6H_4	4-$EtOC_6H_4$	53	14–16
f	4-$MeOC_6H_4$	4-MeC_6H_4	45	12, 14, 15
g	4-$MeOC_6H_4$	4-$EtOC_6H_4$	39	12, 14–16
h	4-BrC_6H_4	4-MeC_6H_4	55	12, 14, 15
i	4-BrC_6H_4	4-$EtOC_6H_4$	47	14, 15

The stereochemistry of reactions of nucleophilic substitution of arenetellurolate anions for the chlorine atom in β-chlorovinylcarbonyl compounds was studied in the example of β-chlorovinyl ketones **4** (R = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-$MeOC_6H_4$),[12, 14, 15] since the configurations of substituents at the double bond of the starting compounds and the derived tellurovinyl ketones **2** could easily be established from the values of coupling constants of olefinic protons. Ketones **4** synthesised by treatment of sodium salts of β-oxoaldehydes **5** with $SOCl_2$ represent a mixture of *Z*- and *E*-isomers where the latter predominate.

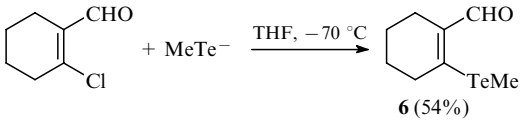


As described earlier,[14, 15] the ratios of *Z*- and *E*-isomers in chlorovinyl ketones **4** depend on the nature of the substituent in position 4 of the phenyl ring and are equal to 0 : 1 (R = 4-BrC_6H_4), 1 : 12 (R = Ph), 1 : 5 (R = 4-MeC_6H_4), 1 : 1,5 (R = 4-$MeOC_6H_4$). However, aryl β-aryltellurovinyl ketones **2a**–**i** prepared from them represent exclusively *Z*-isomers.[12, 14, 15] Thus, substitution of $ArTe^-$ for the chlorine atom results in complete reversal of the configuration of the *E*-isomers of aryl β-chlorovinyl ketones **4** and complete retention in the case of *Z*-isomers. This was rationalised in terms of a two-step vinylic nucleophilic substitution mechanism, *viz*., vinylic substitution through addition–elimination.[17] The first step of this reaction includes addition of highly nucleophilic arenetellurolate anions [18] to the double bond of chlorovinyl ketones, the electrophilicity of the double bonds being enhanced owing to the presence of the oxo group. The conformers **A** stabilised by the coordinative bond O → Te certainly possess the highest stabilities compared with the other conformers existing due to the rotation of the carbanions formed around the simple bond. Subsequent elimination of the chloride ion from conformers **A** yields the *Z*-isomers of aryl β-aryltellurovinyl ketones **2a**–**i**, which are additionally stabilised by the coordinative bond O → Te.[14, 15]

β-Chloro-β-phenylpropenal obtained as a mixture of *Z*- and *E*-isomers in a 9 : 1 ratio [19] reacts with arenetellurolate anions to yield exclusively the *Z*-isomers of compounds **1a**,**b**.[14, 15] The reaction of arenetellurolate anions with 2-chlorocyclohex-1-enecarbaldehyde has the same stoichiometric result, *i.e*., exclusive formation of *Z*-isomers of compounds **1g**–**i** (see Table 1).[14, 15]

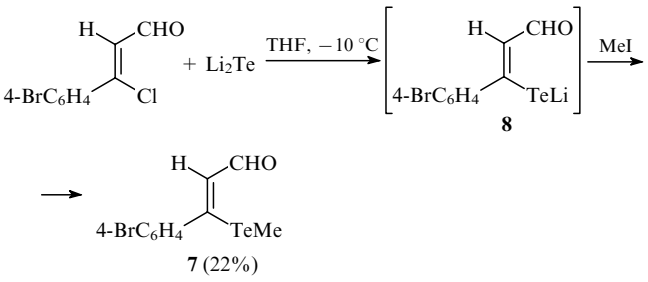
In contrast to chloroacroleins and chlorovinyl ketones nonsubstituted in the α-position, compounds **3** (R^1 = Ph, R^2 = Me, Et) react with arenetellurolate anions to afford mixtures of *E*- and *Z*-isomers of compounds **1c**–**f**; their isomeric ratios vary widely (see Table 1). In this case, the O → Te interaction, which stabilises conformers **A**, competes with the steric repulsion of bulky phenyl and alkyl groups, as a result of which the stereospecificity of the reaction is lost.[14, 15]

Among β-alkyltellurovinylcarbonyl compounds, β-methyltelluroacroleins were the first to be synthesised by nucleophilic substitution of the chlorine atom in β-chlorovinylcarbonyl derivatives.[14, 15, 20] Thus 2-methyltellurocyclohex-1-enecarbaldehyde **6** was prepared by reaction of β-chlorocyclohex-1-enecarbaldehyde with lithium methanetellurolate obtained from methyllithium and tellurium in tetrahydrofuran. This reaction proceeds smoothly only at −70 °C.

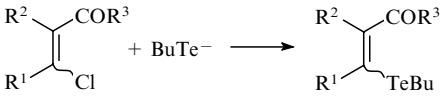


6 (54%)

The approach to the synthesis of β-methyltelluroacrolein **7** is based on the reaction of equimolar amounts of the corresponding β-chloroacrolein with lithium telluride with subsequent alkylation of intermediate lithium tellurolate **8** with methyl iodide.[21]



β-Butyltellurovinyl ketones **9a**–**e** were synthesised by nucleophilic substitution of the chlorine atom in the corresponding β-chlorovinyl ketones **10** using the reaction with the butanetellurolate anion generated by reduction of dibutyl ditelluride with diisobutylaluminium hydride.[22] Compounds **9a**–**e** were obtained as mixtures of *E*- and *Z*-isomers,[22] however, their ratios were not indicated.



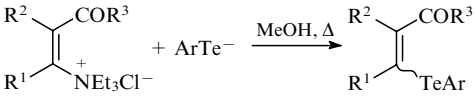
10a–**e** **9a**–**e**

$R^1 = R^3 = Me$, $R^2 = H$(**a**); $R^1–R^3 = (CH_2)_2$, $R^2 = H$ (**b**);
$R^1–R^3 = (CH_2)_3$, $R^2 = H$ (**c**); $R^1 = Me$, $R^2–R^3 = (CH_2)_3$ (**d**);
$R^1 = Me$, $R^2–R^3 = (CH_2)_4$ (**e**).

(β-Acylvinyl)triethylammonium chlorides **11** obtainable in high yields upon treatment of chlorovinylcarbonyl derivatives with triethylamine [23] can be used in the synthesis of β-aryltellurovinyl aldehydes **1** and ketones **2** instead of β-chlorovinylcarbonyl compounds.[14–16] The reactions of compounds **11** with sodium tellurophenolates prepared by reduction of diaryl ditellurides with sodium borohydride are carried out in methanol with subsequent short-term boiling of the reaction mixture (Table 3).

This approach to the synthesis of β-aryltellurovinylcarbonyl compounds is more convenient than that from chlorovinylcarbonyl compounds, since ammonium salts are more storage-stable than their chlorine-containing analogues. Moreover, the preparation of arenetellurolate anions is preparatively more simple, and the yields of the reaction products are usually higher.

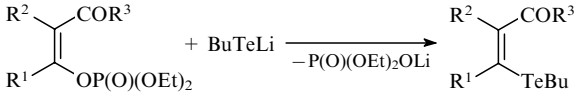
Table 3. Synthesis of β-aryltelluroacroleins and β-aryltellurovinyl ketones from β-acylvinyltriethylammonium chlorides **11**.



11 **1h–j**, **2e**,**g**,**i**,**j**

Compound	R^1	R^2	R^3	Ar	Yield (%)	Ref.
1h	$(CH_2)_4$		H	4-MeC_6H_4	71	14–16
1i	$(CH_2)_4$		H	4-$EtOC_6H_4$	70	12–16
1j	$(CH_2)_4$		H	4-ClC_6H_4	79	14–16
2e	H	H	4-MeC_6H_4	4-$EtOC_6H_4$	79	14–16
2g	H	H	4-$MeOC_6H_4$	4-$EtOC_6H_4$	83	12, 14–16
2i	H	H	4-BrC_6H_4	4-$EtOC_6H_4$	85	14, 15
2j	H	H	Ph	4-MeC_6H_4	86	12, 14–16

Enol phosphates **12** were also used as starting compounds in the synthesis of β-substituted tellurovinylcarbonyl compounds.[24] Their reactions with lithium butanetellurolate prepared from butyllithium and tellurium powder in THF result in β-butyltellurovinyl methyl ketones **9a**,**f**,**g**.

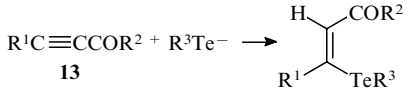


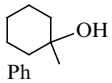
12 **9a**,**f**,**g**

$R^1 = R^3 = Me$, $R^2 = H$(**a**); $R^1 = Ph$, $R^2 = H$, $R^3 = Me$ (**f**);
$R^1–R^2 = (CH_2)_3$, $R^3 = Me$ (**g**)

A large variety of telluroacroleins and tellurovinyl ketones non-substituted in the α-position were prepared by nucleophilic addition of alkane(arene)tellurolate anions generated by reduction of dialkyl(aryl) ditellurides with sodium borohydride in methanol or ethanol to the triple bonds of acetylenic aldehydes or ketones **13** (Table 4).[1,14,15,25,26] The reaction proceeds under

Table 4. Synthesis of β-alkyl(aryl)telluroacroleins and β-alkyl(aryl)tellurovinyl ketones by addition of tellurolate anions to acetylenic carbonyl compounds.



Compound	R^1	R^2	R^3	Yield (%)	*Z* : *E* ratio	Ref.
1a	Ph	H	Ph	90	1 : 0 [a]	14, 15, 25
1b	Ph	H	4-$EtOC_6H_4$	61	1 : 0 [a]	14, 15
1k	H	H	Ph	80	1 : 0 [b]	26
1l	Ph	H	4-MeC_6H_4	76	–	25
1m	Ph	H	4-$MeOC_6H_4$	68	–	25
3b	H	Ph	4-MeC_6H_4	86	1 : 0 [b]	14, 15
3c	H	Ph	4-$EtOC_6H_4$	89	1 : 0 [b]	14, 15
3j	H	Ph	4-$MeOC_6H_4$	71	–	1
3k	Bu	Ph	4-$MeOC_6H_4$	68	–	1, 25
3l	Bu	Me	4-$MeOC_6H_4$	71	–	1
3m		Ph	Ph	84	–	25
3n	Ph	Ph	Ph	86	–	25
3o	Ph	4-$MeOC_6H_4$	Ph	74	–	1
9h	H	H	Bu	84	89 : 11	26

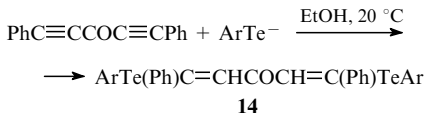
[a] The assignment was made on the basis of the identity of the compounds synthesised to those prepared from β-chloroacroleins. [b] The assignment was made on the basis of coupling constants of olefinic protons in the ^1H NMR spectra.

mild conditions and results in β-alkyl(aryl)telluroacroleins and β-alkyl(aryl)tellurovinyl ketones (yields 60% – 90%).

The stereochemistry of the nucleophilic addition of arenetellurolate anions to the triple bond was studied for the acetylenic derivatives **13**, where R^1 = H, R^2 = H, Ph.[14, 15, 26] It was found that all these reactions yield *Z*-isomers in high yields. In the case of β-aryltellurovinyl phenyl ketones **2b**,**c**, the coupling constants for the alkene protons $^3J_{HH}$ are equal to 8.79 Hz, which corresponds to the *cis*-configuration. The *Z*-configuration of the substituents in β-phenyltelluroacrolein (**1k**) was also determined from the ^{1}H NMR spectra.

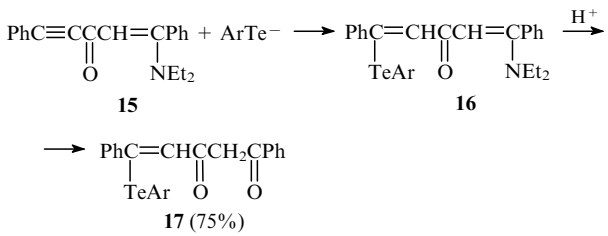
However, reaction of the butanetellurolate anion with propiolaldehyde yields a mixture of *Z*- and *E*-isomers of the aldehyde **9h** in an 89 : 11 ratio.[26] This seems to be due to the lower electronegativity of the butyl substituent as compared with the phenyl one. Indeed, according to quantum-chemical calculations,[27–30] the lengths and, hence, the stabilities of the intramolecular coordinative bond O(N) → Te(II) depend on the electronegativities of substituents at the tellurium atom: the higher this value the shorter the coordinative bond. Weakening of the coordinative bond on going from R = Ph to R = Bu results in partial cleavage of this bond in the butyl derivative and the appearance of the *E*-isomer of compound **9h** in the solution.

Arenetellurolate anions, which are the strongest nucleophiles in the series of structurally related anions ArM^- (M = O, S, Se, Te),[18] react with symmetrical diacetylenic ketones to give only the bisadducts **14** (yields 84% – 88%),[25] whereas alcohols and phenols add to one or both triple bonds depending on the reaction conditions.



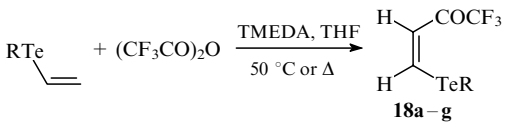
Ar = Ph, 4-MeC_6H_4.

Due to the relatively low electrophilicity of the triple bond in β-aminovinyl ethynyl ketones **15**, they do not react with nucleophiles, such as amines, alcohols and phenols. However, arenetellurolate anions readily add to compounds **15**. Thus ketone **16** was prepared in 68% yield.[25] Acid hydrolysis of this ketone results in the elimination of diethylamine and the formation of diketone **17**.[25]

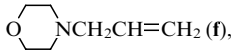


Ar = 4-MeC_6H_4.

A specific synthetic procedure was used to prepare β-trifluoroacetylvinyl tellurides **18a**–**g**.[31] Like other heterosubstituted alkenes (vinyl sulfides, vinyl ethers, *N*-vinylamides, carbazoles, *etc*.) (see Ref. 31 and references cited therein), vinyl tellurides $RTeCH=CH_2$ react with trifluoroacetic anhydride in THF to give ketones **18a**–**g** (yields 50% – 84%). However, in contrast to the previously mentioned heterosubstituted alkenes, the use of catalysts is necessary, among them *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) is the most efficient. The yields of alkylvinyl tellurides **18a**–**d** are higher than in the case of compounds **18e**–**g**.



R = Bu^n (**a**), Bu^i (**b**), $EtO_2C(CH_2)_2$ (**c**), $NC(CH_2)_2$ (**d**), Ph (**e**),

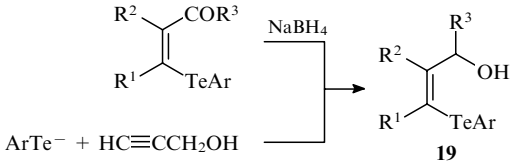


(**f**), PhCH=CH (**g**).

It is of note that the 1,1-disubstituted vinyltelluride, *viz*., 1-butyltelluro-1-phenylethylene, does not enter into this reaction.[31]

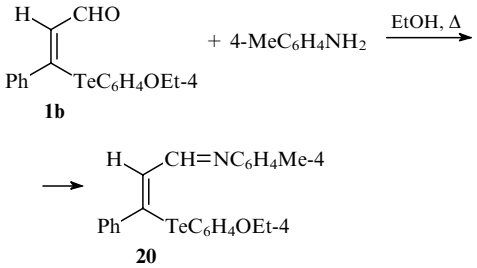
2. Reactions of β-alkyl(aryl)telluroacroleins and β-alkyl(aryl)tellurovinyl ketones

Reactions of β-alkyl(aryl)tellurovinylcarbonyl compounds have been studied relatively little. Like other aldehydes and ketones, they are reduced with sodium borohydride to 3-aryltelluroprop-2-en-1-ols **19**,[13] which can be used as the starting compounds in the synthesis of 5*H*-1,2-oxatelluroles. Compounds **19** (R^1 = R^2 = H) were prepared by nucleophilic addition of arenetellurolate anions to the triple bond of propargyl alcohol.[13, 32, 33]

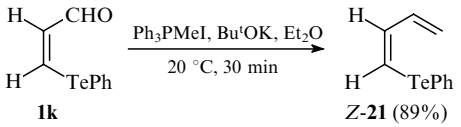


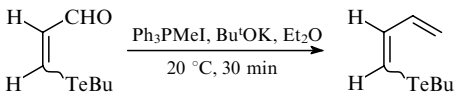
R^1 = R^2 = H, R^3 = Ar = Ph; R^1 = Ph, R^2 = R^3 = H: Ar = Ph, 4-$EtOC_6H_4$; R^1–R^2 = $(CH_2)_4$, R^3 = H: Ar = Ph, 4-$EtOC_6H_4$; R^1 = R^2 = R^3 = H: Ar = Ph, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$.

Azomethine **20** was prepared by condensation of β-aryltelluroacrolein **1b** with *p*-toluidine.[15]



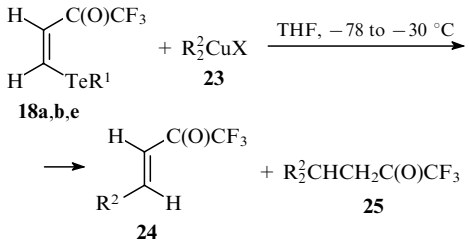
β-Alkyl(aryl)telluroacroleins, particularly compounds **1k** and **9h**, enter into the Wittig reaction with *in situ* generated methylenetriphenylphosphorane to give dienyl tellurides **21** and **22**.[26] The configurations of the starting alkenes are retained.





Z-β-Alkyl(aryl)tellurovinyl trifluoromethyl ketones **18a**,**b**,**e** react with zinc cuprates **23** at low temperatures (from −78 °C to −30 °C) to give *E*-isomers of α,β-unsaturated trifluoromethyl

ketones **24**.[34] However, compounds **24** are obtained in high yields only with cuprates **23** where R^2 = Ar and CH=CHPh. In the case of alkylzinc cuprates, the yields of ketones **24** do not exceed 70%; dialkylated ketones **25** are formed as side products (yields 11%–19%).[34]

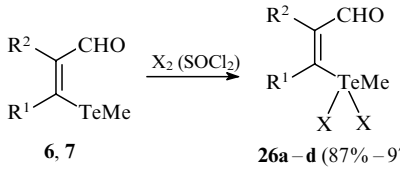


18a,**b**,**e** **23** **24** **25**

R^1 = Bu^n (**a**), Bu^i (**b**), Ph (**e**); R^2 = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$EtO_2CC_6H_4$, PhCH=CH, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$;
X = $(CN)(ZnCl)_2$, ZnCl.

It is noteworthy that the reaction of organocopper derivatives Ph_2CuLi, $Ph_2CuMgBr$, $Ph_2Cu(CN)Li_2$ and $Ph_2Cu(CN)(MgBr)_2$ with ketones **18a**,**b**,**e** is accompanied by the predominant formation of the diphenyl derivatives **25**, whereas ketones **24** are the side products.[34]

Only one reaction of β-alkyl(aryl)telluroacroleins involving the two-coordinate tellurium atom is presently known. Like other vinyl tellurides,[35] β-methyltelluroacroleins **6** and **7** are oxidised to the four-coordinate tellurium derivatives **26a**–**d** by halogens or thionyl chloride under mild conditions (PhH, 0–5 °C).[15, 20, 21]



6, **7** **26a**–**d** (87%–97%)

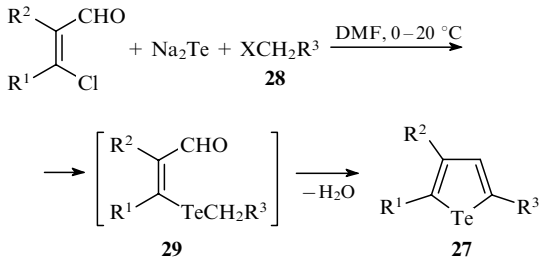
R^1–R^2 = $(CH_2)_4$, X = Cl (**a**), Br (**b**), I (**c**); R^1 = 4-BrC_6H_4, R^2 = H, X = Br (**d**).

3. Synthesis of tellurium-containing heterocycles

a. Tellurophenes

A series of substituted tellurophenes **27** containing strong electron-withdrawing groups in position 2 were synthesised by reaction of β-chloroacroleins with sodium telluride and the α-halogenomethyl derivatives **28**.[5, 36, 37]

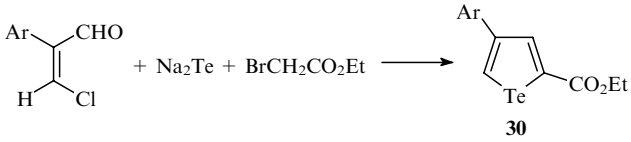
This reaction proceeds under mild conditions and results in the heterocycles **27** in 25%–30% yields. Presumably, β-substituted telluroacroleins **29** are the intermediate products in this reaction.



28 **29** **27**

R^1 = Bu^t, R^2 = H: R^3 = CHO, COMe, CO_2Et, NO_2;
R^1 = 3-$MeOC_6H_4$, 4-$MeOC_6H_4$; R^2 = H, R^3 = CO_2Et;
R^1–R^2 = $(CH_2)_4$: R^3 = COMe, CO_2Et, NO_2;
R^1–R^2 = $(CH_2)_5$, R^3 = CO_2Et; X = Cl, Br.

2,4-Disubstituted tellurophenes **30** were prepared from α-aryl-β-chloroacroleins.[38]

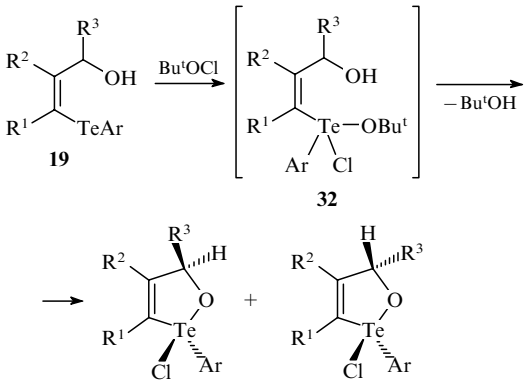


30

The above-described methods for the synthesis of tellurophenes are similar to the reactions used in the synthesis of substituted thiophenes and selenophenes.

b. 2-Aryl-2-chloro-5*H*-1,2-oxatelluroles

3-Aryltelluroprop-2-en-1-ols **19**[13, 32, 33] were used as starting compounds in the synthesis of four-coordinate derivatives of 5*H*-1,2-oxatellurole.[13, 33] Thus 2-aryl-2-chloro-5*H*-1,2-oxatelluroles **31a**,**b** were synthesised in 44%–82% yields by oxidation of alcohols **19** with Bu^tOCl. This reaction seems to proceed through the intermediate formation of σ-telluranes **32** which are further converted into the heterocycles **31a**,**b** with elimination of Bu^tOH.[13]



19 **32** **31a** **31b**

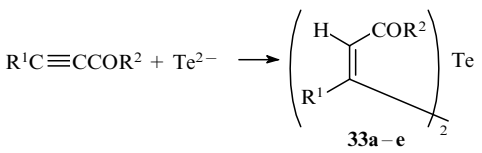
R^1 = R^2 = R^3 = H: Ar = Ph, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$; R^1 = R^2 = H, R^3 = Ar = Ph; R^1 = Ph, R^2 = R^3 = H: Ar = Ph, 4-$EtOC_6H_4$.

Oxatelluroles **31** containing substituents in position 5 of the heterocycle are formed as a mixture of two isomers as can be evidenced from the ^{1}H NMR spectra of these compounds. Thus the signals of the methine protons of 2-chloro-2,5-diphenyl-5*H*-1,2-oxatelluroles are observed as two singlets at δ = 6.02 and 6.27.

4. Bis(β-acylvinyl) tellurides

Of the methods for the synthesis of bis(β-acylvinyl) tellurides that have been studied, the data about the reactions, structures and applications of these compounds in the synthesis of tellurium-containing heterocycles are virtually absent in the literature.

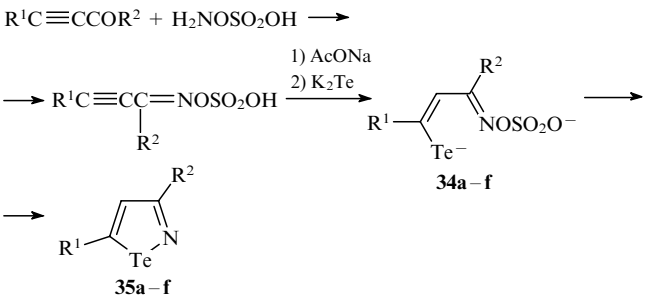
The syntheses of bis(β-acylvinyl) tellurides **33a**–**e**, like those of β-alkyl(aryl)telluroacroleins and β-alkyl(aryl)tellurovinyl ketones, were carried out using the nucleophilic addition of potassium telluride to the triple bond of α-acetylenic ketones.[2] To this end, acetylenic ketones were made to react with potassium telluride and hydroxylamine-*O*-sulfonic acid in an aqueous solution of sodium acetate.



33a–**e**

R^1 = H: R^2 = Me (**a**, 11%), Et (**b**, 6%), Pr (**c**, 3%);
R^1 = R^2 = Me (**d**, traces); R^1 = Ph, R^2 = Me (**e**, 3%).

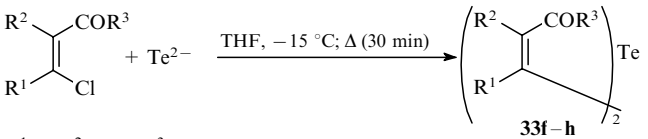
The low yields of ketones **33a**–**e** are due to the competing heterocyclisation of the intermediate oximes **34** into isotellurazoles **35**.[2, 39] Under these conditions, 3-mono- (**35a**–**c**) and 3,5-disubstituted isotellurazoles (**35d**–**f**) are obtained in nearly the same yields (3%–10%) as ketones **33**.



35: R^1 = H: R^2 = Me (**a**, 6%), Et (**b**, 5%), Ph (**c**, 4%);
R^1 = R^2 = Me (**d**, 10%); R^1 = Ph, R^2 = Me (**e**, 7%);
R^1 = CH_2=CH, R^2 = Me (**f**, 5%).

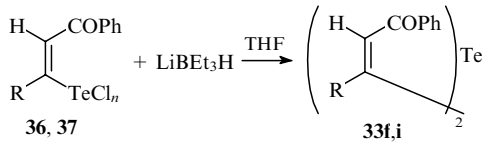
This method is inapplicable to the synthesis of isotellurazoles non-substituted in position 3, since bis(β-cyanovinyl) tellurides $(NCCH=CR)_2Te$ (R = H and Ph), are the only reaction products (yields 20% and 14%) when α-acetylenic aldehydes are used instead of ketones.

Nucleophilic substitution of the telluride anion for the chlorine atom in β-chlorovinylcarbonyl compounds is used in the preparative synthesis of ketones and aldehydes **33**.[14, 15] Lithium telluride, prepared from lithium and elementary tellurium in THF in the presence of catalytic amounts of naphthalene, reacts with β-chloroacroleins and β-chlorovinyl ketones to give compounds **33f–h** in 39%–60% yields.[14, 15]



R^1 = R^2 = H: R^3 = Ph (**f**), 4-MeC_6H_4 (**g**);
R^1–R^2 = $(CH_2)_4$, R^3 = H (**h**).

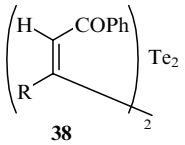
The synthesis of bis(β-benzoylvinyl) tellurides **33f,i** was carried out using β-chlorotellurovinyl phenyl ketones **36** and β-trichlorotellurovinyl phenyl ketones **37**.[4] Reduction of the former with lithium triethylborohydride in THF affords ketones **33f,i** in 53%–92% yields; the yields in the latter case were not indicated.



R = H (**33f**), Ph (**33i**); *n* = 1 (**36**), 3 (**37**).

This method obviously holds little promise for the synthesis of ketones **33f,i**, since chlorotellurium derivatives **36** are prepared in four steps from α-acetylenecarboxylates,[3] and trichlorotellurovinyl ketones are produced upon their oxidation.

Special mention should be made of the unusual course of the reduction of compounds **36** and **37**. Tellurenyl halides[40] and tellurium trihalides[41] devoid of the coordinative bond O(N) → Te are reduced to the corresponding ditellurides. In the case of the chlorotellurium derivatives **36**, ditellurides **38** are formed in trace amounts, apparently due to the presence of strong intramolecular coordinative bonds O → Te in the starting tellurenyl chlorides.

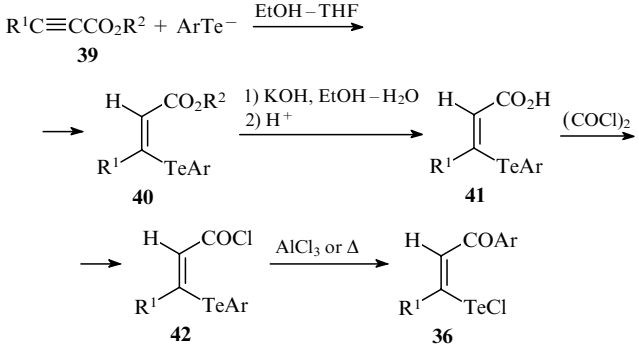


An analysis of the ^{1}H NMR spectrum of ketone **33f**[14, 15] [a ten-proton multiplet of aromatic protons at δ = 7.24–8.10 and an AX system (two two-proton doublets at δ = 8.36 and 9.14, $^3J_{HH}$ = 9.67 Hz)] prompts a conclusion that the benzoylvinyl fragments of this compound exist in conformations with the *cis*-arrangement of the hydrogen atoms.

5. β-Halogenotellurocarbonyl compounds and their analogues; β-halogenotellurovinyl aldimines

a. Synthesis

Aryl β-chlorotellurovinyl ketones **36** are among the most well-studied β-tellurovinylcarbonyl compounds $XTeC(R^1)=C(R^2).COR^3$ where X is an electronegative substituent. They were prepared in four steps starting from α-acetylenecarboxylates **39**.[3, 4, 42–44] The first step includes nucleophilic addition of arene tellurolate anions generated by reduction of the corresponding diaryl ditellurides with sodium borohydride in EtOH–THF to esters **39**. This leads to methyl(ethyl) 3-aryltelluropropenoates **40** (predominantly, *Z*-isomers) (yields 58%–95%).[3] However, ester **40** (R = H, Ar = Ph) is formed as a mixture of *Z*- and *E*-isomers (13 : 1).[3] Hydrolysis of esters **40** with KOH and subsequent acidification of the reaction mixture result in β-(aryltelluro)acrylic (**41**, R = H) or β-(aryltelluro)cinnamic acids (**41**, R = Ph) (yields 68%–95%). Treatment of acids **41** with oxalyl chloride gives 3-(aryltelluro)propenoyl chlorides **42**. The latter are rearranged into ketones **36** (yields 31%–96%) on boiling in deuteriochloroform or by treatment with $AlCl_3$.[3, 4, 42–44] Telluraflavones are formed in some cases in addition to ketones **36** (see below).[42]



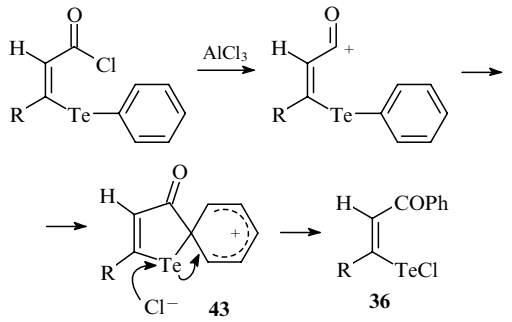
R^2 = Me, Et.

R^1	Ar	Yield (%)	Ref.
H	Ph	82	3
Me	Ph	76	3, 43
Me	4-FC_6H_4	–	43
Me	4-$MeOC_6H_4$	–	43
Me	4-$Me_2NC_6H_4$	31	4, 43
Ph	Ph	81	3, 4
Ph	2-MeC_6H_4	75	3
Ph	3-MeC_6H_4	92	42
Ph	4-MeC_6H_4	92	3
Ph	4-$MeOC_6H_4$	96	3, 4
Ph	3-FC_6H_4	78	42
Ph	3-$MeOC_6H_4$	4	42
Ph	4-$MeCOC_6H_4$	50	3
Ph	1-$C_{10}H_7$	82	3
4-$MeOC_6H_4$	Ph	–	4
2,5-$(MeO)_2C_6H_3$	Ph	70	44
4-$Bu^tC_6H_4$	Ph	–	4

The rates of both thermal and catalytic rearrangements of compounds **42** are governed by the electronic nature of *p*-substituents in the aryl nuclei.[3] Thus in the case of β-(phenyltelluro)-cinnamoyl chlorides, compound **42** (R = Ph, Ar = 4-$MeOC_6H_4$) could not be isolated at all, since it undergoes rearrangement into ketone **36** (R = Ph, Ar = 4-$MeOC_6H_4$) in nearly quantitative yield even at 20 °C. The half-transformation time of the acid chloride **42** (R = Ph, Ar = 4-MeC_6H_4) in boiling $CDCl_3$ is 1 h, whereas that for compound **42** (R = Ar = Ph) is 30 h under

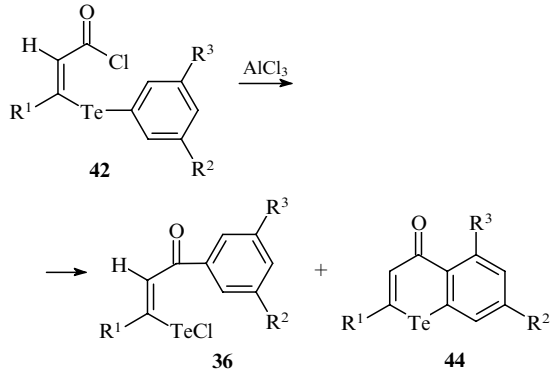
identical conditions. The presence of strong electron-withdrawing substituents (*e.g.*, Ar = 4-$MeCOC_6H_4$) inhibits almost completely the thermal rearrangement, the yield of ketone **36** (R = Ph, Ar = 4-$MeCOC_6H_4$) being < 1% on boiling in $CDCl_3$ for 72 h.

The putative mechanism of the catalytic rearrangements of acid chlorides **42** into compounds **36** involves an attack of the acylium cation on the aromatic carbon atom bound to tellurium (*ipso*-acylation) to yield the spirocyclic σ-complex **43**. Subsequent nucleophilic attack of the chloride ion on the tellurium atom yields ketones **36**.



It should be noted that such rearrangements were first observed for *o*-(aryltelluro)benzoyl chlorides *o*-$ClCOC_6H_4TeAr$ (Ar = Ph, 4-MeC_6H_4, 2-C_4H_3S). Heating of these compounds with $ZnCl_2$ gave (*o*-chlorotelluro)benzophenones *o*-$ClTeC_6H_4$.COAr in high yields.[45–47]

The structures of the rearrangement products of aroyl chlorides **42** depend on the position and the nature of substituents in the ArTe fragments. In the case of *p*-substituted β-(aryltelluro)propenoyl chlorides **42**, the only reaction products are ketones **36**.[3] However, the introduction of donor substituents into the *m*-position of aryl substituents results in the activation of the *o*-positions towards electrophilic attack and prevents *ipso*-acylation, which results in either a mixture of ketones **36** and telluraflavones **44** or only the latter compounds.[42, 44]

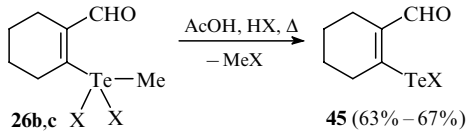


R^1	R^2	R^3	Yield of **36** (%)	Yield of **44** (%)	Ref.
Ph	Me	H	92	0	3
Ph	F	H	78	5	3, 42
Ph	F	F	—	18	42
Ph	OMe	H	4	78	3
Ph	OMe	OMe	0	90	3
4-$MeOC_6H_4$	OMe	H	5	44	44
3,4-$(MeO)_2C_6H_3$	OMe	H	5	68	44
2,5-$(MeO)_2C_6H_3$	OMe	H	5	—	44
4-$MeOC_6H_4$	OMe	OMe	0	52	44
3,4-$(MeO)_2C_6H_3$	OMe	OMe	0	57	44
2,5-$(MeO)_2C_6H_3$	OMe	OMe	0	72	44

The above-described method for the synthesis of ketones **36** has certain limitations: it is a multistep procedure and affords only those aroyl derivatives that are not substituted in the α-position.

A method for the preparation of β-halogenotellurenylvinylcarbonyl compounds based on the use of β-methyldihalogenotellurovinylcarbonyl compounds **26** is devoid of these drawbacks. Until now, such compounds were mostly employed for the preparation of 2-halogenotellurocyclohex-1-enecarbaldehydes **45**,[15, 20] they can undoubtedly be used in the synthesis of vinyltellurenyl halides containing a broad range of substituents in the carbon triad.

Like 2-formylphenyl(alkyl)tellurium dibromides,[48] compounds **26** (their syntheses were discussed in Section II.2) undergo reductive elimination of methyl halide upon boiling in acetic acid in the presence of catalytic amounts of the corresponding hydrohalic acids.[15, 20]

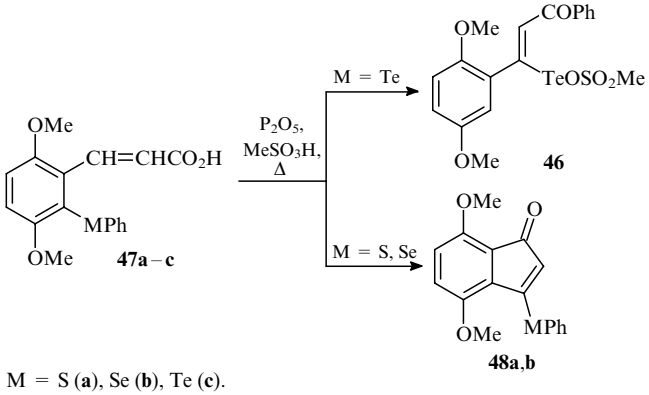


26b,**c** **45** (63% – 67%)

X = Br, I.

It is noteworthy that reductive elimination of methyl halides is extremely sensitive to the admixtures present in the reagents used and is therefore poorly reproducible.

The mesylate derivative **46** is an example of tellurenyl derivatives containing electronegative substituents other than halogen atoms, which has been prepared by direct synthesis.[44] This compound is an unstable oil; it was synthesised by heating a mixture of β-(phenyltelluro)-2,5-dimethoxycinnamic acid (**47c**), phosphoric anhydride and methanesulfonic acid. It is of note that sulfur (**47a**) and selenium analogues (**47b**) undergo cyclisation into benzocyclopentenones **48a**,**b** under identical conditions.[44]

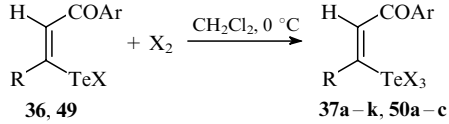


M = S (**a**), Se (**b**), Te (**c**).

b. Reactions

Reactions of (β-halogenotellurovinyl)carbonyl compounds characteristic of the constituent two-coordinate tellurium atom have been studied largely for aryl β-halogenotellurovinyl ketones **36**.

Ketones **36** enter into reduction, oxidation and exchange reactions of chlorine atoms by other anionoid substituents. Aryl β-chlorotellurovinyl ketones **36** and their bromo analogues **49** undergo oxidative addition of chlorine and bromine under mild conditions (CH_2Cl_2, 0 °C) to give aryl β-trichlorotellurovinyl ketones **37a**–**k** and aryl β-tribromotellurovinyl ketones **50a**–**c**, respectively.[4]



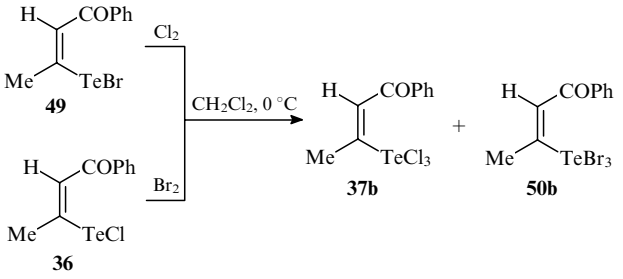
36, **49** **37a**–**k**, **50a**–**c**

37: X = Cl; R = H, Ar = Ph (**a**, 70%); R = Me: Ar = Ph (**b**, 74%), 4-FC_6H_4 (**c**, 92%), 4-$Me_2NC_6H_4$ (**d**, 39%); R = Ph: Ar = Ph (**e**, 66%), 3-FC_6H_4 (**f**, 88%), 4-FC_6H_4 (**g**, 88%), 2-MeC_6H_4 (**h**, 82%), 4-$MeOC_6H_4$ (**i**, 55%); R = 4-$MeOC_6H_4$, Ar = Ph (**j**, 85%); R = 4-$Bu^tC_6H_4$, Ar = Ph (**k**, 79%).

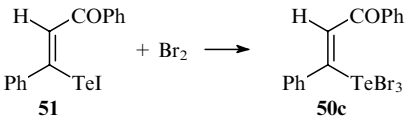
50: X = Br; Ar = Ph: R = H (**a**, 52%), Me (**b**, 70%), Ph (**c**, 89%).

Iodine, possessing the weakest (in comparison with other halogens) oxidating properties, does not oxidise tellurenyl iodides. Thus phenyl β-iodotelluro-β-phenylvinyl ketone ITeC(Ph)=CH. .COPh is not converted into the corresponding tellurium triiodide in a reaction with iodine.

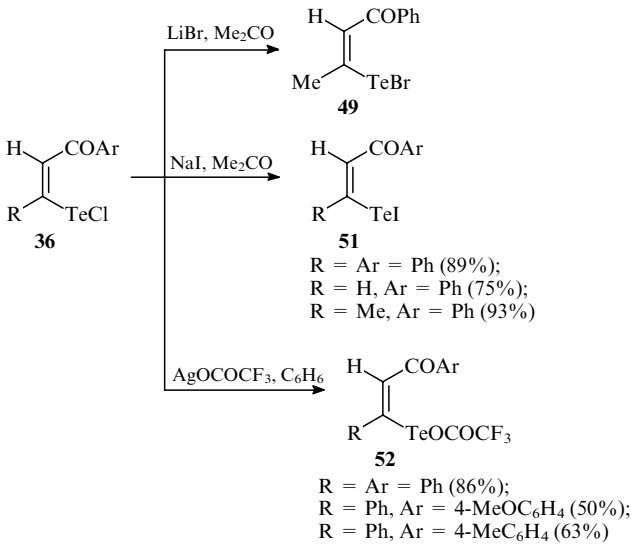
The attempts to prepare mixed tellurium trihalides were unsuccessful. Thus the reaction of tellurenyl bromide **49** (R = Me, Ar = Ph) with chlorine gave a mixture of tellurium trichloride **37b** and tellurium tribromide **50b** in a 2:1 ratio, whereas treatment of tellurenyl chloride **36** (R = Me, Ar = Ph) with bromine yields a mixture of analogous tellurium trihalides, but in a 1:2 ratio.[4]



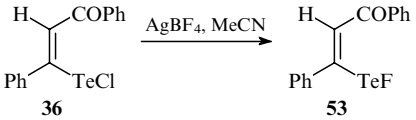
At the same time, the reaction of tellurenyl iodide **51** with bromine results in tellurium tribromide **50c**.[4]



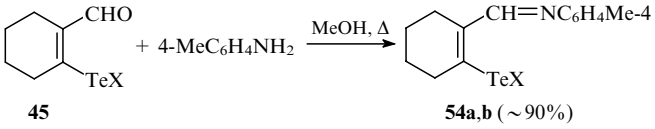
The chlorine atoms in tellurenyl chlorides **36** are highly mobile and readily exchangeable for other anions (Br^-, I^-, CF_3COO^-), which affords the tellurenyl derivatives **49**, **51**, **52** in high yields.[3]



Quite unexpected results were obtained in the reaction of aryl β-chlorotellurovinyl ketone **36** (R = Ar = Ph) with $AgBF_4$ (see Ref. 3). β-Fluorotellurovinyl phenyl ketone **53** was isolated instead of the expected tetrafluoroborate. Obviously, this reaction results in the decomposition of the complex ion BF_4^-, but the reasons for this decomposition have not been established.

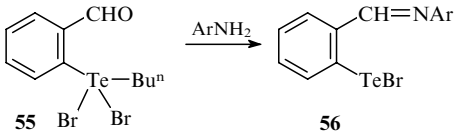


The condensation of aldehydes **45** with aromatic amines (boiling of equimolar amounts of reactants), which affords azomethines **54a**,**b**, is the only well-studied reaction of (β-halogenotellurovinyl)carbonyl compounds **45** involving the carbonyl group.[15,20]



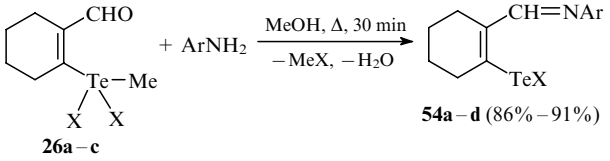
X = Br (**a**), I (**b**).

Earlier,[10] it was shown that the reaction of *o*-butyldibromotellurobenzaldehyde (**55**) with aromatic amines is accompanied by reductive elimination of butyl bromide to give azomethines **56**.



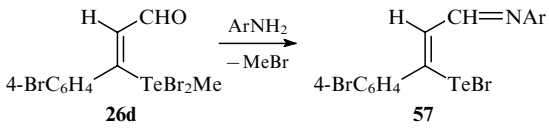
Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$.

2-Methyldihalogenotellurocyclohex-1-enecarbaldehydes **26a**–**c** and aldehyde **56d** react with aromatic amines in a similar manner. The yields of azomethines **24a**–**d**, **57** amount to 86%–91%.[15,20,21]



Ar = 4-MeC_6H_4: X = Cl (**54a**), Br (**54b**), I (**54c**);

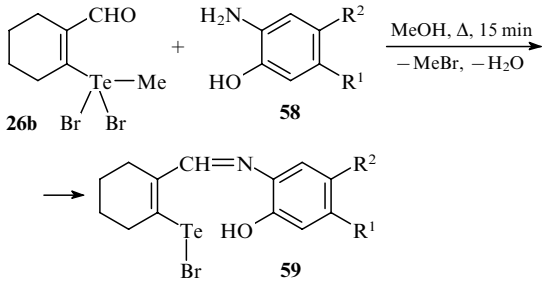
Ar = 4-$MeOC_6H_4$: X = Br (**54d**).



Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$.

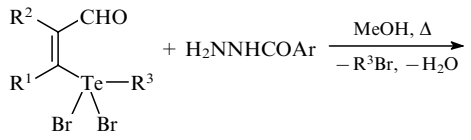
This procedure for azomethine synthesis has certain advantages over those mentioned above, since it excludes the conversion of aldehydes **26** into the tellurenyl derivatives **45**.

o-Aminophenols **58** react with aldehyde **26b** in a similar way: the yields of azomethines **59** vary from 78% to 85%.[49]

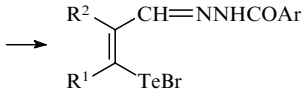


$R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = NO_2$, $R^2 = H$.

Reactions of 2-methyldibromotellurocyclohex-1-enecarbaldehyde **26b** and *o*-butyldibromotellurobenzaldehyde (**55**) with aromatic acid hydrazides proceeds in the same way as with aromatic amines. Short-term (10 min) boiling of equimolar amounts of the reactants results in *N*-aroylhydrazones of 2-bromotellurocyclohex-1-enecarbaldehyde or *o*-bromotellurobenzaldehyde **60**.[50]



26b, **55**



60 (78% – 90%)

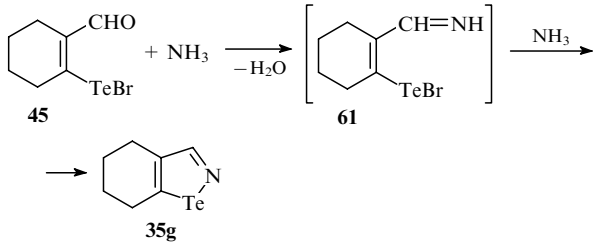
$R^1 - R^2 = (CH_2)_4$, R^3 = Me: Ar = 4-BrC_6H_4, 4-$MeOC_6H_4$;
$R^1 - R^2 = (CH=CH)_2$, R^3 = Bu, Ar = 4-$MeOC_6H_4$.

6. Synthesis of tellurium-containing heterocycles

β-Halogenotellurovinylcarbonyl compounds and their aza analogues were used as starting compounds in the synthesis of tellurium-containing heterocycles comprising one or two heteroatoms in addition to the tellurium atom.

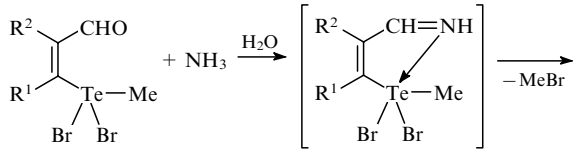
a. Isotellurazoles

The synthesis of isotellurazoles **35a** – **f** by the reaction of α-acetylenic ketones with hydroxylamine-*O*-sulfonic acid and potassium telluride (Section II.4) has significant disadvantages in comparison with other methods due to very low yields of isotellurazoles and the impossibility of obtaining compounds non-substituted in position 3. The procedure for the synthesis of isotellurazole from compounds of the type **45** is devoid of these drawbacks.[20] Thus 4,5-tetramethyleneisotellurazole **35g** was prepared in 70% yield by passage of ammonia through a solution of 2-bromotellurocyclohex-1-enecarbaldehyde **45** in benzene. The putative mechanism of this reaction involves the intermediate formation of imine **61**; dehydrobromination of the latter under the action of ammonia yields isotellurazole **35g**.[21]

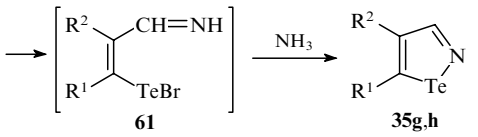


45 **61** **35g**

The synthesis of isotellurazoles from aldehydes **26** as starting compounds is preparatively more convenient, since it excludes the conversion of aldehydes into the tellurenyl derivatives of the type **45**. Passage of ammonia through benzene solutions of tellurium dibromides **26b**,**d** gave isotellurazoles **35g**,**h** in ~ 70% yields.[21] Allowing for the fact that the reaction of tellurium dibromides **26b**,**d** with aromatic amines proceeds through elimination of methyl bromide, a mechanism for the formation of isotellurazoles has been proposed.[21] Its initial step includes the formation of imines **62**, which are further converted into imines **61** by elimination of methyl bromide; their cyclisation into isotellurazoles is described above.



26b,**d** **62**



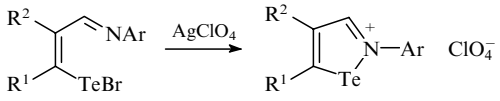
61 **35g**,**h**

$R^1 - R^2 = (CH_2)_4$ (**26b**, **35g**); R^1 = 4-BrC_6H_4, R^2 = H (**26d**, **35h**).

This method for the synthesis of isotellurazoles is similar to that proposed by Renson for the synthesis of isoselenazoles.[51] However, due to the high thermal stability of tellurodibromides **26** (σ-telluranes of the type $R^1R^2TeX_2$), the respective reactions are carried out at room temperature, while those of less stable selenium analogues should be carried out only at −78 °C.

b. *N*-Arylisotellurazolium salts

N-Arylisotellurazolium perchlorates **63** were prepared in 78% – 86% yields by treatment of solutions of aldimines **54** in acetone or DMF with the silver perchlorate – acetonitrile complex in acetone. [21]

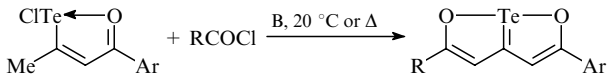


54 **63**

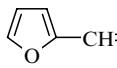
$R^1 - R^2 = (CH_2)_4$: Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$;
R^1 = 4-BrC_6H_4, R^2 = H: Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$.

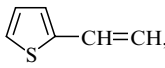
c. 1,6-Dioxa-6*a*-tellurapentalenes and 1-oxa-6-aza-6*a*-tellurapentalenes

Aryl β-chlorotelluro-β-methylvinyl ketones of the type **36** were used as starting compounds in the synthesis of 1,6-dioxa-6*a*-tellurapentalenes **64**.[6,43] Condensation of these compounds with carboxylic acid chlorides in CH_2Cl_2 or MeCN in the presence of excess of a base (triethylamine, pyridine, 2,6-lutidine) gives heterocycles **64** (yields 11% – 85%). This reaction occurs with various (saturated, unsaturated, aromatic, heterocyclic, *etc*.) acid chlorides.



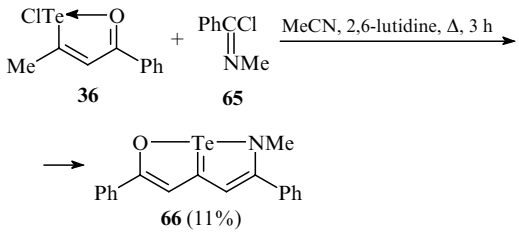
36 **64**

Ar = Ph: R = Me, Ph, 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$;
Ar = 4-FC_6H_4: R = Me, Ph, 4-FC_6H_4, 4-$O_2NC_6H_4$, 4-NCC_6H_4,
4-$MeOC_6H_4$, 2,4-$(NO_2)_2C_6H_3$, 3,5-$(NO_2)_2C_6H_3$, 



Ar = 4-$MeOC_6H_4$: R = Me, 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$;
Ar = 4-$Me_2NC_6H_4$: R = 4-$O_2NC_6H_4$, 4-NCC_6H_4.

The use of imidoyl chloride **65** instead of acid chlorides has led to 1-oxa-6-aza-6*a*-tellurapentalene **66**.[43]

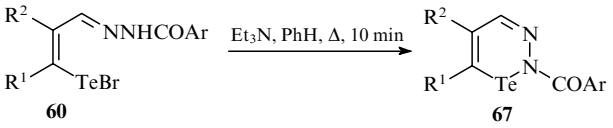


36 **65**

66 (11%)

d. 2-Aroyl-1,2,3-telluradiazines

Dehydrobromination of aldimines is the key step in the synthesis of isotellurazoles. A similar approach was used in the synthesis of 2-aroyl-1,2,3-telluradiazines **67**.[50] These heterocycles were synthesised in 76% – 82% yields by treatment of benzene solutions of *N*-aroylhydrazones **60** with triethylamine.

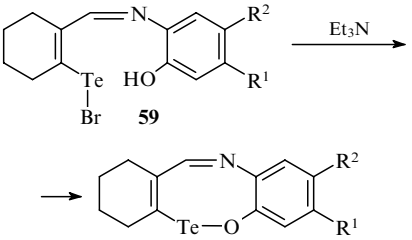


60 **67**

$R^1 - R^2 = (CH_2)_4$: Ar = 4-BrC_6H_4, 4-$MeOC_6H_4$;
$R^1 - R^2 = (CH{=}CH)_2$: Ar = 4-$MeOC_6H_4$.

e. 1,2,6-Oxatellurazocine benzo-derivatives

Benzo-1,2,6-oxatellurazocine derivatives **68** were prepared by dehydrobromination of the corresponding β-bromotellurovinylaldimines **59** in the presence of an equimolar amount of triethylamine with subsequent short-term boiling of the reaction mixture.[49]



68 (71% – 87%)

$R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = NO_2$, $R^2 = H$.

7. β-Trihalogenotellurovinylcarbonyl compounds

The only available data in the literature concerns aryl β-trihalogenotellurovinyl ketones $X_3TeC(R){=}CHCOAr$ (X = Cl, Br).

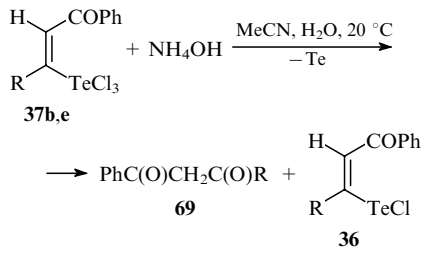
a. Synthesis

The only known method for the synthesis of aryl β-trichlorotellurovinyl ketones **37** and aryl β-tribromotellurovinyl ketones **50**, *viz*., the oxidative addition of chlorine and bromine to aryl β-chloro- (**36**) and aryl β-bromotellurovinyl ketones (**49**), respectively, is described in Section II.5.b.

b. Reactions

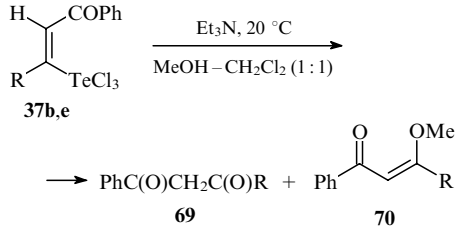
Reactions of aryl β-trihalogenotellurovinyl ketones were studied primarily for the chloro derivatives **37**. The latter are reduced to bis(β-aroylvinyl) tellurides with lithium triethylborohydride and react with various nucleophiles. It should be noted that under the action of hypophosphorous acid as reducing agent tellurotrichlorides **37b**,**e** are reduced to tellurenyl chlorides **36b**,**f**.[4] Of special interest is the striking difference between the structures of the reaction products of aryl β-trichlorotellurovinyl ketones **37** and tellurotrichloride derivatives containing no intramolecular coordinative bonds O → Te with nucleophiles.[41] Reactions of the latter with nucleophiles result in the exchange of anionoid substituents for chlorine atoms or reduction of tellurium trichlorides to ditellurides, no detellurination occurs. The Michaelis addition of nucleophiles to the enone fragment of the ketones **37** proceeds with the elimination of the tellurium atom; sometimes, the trichlorides are reduced to tellurenyl chlorides.

Reaction of tellurium trichlorides **37b**,**e** with aqueous ammonia yields diketones **69**, tellurenyl chlorides **36** and metallic Te.[4]



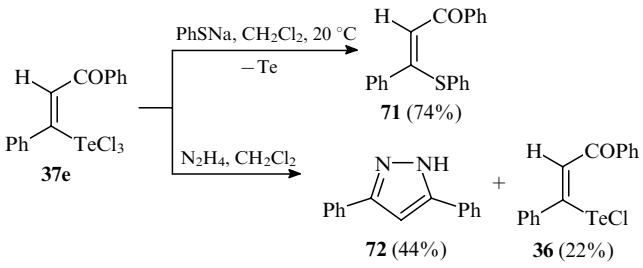
Compound **37**	R	Yield of **69** (%)	Yield of **36** (%)
b	Me	56	13
e	Ph	63	36

Ketones **69** and methyl ethers of enols **70** (a mixture of *Z*- and *E*-isomers) are formed in the reaction of tellurium trichlorides **37b**,**e** with triethylamine.[4]



Compound **37**	R	Yield of **69** (%)	Yield of **70** (%)
b	Me	38	56
e	Ph	15	80

The reaction of tellurium trichloride **37e** with sodium benzenethiolate which proceeds with elimination of the tellurium atoms yields the *Z*-isomer of β-phenyl-β-phenylthiovinyl phenyl ketone **71**. The reaction of tellurium trichloride **37e** with hydrazine gives a mixture of pyrazole **72** and tellurenyl chloride **36** (R = Ph).[4]



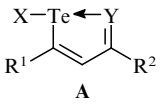
8. β-Methyldihalogenotelluroacroleins

The synthesis of β-methyldihalogenotelluroacroleins was considered in Section II.2. Reductive elimination of methyl halides from these compounds results in β-halogenotelluroacroleins. Reaction with aromatic amines and acid hydrazides yields β-halogenotellurovinylaldimines (Section II.5.b). The use of β-methyldihalogenotelluroacroleins in the synthesis of isotellurazoles was considered in Section II.6.a.

III. Structures and spectral characteristics of β-tellurovinylcarbonyl compounds

β-Tellurovinylcarbonyl compounds are convenient objects for the study of intramolecular coordinative bonds between O or N atoms and tellurium-containing substituents and the effects of these bonds on the structural and chemical properties of compounds under study.

The molecular and crystal structures of five β-tellurovinylcarbonyl compounds of the general formula **A** have been studied [3, 4, 15, 31] using X-ray diffraction analysis (Tables 5 and 6).



A

Compounds containing two-coordinate tellurium atoms (*e.g.*, carbonyl derivatives **1b**, **18c**, **36** and azomethine **20**) possess *Z*-configuration of the C=C bond, which ensures the formation of the intramolecular coordinative bonds O → Te and N → Te. The configuration of the substituents at the Te atom in the above-mentioned compounds can be described as a slightly distorted T-shaped structure, since the value of the angle X—Te—Y is close to 180° (164.4°–170.9°). According to the N-X-L nomenclature,[52] these compounds represent 10-Te-3-telluranes. The lengths of the C—Te bonds in the two-coordinate tellurium derivatives **1b**, **18c**, **36** and **20** (2.06–2.119 Å) and the values of the bond angles X—Te—C (93.6°–98.5°) are similar to those of other two-coordinate tellurium derivatives.[8, 9, 53]

The five-membered tellurium-containing rings in compounds **1b** and **20** are virtually planar; the phenyl rings in these compounds deviate from the planes of the heterocycles by 57.3° and 60.0°, respectively.

In addition to the presence of the intramolecular coordinative bond C=O → Te, the distinguishing feature of the trifluoromethyl derivative **18c** [31] is the interaction of the carbonyl atom of the ethoxycarbonyl group with theTe atom. However, the length of this bond (3.92 Å) exceeds the sum of the van der Waals radii of O and Te (3.70 Å [54]) and can therefore be neglected in the analysis of the polyhedron of the tellurium atom in this compound.

The coordination polyhedron of the Te atom in tellurium tribromide **50c**, a four-coordinate tellurium derivative, represents a trigonal bipyramid; the intramolecular coordinative bond O → Te is not taken into account.[4] Here, the tellurium atom, the vinyl fragment and one bromine atom lie in the equatorial plane, while the other two bromine atoms are in the axial positions. The $Te-Br_{equv.}$ bond (2.513 Å) is shorter than the $Te-Br_{ax.}$ bond (the average length is 2.660 Å). Taking account of the intramolecular coordinative bond O → Te (2.362 Å), the geometry of the bonds at the tellurium atom can be regarded as an octahedron.

In addition to intramolecular interactions, the crystals of compound **50c**, like those of aryltellurium tribromides,[55] contain the intermolecular bond Te···Br (3.757 Å), which enables binding of individual molecules into polymeric chains.

Apart from bond lengths, the intramolecular coordinative bond O(N) → Te is characterised by the covalence factor (χ), which is calculated by the formula [56]

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

where *R* and *r* are the van der Waals and covalent radii of the non-bonded elements A and B and d_{AB} is the distance between the atoms A and B.

Obviously, the higher the value of χ the shorter the bond.

The Te—Y bond lengths in β-tellurovinylcarbonyl compounds (see Table 5, compound **18c** will be mentioned separately) depend on the nature of the substituent X and increase in the following order: Cl < Br_3 < C_6H_4OEt-4 (for Y = O) ≅ C_6H_4OEt-4 (for Y = NC_6H_4Me-4). Depending on the nature of X, similar changes in the bond lengths corroborated by the results of quantum-chemical calculations [27–30] were observed in the case of *o*-tellurinated phenylcarbonyl derivatives and (β-halogenotellurovinyl)aldimines.[7–9]

2-Trifluoroacetylvinyl 2-ethoxycarbonylethyl telluride (**18c**) presents special interest.[31] The intramolecular coordinative bond in this compound (3.22 Å, χ = 0.24) is the longest in the series of organotellurium compounds (*e.g.*, the length of the O → Te bond in aldehyde **1b** is 2.725 Å). The reason for the significant elongation of the O → Te bond in the ethoxycarbonyl derivative **18c** seems to be due to the decrease in the electron density of the oxygen atom of the trifluoroacetyl group which, in turn, is determined by specific electron-withdrawing properties of the trifluoromethyl substituent.

β-Halogenotellurenylvinyl ketones of the general formula RC(TeX)=CHCOAr were studied by ^{125}Te NMR spectroscopy (Table 7).[3, 57]

Two main conclusions can be drawn from the data presented in Table 7. First, the chemical shifts of the Te atoms in these halogenotellurium derivatives are primarily affected by the electronegativity of the halogen atom: the higher the electronegativity the more low-field the ^{125}Te signal. The nature of substituents at

Table 5. The bond lengths in compounds of the type **A** (in Å).

Compound	R^1	R^2	X	Y	C—Te	Te—X	$C(R^1)=CH$	$CH-C(R^2)$	$C(R^2)=Y$	Y → Te	χ	Ref.
1b	Ph	H	C_6H_4OEt-4	O	2.101	2.124	1.368	1.437	1.219	2.725	0.59	15
18c	H	CF_3	$(CH_2)_2CO_2Et$	O	2.06	2.14	1.34	1.42	1.24	3.22	0.24	31
36	Ph	C_6H_4OMe-4	Cl	O	2.08	2.47	1.354	1.425	1.27	2.19	0.95	3
20	Ph	H	C_6H_4OEt-4	NC_6H_4Me-4	2.119	2.138	1.336	1.442	1.278	2.771	0.58	15
50c	Ph	Ph	Br_3	O	2.175	2.513 [a] 2.660 [b]	1.33	1.47	1.26	2.362	0.83	4

Note. χ is the covalence factor (see text). [a] $TeTe-Br_{equiv.}$ bond length. [b] Average length of the $Te-Br_{ax.}$ bond.

Table 6. The values of the bond angles in compounds of the type **A** (in degrees).

Compound	R^1	R^2	X	Y	$X-Te-C(R^1)$	$Te-C(R^1)=CH$	$C(R^1)=CH-C(R^2)$	$CH-C(R^2)=Y$	$C(R^2)=Y\rightarrow Te$	$Y\rightarrow Te-X$	Ref.
1b	Ph	H	C_6H_4OEt -4	O	98.5	119.4	122.4	123.7	103.2	168.3	15
18c	H	CF_3	$(CH_2)_2CO_2Et$	O	94.1	126	112	124	—	—	31
36	Ph	C_6H_4OMe-4	Cl	O	93.6	113.7	118.6	116.8	114.2	170.9	3
20	Ph	H	C_6H_4OEt-4	NC_6H_4Me-4	95.6	120.5	125.1	120.7	104.5	164.4	15
50c	Ph	Ph	Br_3	O	95.0 [a]	114.0	121.1	118.4	111.9	—	4

[a] The $Br_{equiv.}-Te-C$ angle.

Table 7. The ^{125}Te NMR spectra of compounds RC(TeX) = CHCOAr in CD_2Cl_2.

R	Ar	X	δ /ppm	Ref.
Me	Ph	Cl	1744 [a]	3, 57
Me	Ph	Cl	1726	50
Me	Ph	Br	1691 [a]	3, 57
Me	Ph	Br	1672	50
Me	Ph	I	1510	3
Ph	Ph	Cl	1697	57
Ph	Ph	Br	1672	57
Ph	Ph	I	1501	57
Ph		Cl	1692	57
Ph		Br	1654	57
Ph	2,5-$(MeO)_2C_6H_3$	I	1484	57

[a] Bis(diethylcarbamato)tellurium served as the standard; the δ ^{125}Te values are given relative to Me_2Te, these are calculated according to the formula $\delta(Me_2Te) = \delta[Te(S_2CNEt_2]_2 + 833$.

the carbon atoms only weakly affects the δ ^{125}Te value (the maximum δ value does not exceed $\sim$ 50 ppm).

IV. Conclusion

The data presented in this review suggest that the chemistry of β-tellurovinylcarbonyl compounds has progressed considerably in recent years. This can be exemplified by the development of procedures for the preparative synthesis of these compounds and azomethines prepared from them as well as by studies of the reactivity of β-tellurovinylcarbonyl compounds and the effect of the intramolecular coordinative bond O(N) → Te on the reaction features. The use of β-tellurovinylcarbonyl compounds and related aldimines has made it possible to develop preparative procedures for the synthesis of isotellurazoles, *N*-arylisotellurazolium salts and novel tellurium-containing heterocycles, such as 5*H*-1,2-oxatelluroles, 1,6-dioxa-6*a*-tellurapentalenes, 1,2,3-telluradiazines and 1,2,6-oxatellurazocines.

Further investigations in this field will presumably be carried out along the following lines:

1. Synthesis of novel β-tellurovinylcarbonyl compounds (ditellurides, telluronium ylides, tellurimides, telluronium salts).

2. In-depth studies of reactions of β-tellurovinylcarbonyl compounds which have been studied insufficiently even for known compounds.

3. Further studies of possible applications of compounds considered and newly prepared in the synthesis of miscellaneous tellurium-containing heterocycles.

4. Synthesis of complex compounds including metal chelates containing the coordinative site MN_2Te_2 from β-tellurovinyl aldimines.

5. Systemic studies of the effect of the nature of tellurium-containing substituents and donor sites (COR, CH = NR) on the lengths and stabilities of the intramolecular coordinative bonds O → Te and N → Te.

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